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# Establishment of Authenticity and Typicality of Sugarcane from Madeira Island, and its Derivative Sugarcane Honey, Based on Molecular, Chemical and Chemometric Analysis

DOCTORAL THESIS

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DOCTORATE IN CHEMISTRY - SPECIALITY IN FOOD CHEMISTRY

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## ABSTRACT

Food authenticity has become a worldwide concern, foresting the importance of the development of strategies to guarantee the quality and safety of food products.

The purpose of this doctoral thesis was the establishment of the typicality and authenticity of sugarcane cultivars from Madeira Island, and its main derivative, sugarcane honey. The followed strategy was based on the identification of typical volatile, sugars and furan derivatives profiles in sugarcane honey processed by the certified producer *Fábrica Mel-de-Cana Ribeiro Sêco*, and compare it with sugarcane-based syrups from non-certified regional producers and from producers from different geographical regions. Also, the typical volatile profile throughout all stages of sugarcane honey processing were identified during four years, allowing the evaluation of influence of each stage in the formation of its typicality. In addition, the typical volatile profile of all sugarcane cultivars currently cultivated in Madeira Island were identified, namely *amarela*, *canica*, *roxa*, *radiada*, *verde* and *violeta*.

Different analytical methodologies based on effective extractive techniques and high-resolution chromatographic methods were successfully developed, optimized and validated, namely solid-phase microextraction combined with gas chromatography-mass spectrometry for the volatile profile, microextraction by packed sorbent combined with ultra-high performance liquid chromatography with diode-array detector for the furan derivatives profile, and ultrasound-assisted liquid-liquid extraction combined with liquid chromatography with a refractive index detector for sugars profile. Furthermore, an innovative and powerful Quality-by-Design approach was selected for development of the methodologies used for quantitation of furan derivatives and SGs. An exhaustive chemometric analysis based on *one-way* ANOVA, principal component analysis, partial least squares, linear discriminant analysis and hierarchical clustering analysis was successfully applied to recognize the typical profiles of sugarcane honey.

This doctoral thesis represents the first attempt to define the typicality, authenticity and traceability of sugarcane honey from Madeira Island, providing a highly valuable information to support its European Union certification.


**Keywords:** *sugarcane cultivars, sugarcane honey, typicality, authenticity*

## RESUMO

A autenticidade alimentar tornou-se uma preocupação mundial, evidenciando a importância do desenvolvimento de estratégias para garantir a qualidade e segurança dos produtos alimentares.

O objetivo do presente doutoramento foi estabelecer a tipicidade e autenticidade das cultivares de cana-de-açúcar da Ilha da Madeira, e do seu principal derivado, o mel-de-cana. A estratégia seguida baseou-se na identificação de perfis típicos de voláteis, açúcares e derivados do furano no mel-de-cana processado pela empresa certificada Fábrica Mel-de-Cana Ribeiro Sêco, e compará-lo com xaropes de cana-de-açúcar de produtores regionais não certificados e produtores de diferentes regiões geográficas. Também foram identificados os perfis voláteis típicos ao longo de todas as etapas de processamento do mel-de-cana, permitindo avaliar a influência de cada etapa na formação de sua tipicidade. Além disso, foram identificados os perfis voláteis típicos de todas as cultivares de cana-de-açúcar atualmente cultivadas na Ilha da Madeira, nomeadamente *amarela*, *canica*, *roxa*, *radiada*, *verde* e *violeta*.

Diferentes metodologias analíticas baseadas em técnicas extrativas e métodos cromatográficos foram desenvolvidos, otimizados e validados com sucesso, nomeadamente a microextração em fase sólida combinada com cromatografia gasosa e espectrometria de massa para perfil volátil, microextração por sorvente empacotado combinado com cromatografia líquida de ultra-alto desempenho com detetor díodos para perfil de derivados de furano, e extração líquido-líquido assistida por ultrassom combinada com cromatografia líquida com detetor de índice de refração para perfil de açúcares. Além disso, uma abordagem inovadora e poderosa de *Quality-by-Design* foi selecionada para o desenvolvimento das metodologias usadas para quantificação de derivados de furano e açúcares. A análise quimiométrica exaustiva baseada em ANOVA unilateral, análise de componentes principais, mínimos quadrados parciais, análise discriminante linear e análise de agrupamento hierárquico foi aplicada com sucesso para o reconhecimento de perfis típicos de mel-de-cana.

O presente doutoramento representa a primeira tentativa de definir a tipicidade, autenticidade e rastreabilidade do mel-de-cana, fornecendo uma informação altamente valiosa para apoiar a sua certificação na União Europeia.


**Palavras-chave:** *cultivares de cana-de-açúcar, mel-de-cana, tipicidade, autenticidade*

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## ABBREVIATIONS

AA – Amino Acids

AAO – Ascorbic Acid Oxidase

AAT – Alcohol Acyltransferase

ACT – Acetone

ACN – Acetonitrile

ADH – Alcohol Dehydrogenase

ANNs – Artificial Neural Networks

ANOVA – Analysis of Variance

ASY – Peak Asymmetry

ATP – Analytical Target Profile

BR – Browning Reaction

CAC – Codex Alimentarius Commission

CAD – Charged Aerosol Detection

CAR/PDMS – Carboxen/Polydimethylsiloxane

CDF – Canonical Discriminant Function

CHD - Carbohydrate

CE – Capillary Electrophoresis

CFDA – China Food and Drug Administration

CFIA – Canadian Food Inspection Agency

CMA – Critical Method Attribute

CMP – Critical Method Parameters

Cpk – Process Capability Index

CQM – Centro de Química da Madeira

CV – Cross Validation

DA – Desirability Analysis

DART – Direct Analysis in Real Time

DLLME – Dispersive Liquid-Liquid Microextraction

DoE – Design of Experiment

DVB/CAR/PDMS – Divinylbenzene/Carboxen/Polydimethylsiloxane

EBR – Enzymatic Browning Reaction

EC – European Commission

EFSA – European Food Safety Authority

ELSD – Evaporating Light Scattering Detector

EMA – European Medicines Agency

EU – European Union

EtOH – Ethanol

FA – Formic Acid

FAO – Food and Agriculture Organization of the United Nations

FD – Furanic Derivative

FDA – Food and Drug Administration

FFD – Full Factorial Design

FID – Flame Ionization Detector

FLD – Fluorescence Detector

FRS – Fábrica Mel-de-Cana Ribeiro Sêco

FNME – Fibre-Packed Needle Microextraction

FRU – Fructose

FSANZ – Food Standards Australia New Zealand

FSSAI – Food Safety and Standards Authority of India

FT – Fourier Transformation

GC – Gas Chromatography

GLU – Glucose

GHP – Good Hygiene Practices

GMP – Good Manufacturing Practices

HACCP – Hazard Analysis Critical Control Point

HCA – Hierarchical Cluster Analysis

HPAEC – High-Performance Anion Exchange Liquid Chromatography

HPLC – High-Performance Liquid Chromatography

HPTLC – High-Performance Thin Layer Chromatography

HS – Headspace Mode

ICH – International Conference on Harmonization

IP – Intermediate Precision

IS – Internal Standard

ISO – International Organization for Standardization

IR – Infrared Spectroscopy

kNN – k-Nearest Neighbours

KS – Knowledge Space

LC – Liquid Chromatography

LDA – Linear Discriminant Analysis

LLE – Liquid-Liquid Extraction

LLME – Liquid-Liquid Microextraction

LOD – Limit of Detection

LOQ – Limit of Quantitation

LOX – Lipoxygenase

MAE – Microwave-Assisted Extraction

MALDI-TOF – Matrix-Assisted Laser Desorption Ionization Time-of-Flight

MAN – Mannose

MeOH – Methanol

MEPS – Microextraction by Packed Sorbent

MIP – Molecular Imprinted Polymer

MIR – Mid-Infrared Spectroscopy

MLDR – Maillard Reaction

MLR – Multiple Linear Regression

MODR – Method Operable Design Region

MS – Mass Spectrometry

NEBR – Non-Enzymatic Browning Reaction

NIR – Near-Infrared Spectroscopy

NMR – Nuclear Magnetic Resonance

OPLS – Orthogonal Partial Least Squares

PA – Polyacrylate

ASY – Peak Asymmetry

PA – Polyacrylate

PAD – Pulsed Amperometry Detector

PC – Principal Component

PCA – Principal Component Analysis

PDA – Photo Diode Array

PDMS/DVB – Polydimethylsiloxane/Divinylbenzene

PDMS – Polydimethylsiloxane

PDO – Protected Designation of Origin

PGI – Protected Geographical Indication

PLS – Partial Least Squares

PLS-R – Partial Least Squares Regression

POX – Peroxidase

PPO – Polyphenol Oxidase

PR – Peak Resolution

PRA – Pareto Ranking Analysis

PTR-MS – Proton-Transfer-Reaction Mass Spectrometry

QbD – Quality-by-Design

QMS – Quality Management Systems

QRA – Quality Risk Assessment

QuEChERS – Quick, Easy, Cheap, Effective, Rugged, and Safe

RASFF – Rapid Alerts System for Food and Feed

RF – Random Forests

RHA – Rhamnose

RI – Refractive Index Detector

ROC – Receiver Operating Characteristic

RPA – Relative Peak Area

RS – Reference Standards

RSD – Relative Standard Deviation

RSM – Response Surface Methodology

RT – Retention Time

SBSE – Stir Bar Sorptive Extraction

SC – Sugarcane

SCH – Sugarcane Honey

SIMCA – Soft Independent Modelling by Class Analogy

SPDE – Solid Phase Dynamic Extraction

SPE – Solid Phase Extraction

SPME – Solid Phase Microextraction

STKD – Strecker Degradation

SUC – Sucrose

SVMs – Support Vector Machines

TEA – Triethylamine

TOF-MS – Time-of-Flight Mass Spectrometry

TPA – Total Peak Area

TRIPS – Trade-Related Aspects of Intellectual Property Rights

TRPA – Total Relative Peak Area

TSG – Traditional Specialties Guaranteed

TVA – Total Variance

UN – United Nations

UAE – Ultrasound-Assisted Extraction

USA – United States of America

USA-LLE – Ultrasound-Assisted Liquid-Liquid Extraction

USDA – United States Department of Agriculture

UHPLC – Ultra-High-Performance Liquid Chromatography

UV – Ultraviolet Detector

UV-Vis – Ultraviolet-Visible Spectroscopy

VIP – Variable Importance in Projection

VOC – Volatile Organic Compound

WHO – World Health Organization

WIPO – World Intellectual Property Organization

WTO – World Trade Organization

XYL - Xylose

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# OUTLINE

## Chapter 1. General Introduction

### Section 1.1. Scope and Propose

The scope and propose of the doctoral thesis, and its frame with the strategic vision of the company, are described in this section.

### Section 1.2. Strategy and Experimental Design

The followed strategy and the respective main objectives, and also the selected experimental design used, are described in this section.

## Chapter 2. State of Art

### Section 2.1. Current Trends and Regulatory Framework on the Food Authenticity

A review of main analytical methodologies and chemometric approaches in food fingerprinting, and the current legislation on the food authentication domain, are revised in this section, being provided through the following publication:

Sónia Medina, Rosa Perestrelo, Pedro Silva, Jorge A. Pereira, José S. Câmara. *Current trends and recent advances on food authenticity technologies and chemometric approaches*. Trends in Food Science & Technology, Volume 85, Pages 163-176, 2019. [IF: 11.077] DOI: https://doi.org/10.1016/j.tifs.2019.01.017

## Chapter 3. Volatile Fingerprinting

### Section 3.1. Development of Methodology for Volatile Fingerprinting

The proceedings of development, optimization and validation of the methodology based on solid phase microextraction in headspace mode combined with gas chromatography mass spectrometry for fingerprinting of volatile profile were described in this section, being provided through the following publication:

Pedro Silva, Jorge Freitas, Catarina L. Silva, Rosa Perestrelo, Fernando M. Nunes, José S. Câmara. Establishment of authenticity and typicality of sugarcane honey based on volatile profile and multivariate analysis, Food Control, Volume 73, Part B, Pages 1176-1188, 2017. [IF: 4.258] DOI: https://doi.org/10.1016/j.foodcont.2016.10.035

### Section 3.2. Volatile Fingerprinting of Sugarcane Cultivars

Fingerprinting of the volatile profile of sugarcane cultivars from Madeira Island to establish its authenticity and typicality were described in this section, being provided through the following publication:

Pedro Silva, Jorge Freitas, Fernando M. Nunes, José S. Câmara. *Chemical differentiation of sugarcane cultivars based on volatile profile and chemometric analysis*. Journal of Agricultural and Food Chemistry, Volume 69, Pages 3548-3558, 2021. [IF: 4.192] DOI: https://doi.org/10.1021/acs.jafc.0c07554

### Section 3.3. Volatile Fingerprinting throughout the Sugarcane Honey Processing

Fingerprinting of volatile profile throughout all stages of sugarcane honey processing to evaluate the influence of each stage in the typicality of sugarcane honey were described in this section, being provided through the following publication:

Pedro Silva, Jorge Freitas, Fernando M. Nunes, José S. Câmara. *Effect of processing and storage on the volatile profile of sugarcane honey: a four-year study*. Food Chemistry, Accepted, Ref. FOCH_130457, 2021. [IF: 6.306] DOI:

https://doi.org/FOCH_130457

### Section 3.4. Volatile Fingerprinting of the Sugarcane Honey

Fingerprinting of volatile profile of the sugarcane honey produced by a regional certified producer and compare it with syrups from non-certified regional producers and with producers from different geographical regions to establish its authenticity and typicality on the global market were described in this section, being provided through the following publication:

Pedro Silva, Jorge Freitas, Fernando M. Nunes, José S. Câmara. *A predictive strategy based on volatile profile and chemometric analysis for traceability and authenticity of sugarcane honey on the global market*. Foods, Submitted, 2021. [IF: 4.092] DOI:

https://doi.org/XXX

## Chapter 4. Furan Derivatives Fingerprinting

### Section 4.1. Development of Methodology for Furan Derivatives Fingerprinting

The proceedings of development, optimization and validation of the methodology based on microextraction by packed sorbent combined with ultra-high-performance liquid chromatography

with diode-array detector for fingerprinting of furan derivatives profile were described in this section, being provided through the following publication:

Pedro Silva, Catarina L. Silva, Rosa Perestrelo, Fernando M. Nunes, José S. Câmara. *A useful strategy based on chromatographic data combined with quality-by-design approach for food analysis applications. The case study of furanic derivatives in sugarcane honey*. Journal of Chromatography A, Volume 1520, Pages 117-126, 2017. [IF: 4.049] DOI: https://doi.org/10.1016/j.chroma.2017.09.019

**Section 4.2. Furan Derivatives Fingerprinting of the Sugarcane Honey**

Fingerprinting of furan derivatives profile of the sugarcane honey produced by a regional certified producer and compare it with syrups from non-certified regional producers and with producers from different geographical regions to establish its authenticity and typicality on the global market were described in this section, being provided through the following publication:

Pedro Silva, Catarina L. Silva, Rosa Perestrelo, Fernando M. Nunes, José S. Câmara. *Fingerprint targeted compounds in authenticity of sugarcane honey – An approach based on chromatographic and statistical data*. LWT - Food Science and Technology, Volume 96, Pages 82-89, 2018. [IF: 4.006] DOI:

https://doi.org/10.1016/j.lwt.2018.04.076

## Chapter 5. Sugars Fingerprinting

**Section 5.1. Development of Methodology for Sugars Fingerprinting**

The proceedings of development, optimization and validation of the methodology based on ultrasound-assisted liquid-liquid extraction combined with liquid chromatography with a refractive index detector for fingerprinting of sugars profile were described in this section, being provided through the following publication:

Pedro Silva, Catarina L. Silva, Rosa Perestrelo, Fernando M. Nunes, José S. Câmara. *Application of Quality-by-Design Approach in the Analytical Method Development for Quantification of Sugars in Sugarcane Honey by Reversed-Phase Liquid Chromatography*. Food Analytical Methods, Volume 13, Pages 1634-1649, 2020. [IF: 2.667] DOI:

https://doi.org/10.1007/s12161-020-01767-7

### Section 5.2. Sugars Fingerprinting of the Sugarcane Honey

Fingerprinting of sugars profile of the sugarcane honey produced by a regional certified producer and compare it with syrups from non-certified regional producers and with producers from different geographical regions to establish its authenticity and typicality on the global market were described in this section, being provided through the following publication:

Pedro Silva, Fernando M. Nunes, José S. Câmara. *Assessment of authenticity of Sugarcane Honey based on sugar profile and chemometric analysis*. Journal of Food Composition and Analysis, Submitted, 2021. [IF: 3.721] DOI:

https://doi.org/XXX

## Chapter 6. Conclusions and Future Perspectives

### Section 6.1. Conclusions

The main conclusions of thesis are highlighted in this section, comprising all issues that have been discussed in detail throughout the previous chapters.

### Section 6.2. Future Perspectives

The future perspectives of the results achieved in the doctoral thesis, and ongoing results of work started but not finished in the doctoral thesis, are discussed in this section.

# CHAPTER 1. GENERAL INTRODUCTION

## SECTION 1.1. SCOPE AND PROPOSE

*Scope*

The scope of doctoral thesis was the introduction of scientific knowledge and technological development in the sugarcane (SC) sector of Madeira Island through the cooperation between the main sector company, the *Fábrica Mel-de-Cana Ribeiro Sêco de V. Melim, Lda, (FRS),* and the research center with the highest recognition of merit at the University of Madeira, the *Centro de Química da Madeira (CQM),* in order to obtain a robust and valuable information to support the European Union (EU) certification of SC honey (SCH), promoting its international valorization and worldwide expansion, and consequently, enhancing the internationalization of FRS.

*Propose*

The propose of doctoral thesis was the establishment of authenticity and typicality of SC cultivars cultivated in Madeira Island, and principally, of its main derivative SCH, based on the fingerprinting of volatile organic compounds (VOCs), furan derivatives (FDs) and sugars (SGs) profiles.

## SECTION 1.2. STRATEGY AND EXPERIMENTAL DESIGN

*Strategy*

The strategy followed in doctoral thesis consists in three main objectives:

(i) Fingerprinting of VOCs, FDs and SGs profiles of the SCH from the certified producer FMCRS, and compare it with SC-based syrups from non-certified regional producers and producer from different geographical regions, to establish the typicality and authenticity of the SCH on the global market;

(ii) Fingerprinting of VOCs profile throughout all stages of SCH processing during four years to evaluate the influence of each stage in the typicality of SCH;

(iii) Fingerprinting of typical VOCs profile of all SC cultivars currently cultivated in Madeira Island for its differentiation and classification, to support the establishment of typicality and authenticity of SCH.

*Experimental design*

The experimental design selected for the fingerprinting of typical profiles in order to achieve the EU certification of SCH product was described in the framework showed in Figure 1.

**Figure 1. Experimental design selected for the fingerprinting of typical profiles.**

# CHAPTER 2. STATE OF ART

# SECTION 2.1. CURRENT TRENDS AND REGULATORY FRAMEWORK ON THE FOOD AUTHENTICITY

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Review

## Current trends and recent advances on food authenticity technologies and chemometric approaches

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*Abstract*

Food frauds and counterfeit products produced to obtain economic advantages have become a growing concern over the last decade. The assessment of food safety and authenticity constitute a powerful tool to mitigate this problem and protect public health. Nevertheless, the growing sophistication of fraudulent practices requires a continuous update and improvement of the analytical methodologies. In this context, the advances and novel techniques and chemometric approaches reported since 2016 are discussed regarding their potential use in food authentication. This review details the main analytical techniques applied in the extraction, detection and identification of metabolites to obtain food fingerprints, emphasizing the advantages and drawbacks of each approach with practical examples. Additionally, the current legislation on food authentication has also been revised. Gas chromatography (GC) coupled mass spectrometry (MS), liquid chromatography coupled time-of-flight mass spectrometry (TOF-MS) and nuclear magnetic resonance (NMR) followed by principal component analysis (PCA) and partial least squares (PLS) with linear discriminant analysis (LDA) are the most often reported analytical methodologies to discriminate between authentic and non-authentic foodstuffs using chemical fingerprints. More recently, novel and promising statistical methods with high classification power, such as soft independent modelling by class analogy (SIMCA) and k-nearest neighbours (kNN), are being already applied. Overall, the development of non-destructive, on-site and real-time analytical procedures able to deliver fast and unambiguous food authentication results will continue to be the goal driving food research.

Keywords: food fingerprints, food authentication, legal framework, analytical techniques, chemometric methods

## 1. *Introduction*

Food adulteration is potentially harmful to human health and so food safety and quality control constitute an important issue in food chemistry and related subjects. For this reason, the main players in the food chain, regulatory authorities, food processor, retailers and consumers, are very interested in the certification of food authenticity. To achieve this, different analytical techniques have become extremely appealing. Nevertheless, from a commercial and legal point of view, regulatory authorities are requested to continuously update the analytical methods and conditions allowed to validate the authenticity of a certain the product as this may support law enforcement actions [1].

The chemical composition (fingerprint) of foodstuffs is an excellent indicator of their quality, origin, authenticity and/or adulteration. Variations of these fingerprints may indicate changes in the metabolites levels caused by different conditions, as alterations in the production systems, geographical origin of the raw materials, storage conditions or adulteration practices [2]. For this reason, food fingerprints constitute a powerful tool to monitor food authenticity, as we very recently reviewed [3]. In this regard, the major food fraud alerts and common types of food frauds have been collected in a recent review [4]. Accordingly, different chemometric and statistical approaches have been described in the literature to optimize the experimental design and extract useful information from large and complex datasets in food authentication challenges [5–8]. Nevertheless, there is little information concerning the best sample extraction and analytical methods for food authenticity purpose, which processed with the suitable chemometric approach will allow us to reach valid conclusions from data that otherwise would be very hard to understand. In this regard, the main aim of this review is to give a detailed overview of recent developments in the experimental workflow -sample extraction techniques, analytical methodologies, and multivariate analysis-to assess food authenticity. This includes a critical discussion of the advantages and disadvantages of each technology, as well as examples of application to try to solve food authentication issues. In turn, this will contribute to improve the current lack of knowledge for the choice of the “best” technical methodology and upgrade the implementation of the existing legal framework on food authentication.

## 2. *The current regulatory framework and databases in food authenticity*

Food authenticity can be defined by the legal recognition of distinctive characteristics of a genuine food product, being its uniqueness, quality, safety, and traceability guaranteed by a certification regulatory framework. Usually, this certification is a bureaucratic and rigorous process involving a large number of entities, including the scientific community, governmental organizations, food producers and consumers [1].

Regarding this, the Codex Alimentarius Commission (CAC) is the coordination authority of the Food Standards Programme from the joint Food and Agriculture Organization of the United Nations (FAO) and World Health Organization (WHO). Nevertheless, remain entities and regulatory frameworks are very different from region to region. In EU, food certification legislation is defined by the European Commission (EC) Directives and Regulations produced by the European Food Safety Authority (EFSA). EFSA was established in February 2002 and it is funded since then by the EU Regulation (EC) 178/2002. Nevertheless, it is an independent organism, not depending of the European institutions (Commission, Council, and Parliament) and EU Member States. In turn, the United States of America (USA) food certification regulatory framework is based on regulations designated as "Acts". These are managed by a more complex structure involving the federal organizations FDA and United States Department of Agriculture (USDA). The Food and Drug Administration (FDA) is the scientific regulatory agency within the Department of Health and Human Services, coordinating the regulations and respective control involving the quality, safety and traceability of most food products. This specific control is performed by the Centre for Food Safety and Applied Nutrition. USDA, the other organization involved in the regulatory framework for food safety and certification, is responsible for the inspection and control of food safety standards. Within the USDA organic, this task is managed by the Food Safety and Inspection Service for meat, poultry, and eggs products, while the agricultural products are controlled by the Agricultural Marketing Service. Interestingly, Australia and New Zealand share a common food regulation authority, the Food Standards Australia New Zealand (FSANZ). Beyond the referred institutions, there are other national food regulatory organizations around the world, such as China Food and Drug Administration (CFDA), Food Safety and Standards Authority of India (FSSAI) and Canadian Food Inspection Agency (CFIA). The authenticity certification of foodstuffs is based on traceability systems to guarantee their genuineness, being mainly related to three issues: (a) quality and safety (food standards, good manufacturing practices, labelling, and adulteration ingredients); (b) geographical indication (species, crops, processing conditions) and (c) production systems (organic vs. conventional, traditional procedures).

### *2.1. Food quality and safety*

Currently, the Hazard Analysis Critical Control Point (HACCP) is the most effective regulatory framework to certify the food chain supply safety and quality, being recommended in the Codex Alimentarius standard published by CAC. In addition, Good Hygiene Practices (GHP) and Good Manufacturing Practices (GMP) procedures are also used as preventive control systems for HACCP. The International Organization

for Standardization (ISO) standards series for Quality Management Systems (QMS) developed by ISO is also a food safety management system widely used. The ISO 9001 (2000), for instance, defines the standard model for quality management in food processing and storage, while the ISO 22000 (2005) specify the requirements for safety control and management system in the food chain. The EFSA and FDA also recommended the application of HACCP and ISO standards as management systems in food quality and safety. Moreover, there are specific food regulatory frameworks for each region. As already refereed, EFSA was created by the EU Regulation (EC) 178/2002 and includes a set of laws and guidelines for food quality and safety assurance, designed as General Food Laws. This regulation establishes that the safety of all food products within EU market is mandatory. Moreover, to prevent the adulteration on labelling and ingredients composition, the Article 16 also indicates the specific regulations related with food and feed labelling, advertising and presentation. This control includes all aspects of the food shape, appearance and even the packaging materials used and the form this information is available to the consumers. In USA, FDA published the Food Code, which was described as "a model to develop or update their own food safety rules and to be consistent with national food regulatory policy". Meanwhile, the regulation about the food products traceability was defined in the Public Health Security and Bioterrorism Preparedness and Response Act of 2002. More recently, in 2011, the Food Safety Modernization Act defined by FDA, established several rules to prevent foodstuffs adulteration and to ensure food products quality and safety. This includes the food facilities registration, hazard analysis and risk-based preventive controls, standards for products safety, protection against intentional adulteration, sanitary transportation, food allergy and new dietary ingredients. The authentication of food products based on its quality and safety involves several steps and analytical procedures to verify that the composition of a given product is in accordance with the nutritional information, quality, and safety described in the labelling of the respective package.

### *2.1.1. Geographical indication*

The protection of the geographical indication has become one of the main means for the certification of food authenticity, being used to recognize the unique and distinctive characteristics to protect the quality and reputation of products originating from certain geographical regions. In this context, EU has a regulatory framework based on Regulation (EC) 510/2006 for the certification of regional food products, namely the Protected Designation of Origin (PDO) and Protected Geographical Indication (PGI). Both certifications have specific and rigorous requirements. Briefly, the PDO certification establishes that the product must be specific from a given region or eventually country. This geographical environment and related natural and

human characteristic must define the uniqueness of the product. Finally, also the production itself has to occur in a specific region. For application of PGI, the product needs to fulfil similar requirements to PGO products, except that the production is more flexible and can be only partially performed in the protected region. In addition, EU, through the Regulation (EC) 1257/1999, also certificates products originating from specific areas, such as Mountain or Island products. In these cases, the raw materials and the feedstuffs to feed the animals come essentially from the designated areas. In the case of processed products, they must be produced in these areas. In opposition to EU scenario, there isn't an authenticity regulatory framework in USA to protect the products produced from a specific geographic area. Instead, they are generally used as subsets of trademarks. Moreover, there are even certain products produced in USA that abusively branded with designation that correspond to EU products with geographical indication. This lack of legislation about the authenticity certification for regional products complicates the recognition of EU certifications by organizations from other countries. To overcome this problem, the World Trade Organization (WTO) through the agreement on Trade-Related Aspects of Intellectual Property Rights (TRIPS), produced a regulatory framework to harmonize the authentication legislation between different trade agreements. Accordingly, WTO defines in Article 22 (1) the geographical indication as "indications which identify a good as originating in the territory of a member, or a region or locality in that territory, where a given quality, reputation or other characteristic of the good is essentially attributable to its geographical origin". Meanwhile, TRIPS are now under by the World Intellectual Property Organization (WIPO) administration. This is the United Nations (UN) agency that is establishing a framework for an international intellectual property system able to foster "innovation and creativity for the benefit of all". The geographical indication was defined by WIPO as "a sign used on products that have a specific geographical origin and possess qualities or a reputation that are due to that origin". In any case, and in what concerns to this review, the attribution of a protected geographical indication must be supported in analytical methodologies demonstrating that the specificity and genuineness of the products come from the conditions of the region of origin.

### *2.1.2. Manufacturing methods*

The certification of food products authenticity can also be based on the manufacturing methods, such as organic production or traditional procedures. Thereby, EU certificates the authenticity of food products manufactured by traditional methods through the Traditional Specialties Guaranteed (TSG) certification (Regulation (EC) 509/2006). TSG certificates food products obtained through traditional practices or using traditional raw materials or ingredients. On the other hand, the certification of organic production is perhaps

the most widely used in the world, and almost all countries have already legislated in this topic. In EU, the certification of organic production was defined by Regulation (EC) 834/2007, and involve different aspects as (a) the appropriate design and management of biological processes based on ecological systems and using natural resources which are internal to the system; (b) a restriction in the use of external inputs that should be limited to (i) inputs from organic production; (ii) natural or naturally-derived substances; (iii) low solubility mineral fertilizers; and (c) the strict limitation of the use of chemically synthesized inputs. In USA, this topic is covered by the Organic Foods Production Act of 1990, from USDA, which establishes that any food product labelled as organically produced must (a) be obtained without involving synthetic chemicals; (b) be produced on land free from any prohibited substances, including synthetic chemicals, at least during three years before the products harvesting; and (c) be produced and handled according to the strict guidelines of the organic plan involving the producer, the product handler and the certifying agent. Overall, there may be differences between the EU and the USA regarding the products from organic production, but the principles are the same.

*2.2. Databases related to food authentication*

The EU policy on agricultural product quality is largely supported by DOOR, a database for the origin and registration of PDOs, PGIs, and TSGs. DOOR provides information about technologies for the knowledge of public data related with the protected foodstuffs. In this sense, in the last year (from May 2017 to May 2018) have been registered 12 PDOs, 22 PGIs and 2 TSGs. Two additional databases cover wines (E-Bacchus) and spirit drinks (E-spirit drinks). To handle these databases, the Rapid Alerts System for Food and Feed (RASFF) allows online interactive quests. This is an important tool that makes the RASFF notifications public available, not only of recent information, as well for any issue reported in the past. So, a search in the RASFF portal for the 5-year period (2011-2016) showed 665 notifications that were categorized as being adulteration or fraud. Many of these alerts relate to the absence of proper documentation such as detection of fraudulent health certificates, suggesting attempts to export products that have not undergone proper checks or may not be fit for human consumption. USA also has a service very similar to the RASFF database in what concerns to the detection of fraudulent food products. The US Food Fraud Database provides a continuously updated collection of ingredients and related reports gathered from scientific literature, regulation reports and judicial records. This database contains relevant information to governments, agencies or individual companies to identify specific food ingredients and vulnerable

categories to adulteration. According to this database, olive oil, milk, honey and saffron are the most common targets for adulteration [9].

## 3. *Experimental workflow for food authentication purpose*

Food products are complex matrices containing from hundreds to thousands of volatile, semi-volatile and non-volatile compounds. Therefore, food authentication is a hot topic requiring an integrated metabolomic workflow that should involve a carefully selection of the best sample processing procedures, the suitable analytical methods, reliable and unbiased chemometric analysis and unambiguous metabolite identification [5,8]. In recent years, the number of publications related to food fingerprints has substantially increased as a result of the improvements in the extraction techniques and analytical instruments that have allowed a more comprehensive analysis and better and more robust chemometric analyses [10–12].

### *3.1. Sample extraction techniques*

The sample preparation is a crucial step in food fingerprints and the quality of the analytical results has often been directly correlated to the extraction technique employed in the experimental layout used. In addition, a more efficient sample pre-treatment enriches the method selectivity and sensitivity, protects the analytical columns and decreases the matrix effect, allowing the collection of better results. As foods are complex matrices and some target analytes are present at trace levels (low concentrations), a sample preparation step in the experimental workflow is often required [13]. The extraction methods more often reported in food fingerprinting are liquid-liquid extraction (LLE), microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE), solid phase extraction (SPE), stir bar sorptive extraction (SBSE), solid phase microextraction (SPME), microextraction by packed sorbent (MEPS), and quick, easy, cheap, effective, rugged, and safe (QuEChERS), as shown in Figure 2.

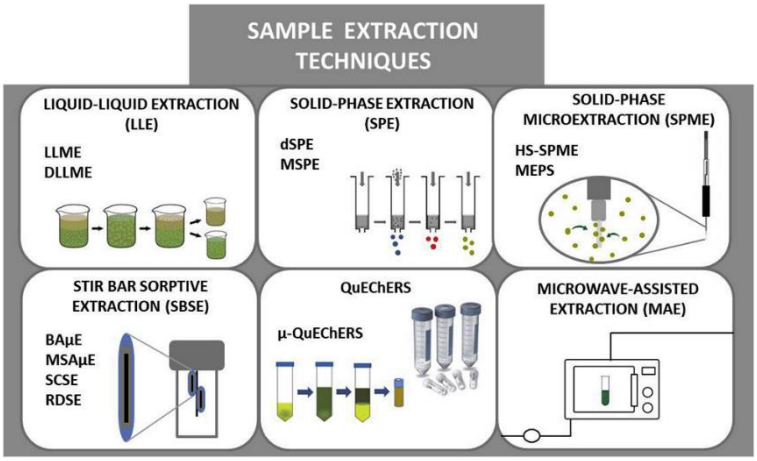


**Figure 2. Different extraction methods applied in the field of food authenticity.**

Nevertheless, among these sample extraction techniques, the microextraction techniques (e.g., SPME, MEPS, QuEChERS) are becoming more popular in food fingerprints due to several factors, including reduced labour time and costs, as well as low sample and solvent volumes requirements, making them more environmental friendly [14]. The main features (pros and cons) of sample extraction techniques are displayed in Table S1 (Supplementary Figure).

### *3.1.1. LLE*

LLE involves the analytes partitioning between two immiscible phases (organic and aqueous phase). Although very simple, LLE presents several disadvantages. After mixing, exhaustive recoveries are required to extract the target analytes. Moreover, LLE requires large amounts of organic solvents, is time-consuming and lower recoveries are usually obtained. Therefore, analysts were confronted with the challenge of developing analytical procedures without these drawbacks and liquid-liquid microextraction (LLME) is becoming a natural evolution of LLE. LLME is a suitable approach to conventional solvent-based extraction techniques, since is more cost-effective, involving a lower solvent consumption (microliter volumes), being therefore eco-friendlier. However, there are still disadvantages in LLME technique, including long extraction times and low enrichment factors [15]. Dispersive liquid-liquid microextraction (DLLME) was developed as a new type of LLME to analyse organic compounds. It is a triphasic extraction system in which a mixture of the extraction solvent and disperser solvent (in optimized ratios) is injected into the sample using a syringe or a micropipette, thus producing a cloudy solution [16]. This dispersion process significantly improves the extraction kinetics by increasing the contact surface between the extractant and the sample. Subsequently, phase separation is performed by centrifugation or by decreasing the solution temperature [17]. The main advantages of DLLME with respect to LLE and LLME techniques are low solvent and sample volumes, rapid equilibration times, very short extraction times (often less than a minute) and an high enrichment factor, attributed to the high phase ratio of the aqueous sample to the extraction solvent [18]. An important drawback in DLLME is that the extraction solvents are often organic and highly toxic (e.g., chlorobenzene, chloroform or carbon tetrachloride). To avoid this, in 2008, ionic liquids (ILs) were used as a green alternative to conventional organic solvent in DLLME. ILs exhibit many unique physical properties, including negligible vapor pressures (low volatility), good solubility for organic and inorganic compounds, non-flammability, high thermal stability, tunable viscosities and a wide temperature range in the liquid phase that make them particularly suitable for DLLME [18,19]. Nowadays, several variations of original DLLME method are being used, such as DLLME based on the solidification of floating organic drop, ultrasound assisted-DLLME,

vortex-assisted assisted-DLLME, alcoholic assisted-DLLME, solvent terminated-DLLME, among others, followed by different chromatographic, spectroscopic or hyphenated techniques to analyze water and food samples [17,20,21].

### *3.1.2. SPE*

SPE has gradually replaced the conventional LLE because it prevents most of the common problems encountered with LLE and improves quantitative recovery yields. The principle of SPE is very similar to LLE, but instead of two immiscible liquid phases, SPE involves partitioning between a liquid and a solid phase. So, SPE enables the extraction, clean-up and concentration of target analyte prior to its quantification, and can be used for many purposes such as desalting, derivatization and class fractionation [22]. Thus, SPE technique has been used in food and beverages characterization to detect key metabolites in different matrices like wine, honey, oregano or coffee, among others [23]. Over the past decade, SPE has rapidly developed and improved to overcome its disadvantages (e.g., large volumes of the sample solution, elution solvents and time-consuming), which often decrease the analysis accuracy. Currently, miniaturized solid phase extraction, such as μSPE, dispersive SPE, magnetic SPE), immunoaffinity-SPE, and molecularly-imprinted SPE, have been developed and become very popular in food analysis [24,25]. Compared to conventional SPE, these extraction techniques show several advantages such as a shorter time of extraction, lower consumption of sorbents (10-35 mg), lower volume of organic solvents (50-500 μL), and higher selectivity and sensitivity [22,24].

### *3.1.3. SPME*

SPME was originally introduced in the early 1990s as a solvent-free sample preparation technique that can integrate sampling, extraction, concentration and injection into one single step, minimizing potential sources of analytes instability [26]. This procedure is an equilibrium technique involving the analytes partitioning between the sample matrix and the extraction phase, followed by the analytes desorption into an analytical instrument. So, SPME compared to LLE and SPE shows several advantages such as reduced analysis time, disposal cost or low sample and solvent volumes [27]. The main disadvantages of SPME technique are the limited stationary phases (fiber materials) commercially available [28]. However, it has been overcome with the introduction in the market of new extraction phases and devices, increasing SPME application in food analysis [14]. Numerous new materials are currently being developed for SPME fiber coatings, such as graphene aerogel-mesoporous carbon composites, titanium oxide composites, amine-functionalized material, carbon nanotubes, molecular imprinted polymers (MIPs), metal-organic

frameworks, sol-gel coatings, among others, which should be carefully selected according to the purpose of the analysis and the analytical instrument (e.g., use of thermally stable fibers for GC) [29,30]. In addition, particle-loaded coatings prepared by spray and dip coating methods have also gained attention as SPME coatings for several applications [31]. The first SPME applications involved the so-called fiber geometry, which was composed by a fused silica rod supporting a polymeric coating suitable for direct immersion, headspace (HS) and membrane protection extraction [32]. Then, in-tube SPME was introduced with some modifications as a wire-in-tube with a stainless-steel wire placed into the extraction capillary. This modification improved the extraction efficiency since the capillary volume was significantly reduced leading to the target analytes preconcentration and simplifying the automation, particularly the LC instrumentation [31]. Beyond in-tube SPME, recent advances HS-SPME have been developed, such as in-needle SPME [33], in-tip SPME or vacuum-assisted HS-SPME [26]. In this regard, in-needle SPME technique includes solid phase dynamic extraction (SPDE), MEPS and fibre-packed needle microextraction (FNME) [34]. Compared with SPME, these extraction procedures have several advantages, namely, the large coating volume, concentration capacity, lower extraction time and better repeatability and mechanical stability. MEPS is a miniaturization of the conventional SPE technique, in which the sample volume, extraction and washing solvents volumes are significantly reduced. In MEPS, the sorbent (~2 mg) is packed within the syringe (as a plug) or between the barrel and the needle (as a cartridge) and not in a separate column. MEPS can handle small sample volumes (10 up to 5000 μL) and can be connected on-line to different chromatographic techniques [35]. The main advantage of MEPS compared to SPE is that the packed sorbent can be reused many times, up to 100 times or more, depending on the complexity of the sample matrix. Moreover, MEPS can be easily processed to obtain enrichment factors much more interesting than those allowed in conventional SPE, therefore allowing a higher analytical performance. Currently, there are several MEPS sorbents commercially available, such as silica-based C18, C8, and C2 (reversed phase), silica (normal phase), restricted access material, carbon, polystyrene-divinylbenzene copolymer, MIPs, mixed mode, cation exchange, allowing a very broad range of applications [36]. These reasons make MEPS quite popular in food analysis, being particularly tailored for liquid samples as wines [34]. In the in-tip SPME, the solid sorbent is packed in the pipette tip, and so several samples can be handled simultaneously using the commercially available 96-blade configuration systems (thin film on a blade support). The sorbents used for in-tip SPME comprise silica and methacrylate monoliths. In contrast to SPME fibre and in-tube SPME, in-tip SPME better recoveries rates were described for several applications [37]. Although, there are interesting applications

with different variations of SPME, as the analysis of ochratoxin A in wines using in-tube SPME recently described [38] or the SPME-transmission mode methodology reported to analyse pesticides in food specimens [14]. Apart from that, HS-SPME technique continues to be the most popular SPME format. Recent HS-SPME applications are related to the characterization of the volatile profile of a diversity of food samples to differentiate among different date varieties [39] or discriminate between organic and conventional orange juices [40]. There are, nevertheless, very interesting works applying MEPS to food authentication analyses in fortified wines samples [34] or SCH samples [11]. In recent years, MIPs have received considerable attention in analytical chemistry and custom MIPs-MEPS sorbents have been already successfully applied to food safety analysis, for instance, to analyse dimethoate derivates in wheat flour samples [41].

#### *3.1.4. SBSE*

SBSE is a sample preparation technique similar to SPME, also involving an equilibrium-based non-exhaustive extraction. However, the larger volume of the polydimethylsiloxane (PDMS) confers greater surface areas, therefore providing higher extraction efficiencies. In SBSE technique, a magnetic stir bar coated is placed into an aqueous sample (or extract) for a certain extraction time, after this, the stir bar is removed and the analytes are desorbed thermally or with a solvent [42]. SBSE is less well-known than SPME in food analysis, due to the number of coatings commercially available and the difficulty to attain full automation. Several efforts have been done to overcome these drawbacks with the development of dual phase/hybrid twisters, ion-pair and/or alternative new coating materials such as MIPs, monolithics, ethylene glycol modified silicone, magnetic ionic liquid, nanosilica/polydimethylsiloxane, polyurethane, polyacrylate, among others, to increase the selectivity and/or efficiency of the extraction process with improved analytical features [42,43]. In addition, improved versions of SBSE, as stir cake sorptive extraction and rotating-disc sorbent extraction, which may increase the exchange-efficiency mass, and present higher recovery rates and better repeatability and reproducibility, were made available [44]. There are also relevant reports of food fingerprinting using SBSE as sensomic approach from Picard et al. [42], providing useful information about food aroma fingerprints and profiles, particularly in wines samples. Meanwhile, new adsorptive microextraction approaches, bar adsorptive microextraction and multi-spheres adsorptive microextraction, were recently proposed [45]. Bar adsorptive microextraction uses nanostructured sorbents (e.g., activated carbons, polymers) that operate under the floating sampling technology. On the other hand, in multi-spheres adsorptive microextraction, the spherical substrates are fixed to the surface of the device

through thermal treatment. These techniques present a great advantage over SBSE that relates with their flexibility to adapt the most suitable sorbent for each target analyte or classes of compounds [37].

### *3.1.5. QuEChERS*

Traditionally, QuEChERS extraction was focused on the multiresidue pesticide analysis in food matrices, but recently is gaining popularity to extract other compounds in an enormous variety of food products [46]. Essentially, QuEChERS technique involves two steps: i) extraction based on partitioning via salting out, and ii) dispersive solid phase extraction (d-SPE) in order to remove matrix interferences. Thus, QuEChERS combines extraction, separation, and purification of the extract, allowing a sample preparation with minimal loss of analytes in intermediate steps and laboratory ware, as filters, evaporators, sorbents or dehydrating reagents. In addition, QuEChERS technique is relatively fast, eventually allowing a following high throughput analysis (a set of 10-20 samples could be extracted in 30-40 min by a single analyst), it requires low solvent volume, avoids chlorinated solvents and involves a very small waste generation [47]. QuEChERS applications to food matrices involve primarily food adulteration, and QuEChERS has been used as extraction procedure in methodologies to detect illegal additives (ractopamine) in pork meat [48] or ferulic acid metabolites in milk samples [47]. Recently, an improved and miniaturized method (μ-QuEChERS) has been developed as a cost-effective tool, producing minimal amounts of waste disposal in comparison to the classical extraction procedure. This novel method has been used for quality control of baby foods [49].

### *3.1.6. MAE*

MAE combines microwaves power (to stimulate the molecular motion and spin of liquids' molecules with a constant dipole) and traditional solvent extraction. The MAE system contains a flask, a condensing tube, a microwave oven and the magnetic stirrer. This technique presents several advantages compared to conventional and advanced extraction techniques, including a controllable temperature setting, reduced extraction time and solvent costs, high-throughput capability and extraction efficiency [50]. The effective solvent for MAE depends not only on the chemical properties of the target analyte, but also on the dissipation factor, which measures the polarizability of the solvent under MAE and the transformation of absorbing microwaves into heat. For being a good solvent to work under the microwave conditions, the solvent must have high dissipation factor. For this reason, water is seen as a good substitution of organic solvents since it presents a higher dissipation factor [51]. In the context of food analysis, it is worthwhile to refer the use of MAE to obtain food fingerprints in different blueberry cultivars [52] and to characterize disinfection by-products in meat samples [50].

*3.2. Analytical methodologies*

Fingerprinting detection methods used in food science include many important technologies such as chromatographic, hyphenated techniques, spectroscopic, spectrometric, and electrochemical approaches, which are shown in Figure 3.

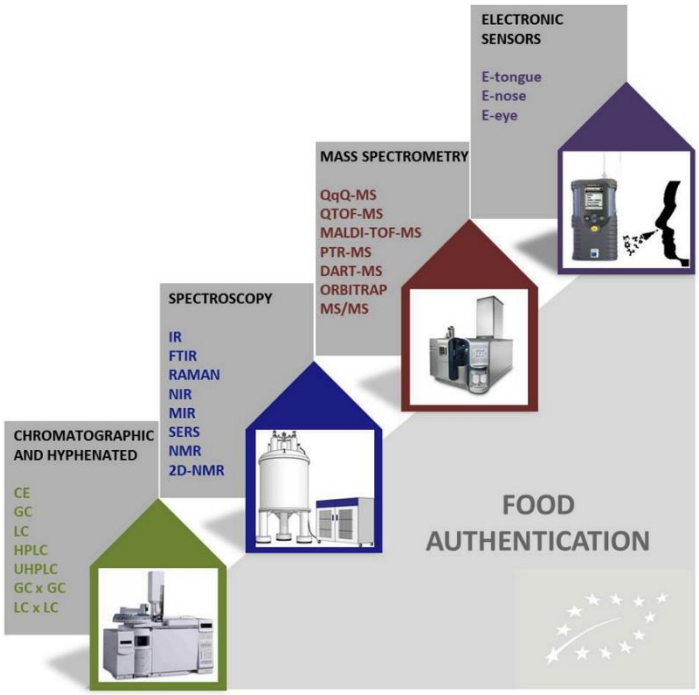


**Figure 3. Analytical techniques employed for monitoring the food authentication.**

However, in recent years, spectroscopic and spectrometric-based studies are the more often reported for food fingerprint analysis [2]. In the following subsections as well as in Table S2, we present a general overview of the most common separation techniques (and chemometric analyses) reported since 2016 to 2018 obtain food fingerprints with the aim of certifying food authenticity.

*3.2.1. Chromatographic and hyphenated techniques*

Chromatographic techniques, as capillary electrophoresis (CE), GC and liquid chromatography (LC) are employed to separate the different components of a mixture. Then, depending on the detection system, each component will generate specific signals suitable for qualitative and quantitative analysis. Chromatographic fingerprint analysis combined with chemometric methods are usually applied throughout the food chain to monitor food authentication issues [53]. Currently, hyphenated techniques combining separation techniques (e.g. GC and LC) with spectroscopic or spectrometric techniques (e.g. MS and NMR) are receiving special attention given their ability to solve complex analytical problems. Hyphenated techniques, although eventually requiring more skills and expertise, are becoming very popular and very useful for food fingerprinting and authenticity and safety certification [54]. In this regard, CE is an electrophoretic technique that separates charged analytes based on their ability to travel through a conductive medium in response to

an applied electric field. The main advantages of CE are the high resolution, speed and low mobile phase volume requirements, being very cost-effective [55]. In contrast, the low reproducibility and sensitivity are the main drawbacks of CE, making this separation technique not appropriate for analyses of target compounds in trace amounts [56]. Nevertheless, CE with photo diode array (PDA) allowed the Argentinean white wines discrimination [55], to determine quality and origin of public drinking waters [57]. More complex applications involving CE-MS include the establishment of the metabolite profiling of orange juice and wines [58] or the analysis of food contaminants in meat [59]. Furthermore, GC is one of the most popular separation techniques used in food science, being described in foodstuff profiling, authenticity, quality assessment and safety. In GC, the sample mixture is vaporized in a heated chamber (without decomposition) and the compounds separated according to their selective interaction with the column material (stationary phase). The compounds migrate through the column under high pressure using a mobile phase, an inert gas (e.g., He, N2) [56]. Two decades ago, two-dimensional GC (2D GC or GC × GC) was introduced as a multidimensional analytical technique. It is characterized by the combination of two columns with different polarities in tandem by a modulator interface. The chromatographic deconvolution overcomes the co-eluting problems common in 1D GC. In addition, GC × GC offers greater sensitivity (particularly if using cryogenic modulation), resolution, selectivity and fast analysis (in the 2nd dimension, the analyses time range from 4 to 8 s) then 1D GC [60]. GC and/or GC × GC can be hyphenated to different detectors, as flame ionization detector (FID), MS or TOF-MS. Among them, GC-MS analysis is becoming the most robust technology to assess the authenticity and safety of a great diversity of food products. This include, for example, the discrimination of honeys from different botanical origins [61], Asiago PDO cheese authentication [60], differentiation of several date varieties [39] and organic orange juices [40] or the adulteration of almond powder samples with apricot kernel [57]. On the other side, in LC, the analytes are separated by a column based on their selective partition between a stationary phase (column material) and a mobile liquid phase. Taking into account the type of stationary phase, the analytes can be separated according to their charge, size, hydrophobicity and molecular mass [56]. High-performance liquid chromatography (HPLC) is the most popular LC technique, being robust and reproducible, but in the last decade the evolution of the HPLC towards miniaturization, using smaller columns and reduced volume of solvents to achieve a faster separation of the target analytes, is making ultra-high-performance liquid chromatography (UHPLC) the new standard in LC. Thus, UHPLC allows similar or high resolution with a much lower analysis time and solvents needs [2]. In addition, UHPLC columns are packed with sub-2 μm particles and the system can operate at higher

pressures (1000 bar). Due to their advantages, UHPLC has gained popularity in profiling studies, including in metabolomics approaches applied to food authenticity. Nevertheless, to improve its potentiality even further, UHPLC can be combined in tandem with mass spectrometry techniques [54]. On the other hand, to overcome the target analytes overlapping, multidimensional liquid-liquid chromatography 2D (LC × LC) represents a suitable tool for analysis of complex food samples [62]. This has been used to discriminate garlics according to their geographic origin [63] and honeys from different botanical origins [64], to authenticate organic carrots [2] or to differentiate different wheat varieties [65].

### *3.2.2. Spectroscopic approaches*

Spectroscopic techniques are based on the interaction of electromagnetic radiation with the matter that composes the food matrix. This technique allows obtaining information related to structural, physical-chemical and composition properties of the sample, through the wavelength or frequency detected in the emitted or absorbed energy spectrum. In food fingerprints, spectroscopic techniques have gained popularity since it is fast, non-destructive, non-invasive, solvent-free, automatic, inexpensive and in some cases, many compounds can be detected simultaneously [1]. Several spectroscopic techniques are available, such as vibrational spectroscopy (infrared (IR), mid-infrared (MIR), near-infrared (NIR), and Raman), ultraviolet-visible (UV-Vis) spectroscopy, NMR, electron spin resonance, X-ray spectroscopy, electron spectroscopy, Mössbauer and thermal spectroscopy. From these, IR, Raman and NMR are the spectroscopic techniques most often reported in food authentication, safety and quality analysis [66–68]. Indeed, the combined used of spectroscopic methods and chemometric strategy has provided powerful tool for detecting food frauds [53].

Vibrational spectroscopy technique is an energy sensitive method based on periodic changes of dipole moments (IR) or polarizabilities (Raman) caused by molecular vibrational of molecules or groups of atoms between 10-12 and 10-15 seconds. So, IR spectroscopy is based on the absorption of electromagnetic radiation, whereas Raman spectroscopy relies upon inelastic scattering of electromagnetic radiation [69]. Vibrational spectroscopy enables to detect known compounds through fingerprint and to identify unknown compounds through functional groups and bonds properties. A special attention should be given to IR spectroscopic techniques, once IR has very intense water absorption. This problem can be overcome by a shorter irradiation time, increasing the number of scans and attenuated total reflectance [70]. Nonetheless, for dehydrated foodstuffs like flours or flour-based product, intense water absorption makes infrared especially useful and it should not be seen as an issue [71]. The application of vibrational spectroscopy in

food authenticity was also significantly increased with the development of analytical methods using Fourier transformation (FT) instrumentation, as FT-IR and FT-Raman [8,72]. Most recent studies using IR technique in food authentication aimed to assess the existence of food adulteration, as the reports involving saffron [9], paprika [73] and açai fruits [74]. Raman provides specific information related to the identification of samples and it is sensitive enough for analytes present at trace amounts. The advances regarding Raman approach, such as surface-enhanced Raman spectroscopy, stimulated Raman scattering, resonance Raman spectroscopy, among others, contribute to increase its popularity in the field of food analysis. From these, surface-enhanced Raman spectroscopy is the most frequent technique used in food analysis, being the one allowing high sensitivity and selectivity for the characterization of a wide range of food products [75]. Moreover, Raman spectroscopy has been applied to control the designation of origin of certain wines [69] or to assess the citrus fruits freshness (using a portable Raman instrument), introducing objective criteria of appreciation and quality control [68]. NIR spectroscopy has been applied in the geographical origin authentication of wine vinegars [8] and in the discrimination of several maize cultivars [76]. In addition, a recent study using a handheld NIR device a simple and portable instrument that may increase the number of screened samples directly in situ, has been applied to assess frauds in fish and even in processed products in a faster and economic way [67]. In another work, NIR, MIR, and Raman spectroscopy were employed to classify wines according to their origin. The findings of this study showed that MIR technology allowed better prediction compared to other ones [77]. Furthermore, the portable devices had similar levels of performance as the benchtop instruments in terms of sensitivity and specificity for classifying authentic or adulterated samples. For instance, handheld Raman devices have been applied for detecting milk powder adulteration [7] or a handheld NIR device was used to detect the presence of lard adulteration in palm oil [78]. NMR is a spectroscopic technique that allows the characterization of the compounds present in a given sample by identifying the carbon-hydrogen frameworks according to the absorption of electromagnetic radiation [79]. So, NMR signals show a diverse array of measurable parameters such as intensity, frequency (normalized to chemical shift), line shape, line width and relaxation times. This technique is used as a useful tool to elucidate molecular structures and to investigate foodstuffs at molecular scale [80]. Proton nuclear magnetic resonance (1H NMR) is the spectroscopy technique most used in the field of food composition analysis, allowing “high-throughput” spectroscopic and structural information on a wide range of molecular compounds. The main disadvantage of this technique is the elevated costs of the instruments and experiments. This is being partially attenuated with the introduction of low-resolution NMR instruments with

frequencies ranging 10-40 MHz. These instruments are much less expensive and easy to use and although providing lower detailed information than the high-resolution instruments, they can retrieve good accuracy. Nevertheless, their sensitivity is less than the one obtained by MS detection [56]. Non-targeted NMR analysis has been used to obtain fingerprinting in several matrices as apples [80] and cinnamon varieties [79], and for the determination of lentils origin [81]. Moreover, both techniques (1H and 13C NMR) have been used together for the identification of lard adulteration in butter samples [82]. Recently, 2D-NMR has been applied for the discrimination of edible vegetable oils according to their botanical origin and for the detection of adulterations by hazelnut oil addition, providing real benefits (in terms of discrimination power) compared with the 1D NMR approach [83].

### *3.2.3. Mass spectrometry technologies*

In general, MS technique is used tandem with chromatographic techniques, such as GC and liquid LC chromatography. Nevertheless, the recent advances in non-chromatographic MS, in particular matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF), proton-transfer-reaction mass spectrometry (PTR-MS) and ambient mass spectrometry techniques, as direct analysis in real time (DART) coupled to MS have led the development of novel methods that enable the complex assessment of food authenticity and adulteration detection [17,84]. In this context, MALDI has a great potential for the fast screening of food quality, safety, and authentication, due to its ability to desorb high-molecular-weight (e.g., peptides, oligosaccharides, oligonucleotides), high accuracy, simplicity, cost-effective and wide mass range (1-300 kDa). In addition, MALDI-MS techniques require a low sample amount and no sample pre-treatment [1]. In MALDI, the sample within the matrix is ionized with a laser beam in an automated mode, generating single protonated ions. Then, these ions are accelerated at a fixed potential and separated based on their mass-to-charge ratio (m/z). Different mass analysers can be tandem connected in MALDI, such as ion trap or TOF analysers, being MALDI-TOF-MS the most often used in food analysis [84]. On the other side, PTR-MS is the most sensitive instruments for real-time monitoring, being able to quantify hundreds of VOCs through proton-transfer reaction with hydroxonium ions and detection by MS. This technique allows the fast detection, near real-time, of several VOCs in complex matrices with low detection limits (LOD < 1 ppt) and soft ionization and does not require any sample preparation. In what concerns to food analysis, PTR-MS has been already used to discriminate wines samples based on their geographical origin [85]. On the other hand, ambient-MS greatly simplified and favoured speed, selectivity, sensitivity, and simplicity of MS analysis, being DART-MS one of the variants of ambient-MS. The ionization process of DART-MS takes place at

atmospheric pressure and present several advantages, such as fast analysis, minimal sample preparation and high salt tolerance. Furthermore, this approach covers compounds deposited or adsorbed on to surfaces or that have been desorbed therefrom into the atmosphere. DART-MS has recently reported in food authenticity, to detect illegal adulterants in red wine [17].

#### *3.2.4. Electronic sensors*

Electronic sensors work by "imitating" the human senses, namely the olfactory sense through the electronic nose (gas sensor), taste sense by electronic tongue (liquid sensor) and vision sense by electronic eye, which is based on computer vision systems and colorimetric techniques. The non-selectivity of the sensors may result in many possibilities for unique signal combinations, patterns or fingerprint [86]. These sensors can be used to characterize multicomponent mixture with both qualitative and quantitate purpose and they require less time and costs than other techniques but they can only recognize a limited number of compounds [87]. So, E-sensors technology combined with chemometric tools is a promising approach for food authenticity assessment and detection of food adulteration. In fact, they are some interesting applications described in food, cosmetic and pharmaceutical industries. Gan et al., [87], for instance, challenged the reliability of two sensors, electronic tongue and nose, against NIR and MIR using honey samples. The authors demonstrated that the electronic-tongue sensor was the most effective approach in the confirmation of the botanical origin of different honeys, as well as in the detection of raw honey adulterations. More recently, Buratti et al. [86], demonstrated the potential of electronic-nose, tongue and eye for the characterization of edible olive oil and assessment of its shelf life.

### *3.3. The role of chemometric approaches in the characterization of food fingerprints*

Modern analytical methodologies applied to food fingerprinting, contrarily to target analysis, generate a large amount of data that is not easy to understand. This requires complex statistical analysis, which we can broadly define as chemometric, to modulate multivariate data and extract chemically relevant information. In the last decade, many chemometric applications coupled with conventional and innovative analytical measurements, have been developed for quality assessment, product traceability, definition of geographic origin and detection food frauds and adulterations [5]. Generically, the chemometric layout is applied when large amounts of data (high number of variables) are obtained and data dimensionality reduction procedures are required. The chemometric tools can be organized into three categories: (i) exploratory analysis; (ii) classification/discriminant analyses; and (iii) regression analyses/prediction models.

### *3.3.1. Exploratory analysis*

Also known as non-supervised approach, it involves algorithms that cluster the data into groups without prior information of group relationship and visualize the data to highlight their differences and similarities. Hierarchical cluster analysis (HCA) and PCA are the most common exploratory methods used in food fingerprint [5]. PCA is an approach for dimension reduction that uses linear combinations of the original variables, to retrieve fewer and new variables called principal components (PCs). PCs explain the maximum variance of the data used, enabling to better visualize the variation present in a dataset. Moreover, PCA identifies the variables responsible for the discrimination pattern through the PCs loading. PCA was successfully used in food fingerprint to discriminate agricultural production systems [54], the geographical origin of legumes samples [81] or to evaluate saffron adulteration with others plant-derived products [9]. Hierarchical clustering analysis (HCA) is a clustering method in which the samples are organized in clusters considering their nearness in the multidimensional space. The result of HCA is presented in a dendrogram [5]. This statistical approach was used, for instance, to assess the effect of the geographic origin on mushrooms [88] and SCH [11], and to certificate the authenticity of commercial spices [89].

### *3.3.2. Class modelling and discriminant analysis*

Supervised methods are used to classify and discriminate samples considering all pattern of features [12]. This includes methods as PLS-DA, orthogonal partial least squares with discriminant analysis (OPLS-DA), LDA, artificial neural networks (ANNs), support vector machines (SVMs) and SIMCA. From these, PLS-DA and LDA are the most often used discriminant approaches in food fingerprint. PLS-DA has been recently used to discriminate olive oil and white rice samples according to their geographic origin [90,91]. In turn, LDA was used to discriminate honey samples from different botanical origin [61,92] and to detect the adulteration of saffron samples [93]. Variable importance in projection (VIP) is another well-known method for finding significant variables in complex data. This method selects variables from the PLS model by calculating the VIP score for each variable and it removes non-important variables with VIP score below a predefined threshold (default = 1) and it has been applied, for instance, to detect saffron adulteration [94]. LDA uses linear combinations of the original variables to achieve class discrimination, therefore maximizing the ratio between-class vs. within-class variance [95]. The main disadvantage of LDA, however, is that it requires a lower or equal number of variables and samples. Nevertheless, this problem can be easily solved employing PCA or feature selection procedures like stepwise forward variable selection [10,96]. ANNs has proved useful in agro-food science and technology, particularly in olive oil industry [97]. SIMCA analysis

is a class modelling technique ("soft" classification) that requires prior analysis by PCA [5]. This approach has been applied to classify honey types by their botanical and geographical origin [66] and species of fish samples [67]. Other interesting approaches include data driven SIMCA, which has been recently applied to Colombian coffee authentication by geographical origin [98] and one-class SIMCA, that was shown to be effective to detect paprika samples adulteration [73]. Recently, biomimetic pattern recognitions has been applied to establish identification models and it has shown to be more stable and robust than SIMCA in the identification of seed maize varieties [76]. A simple method that may be used for a small number of samples is the kNN. It may be used for classification of categorical data variables and regression for continuous variables, although kNN is not accurate when there are many features [5], but it may be a useful tool. For example, kNN has been applied to classify results on açaí adulterations [74] and to discriminate among the botanical origin of vegetables oils [86]. Finally, it should be mentioned the receiver operating characteristic (ROC) curves. These are computed to express the balance between sensitivity and specificity, representing the area under the ROC curve the overall ability of the test. An ideal model should have an area of 1.00, which occurs, for instance, when there is complete separation of two agricultural production systems (organic and conventional). ROC curves were used to distinguish organic and conventional carrot samples [2] and to discriminate between common and durum wheat with an authenticity purpose [65]. Furthermore, Random Forests (RF) is a powerful and well-established classifier and it presents high classification accuracy in untargeted metabolomics assays. It has been successfully applied to discriminate white rice by its geographical origin [91].

In this respect, Oliveri, [99] concluded that discriminant methods seek a delimiter between two – or more – classes, using a contribution from all of the classes considered. For that, all of the classes must be correctly defined and samples included should be representative of each class. This is extremely important when the focus is on a single class like, for instance, cases involving food authentication issues [99]. Nevertheless, Rodionova et al. [100] in a detailed review about chemometric methods applied to food authentication, declared that discrimination methods are inappropriate for solving authentication issues and only one-class classifiers should be used for this purpose and particularly SIMCA shows more reliable results [100]. Therefore, it is a very difficult task to select the "best" statistical model because of all of them present negative and positive characteristics [5].

### *3.3.3. Regression analyses/prediction models*

Partial least squares regression (PLS-R) is the approach most commonly used in chemistry and technology fields, and it is a suitable approach to establish a possible relationship between two matrices (e.g., a latent variable approach for modelling the covariance structures in these two matrices) through a linear multivariate model. PLS-R analysis retrieves an equation that predicts Y values (classical parameters) based on X values (e.g., GC-MS dataset) and this tool is particularly relevant for sample sets in which the number of independent variables is much larger than that of the dependent variables. Overall, the main advantage of PLS-R is the minimization of the overfitting issue obtained with multiple regressions. Multiple linear regression (MLR) and SVM regression are other regression methods that are less used [101]. Nevertheless, SVM has been used to detect adulteration practices in edible bird's nest with satisfactory classification ability [102]. The model validation needs to be performed to demonstrate its feasibility to predict the desirable parameter. This validation procedure can be performed through cross-validation (e.g., leave-one-out cross-validation and k-fold cross-validation) or external validation. The PLS-R models performance is assessed via the correlation coefficient I and determination coefficient ($R^2$) between predicted and measured data, the root mean square error of calibration and the root mean square error of prediction. A good model should have high R2, low root mean square error of calibration, low root mean square error of prediction and a small difference between these two errors [103].

## *4. Conclusions*

The selection of the best analytical and statistical approaches is not an easy task. It will depend on the specific food authenticity issue, since all methodologies present both benefits and disadvantages. In this context and considering the recent reports, analytical technologies as GC-MS, UHPLC-TOF-MS and NMR tandem with PCA and PLS-DA are the most frequently methodologies used to resolve issues related with food authenticity. Although, the use of innovative statistical methods with high classification power (SIMCA and kNN) is growing, it is still necessary the development not only of non-destructive analytical techniques for on-site and real-time procedures, but also “user-friendly” chemometric approaches to guarantee a rapid, simple, and unequivocal food authentication. Likewise, the development of updated and interconnected databases that allow identifying vulnerabilities and containing information about of food authentication markers as well as sophisticated analytical method is also essential to combat food frauds.

# CHAPTER 3. VOLATILE PROFILE

## SECTION 3.1. DEVELOPMENT OF METHODOLOGY FOR VOLATILE FINGERPRINTING

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# Establishment of authenticity and typicality of sugarcane honey based on volatile profile and multivariate analysis

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*Abstract*

SCH is a black syrup produced in Madeira Island widely known for their excellent quality being used in traditional pastry and confectionery. However, its notoriety has been affected by circumstances in which some producers do not guaranty the product quality. The purpose of this study was to establish, for the first time, the volatomic profile of SCH produced by certified and non-certified producers in order to define their authenticity and typicality as useful platform to ensure SCH safety, protect consumer interests and fight the continuous problems of food fraud and adulteration. HS-SPME/GC-MS was applied as high throughput approach for extraction, separation and identification of SCH volatile compounds. The extraction technique was optimized for nature of stationary phase, extraction temperature, extraction time, and validated according with IUPAC and AOAC guidelines. Different volatomic fingerprints for SCH from certified and non-certified producers were recognized, being identified up to 87 VOCs belonging to distinct chemical classes, mainly aldehydes, alcohols, ketones and furans. One-way analysis of variance (ANOVA) analysis showed the existence of 18 VOCs with statistically significant differences between volatile profiles from certified and non-certified producers. PCA and LDA differentiate and discriminate the samples from both type of producers. According to the obtained results, the followed strategy revealed an effective way to establish the authenticity and typicality of SCH, providing useful information to producers that might therefore be used to improve the SCH quality and a powerful platform to promote a European certification application.

Keywords: sugarcane honey, volatile profile, HS-SPME/GC-MS, authenticity, typicality

## 1. *Introduction*

SCH, known as *"mel-de-cana"*, is a black syrup produced from fresh SCs (*Saccharum officinarum L.*) in Madeira Island, Portugal and is part of the historical and cultural patrimony of the Island. The plantations of SC are as old as the first steps made by men in the transformation of the island's landscape. Widely recognized by its excellent quality and unique organoleptic properties, can be used in traditional pastry and confectionery, as well as in cook meat, fish, salads or even used for medicinal purposes. Is a powerful source of proteins, minerals (Fe, Ca, Mg, Cu), vitamins (niacin, riboflavin and thiamin) and fibers. The SCH production process consists of three main steps: (i) cold mechanical pressing of fresh SC stalks to produce SC juice; (ii) filtering and heating procedures followed by another filtering of juice that ensures a flawless rigor in the process of product improvement; and (iii) new heating and filtration of syrup until obtain a viscous and crystalline black syrup. In the last step SC syrup is placed in a reservoir where it sits and cools down naturally. Although syrups, molasses and treacle's are obtained as by-products of SC, their production processes differ greatly which consequently imparts a differentiated chemical composition [104]. Many factors, such as SC cultivars, agricultural treatments, soil and climatic conditions, as well as the manufacturing process, packing and storage conditions should be considered in order to obtain a final product with high quality [105]. The local government created a regional production certification brand in order to distinguish the SCH from others syrups. However, several SCH samples that not followed the traditional production process and/or not used the regional cultivars have been detected on the market, affecting its notoriety.

Food adulteration is a matter of great concern. The use of raw materials of poor quality, additives or inadequate processes, favours to the production of low-quality products [106]. Thus, the implementation of certified quality systems with more transparent and verifiable control in the production and storage processes is essential for food control and guarantee of higher-quality products [107,108]. To ensure the authenticity of local products, such as SCH, the EU introduced legislation that protects the specific geographical origin in addition to the traditional processes of transformation of regional agro-food products. In this context can be assigned three types of certification: PDO, PGI and TSG [107,109,110]. Unfortunately, till now the SCH has no EU certification. The lack of a complete characterization of its physical-chemical and organoleptic characteristics hampers their potential application for certification. Thus, it is of outmost importance develop tools for characterizing the SCH allowing EU certification and providing a stricter control of authenticity on the market.

Recent developments of advanced analytical strategies in food science play a crucial role in investigation of topics considered unapproachable few years ago. In this context, the study of genomic, transcriptomic, proteomic, and/or metabolomic in agro-food areas leaded to a new discipline, the Foodomics [111–113], which appears as a new approach to solve some of the new challenges that modern food safety, quality, traceability and authenticity, have to face [111,114].

One of recent approaches of Foodomics supported on MS-based techniques is the establishment of the volatomic profile of food and food-related products. This approach is based on the identification of VOCs established on their unique mass fragments spectrum. The VOCs play a relevant role in agro-food science, being responsible for the sensory characteristics (aroma and flavor) of food products, allowing not only to assess the geographical origins, but also determine the product quality and authenticity [105,115,116]. Although, some VOCs identified in SC juice are also present in SC heated-products (molasses and treacle's), most of VOCs are produced by non-enzymatic browning reactions (NEBRs) via Maillard reaction (MLDRs), Strecker degradation (STKD) and caramelization, during heating of the syrup and by microbial activity on sugary components during storage [117–120].

Thus, the exclusive use of regional SC cultivars, its cultivation under specific soil and climatic conditions of Madeira Island, the use of traditional production processes with predefined temperatures and times, and the storage conditions established by government entities, gave rise to similarities in VOCs that might create a “fingerprint” of SCH, allowing its authentication. Furthermore, the establishment of volatile profile is a widely used approach in food industry for determining the geographical origin, evaluate the product authenticity and detection of adulterations from various food products [110,121–125]. Verzera et al. [126] used HS-SPME/GC-MS to show the importance of chiral volatile compounds for the determination of orange honey authenticity, while Condurso et al. [127,128] reported the useful of volatiles for the characterization of capers from different geographic origin. In addition, Nicolotti et al. [109,116] determined the quantitative fingerprinting of food matrices using divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) coating. Oliveira et al. [106] reported the multivariate class modelling for the verification of food-authenticity claims, whereas Beltrán et al. [121] carried out the monitoring of the oxidation of almond oils and applied the volatile compounds for determination cultivar authenticity. Furthermore, Cajka et al. [129] used HS-SPME/GC-MS on the recognition of beer brand based on multivariate analysis of volatile fingerprint obtained by SPME/GC-MS.

The aim of this study was to establish the volatomic composition of SCH obtained from certified, non-certified and homemade producers by HS-SPME/GC-MS, in order to develop a useful approach to establish its authenticity and typicality as a tool to protect consumer interests and to prevent frauds and adulteration that affect its notoriety The HS-SPME technique was optimized by univariate experimental design based on fiber coating, extraction temperature and extraction time parameters. The analytical methodology was validated according with IUPAC [130] and AOAC [131] guidelines. The existence of VOCs with statistically significant differences between different producers was assessed by one-way ANOVA test. The differentiation and discrimination patterns between volatile components from certified, non-certified and homemade producers based on volatomic pattern was performed by PCA and LDA, respectively.

## *2. Materials and methods*

### *2.1. Materials and reagents*

Sodium chloride was obtained from Panreac (Barcelona, Spain); 2,3-butanedione, hexanal and decanal were purchased from ACROS Organics (Geel, Belgium), whereas furfural, 1-(2-furanyl)-ethanone, 2-furanmethanol, 2-methyl-1-propanol, 2-methyl-1-butanol and 4-heptanone were purchased from Sigma-Aldrich (St. Louis, Missouri, USA). SPME holder for manual sampling of SPME fiber and the respective five fibers, namely the divinylbenzene/carboxen/polydimethylsiloxane, with 50/30 μm film thickness (DVB/CAR/PDMS), carboxen/polydimethylsiloxane with 75 μm film thickness (CAR/PDMS), polydimethylsiloxane/divinylbenzene with 65 μm film thickness (PDMS/DVB), polydimethylsiloxane with 100 μm film thickness (PDMS), and polyacrylate with 85 μm film thickness (PA) were purchased from Supelco (Bellefonte, PA, USA).

### *2.2. Samples*

SCH samples (N = 16) were picked at Madeira Island, Portugal. Eight samples were obtained from a certified producer, four were obtained from non-certified producer and four from a homemade producer. Commercial SCH samples from certified producer were collected at FMCRS in April 2013, 2014 and 2015, Madeira Island, Portugal, being stored in factory facilities until further analysis. SCH samples from the non-certified producer were purchased in May 2015, while SCH samples from homemade producer were purchased in April 2015. Sample name, code, production type, production year, geographical area and authenticity certification are presented in Table S3. (All SCH samples were stored under stable conditions at 4 °C) until analysis.

*2.3. SPME procedure*

VOCs extraction from SCH samples was performed using a SPME fiber attached to a manual HS-SPME holder. The effect of sample dilution was tested (1:1, 2:1 and 3:2 w/v) in order to avoid problems related with sample viscosity and thus obtain reproducible results. Based on the results (data not shown), the ratio 3:2 in sample dilution showed good reproducibility and precision. Thus, all samples were previously diluted using 15 g of SCH in 10 mL of deionized water ($H_2O^d$) and stored at 4 °C in aliquots of 5 ml. For each analysis, these aliquots were placed into an 8 mL glass vial, followed by addition of 60 mg NaCl to increase ionic strength of the sample. Under magnetic agitation (600 rpm), the SPME fiber was exposed in the sample HS according the optimum extraction parameters. The target compounds extracted by SPME were thermally desorbed by inserting the fiber directly into the GC injector at 250 °C in splitless mode for 10 min. Triplicate analysis were performed for all experiments. Blanks, corresponding to the analysis of coating fibers that were not submitted to any extraction procedure, were run between sets of three analysis.

The optimization of HS-SPME technique was performed by application of univariate experimental design on three experimental parameters with influence in extraction efficiency, namely the fiber coating, extraction temperature and extraction time [132,133]. The selection of fiber coating was based on extraction efficiency of each available fiber, namely DVB/CAR/PDMS, CAR/PDMS, PDMS/DVB, PDMS and PA. The fibers were conditioned before use by insertion into the GC injector, as recommended by the manufacturer instructions. The dependence of the extracted number of VOCs on the extraction temperature and extraction time was studied using sorption temperatures between 30 and 80 °C for different times 30, 45, 60 and 75 min. The optimum extraction parameters conditions were selected based on number of identified compounds, total peak area (TPA) and reproducibility. The optimized conditions were used for next all experiments.

*2.4. GC-MS conditions*

The Agilent Technologies 6890N Network GC system (Santa Clara, California, USA) was equipped with a 60 m × 0.25 mm I.D. × 0.25 μm film thickness, BP-20 (SGE, Dortmund, Germany) fused silica capillary column and interfaced with an Agilent 5975 quadrupole inert mass selective detector (Santa Clara, California, USA). It was employed the following chromatographic protocol for separation before MS analysis: 40 °C for 2 min, then was increased at 0.25 °C $min^{-1}$ until 45 °C with a 2 min hold, after was increased at 4 °C $min^{-1}$ to 70 °C with a 2 min hold, was increased again at 3 °C $min^{-1}$ to 130 °C with a 2 min hold, and finally, was increased at 3 °C $min^{-1}$ to 220 °C, this final temperature was maintained during 7 min, for a total GC run

time of 91.25 min. Column flow was constant at 1 mL min-1 using He (Helium N60, Air Liquid, Portugal) as carrier gas at a purity of 99.999%. The injection port was operated in the splitless mode and held at 250 °C. For the 5975 MS system, the operating temperatures of the transfer line, quadrupole and ionization source were 270, 150 and 230 °C respectively; electron impact mass spectra were recorded at 70 eV ionization voltages and the ionization current was 10 μA. The acquisitions were performed in Scan mode (30-300 m/z). The electron multiplier was set to the auto tune procedure. Compound identification was accomplished through manual interpretation of spectra and matching against the Agilent MS ChemStation Software, equipped with a NIST05 mass spectral library with a similarity threshold higher than 75% and comparison with commercially standards when available. The results are presented as relative peak area (RPA), which were calculated by dividing the TPA values of VOCs by the TPA value of internal standard (IS).

### *2.5. Analytical method validation*

The analytical method was validated for the following parameters: calibration function and linearity, precision, accuracy, matrix effect, ruggedness, limits of detection (LOD) and quantitation (LOQ), according to recommendations from literature [134,135], IUPAC [130] and AOAC [131] guidelines. In order to obtain a comprehensive validation of the analytical method, we selected the most abundant and representative volatiles for each chemical group identified in SCH samples: 2,3-butanedione (ketones), 2-methyl-1-propanol and 2-methyl-1-butanol (alcohols), hexanal and decanal (aldehydes), furfural, 1-(2-furanyl)-ethanone and 2-furanmethanol (furans). 4-Heptanone was selected as IS. Standards and IS stock solutions were prepared daily by adding a specific volume of each standard into a flask with $H_2O^d$ to a total volume of 50 mL. A certified SCH sample, coded as FRS14A1, was used for validation proposes. The HS-SPME extractions were performed as described previously using 5 mL of each standard solution. All analysis were performed in triplicate.

#### *2.5.1. Calibration function and linearity*

The calibration function was constructed through the standard calibration curves prepared with six different concentrations of each standard used. The concentration range is shown in Table 1. Each concentration was performed in triplicate at different days in a random order. The calibration curves were constructed by plotting the RPAs versus concentration, giving the values of slope along with the intercept and correlation coefficient for each calibration curve. The test of suitability of a linear or non-linear function model obtained from calibration curves was evaluated by estimation of purely experimental variance and lack-of-fit variance error sum squares, and Fisher variance ratio (F-test).

*2.5.2. Precision and accuracy*

The precision was determined by repeatability and intermediate precision of the analytical method, measuring the inter- and intra-day variation, respectively. The intra-day variation was determined by assaying ten replicates on the same day of the sample under study, and inter-day variation was performed by assaying four replicates during three days. The precision was expressed as the percentage of % RSD. The accuracy was determined through percentage of recovery. The recovery was obtained by comparing the known theoretical concentration added to sample ($C_{theoretical}$) with the experimental concentration ($C_{experimental}$) of standards in a sample spiked at low, medium and high concentrations levels. The $C_{experimental}$ was calculated by difference between the peak areas of the standards in spiked sample and the peak areas from sample without spiking. The concentration range is shown in Table 2. The recovery was calculated using the following equation:

$$\% \text{ recovery} = (C_{experimental}/C_{theoretical}) \text{ x } 100$$

*2.5.3. Ruggedness and matrix effect*

The ruggedness was tested by deliberately introducing of small changes to the extraction procedure and examining the effect on the results. The extraction temperature was changed to 58 and 62 °C, and extraction time was changed to 58 and 62 min. The % RSD obtained from changed parameters were compared with the results from extraction performed with optimized parameters. The matrix effect was determined by applying the method of "standard additions" to a sample under study, which was calculated by comparison of the slopes obtained by calibration curves of standards in sample and solvent-based matrix ($H_2O^d$). The calibration functions for both matrixes were constructed on similar way, the standard calibration curves were prepared with six different concentrations of each standards used. The concentration range is shown in Table 2. The matrix effect was calculated using the following equation:

$$\text{Matrix effect} = (\text{Slope}_{Sample}/\text{Slope}_{Solvent}) \times 100$$

*2.5.4. LOD and LOQ*

The approach used to estimate LOD and LOQ is based on the quotient of two analytical parameters of calibration function, namely the standard deviation (σ) of the intercept of calibration curve and the slope of a regression curve. The LOD and LOQ were calculated using the following equations:

$$\text{LOD} = 3.3 \times \sigma/\text{slope} \qquad \text{LOQ} = 10.0 \times \sigma/\text{slope}$$

*2.6. Statistical analysis*

Data processing was performed using the IBM SPSS 22.0 Statistics software (Armonk, NY, USA) and the StatSoft STATISTICA 12.0 (2013) software (Tulsa, OK, USA). Comparison of means of RPAs was achieved by ANOVA in order to determine those VOCs that are significant in differentiating of certified and non-certified samples of SCH. PCA and LDA were carried out on RPAs of VOCs selected by ANOVA to evaluate differences among the studied groups. For LDA analysis a backward selection method was used with a $p < 0.05$. For CV a leave-one-out strategy was used.

## *3. Results and discussion*

*3.1. HS-SPME optimization*

The HS-SPME is recommended for volatile extraction and have been routinely used for several years in volatile profiling of processed food products, such as wine [136], beer [129], liquors [123], vinegar [124] and honeys [122,126]. The HS mode comparing with immersion mode, enables that the VOCs be recovered from vapor phase above the sample, protecting the fiber from damages caused by components of sample matrix and excluding possible interferences from own sample or from the adjustment of extraction conditions (ex. salt addition or pH adjustment) [122,137]. However, some parameters, such as fiber coating, extraction temperature and extraction time, have a great influence in extraction efficiency of HS-SPME and they must be necessarily optimized. For these reasons, these parameters were optimized in this study.

The fiber coating is one of the most important parameters in the HS-SPME extraction efficiency, since this is based on the equilibrium distribution of compounds between the sample and extraction phase (fiber). The matrix effect of each coating is determined by its corresponding polarity and affinity for the target compounds [133]. The most common fiber coatings are PA, PDMS and DVB, and are available in a single type of coating (PA and PDMS), or a mixture of coatings (CAR/PDMS, PDMS/DVB and DVB/CAR/PDMS). PDMS coating is recommended to the analysis of nonpolar compounds, whereas PA is more suitable to extract the polar ones. Although does not exist DVB available in single mode, is also a polar porous solid coating and consequently efficient in extracting polar compounds such as disulfides and trisulfides. The mixed coatings provide high extraction efficiencies for a wide range of compounds with

different polarities and molecular weights [137,138]. The selection of fiber coating was performed based on the number of VOCs identified, TPA and reproducibility. The results are presented in Figure 4.

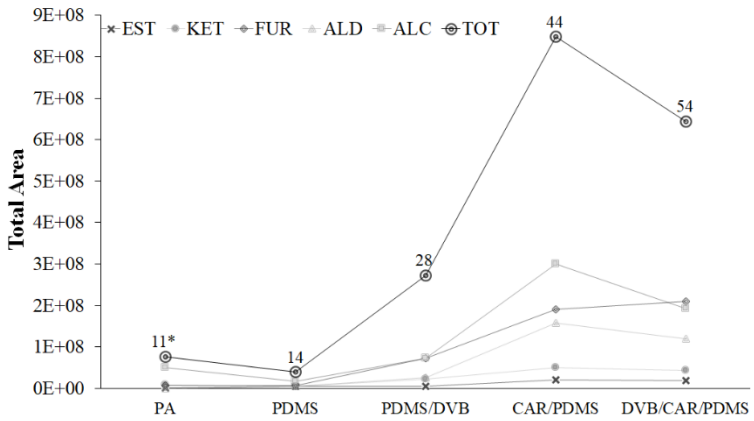


**Figure 4. The influence of the fiber coating on the HS-SPME efficiency.**

Among the tested fibers the extraction efficiency of SCH volatiles follows the order: DVB/CAR/PDMS (54) > CAR/PDMS (44) > PDMS/DVB (28) > PDMS (14) > PA (11), while the TPA decreased in the following order: CAR/PDMS > DVB/CAR/PDMS > PDMS/DVB > PA > PDMS. Although, CAR/PDMS present the highest TPA, influenced mainly by alcohols and aldehydes, DVB/CAR/PDMS has a significantly high number of identified compounds compared to CAR/PDMS, namely furans (e.g. 2,2'-methylenebis[5-methyl-furan and 5-(hydroxymethyl)-2-furancarboxaldehyde), aldehydes (e.g. nonanal, decanal and benzaldehyde) and alcohols (e.g.1-octanol and phenylethyl alcohol). This result can be explained by the fact that DVB/CAR/PDMS has a triple coating, while CAR/PDMS has only two coating types, wherein the large affinity of DVB coating for polar compounds gives the DVB/CAR/PDMS an excellent ability to the extraction of polar compounds such as alcohols, aldehydes, ketones and esters. Based on obtained results DVB/CAR/PDMS was selected for further assays. Several studies [109,116,118,122,126–128] reported the wide use of DVB/CAR/PDMS coating to establish the volatile composition of several foods, verify food authenticity and characterize food products from different geographic origin.

The extraction time is a key parameter to optimize the effectiveness of HS-SPME. An optimal approach is to allow the analyte to reach the equilibrium between the sample and the fiber coating. A time profile of the sorption of SCH was determined using extraction times of 30, 45, 60 and 75 min at 40 °C using DVB/CAR/PDMS fiber. The results are shown in Figure 5.

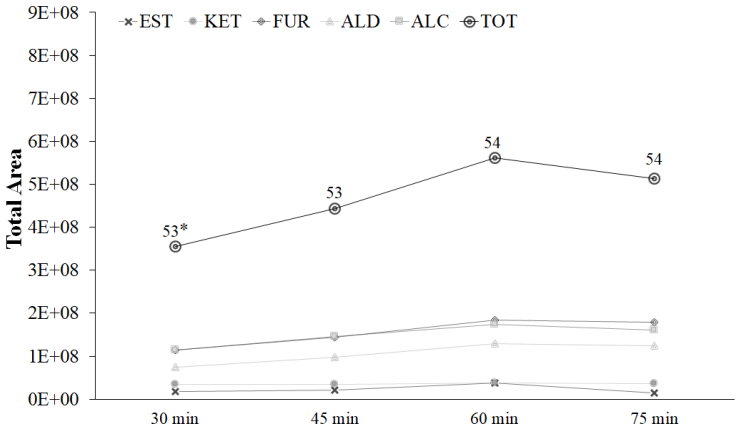


**Figure 5. The influence of the extraction time on the HS-SPME efficiency.**

It is observed that a typical sorption profile consists of an initial rapid partitioning followed by a slower uptake and finally a steady-state equilibrium between the fibre and the vapor phase of the analyte. The number of identified VOCs does not change significantly among the studied extraction times. The peak area increases from 30 to 60 min and remain almost constant till 75 min. However, some VOCs do not follow this trend, namely esters (ethyl acetate, phenylmethyl acetate and 2-phenylethyl acetate) and alcohols (2-methyl-1-propanol and 1-octanol) for which the peak areas decreased for extraction times higher than 60 min. According to the obtained results 60 min was the extraction time selected for further analysis. Long extraction times are inappropriate, since it might lead to sample deterioration by enzymatic and/or physical-chemical reactions, which can result in changes on volatile profile. On the other hand, small extraction time favours the extraction of volatiles compounds comparing to semi-volatiles.

The extraction temperature is also a critical parameter on extraction efficiency of HS-SPME. Low extraction temperatures will increase the retention of compounds with high volatility while high temperatures will lead to an increase of the sorption efficiency of semi-volatile compounds [122]. The optimization of extraction temperature was performed using sorption temperatures between 30 and 80 °C for an extraction time of 60 min using DVB/CAR/PDMS using sorption temperatures between 30 and 80 °C for different times 30, 45, 60 and 75 min. The results are showed in Figure 6.

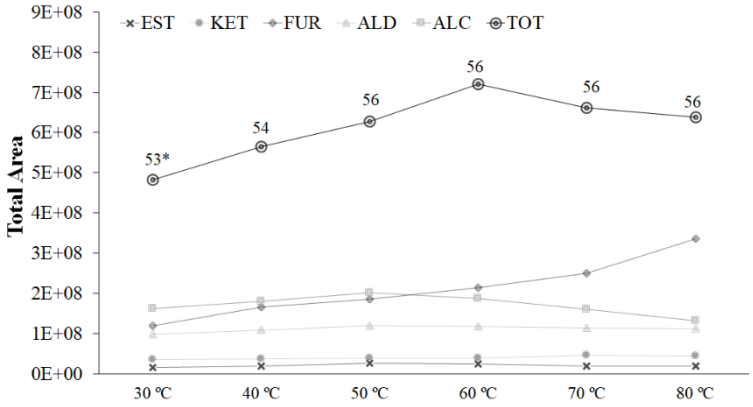


**Figure 6. The influence of the extraction temperature on the HS-SPME efficiency.**

The number of identified VOCs significantly increased between 30 °C (53) and 60 °C (56), and remained constant until 80 °C. The phenylethyl alcohol was identified only at extraction temperatures higher than 40 °C, while 2,5,5-trimethyl-1-cyclopenten-1-one and 1-decene were identified only above 50 °C. The TPA from identified VOCs presents a slight increase from 30 °C to 60 °C, following a little decrease until 80 °C. The results indicate that the maximum of extraction effectiveness was reached at final temperature of 60 °C. Furthermore, in case of samples with large amounts of SGs, such as SCH, an intermediate temperature should be adopted in order to avoid sample degradation and production of undesirable compounds by thermal degradation. Although most of VOCs from SCH, molasses and treacle are products from MLDRs, STKD and caramelization, the continuous exposure of sample to high temperatures can form new degradation products, changing the real volatile profile of SCH samples [118,119]. Thus, using an extraction temperature of 60 °C for 60 min and DVB/CAR/PDMS as coating provides a good equilibrium between fiber sorbent and volatile faction, leading to an effective and robust extraction of VOCs from SCH samples.

*3.2. Analytical method validation*

The validation is an essential step for development of an analytical method which is intended to produce accurate and precise results with adequate strength to be used as a reliable tool for routine analysis [135]. In order to verify the analytical performance of the analytical method, calibration function and linearity, precision, accuracy, matrix effect, ruggedness, LOD and LOQ, were determined.

The calibration function and linearity were evaluated for a representative range of standard concentrations. The calibration curves were plotted as RPA vs concentration, giving the function model and correlation coefficient for each calibration curve. The F-test was performed in order to check the suitability of function model. The results are summarized in Table 1.

The correlation coefficient, in linear function model, ranging between 0.9621 (2-furanmethanol) and 0.9989 (decanal). Apparently, the developed analytical method showed a good linear correlation. However, the results of F-test revealed that linear function model is not suitable to describe the observed data due to some significant lack of fit, since the ratio Ftheo/Fexp values are less than 1.0 for all target standards. Alternatively, a polynomial function model is proposed to describe the data obtained from the calibration curve. According to the literature data [135], the use of polynomial standard curves (y = a × 2 + b ×  + c) are recommended for a wide range of concentrations. The correlation coefficient values obtained from polynomial function model are higher than 0.9991 (2-methyl-1-butanol). In addition, results obtained for the F-test (ratio $F_{theo}/F_{exp} > 1.0$) indicates that the polynomial function is adequate to describe the concentration-response relationship of HS-SPME/GC-MS analytical methodology.

The results for precision, accuracy, matrix effect, ruggedness, LOD and LOQ are summarized in Table 2. The precision was very satisfactory (RSD < 14 %), with values below the maximum described in guidelines (15 %) [130,131]. The repeatability values ranged from 2.7 to 8.1% and the intermediate precision values varied between 3.2 and 13.6%, wherein the lowest value was obtained for decanal and the highest for 2-furanmethanol. The analytical method also showed good values for recovery for all standards, ranging between 86.4 (2-methyl-1-propanol) and 107.6 (2-furanmethanol), being within acceptable recovery limits from literature guidelines (70-125%) [130,131]. The matrix effect was determined through standard additions method. From the obtained results it can be assumed that there is a slight matrix effect with values ranging between 79.2% (furfural) and 114.6% (2-methyl-1-butanol). Considering the high complexity of the SCH samples the effect of matrix is insignificant. The ruggedness was estimated by introduction of small changes in extraction temperature (−/+2 °C) and extraction time (−/+2 min). A slight variation in these experimental parameters has no remarkable influence on analytical response which reveal the ruggedness of the extraction procedure. The determination of LOD and LOQ was based on the standard deviation and the slope of a regression curve for each standard. The results expressed in μg $Kg^{-1}$, are showed in Table 2. The lowest LOD and LOQ was for decanal, hexanal and benzaldehyde, ranging from 0.17-0.36 μg $Kg^{-1}$ and 0.51-1.08 μg $Kg^{-1}$, respectively. On the other hand, the highest values were for 2-furanmethanol with a maximum of 21.78 μg $Kg^{-1}$ (LOD) and 66.01 μg $Kg^{-1}$ (LOQ).

**Table 1. Calibration function and linearity results.**

| RT (min)[a] | VOCs | Concentration Range (µg $L^{-1}$) | Linear | | | | Polynomial | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Regression Equation | Correlation Coefficient ($r^2$) | $F_{exp}$ Value[b1] | Ratio[c1] $F_{theo}/F_{exp}$ | Regression Equation | Correlation Coefficient ($r^2$) | $F_{exp}$ Value[b2] | Ratio[c2] $F_{theo}/F_{exp}$ |
| 10.58 | 2,3-Butanedione | 5.0 - 495.0 | y = 0.0030x + 0.1162 | 0.9914 | 27.0 | -23.9 | y = -2E-06$x^2$ + 0.0041x +0.0554 | 0.9996 | 3.1 | 0.4 |
| 17.05 | Hexanal | 1.6 - 163.0 | y = 0.0352x + 0.2237 | 0.9902 | 143.6 | -140.5 | y = -8E-05$x^2$ + 0.0479x + 0.0197 | 0.9994 | 1.4 | 2.1 |
| 22.24 | 2-Methyl-1-propanol | 40.1 - 4010.0 | y = 0.0012x + 0.5740 | 0.9704 | 935.3 | -932.2 | y = -2E-07$x^2$ + 0.002x + 0.1918 | 0.9998 | 3.0 | 0.5 |
| 31.82 | 2-Methyl-1-butanol | 4.1 - 408.0 | y = 0.0187x + 0.9527 | 0.9705 | 1303.8 | -1300.7 | y = -3E-05$x^2$ + 0.0309x + 0.3659 | 0.9991 | 2.4 | 1.1 |
| 48.17 | Furfural | 5.8 - 580.0 | y = 0.0045x + 0.1030 | 0.9949 | 120.5 | -117.4 | y = -2E-06$x^2$ + 0.0056x + 0.0239 | 0.9995 | 3.0 | 0.5 |
| 49.81 | Decanal | 1.7 - 166.0 | y = 0.0306x + 0.0519 | 0.9989 | 3.9 | -0.8 | y = -2E-05$x^2$ + 0.0335x + 0.0046 | 0.9995 | 3.4 | 0.1 |
| 50.05 | 1-(2-Furanyl)-ethanone | 21.6 - 2160.0 | y = 0.0057x + 0.6381 | 0.9859 | 303.2 | -300.1 | y = -1E-06x2 + 0.008x + 0.0623 | 0.9999 | 2.1 | 1.4 |
| 50.83 | Benzaldehyde | 2.1 - 209.0 | y = 0.0099x + 0.0539 | 0.9965 | 71.6 | -68.5 | y = -1E-05$x^2$ + 0.012x + 0.0105 | 0.9997 | 1.3 | 2.2 |
| 57.34 | 2-Furanmethanol | 113.0 - 11300.0 | y = 0.0001x + 0.1386 | 0.9621 | 9221.7 | -9218.6 | y = -7E-09$x^2$ + 0.0002x + 0.0200 | 0.9994 | 1.0 | 2.5 |

[a] Retention time (minutes) in ion chromatograms obtained by GC-MS.
[b1] The Fisher value calculated experimentally with 12 degrees of freedom of experimental error and 4 degrees of freedom of lack of fit of function.
[b2] The Fisher value calculated experimentally with 12 degrees of freedom of experimental error and 3 degrees of freedom of lack of fit of function.
[c1] The Fisher value calculated experimentally is compared against the critical value of Fisher theoretical at the 95% with 12 degrees and 4 of freedom degrees. If the experimental data set describes a proposed function calibration of the form given then the condition $F_{theo.} > F_{exp}$ must be fulfilled.

**Table 2. Accuracy, precision, ruggedness, matrix effect, LOD and LOQ results.**

| RT (min)[a] | Compounds | Concentration range (µg/L) | Accuracy | Precision | | Ruggedness | | Matrix Effect (%) | LOD (µg/Kg) | LOQ (µg/Kg) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Recovery (%) | Repeatability (% RSD) | Intermediate Precision (% RSD) | Time (% RSD) | Temperature (% RSD) | | | |
| 10.58 | 2,3-Butanedione | 5.0[LL] | 86.5 | 3.9 | 6.8 | 7.5 | 4.4 | 96.8 | 0.91 | 2.75 |
| | | 49.5[ML] | 93.8 | | | | | | | |
| | | 198.0[HL] | 96.8 | | | | | | | |
| 17.05 | Hexanal | 1.6 | 93.2 | 3.4 | 5.0 | 7.2 | 1.1 | 100.9 | 0.23 | 0.71 |
| | | 16.3 | 99.7 | | | | | | | |
| | | 81.4 | 100.7 | | | | | | | |
| 22.24 | 2-Methyl-1-Propanol | 40.1 | 86.4 | 4.2 | 9.1 | 8.3 | 1.2 | 106.3 | 0.17 | 0.51 |
| | | 401.0 | 94.8 | | | | | | | |
| | | 1604.0 | 96.2 | | | | | | | |
| 31.82 | 2-Methyl-1-Butanol | 4.1 | 91.2 | 2.9 | 4.9 | 7.2 | 5.6 | 114.6 | 0.36 | 1.08 |
| | | 40.8 | 95.7 | | | | | | | |
| | | 163.0 | 97.1 | | | | | | | |
| 48.17 | Furfural | 5.8 | 99.8 | 4.7 | 9.0 | 7.5 | 1.9 | 79.2 | 0.49 | 1.48 |
| | | 58.0 | 103.5 | | | | | | | |
| | | 232.0 | 105.2 | | | | | | | |
| 49.81 | Decanal | 1.7 | 95.7 | 2.7 | 3.2 | 8.6 | 7.7 | 82.6 | 2.86 | 8.65 |
| | | 16.6 | 96.7 | | | | | | | |
| | | 83.0 | 100.1 | | | | | | | |
| 50.05 | 1-(2-Furanyl)-Ethanone | 21.6 | 99.8 | 5.0 | 7.2 | 10.0 | 2.6 | 79.6 | 1.13 | 3.43 |
| | | 216.0 | 100.8 | | | | | | | |
| | | 1080.0 | 107.0 | | | | | | | |
| 50.83 | Benzaldehyde | 2.09 | 91.0 | 3.1 | 5.7 | 9.0 | 2.2 | 101.3 | 21.78 | 66.01 |
| | | 20.9 | 98.9 | | | | | | | |
| | | 104.4 | 100.4 | | | | | | | |
| 57.34 | 2-Furanmethanol | 113.0 | 98.5 | 8.1 | 13.6 | 4.3 | 4.5 | 112.9 | 1.24 | 3.75 |
| | | 1130.0 | 102.8 | | | | | | | |
| | | 5650.0 | 107.6 | | | | | | | |

[a] Retention time (minutes) in ion chromatograms obtained by GC-MS.
[LL] Concentration of compound in low level.
[ML] Concentration of compound in medium level.
[HL] Concentration of compound in high level.

*3.3. Establishment of volatile profile from SCH*

The application of HS-SPME/GC-MS method with optimal experimental conditions and validated parameters to sixteen SCH samples allowed the identification of 87 VOCs from a wide of chemical classes, namely alcohols, aldehydes, carboxylic acids, furans, esters, ketones, nitrogen compounds, phenols, sulfur compounds and terpenoids. The NIST database and common names, ID number, CAS number, abbreviations, molecular formula and retention time (RT) of identified VOCs are described in Table S4. The average peak areas, % RSD and chemical classes of identified VOCs for each SCH sample are summarized in Table S5. The chemical classes with highest contribution for the volatile profile of SCH samples from certified and non-certified producers are alcohols, aldehydes, esters, furans and ketones, following this order. Alcohols contribution is strongly influenced by high abundance of ethanol and some higher alcohols namely 2-methyl-1-propanol, 2-methyl-1-butanol and 3-methyl-1-butanol. The 2-methyl-propanal, 2-methyl-butanal and 3-methyl-butanal are the VOCs in more abundance for aldehydes. Ethyl acetate is clearly the most abundant VOC for esters, followed by phenylmethyl acetate and 2-phenylethyl acetate in lesser amounts. The most abundant furans are dihydro-2-methyl-3(2H)-furanone and 1-(2-furanyl)-ethanone, whereas 1-(1H-pyrrol-2-yl)-ethanone and 1-hydroxy-2-propanone are most representative ketones to SCH volatile profile.

Due to the wide variability of volatile profiles obtained for SCH samples under study, only 33 of 87 VOCs identified are common to all SCH samples, three volatile compounds were exclusively identified in the samples of certified producer while 28 volatiles in samples of non-certified producer. The fragment ion m/z values with the highest abundance within each fragmentation pattern, identification mode, abundance match according to the NIST database, peak area range (minimum, maximum and mean values) and percentage of occurrence frequency of identified VOCs are listed in Table S6.

Most of VOCs identified in the volatile profile of SCH samples were reported previously in SC-related products, such as juice [139,140], brown sugar [141], molasses [142] and treacle [118]. Although being obtained through different production processes, their volatile profiles have similarities and derive mainly from the SC, production process and storage process [143]. Some volatile compounds are crucial in pollination, plant-plant signaling and protection against abiotic (ex. high light, temperature, oxidative stress stresses) and biotic stress (ex. herbivores, pathogens) [144]. Although, there are no studies conducted on the VOCs composition of SC, the raw juice has the most representative VOCs from the plant. Interestingly, 18 of VOCs recognized on SCH samples were reported previously in SC juice, such as alcohols (ethyl

alcohol, 2-methyl-1-propanol, 3-methyl-1-butanol and benzyl alcohol), aldehydes (3-methyl-butanal, hexanal, heptanal, octanal, 2-heptenal, nonanal and benzaldehyde), esters (ethyl acetate and ethyl ester butanoic acid) and terpenoids (d-limonene, 1-methyl-4-(1-methylethyl)-benzene and α,α-4-trimethyl-3-cyclohexene-1-methanol), phenols (phenol) and sulfur compounds (dimethyl sulfide) [139,140]. An important source of VOCs in SCH is formed during the storage processes through the so-called browning reactions (BRs) and microbial activity.

BRs, are some of the most important phenomena for the formation of aroma and flavor in food, and occurs mainly via two pathways: enzymatic and non-enzymatic processes. The enzymatic browning reactions (EBRs) usually occurs via oxidation of food components (e.g. carbohydrates (CBHs), proteins and lipids) in storage of raw plant related-products, such as SC juice, as consequence of polyphenol oxidase and phenol peroxidase enzymes action on polyphenols that leads to the quinones formation [145]. However, for SC-related products that undergo heat processing, such as syrups, molasses and treacle's, the EBRs are hampered by high temperatures used in production process that leads to inhibition of most enzymes. In addition, some thermal degradation products (from MLDRs) have also ability to retard lipid oxidation and to inhibit certain oxidoreductases such as oxidase, peroxidase, superoxide and hydrolase activity [146]. On the other hand, the NEBRs are responsible for the formation of a large number of VOCs. The NEBRs of heated-sugary products primarily occurs through the thermal degradation by MLDR, STKD and caramelization. All of these reactions have various interactions between them and always involves the degradation of reducing SGs, especially of glucose (GLU) and fructose (FRU) from the sucrose (SUC) hydrolysis. The MLDRs occurs between reducing SGs and compounds possessing a free amino group (e.g. AA, peptide, protein) promoted at high temperatures (70-110 °C) that promotes the formation of melanoidins and low molecular weight compounds [147]. The volatiles arising from MLDRs are essentially formed by three pathways: sugar dehydration/fragmentation, AA degradation and further condensation of the formed products. The sugar dehydration/fragmentation compounds are products of the reactions by the breakdown of the Amadori or Heynes intermediates, such as furans, pyrones, cyclopentenes, dicarbonyl compounds and acids. The AA degradation compounds result from the STKD occurring between amino acids (AAs) and α-dicarbonyl compounds (such as aldehydes), sulfur and nitrogen-containing compounds. Finally, these products are able to reactions at subsequent stages of the MLDRs producing pyrroles, pyridines, pyrazines, imidazoles, oxazoles, thiazoles, thiophenes, dithiolanes, trithiolanes, dithianes, trithianes and furanthiols [117–119]. Additionally, some VOCs, such as furans, can be released upon the

thermal degradation of melanoidins in late stages of MLDRs [147]. Several volatiles compounds from Maillard and Strecker reactions were identified in SCH samples under study, namely aldehydes (acetaldehyde, benzaldehyde, 2-methyl-propanal, 2-methyl-butanal and 3-methyl-butanal), furans (furfural, 1-(2-furanyl)-ethanone, 2-furanmethanol and 5-(hydroxymethyl)-2-furancarboxaldehyde), nitrogen compounds (2,6-dimethyl-pyrazine and 2,3,5-trimethyl-pyrazine) and carboxylic acids (acetic acid) [117]. Another source of VOCs from SC related-products could be the microbial activity of yeast and bacteria. The microbial activity on food products normally occurs by transformation of SGs into simple acids, alcohols and carbon dioxide through primary carbon metabolism of fermenting microbes [148]. Several VOCs recognized previously from fermentation were identified in SCH samples, namely alcohols (ethyl alcohol, 2-methyl-1-butanol, 3-methyl-1-butanol and phenylethyl alcohol), carboxylic acids (acetic acid, also identified as MLDRs product), esters (2-phenylethyl ester acetic acid) and sulfur compounds (dimethyl sulfide) [118,120]. Although still remain undiscovered the origin of some VOCs identified in our study, the results suggest that the SCH volatile profile is highly influenced by raw materials, production process and storage. Therefore, similarities in these conditions can result in similar volatile profiles. On the other hand, different conditions cause large differences in volatile profile. Thus, the establishment of volatile profile might be a useful approach for distinguishing SCH samples according to type of producer.

### *3.4. Statistical analysis of volatile profile from SCH*

The potential of volatile profiling as useful approach to establishment of authenticity and typicality of SCH was evaluated through application of statistical analysis.

The One-way ANOVA ($p < 0.05$) was performed in order to determine the VOCs with statistically significant differences between samples from certified and non-certified producers. Eighteen of identified VOCs showed statistically significant differences. The significance values (p and Z parameters), mean peak

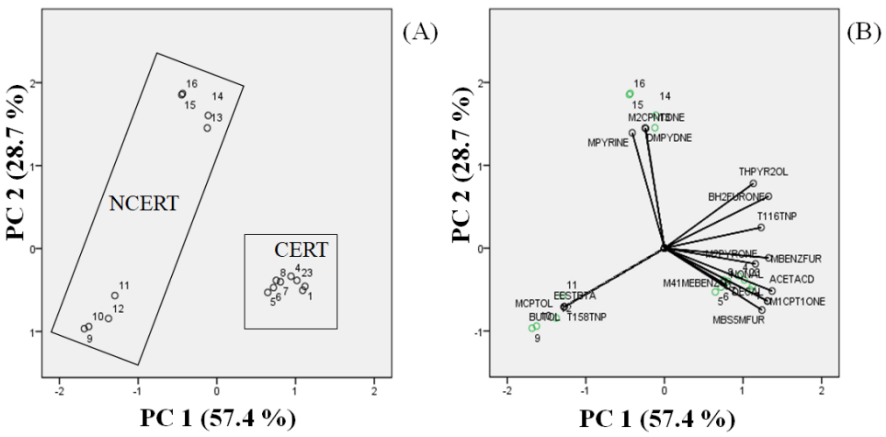


**Figure 7. The PCA score plot of all samples (A) and the 18 selected VOCs (B).**

areas and percentage of change between producers are summarized in Table S7. The VOCs with lowest p-values are acetic acid, 2,2'-methylenebis[5-methyl-furan and 1-(2-methyl-1-cyclopenten-1-yl)-ethanone. The former VOCs were previously identified in SC heated-products, namely brown sugar [141], molasses [142] and treacle [118]. The 1-(2-methyl-1-cyclopenten-1-yl)-ethanone was identified for the first time in heated-SC products, being present only in the volatile profile of certified samples. Seven of 18 VOCs, namely ethyl ester butanoic acid, 1-butanol, 3-methyl-pyridazine, 4,6-dimethyl-pyrimidine, 3-methyl-cyclopentanol, 2-methyl-2-cyclopenten-1-one and 1,2,3,4-tetrahydro-1,5,8-trimethyl-naphthalene, were identified exclusively in samples from non-certified producers. Among the identified VOCs, nonanal (83.1%) showed the major difference between SCH of certified and non-certified producers. This compound was previously reported in SC juice [139,140] and brown sugar [141]. Eighteen VOCs with significant differences between producers were submitted to a PCA in order to obtain differentiation between samples according to production process (certified vs non-certified). The PCA score plot of the samples and score plot of the samples including variables (VOCs) are showed in Figure 7 (A) and (B), respectively.

The PCA score plot of SCH samples showed a good separation between certified producer and non-certified producers, generated by two principal components (PC1 and PC2) that explain 86.1% of the total variance (TVA). Moreover, it is possible to observe in Figure 7 (A) the presence of well-defined clusters belonging to certified (CERT), non-certified and homemade producers (NCERT). Despite, the importance of the 18 VOCs for building the PCA model, only 8 have strong influence on the position of cluster of samples from certified production, namely 1-methyl-2-pyrrolidinone, 2-methyl-benzofuran, nonanal, acetic acid, 1-methyl-4-(1-methylethyl)-benzene, 1-(2-methyl-1-cyclopenten-1-yl)-ethanone and 2,2'-methylenebis[5-methyl-furan. These statistical results demonstrate that SCH samples set can be separated according to production process. In order to develop classification rules for the assignment of samples from certified and non-certified producers, the LDA was used as a supervised pattern recognition method. After applying LDA with backward removal of variables previously selected in PCA analysis, a discriminant function was calculated (Wilk's Lambda = 0.003992, $p < 0.0000001$). The scatter plot of the SCH samples classified according to the discriminant function are showed in Figure 8.

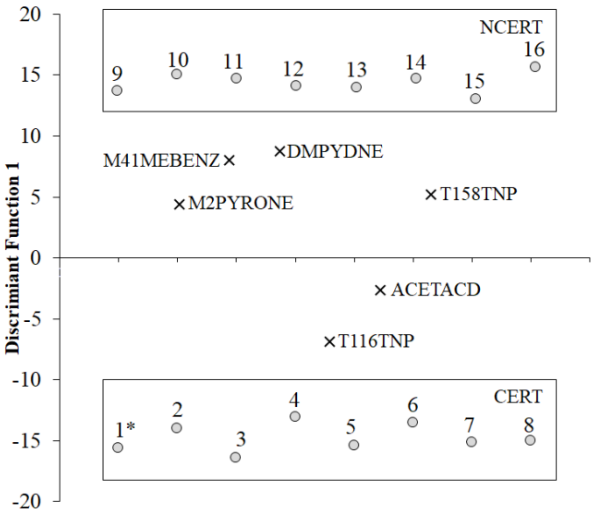


**Figure 8. The LDA score plot of all samples and the selected six VOCs.**

The samples from certified and non-certified producers form two clearly defined groups with a classification rate of 100%. Validation of the model was performed by leave-one-out CV. Recognition ability, calculated as the percentage of members of the training set that were correctly classified, and prediction ability, calculated as the percentage of members that were correctly classified, were 100% in both cases. The standardized discriminant function coefficients, and the variables selected by the method that contributed to the prediction of group membership are showed in Figure 8. 1,2,3,4-Tetrahydro-1,1,6-trimethyl-naphthalene and acetic acid are the variables that most contributed for certified SCH samples class membership, while 1-methyl-2-pyrrolidinone, 1-methyl-4-(1-methylethyl)-benzene, 1,2,3,4-tetrahydro-1,5,8-trimethyl-naphthalene and 4,6-dimethyl-pyrimidine are the variables most associated to non-certified producers samples class membership. Thus, a successful discriminant classification of samples was achieved, showing that the volatile profiling can be useful approach for establishment of authenticity and typicality of SCH.

## *4. Conclusions*

The food authenticity has become a global problem, increasing the importance of identification of markers in order to guarantee the food quality and consumer safety. The developed, optimized and validated HS-SPME$_{DVB/CAR/PDMS}$/GC-MS methodology demonstrated a useful approach for profiling of SCH volatile composition, providing an effective tool for differentiation and discrimination between SCH samples from certified and non-certified production processes. Although, this study represents the first application for establishment the volatomic profiling of SCH from Madeira Island, the results are very promising in order to support its application to EU certification. However, more and deep studies are needed to understand the influence of several factors in volatile profile of SCH. In particular, the study of the VOCs emitted/produced

by different varieties of SC cultivated at Madeira Island, as well the development of SCH during production and storage, from the SC crushing until the finished product. Thus, a stricter control of the production and storage processes of SCH can be achieved ensuring its authenticity and typicality, and contributing to avoid fraudulent situations expressed by commercialization of its adulterated products.

## SECTION 3.2. VOLATILE FINGERPRINTING OF SUGARCANE CULTIVARS

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# Chemical Differentiation of Sugarcane Cultivars Based on Volatile Profile and Chemometric Analysis

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*Abstract*

SC is a perennial grass widely cultivated in tropical and subtropical regions. However, its cultivation in Europe is residual, where Madeira Island, Portugal, is the only region where SC continues to be extensively cultivated. For the first time, the volatile profiles of regional cultivars were established by SPME/GC-MS. Different volatile profiles for each cultivar were recognized, identifying 260 VOCs belonging to 15 chemical classes, such as aldehydes, alcohols, ketones, hydrocarbons, esters, and terpenes. Chemometric analysis procedure, namely, one-way ANOVA with Tukey's test, PCA, PLS, LDA, and HCA, allowed the differentiation between all regional cultivars. This study represents an important contribution for the maintenance of biodiversity and subsistence of the SC industry in Europe. Furthermore, it is also a valuable contribution to establish the typicality of traditional SC-based products, such as SC honey.

Keywords: sugarcane, cultivar, volatile organic compound, differentiation, chemometric analysis

## 1. Introduction

SC is a large perennial grass widely cultivated in tropical and subtropical regions. It is a high value crop due to brief yield production cycle (10-14 months) and high content of SUC, which is the primary raw material for sugar production and biofuel production. Furthermore, SC is a multipurpose crop commonly used as the main ingredient in several food products, such as syrup, molasses, and spirits, and also for animal feed and biomaterial manufacturing [149–152]. Taxonomically, SC is positioned into the family Poaceae (or Gramineae), under the genus Saccharum, being constituted by the inter-breeding of six species, namely, *Saccharum officinarum*, *Saccharum barberi*, *Saccharum sinense*, *Saccharum robustum*, *Saccharum spontaneum*, and *Saccharum edule* [150]. Although the modern cultivars contain some genetic information from these six species, the main part of its genetic pool arises from hybridization between *S. officinarum* (high SUC content) and *S. spontaneum* (high abiotic stress resistance). Nevertheless, *S. officinarum*, known as "noble cane", is responsible for 80% of the genome due to the continuous intra-breeding to increase the SUC content, leading to a breeding process described as "nobilization". The comprehension of the SC pathway since ancient times to modern cultivars is complex and challenging due to its polyploid nature, huge genome size, high hybrid variability, and multi-specific origin [150–153].

Although SC was a historically important crop in Southern Europe, mainly in the Mediterranean area, and later, in the Atlantic islands, such as the Canaries and Madeira archipelagos, since its introduction by navigators from Portugal and Spain at the early 16th century in the Caribbean, Central, and South America, a sharp decline has occurred on its cultivation until today, culminating almost in its disappearance in Europe [154,155]. The current cultivation of SC in Europe is limited to small areas in southern Spain and Portugal, where the Madeira Island (Portugal) represents the last cluster of the once thriving European SC industry. There, SC continues to be cultivated extensively since its introduction in the early 14th century, where the main purpose was sugar production until the 17th century. From there until now, SC was used in the manufacturing of two main traditional food products: *"mel-de-cana"*, a black syrup, also called SC honey (SCH), and *"aguardente"*, a SC rum. Subsequently, both products are used as the main ingredient in traditional pastry/confectionery and regional brandies/spirits, respectively [11,33].

The centenary cultivation of SC in volcanic soils under the Atlantic climatic conditions of Madeira Island can lead to specific regional cultivars. However, these cultivars can be closely related to the primary cultivars brought to the American continent due to relative agronomic isolation common in small and distant islands. In fact, the first SC plants cultivated in Brazil were brought from Madeira Island, later being

dispersed throughout all South America [152,153]. So, the analysis of SC cultivars grown in Madeira Island can provide valuable information of the ancient European cultivars, as well about the early cultivars planted in the America, being an important biodiversity pool in order to understand the genetic and taxonomic connections of SC between the two continents. Besides the contribution to biodiversity maintenance, the analysis of regional cultivars also has economic importance. The exclusive use of regional SC cultivars can give rise to unique organoleptic and nutritional proprieties in the traditional products previously described, contributing to the appreciation and authentication not only of the products themselves but principally for the maintenance of one of the last SC industries in Europe.

One of the most applied approaches for differentiating cultivars in agro-food science is the molecular characterization based on the volatile profile. There, a wide range of VOCs are identified based on their unique mass fragment spectrum, which is expected to form a specific volatile profile for each cultivar highly influenced by the predecessor cultivars, soil proprieties, agronomic practices, and climatic conditions. Moreover, the volatile profile gives useful information about the sensory characteristics, such as aroma and flavor, allowing the evaluation of the quality and postharvest life [152]. Recently, the VOC profiling was widely recognized as a valuable tool for cultivar differentiation of grass crops, such as barley [156], wheat [157], and rice [158].

For the first time, we aim to differentiate chemically six SC cultivars from Madeira Island, Portugal, empirically named by regional farmers as *amarela* (AMA), *radiada* (RAD), *roxa* (ROX), *verde* (VER), *violeta* (VIO), and *canica* (CAN), throughout the establishment of its volatile profile by HS-SPME/GC-MS method and further chemometric analysis. The HS-SPME/GC-MS method was previously developed, optimized, and fully validated in our previous study [159]. The chemometric analysis was based on previously developed procedures in our previous studies [11,33], with some modifications. The establishment of the volatile profile of regional cultivars represents an important contribution for the maintenance of the genetic pool and biodiversity heritage. Furthermore, this study can be a valuable input to establish the typicality of traditional SC-based products, such as SCH, guaranteeing its quality, authenticity, safety control, and, consequently, a potential application to the EU certification, namely, the PDO and PGI, promoting the subsistence of sugar industry not only in Madeira Island, Portugal, but also in Europe.

## 2. Materials and Methods

### 2.1. Samples

SC samples (N = 12) were harvested at Madeira Island, Portugal, where AMA, RAD, ROX, VER, and VIO cultivars were picked in Ribeira Brava, the southern part of Madeira Island, and CAN cultivar were picked in Porto da Cruz, Machico, the northern part of Madeira Island. The samples of all cultivars were harvested in triplicate (three replicates, N = 13) for 2 years, 2015 and 2017, and stored under stable conditions at 4 °C until aliquoting process. After the end of harvest session, the SC samples were mechanically squeezed by cold pressing to obtain SC juice. Then, the SC juice was transferred to 50 mL amber glass bottles in 25 mL aliquots and stored at −80 °C until analysis. The identification (ID) replicate number, ID replicate code, ID sample code, ID variety code, variety empirical name, harvest year, and geographical are presented in Table S8.

### 2.2. Chemicals

Sodium chloride was acquired from Panreac (Barcelona, Spain). The internal standard (IS), 4-heptanone, and the reference standards (RS) described in Table S9 were purchased from Sigma-Aldrich (Missouri, USA).

### 2.3. Materials and Software

SPME holder for the manual sampling of SPME and the fiber DVB/CAR/PDMS with 50/30 μm film thickness were purchased from Supelco (Pennsylvania, USA). Ultrapure deionized water ($H_2O^d$) purified with a Milli-Q ultra-pure water system from Millipore (Massachusetts, USA). The MAXI MIX Vortex Mixer was acquired from Thermo Scientific (Massachusetts, USA). All data analysis and statistical processing were performed using the STATSOFT STATISTICA 12.0 (2013) software (Tulsa, USA).

### 2.4. SPME Procedure

The SPME procedure used for VOC extraction from SC samples was based on our analytical method previously developed, optimized, and validated [159]. Briefly, 20 mL of sample was daily placed into a 50 mL polytetrafluoroethylene centrifuge tube and mechanical homogenized for 1 min and stored at 4 °C in aliquots of 5 mL. Then, these aliquots were transferred to an 8 mL glass vial with 60 mg of NaCl and 5 μL of IS (1 μL $L^{-1}$) previously added, which was placed in a thermostatic bath at 30 °C for 5 min for sample temperature equilibrium. The SPME was performed in HS mode, where the fiber DVB/CAR/PDMS was attached to a manual SPME holder and exposed in the sample HS for 60 min at 30 °C under magnetic

agitation (600 rpm). The VOCs extracted by SPME were thermally desorbed by the fiber direct insertion into the GC injector at 250 °C in splitless mode for 10 min. The fiber was daily conditioned for 15 min at 250 °C into a GC injector to avoid contamination by unwanted interferents. Triplicate experiments were performed for all samples under analysis. Blank experiments were performed before the analysis of each sample, where the fiber was directly placed into GC injector without being subjected to any SPME extraction procedure.

*2.5. GC-MS Analysis*

The analysis of extracted VOCs was carried on an Agilent Technologies 6890N Network GC system (California, USA) equipped with a BP-20 fused silica capillary column with 60 m × 0.25 mm I.D. × 0.25 μm film thickness (Dortmund, Germany) and interfaced with an Agilent 5975 quadrupole inert mass selective detector (Santa Clara, California, USA). The protocol employed for column oven temperatures was 40 °C for 2 min and then was increased at 0.25 °C $min^{-1}$ until 45 °C with a 2 min hold, then was increased at 4 °C $min^{-1}$ to 70 °C with a 2 min hold, was increased again at 3 °C $min^{-1}$ to 130 °C with a 2 min hold, and finally was increased at 3 °C $min^{-1}$ to 220 °C. This final temperature was maintained for 7 min for a total GC run time of 91.25 min. Column flow was constant at 1 mL min–1 using He carrier gas at a purity of 99.999% (helium N60, Air Liquide, Portugal). The injection port was operated in the splitless mode and held at 250 °C. For the 5975 MS system, the operating temperatures of the transfer line, quadrupole, and ionization source were 270, 150, and 230 °C, respectively. Electron impact mass spectra were recorded at 70 eV ionization voltages and the ionization current was 10 μA. The electron multiplier was set to the autotune procedure. The acquisitions were performed in the scan mode (30-300 m/z). VOC identification was based on visual interpretation of spectra through the Agilent MS ChemStation Software and confirmed comparing each VOC mass spectra with the NIST14 Mass Spectral Library (2014), which is successfully identified when the similarity threshold was higher than 75%. In addition, some VOCs were also identified using a RS, where each VOC was individually analyzed by GC-MS. The TPA values were obtained by target ion quantitation protocol. The VOCs were semi-quantitate by dividing the TPA value of each VOC by the TPA value of the IS and expressed as RPA.

*2.6. Chemometric Analysis*

The chemometric analysis was based on previously developed procedures in our previous studies [11,33]. with some modifications according to recommendations for analytical applications [53,160]. One-way ANOVA was performed to determine the VOCs with statistically significant differences ($p < 0.05$)

based on its variance level between RPA values of all SC samples. Additionally, the Tukey post-hoc test was also performed to confirm the VOCs with statistically significant differences ($p < 0.05$) between RPA values of SC samples from two pairs of cultivars. PCA and PLS analysis were applied on RPA values of VOCs dataset in order to obtain the preview of differentiation/correlation structure based on the variance of samples from all cultivars during 2015 and 2017, without classification and with classification according to the cultivar, respectively. A V-fold with a V-value fixed in 7 was used for cross-validation. LDA was applied as a supervised pattern recognition method for variable selection in order to achieve a matrix composed by the lower number of VOCs that allows the correct classification of all samples under analysis for the group assignment (AMA, RAD, ROX, VER, VIO, and CAN). A backward selection method (p value of 0.05 to enter and 0.05 to remove) was used to determine the most predictive VOCs and remove the least predictive from analysis, where a classification structure is obtained based on canonical discriminant functions (CDFs). A V-fold with a leave-one-out strategy was applied for cross-validation. LDA is a highly recommended method to reduce the dimensionality of higher dimension matrix into a lower dimension matrix by removal of less predictive variables preserving the interclass separation (classification structure) [53,160]. A matrix reduction procedure was applied prior to LDA, where the matrix was reduced to 20% of initial dimension based on F-value from one-way ANOVA between all samples. Alternatively, a matrix reduction procedure based on the VIP scores from the PLS analysis was also applied. Thus, the 52 VOCs with higher F-value and VIP score were selected, respectively. Finally, a second PLS analysis and HCA were applied on RPA values of the most predictive VOCs. PLS based on dataset from the reduced matrix was performed to verify the differentiation/correlation structure between all samples when classified according to SC cultivar and compare with structure obtained from PLS performed with the complete matrix. HCA was performed in order to determine the Euclidean linkage distances between all samples and complete an appropriate and visual measure of distance and linkage criterion between SC cultivars based only in the most predictive VOCs. All data analysis and statistical processing were performed using the STATSOFT STATISTICA 12.0 (2013) software (Tulsa, USA).

## *3. Results and Discussion*

### *3.1. Establishment of Volatile Profiles from SC Cultivars*

Through the application of HS-SPME/GC-MS method to all SC samples under analysis in a 2-year study (2015 and 2017), it was possible to establish, for the first time, the volatile profile of six different SC cultivars from Madeira Island, Portugal. The ID number, RT, target ion, match percent, IUPAC name, NIST

database name, abbreviation, CAS number, molecular formula, and main chemical class of VOCs identified through analysis of SC samples during 2015 and 2017 harvest years are described in Table S9. Also, the mean RPA values and the respective % RSD of each VOC identified in AMA, RAD, and ROX and in VER, VIO and CAN cultivars are summarized in Table S10 (A) and (B), respectively. The typical GC-MS chromatograms for each SC cultivar are presented in Figure S1 (Supplementary Figure).

### *3.1.1. Number of VOCs*

The analysis of all samples from six regional SC cultivars allowed the identification of 260 different VOCs. Although there may be a wide disparity in RPA values, all VOCs were recognized in all samples under analysis. This may be due to the procedure used for VOC identification, where all 260 VOCs were searched in all samples based on a stage-by-stage follow-up strategy. The mean, minimum, and maximum values of RPA for all VOCs identified in each SC cultivar are summarized in Table S11.

As expected, 88 (33.8%) of the 260 VOCs were also previously identified in other SC-based products, where 56 (21.5%) in juice, 34 (13.1%) in sugar, 16 (6.2%) in treacle, 20 (7.7%) in molasses, 45 (17.3%) in syrup, 42 (16.2%) in rum or spirits, 3 (1.2%) in infusion, and 4 (1.4%) in alcoholic fermented beverages. Also, 36 (14.2%) VOCs were previously recognized in SCH samples [159]. Nevertheless, 173 (66.5%) VOCs were identified for the first time in food products from SC. This information and respective references are summarized in Table S12.

Interestingly, some of the 260 VOCs were previously identified in raw juice and thermal-processed products (e.g.., sugar, treacle, molasses, and syrup), such as dimethyl sulfide (DMSULFI), 3-hydroxy-2-butanone (HXY3BT2ONE), 1-hydroxy-2-propanone (HXY1PP2ONE), dimethyl sulfoxide (DMSULFO), and furfuryl alcohol (FURFOL), while other VOCs were recognized in raw juice and fermented products (e.g.., rum, spirit, and wine-like beverage), namely, 2-heptanol (HPT2OL), 1-hexanol (HX1OL), 2-octanol (OCT2OL), 1-octen-3-ol (OCT3E1OL), and β-ionone (BIONNE). Moreover, some VOCs were recognized in most of the SC-based products, being identified in raw juice, thermal processed and fermented products, such as 3-methyl-butanal (M3BTAL), ethyl alcohol (ETOL), 2,3-butanedione (BT23DONE), hexanal (HXAL), 2-methyl-1-propanol (M2PP1OL), 3-methyl-1-butanol (M3BT1OL), nonanal (NONAL), furfural (FURAL), ethanoic acid (ETNOIC), mequinol (MEQNOL), and benzeneethanol (BENZETOL) and 2-methoxy-4-vinyl-phenol (MXY2VYL4PHEOL). These findings are indicative that some VOCs from raw SC are still present in thermal processed and/or fermented products, demonstrating that the volatile analysis

of specific cultivars can be a useful tool for the determination of the typicality and authenticity of SC products based on these same cultivars. On the other hand, some VOCs are apparently sensitive to thermal or fermentation processing, being only identified in raw juice, namely, 2-propanone (PP2ONE), 1-penten-3-one (PT1E3ONE), 2-pentanol (PT2OL), 2-heptanone (HPT2ONE), trans-2-pentenol (TPT1E2OL), cis-2-pentenol (CPT1E2OL), 2-pentene (PT2ENE), cis-3-hexen-1-ol (CHX1E3OL), trans-2-octenal (TOCT2EAL), trans,trans-2,4-heptadienal (TTHPT22DEAL), 2-nonanol (NON2OL), β-myrcene (BMYRCNE), trans-2-octen-1-ol (TOCT1E2OL), α-terpineol (ATERPINOL), and nonanoic acid (NONOIC).

### *3.1.2. Main VOCs*

Although each one of the 260 VOCs contributed for the establishment of the volatile profile of all SC cultivars, its RPA values had a wide range, ranging between 0.03 and 3000. Thus, the 20 VOCs with higher RPA values for each SC cultivar were selected in order to determine the main contributors to volatile profile. The RPA values of the 20 main VOCs for AMA, RAD, ROX, VER, VIO, and CAN cultivars during 2015 and 2017 are described in Figure 9 (A), (B), (C), (D), (E) and (F), respectively.

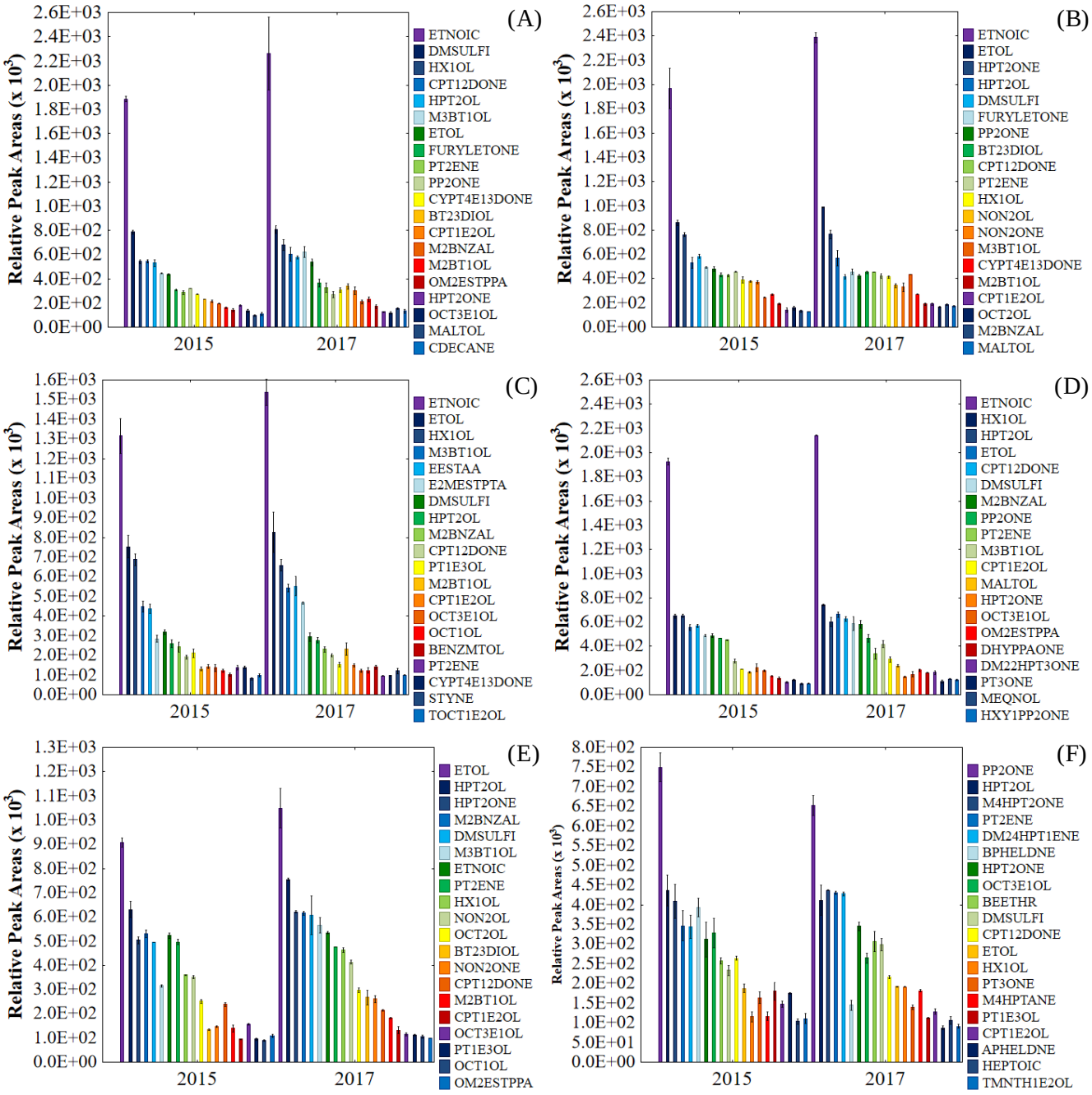


**Figure 9. The RPA values of the 10 main VOCs for *amarela* (A), *radiada* (B), *roxa* (C), *verde* (D), *violeta* (E) and *canica* (F) SC cultivars during 2015 and 2017 harvest years.**

Based on the analysis of the 20 main contributors to the volatile profile for each SC cultivar, 43 different VOCs were selected. From these, only seven were common to all cultivars, namely, DMSULFI, HX1OL, 1,2-cyclopentanedione (CPT12DONE), HPT2OL, ETOL, PT2ENE, and CPT1E2OL. On the contrary, 18 VOCs were selected as main contributors only in a specific SC cultivar, such as cyclodecane (CDECANE) for AMA; ethyl acetate (EESTAA), 2-ethyl methyl ester pentanoic acid (E2MESTPTA), benzenemethanol (BENZMTOL), styrene (STYNE), and TOCT1E2OL for ROX; 1,3-dihydroxy-2-propanone (DHYPPAONE), 2,2-dimethyl-3-heptanone (DM22HPT3ONE), MEQNOL, 1-hydroxy-2-propanone (HXY1PP2ONE), and 4-methyl-2-heptanone (M4HPT2ONE) for VER; and 2,4-dimethyl-1-heptene (DM24HPT1ENE), β-phellandrene (BPHELDNE), tert-butyl ethyl ether (BEETHR), 4-methyl-heptane

(M4HPTANE), α-phellandrene (APHELDNE), heptanoic acid (HEPTOIC), and trans-p-2-menthen-1-ol (TMNTH1E2OL) for CAN. None of the main VOCs were exclusively found for RAD and VIO cultivars. Remarkably, three VOCs, ETNOIC, 3-methyl-1-butanol (M3BT1OL), and 2-methyl-benzaldehyde (M2BNZAL), were classified as the main contributor only in cultivars picked in Ribeira Brava, the southern part of Madeira Island, having potential as markers for this geographic area, which is characterized by higher temperatures and less precipitation than the northern part of the island. In fact, ETNOIC was the main contributor to the volatile profile of AMA, RAD, ROX, and VER cultivars, presenting RPA values considerably higher than the other main VOCs. Possibly, the southern climatic conditions are more favorable to the formation of ETNOIC through natural action of bacteria on the SGs and alcohols [161].

### *3.1.3. Chemical Class Classification of VOCs*

A wide diversity of chemical classes was recognized through the VOC profiling of regional SC cultivars, being fundamental its classification into different groups to characterize the volatile profile of each SC cultivar. The classification group based on the main chemical class of each VOC is described in Table S9. The number of VOCs, RPA, and total relative peak area (TRPA) values of main chemical classes identified in SC samples are summarized in Table S13. The contribution (RPA and TRPA values) of each classification group assigned according to the chemical class is presented in Figure 10 (A) and (B), respectively.

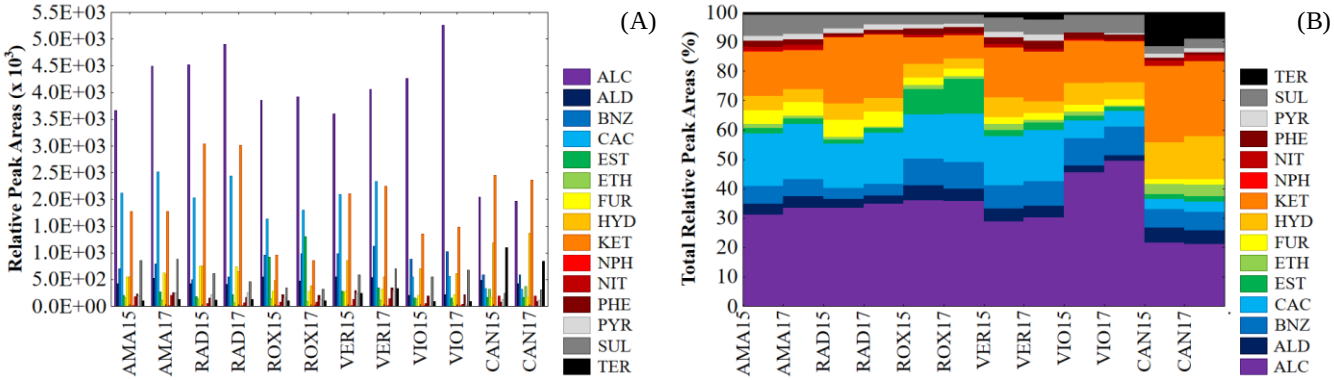


**Figure 10. The contribution, RPA (A) and TRPA (B) values, of each classification group assigned according to the chemical class for all SC cultivars during 2015 and 2017 harvest years.**

Throughout the classification of all 260 VOCs, 15 different chemical classes were recognized, namely, alcohol (ALC), aldehyde (ALD), benzene (BNZ), carboxylic acid (CAC), ester (EST), ether (ETH), furan (FUR), hydrocarbon (HYD), ketone (KET), naphthalene (NPH), nitrogen (NIT), phenol (PHE), pyran (PYR), sulfur (SUL), and terpene/terpenoid (TER).

Surprisingly, VOCs from all these chemical classes were found in cultivars from other grass crops, such as barley [156], wheat [157], rice [158], oat [162], and rye [162]. Some of these chemical classes are commonly linked to plants, and therefore, their VOCs are expected to be found in grass cultivars. BNZ and TER derivatives play a key role in plant biochemistry, such as plant–environment interactions and abiotic stress response, being derived from well-known benzenoid and terpenoid pathways [163]. Although its synthesis is not well established, being probably derivatives from the oxidation of fatty acids, VOCs from ALC, ALD, CAC, EST, HYD, and KET were also commonly found in various plant tissues and contribute in diverse physiological processes [164–166]. On the other hand, for some classes, it is difficult to explain their origin and purpose in grass crops. FUR, PYR, NIT, NPH, and PHE were normally related to thermal degradation (e.g.., MLDRs) of plant components (e.g.., SGs, AAs, and fatty acids) [117,167] and biomass burning [168]. Also, ALD, KET, and HYD can be related to these two processes. A potential explanation is the common use of fires to clean the land from weeds and waste in grass crops, which generated VOCs from pyrolysis of plant components (e.g.., SGs, AAs, cellulose, lignin, starch, among others). Another explanation may be the occurrence of thermal degradation in vivo of SC components, such as SGs (high content) and AAs, due to the high temperatures which the SC stalks are subjected to during the days with more sunlight incidence. For example, the occurrence of MLDRs in vivo during the ripening of fruits was previously detected [169]. In addition, VOCs from ALC, CAC, EST, ETH, and SUL classes could also be formed by the microbial activity of yeast and bacteria in plant tissues [166] or plant-based foods [148].

Based on the results described in Figure 10 (A) and (B), the contribution of all chemical classes to volatile profile differs widely from cultivar to cultivar, which obtained an exclusive volatile profile in terms of class contribution for each cultivar. Once again, the higher contribution differences were verified between the CAN cultivar and the southern cultivars. For example, the ALC class has the highest contribution for AMA, RAD, ROX, VER, and VIO cultivars while the KET class for CAN. Moreover, the contribution of TER, HYD, and ETH classes was considerably higher in CAN cultivar, while the CAC contribution was superior in the southern cultivars. However, some differences were also observed in the southern cultivars. For example, the ROX cultivar presented expressively higher TRPA value for EST class while showed the lower contribution of KET class. Likewise, the VIO cultivar presented TRPA values for PYR class almost 10 times lower than the other cultivars. There, results obtained suggest an apparent differentiation in the chemical class of volatile profiles among all regional SC cultivars.

### *3.2. Chemometric Analysis of Volatile Profiles from SC Cultivars*

Chemometric analysis procedure, namely, one-way ANOVA with Tukey's test, PCA, PLS analysis, LDA, and HCA, was applied in order to achieve the differentiation between all regional SC cultivars. Furthermore, similar chemometric analysis procedures have been successfully applied for differentiation of cultivars based on volatile profile [39,170,171].

### *3.2.1. One-Way ANOVA with Post-hoc Tukey's Test*

One-way ANOVA was performed to assess the existence of statistically significant differences between all SC cultivars for each VOC based on its RPA value variance level, while the post-hoc Tukey's test was done to determine the statistically significant differences between RPA values of SC samples, comparing pairs of cultivars (e.g. all combinations between one specific cultivar and each one of the other cultivars). The one-way ANOVA with post-hoc Tukey's test results, namely, probability (P) and Fischer (F) values, between all cultivars and for each pair of SC cultivars are summarized in Table S14.

Of the all 260 VOCs, only 3,5,5-trimethyl-2-cyclopenten-1-one showed no statistically significant difference ($P > 0.05$) in RPA values among all SC cultivars. Among the 259 VOCs with statistically significant differences ($P < 0.05$), 133 VOCs (51.2%) presented high differences (F values $\geq 100$) between all cultivars, where eight VOCs (3.1%) demonstrated very high significant differences (F values $\geq 1000$), namely, 4,4-dimethyl-2-pentanone (DM44PT2ONE), M4HPT2ONE, DM23HX2OL, 3-ethyl-2-methyl-1,3-hexadiene (E3M2HX13DENE), menthol (MNTHOL), benzeneacetaldehyde (BENZACETAL), 2-undecanol (UNDEC2OL), and 2-acetylpyrrole (ACTLPYROLE).

According to the results from post-hoc Tukey's test described in Table S14, a substantial dissimilarity was found in volatile profiles between all SC cultivars. Again, the CAN cultivar showed the higher dissimilarity level, the cultivar with the largest number of VOCs with significant differences in the RPA values for all pairs formed with each one of the other cultivars (CAN vs RAD, CAN vs ROX, CAN vs VER, and CAN vs VIO). That is, the CAN cultivar presented 115 (44.2%) VOCs with statistically significant differences for AMA, RAD, ROX, VER, and VIO cultivars simultaneously. Also, the ROX cultivar presented some dissimilarity from the remaining cultivars, in which 83 (31.9%) VOCs had significant differences. In minor extension, both AMA and VER cultivars presented 59 (22.7%) VOCs, followed by VIO cultivar with 51 (19.6%) VOCs and RAD cultivar with 49 (18.8%) VOCs. Unexpectedly, only TTHPT22DEAL demonstrated statistically significant differences for all combinations of pairs between the six cultivars. Contrariwise, some VOCs only presented significant differences for all

combinations completed with one specific cultivar. For example, 15 VOCs only showed significant differences between the CAN cultivar and each one of the southern cultivars, namely, hexane (HXANE), BEETHR, M4HPTANE, 2-methyl-2-heptene (M2HPTENE), DM24HPT1ENE, 2,3,4-trimethyl-hexane (TM234HXANE), 2,6-dimethyl-nonane (DM26NNANE), 4-methyl-2-pentanone (M4PT2ONE), 2-methy-2-butanol (M2BT2OL), APHELDNE, BPHELDNE, 4,6-dimethyl-2-heptanone (DM46HPT2ONE), 1,3-bis(1,1-dimethylethyl)-benzene (BI13DME11BNZ), 5-methyl-2-heptanone (M5HPTAONE), and 1,5-cyclooctanedione (CYOCTD15ONE). For ROX cultivar, nine VOCs were specific for these cultivars, specifically ethyl propanoate (EESTPA), ethyl 2-methylpropanoate (M2EESTPA), propyl acetate (PESTAA), 2-methyl-propyl acetate (M2PESTAA), 2-methyl-3-buten-2-ol (M3BT2OL), methyl 3,3-dimethylbutanoate (DM33MESTBA), 2-hexanone (HX2ONE), PT2OL, and E2MESTPTA. Interestingly, most of the compounds specific to the CAN cultivar belong to the chemical class groups of KET, HYD, and TER, while for the ROX cultivar, they belong mostly to the EST group. For remaining cultivars, 2-methyl-2-cyclopenten-1-one (M2CY2PT1EONE) and 2-propenoic acid (PPE2NOIC) were specific for AMA cultivar, while for VER cultivar, ethylene glycol ethyl ether (ENGOLEETHR) and cis-p-2-menthen-1-ol (CMNTH1E2OL) were specific, and only 3-octen-2-one (OCT2E3ONE) was specific for RAD cultivar. None of the VOCs have specificity for VIO cultivar combinations.

### *3.2.2. PCA and PLS*

PCA and PLS analyses were performed to preview the differentiation/correlation structure based on the variance of samples from all SC cultivars during 2015 and 2017, without classification and with classification accordingly, respectively. The PCA and PLS information is summarized in Table S15. The loading results and VIP scores of PCA and PLS analysis for each variable (VOCs) are described in Table S16, while the loading results of all cultivar samples (PCA) and six cultivar centroids (PLS) are described in Table S17. The PCA and PLS score results of all samples under analysis are described in Table S18. The PCA loading line plots of all cultivar samples for PC1, PC2, and PC3 are shown in Figure S2 (A), (B) and (C), respectively. The PLS loading line plots of six cultivar centroids for PLS1, PLS2, and PLS3 are shown in Figure S2 (D), (E) and (F), respectively. The PCA loading 3D plots of all cultivar samples and all variables for PC1, PC2, and PC3 are shown in Figure 11 (A) and (B), respectively. The PLS loading 3D plots of the six cultivar centroids and all variables for PLS1, PLS2, and PLS3 are shown in Figure 12 (A) and (B), respectively.

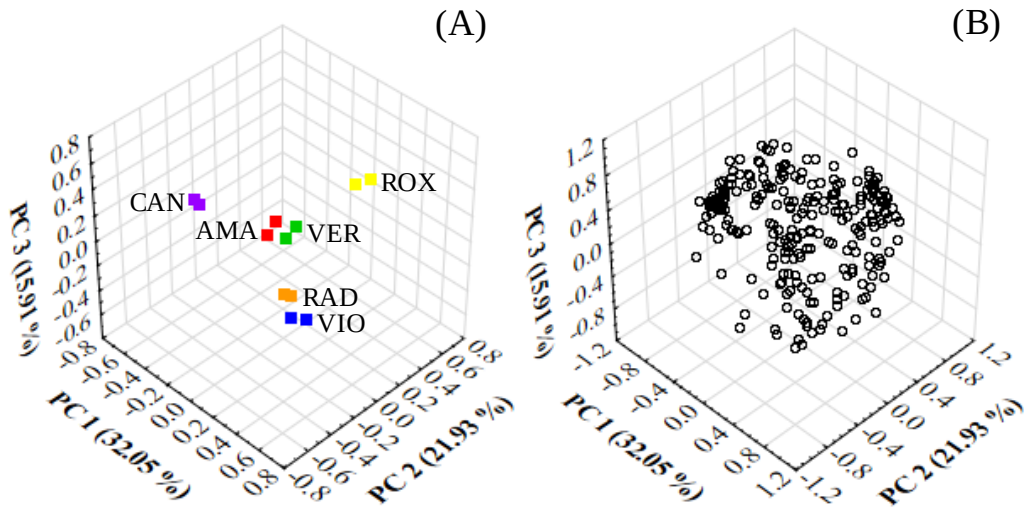


**Figure 12. The PCA loading 3D plot of all cultivar centroids (A) and the selected 259 VOCs (B) for the three main components.**

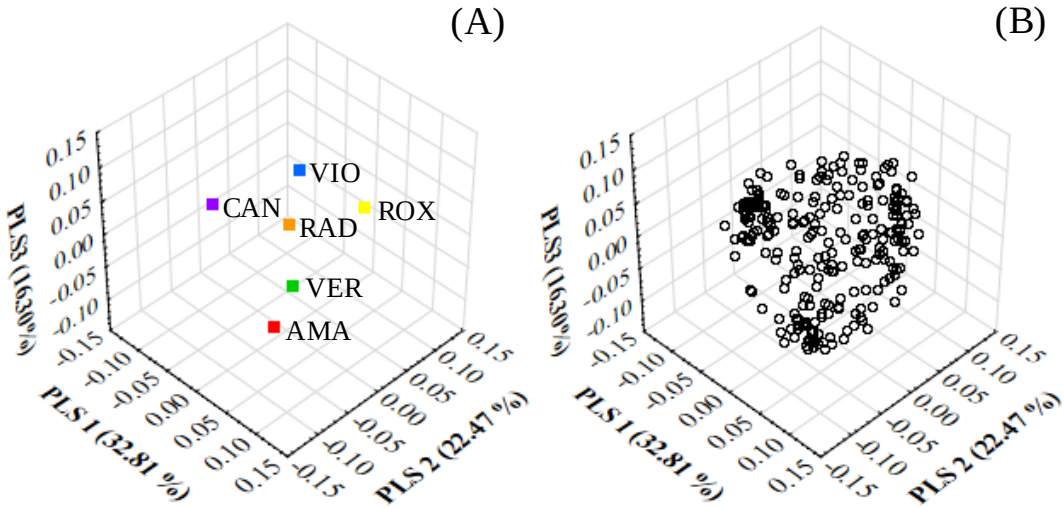


**Figure 11. The PLS loading 3D plot of all cultivar samples (A) and the selected 259 VOCs (B) for the three main components.**

The PCA analysis based on PC1, PC2, and PC3 explained 69.9% of TVA, where the sum of all the 14 components explained 99.5%. The projection of structure based on PC1, PC2, and PC3 loading results demonstrated the formation of precise sample groups (2015 and 2017) according to SC cultivar, namely, AMA, RAD, ROX, VER, VIO, and CAN groups. There, a visual differentiation between all cultivar groups was observed, where CAN and ROX cultivars are clearly separated from the other cultivars. In PC1 projection (32.0% TVA), CAN cultivar demonstrated a high variance from the southern cultivars, while ROX cultivar showed a slight variance for the other southern cultivars. For PC2 projection (21.9%), the ROX cultivar presented a high variance from all the other regional cultivars. Also, in PC2 projection, AMA cultivar exhibited a substantial variance from the RAD, VER, VIO, and CAN cultivars. Finally, in PC3 projection (15.9%), a considerable variance was observed between all cultivars, principally for RAD and VIO cultivars.

A PLS analysis was performed to evaluate the variance between samples when classified according to SC cultivar, being classified as centroid-AMA (C-AMA), centroid-RAD (C-RAD), centroid-ROX (C-ROX), centroid-VER (C-VER), centroid-VIO (C-VIO), and centroid-CAN (C-CAN). The PLS analysis based on PLS1, PLS2, and PLS3 explained 71.6% of TVA, where the sum of all the 18 components explained 99.7%. All cultivar centroids were clearly apart from each other, while the results of PLS analysis were very similar to those obtained in the PCA in terms of variance due to the reduced intra-variance of samples from the same cultivar. This low intra-variance for each cultivar can be verified through analysis of PCA and PLS scores of all samples described in Table S18. Thus, in PLS1 projection (32.8%), the higher variance was observed between CAN cultivar and the southern cultivars, while in PLS2 projection (22.5%), the higher variance was observed for the ROX cultivar. For PLS3 projection (16.3%), all cultivar centroids were well separated, where the higher variance was observed between VIO and RAD cultivars from the other cultivars. Both PCA and PLS projections indicated that the volatile profile can be an effective strategy to differentiate molecularly the six SC regional cultivars.

Although the PLS projection, as well the PCA projection, was based on all 259 VOCs, each one influenced differently the projection of centroids, being possible to recognize the contribution of each VOC for the projection of a specific cultivar centroid. The 3D plot constructed with three main component loading results for all VOCs under analysis showed that a high number of VOCs influenced the projections of CAN and ROX cultivars. Interestingly, the CAN projection was highly influenced by VOCs belonging to KET, HYD, and TER chemical classes, namely, by VOCs previously mentioned in the ANOVA test, such as M4PT2ONE, DM46HPT2ONE, M2HPTENE, DM24HPT1ENE, APHELDNE, and BPHELDNE. Likewise, ROX projection was very influenced by VOCs also referred in the ANOVA test, mainly belonging to EST chemical class, such as EESTPA, M2EESTPA, PESTAA, M2PESTAA, and E2MESTPTA. Also, VIO projection was influenced by some VOCs, namely, HPT2ONE, 5-methyl-4-hexen-3-one (M5HX3E4ONE), OCT2OL, NON2OL, and cis-5-decenol (CDEC5E1OL). Although the projections of the remaining regional cultivars were directly influenced by a smaller number of VOCs, some can be highlighted by their high influence on the projection of a specific cultivar, namely, 2,3-pentanedione (PTDONE) and MALTOL for AMA cultivar, 2-methyl-furan (M2FUR) for RAD cultivar, and 1-decanol (DEC1OL) for VER cultivar. Thus, the specificity of these VOCs for a single cultivar could represent a potential marker of this specific cultivar.

### *3.2.3. LDA*

LDA was performed as a supervised pattern recognition method to achieve classification rules for the cultivar assignment of all samples under analysis based only in the most predictive VOCs. The matrix reduction procedure based on the VIP scores presented poor results to PLS and HCA analysis, showed in Figure S3 (A) and (B), and was therefore disregarded. The LDA information of the selected 52 VOCs based on the VIP scores are summarized in Table S21. The LDA information and CDF coefficients of the selected 52 VOCs based on F-value from one-way ANOVA test are summarized in Table 3.

**Table 3. Results of variables from LDA after matrix reduction method to 20 % of original dimension according with higher F values obtained from One-way ANOVA test based on the RPA of the identified VOCs in SC samples.**

| Volatile Organic Compounds | Abbreviations | ANOVA | | LDA | | | |
|---|---|---|---|---|---|---|---|
| | | F[1] | W[2] | F[3] | CDF[4] | | |
| | | | | | 1 | 2 | 3 |
| Menthol | MNTHOL | 1781.56 | 1.13E-04 | 1.42E+04 | -0.0022 | -0.0015 | 0.0015 |
| 4.4-Dimethyl-2-Pentanone | DM44PT2ONE | 1684.33 | 2.02E-11 | 1.12E+11 | -0.0025 | -0.0017 | 0.0018 |
| 2-Acetylpyrrole | ACTLPYROLE | 1508.90 | | Removed from analysis. | | | |
| 2.3-Dimethyl-2-Hexanol | DM23HX2OL | 1243.14 | 2.24E-11 | 1.01E+11 | -0.0021 | -0.0015 | 0.0017 |
| 2-Undecanol | UNDEC2OL | 1153.59 | | Removed from analysis. | | | |
| 3-Ethyl-2-Methyl-1.3-Hexadiene | E3M2HX13DENE | 1111.23 | 4.51E-12 | 4.98E+11 | 0.0009 | -0.0032 | -0.0021 |
| 4-Methyl-2-Heptanone | M4HPT2ONE | 1066.87 | 6.50E-04 | 2.46E+03 | -0.0019 | -0.0014 | 0.0013 |
| Benzeneacetaldehyde | BENZACETAL | 1009.48 | 9.62E-12 | 2.34E+11 | -0.0002 | 0.0001 | 0.0052 |
| 4-Amino-Phenol | AMIPHEOL | 886.23 | | Removed from analysis. | | | |
| 2-Ethylhexyl Ester Octanoic Acid | EHESTOA | 873.20 | 5.01E-12 | 4.49E+11 | 0.0024 | 0.0011 | -0.0059 |
| cis-5-Decenol | CDEC5E1OL | 706.67 | | Removed from analysis. | | | |
| 2-Nonanol | NON2OL | 695.37 | 2.43E-12 | 9.24E+11 | 0.0012 | -0.0014 | -0.0021 |
| 2.4.5-Trihydroxypyrimidine | THDXYPYMNE | 637.12 | | Removed from analysis. | | | |
| cis-Piperitol | CPIPETOL | 596.97 | | Removed from analysis. | | | |
| 2-Phenoxy-Ethanol | PHENXYOL | 592.27 | | Removed from analysis. | | | |
| Propanoic Acid | PPANOIC | 582.46 | 6.87E-12 | 3.28E+11 | -0.0009 | 0.0012 | -0.0025 |
| Undecanoic Acid | UNDECOIC | 561.56 | | Removed from analysis. | | | |
| 1-(2-Furanyl)-Ethanone | FURYLETONE | 560.99 | 4.38E-12 | 5.13E+11 | 0.0011 | 0.0014 | 0.0016 |
| 1-Methyl-4-Piperidinone | M1PIP4DIONE | 558.99 | | Removed from analysis. | | | |
| 3-Methyl-1.2-Cyclopentanedione | M3CPT12DONE | 544.81 | | Removed from analysis. | | | |
| 4-Methylimidazole | M4IMDZOLE | 543.79 | | Removed from analysis. | | | |
| Nonanoic Acid | NONOIC | 534.87 | | Removed from analysis. | | | |
| 2-Methoxy-4-Vinyl-Phenol | MXY2VYL4PHEOL | 531.37 | | Removed from analysis. | | | |
| β-Myrcene | BMYRCNE | 526.99 | 1.22E-11 | 1.84E+11 | -0.0012 | -0.0014 | 0.0015 |
| 3-Methyl-2-Pentanol | M2PT2OL | 504.97 | 7.52E-12 | 2.99E+11 | -0.0007 | -0.0004 | 0.0015 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 3-Hydroxy-2.3-Dihydro-Maltol | HX3DH23MALTOL | 492.74 | Removed from analysis. | | | | |
| 2-Cyclohexenol | CHEX2E1OL | 443.59 | Removed from analysis. | | | | |
| Phoracanthol | PHOCATHOL | 432.85 | 6.74E-13 | 3.34E+12 | 0.0022 | 0.0019 | 0.0003 |
| Linalool | LINOL | 384.56 | 1.25E-11 | 1.80E+11 | 0.0006 | 0.0012 | 0.0031 |
| 4-Cyclopentene-1.3-dione | CYPT4E13DONE | 365.04 | 1.26E-11 | 1.79E+11 | 0.0008 | 0.0015 | 0.0021 |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | FURYLHXYEONE | 356.33 | Removed from analysis. | | | | |
| 2-Methyl-Crotonal | M2CROTNAL | 350.13 | 1.80E-11 | 1.25E+11 | -0.0004 | 0.0008 | -0.0018 |
| Ethylene Glycol Butyl Ether | ENGOLBETHR | 349.45 | 1.62E-11 | 1.39E+11 | 0.0004 | 0.0013 | 0.0006 |
| 2-Methy-2-Butanol | M2BT2OL | 342.89 | 9.94E-12 | 2.26E+11 | -0.0011 | -0.0009 | 0.0009 |
| cis-4-Decenol | CDEC4E1OL | 327.97 | Removed from analysis. | | | | |
| 2.4-Dimethyl-1-Heptene | DM24HPT1ENE | 324.27 | Removed from analysis. | | | | |
| Triethylene Glycol | TETYNEGLOL | 304.57 | Removed from analysis. | | | | |
| 1-Nonanol | NON1OL | 298.22 | 4.43E-12 | 5.08E+11 | 0.0009 | -0.0011 | -0.0016 |
| trans-2-Nonene | TNONENE | 293.65 | Removed from analysis. | | | | |
| Heptanoic Acid | HEPTOIC | 289.77 | Removed from analysis. | | | | |
| Octanal | OCTAL | 289.51 | Removed from analysis. | | | | |
| Pentanal | PTNAL | 288.09 | 2.42E-11 | 9.30E+10 | -0.0011 | -0.0007 | 0.0008 |
| p-Methoxy-Styrene | PMTXYESTYNE | 285.67 | Removed from analysis. | | | | |
| 4.6-Dimethyl-Dodecane | DM45DODCANE | 274.61 | Removed from analysis. | | | | |
| 5-Methyl-2-Hexanone | M5HX2AONE | 274.44 | 1.90E-11 | 1.19E+11 | -0.0007 | 0.0000 | 0.0017 |
| trans-2-Nonen-1-ol | TNON1E2OL | 270.13 | 6.21E-12 | 3.62E+11 | -0.0011 | -0.0007 | 0.0007 |
| 5-Hydroxy-Maltol | HX5MALTOL | 269.56 | Removed from analysis. | | | | |
| 2-Heptanone | HPT2ONE | 266.55 | Removed from analysis. | | | | |
| Furfuryl Formate | FURYLFMTE | 266.49 | Removed from analysis. | | | | |
| 2-Ethyl Hexanoic Acid | E2HEXOIC | 264.43 | Removed from analysis. | | | | |
| trans-2-Octen-1-ol | TOCT1E2OL | 255.47 | 9.66E-12 | 2.33E+11 | 0.0001 | 0.0007 | -0.0006 |
| 2-Methyl-Benzaldehyde | M2BNZAL | 255.45 | Removed from analysis. | | | | |

[1]F - Fischer value from One-way ANOVA test.
[2]W - Wilks value from Linear Discriminant Analysis.
[3]F - Fischer value from Linear Discriminant Analysis.
[4]CDF - Canonical Discriminant Function Coefficients.

The CDF coefficients and highest probability classification results of all samples are summarized in Table S19. The LDA line plots of all cultivars classified according to CDF1, CDF2, and CDF3 are shown in Figure S4 (A), (B) and (C), respectively. The LDA line plot of selected variables for CDF1, CDF2, and CDF3 are shown in Figure S4 (D), (E) and (F), respectively. The CDF coefficient 3D plots of the six cultivar centroids and selected variables for CDF1, CDF2, and CDF3 are presented in Figure 13 (A) and (B), respectively.

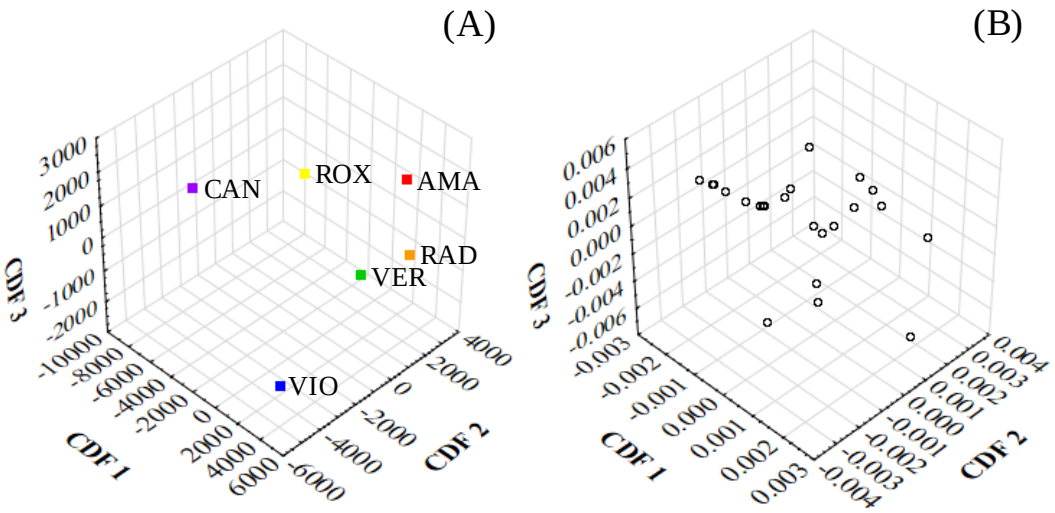


**Figure 13. The LDA loading 3D plot of all cultivar centroids (A) and the 23 most predictive VOCs (B) for the three main components.**

Throughout all the 30 steps of the backward selection method ($p < 0.05$), 29 VOCs were removed. Consequently, LDA analysis results were based on 23 VOCs, namely, MNTHOL, DM44PT2ONE, 2,3-dimethyl-2-hexanol (DM23HX2OL), E3M2HX13DENE, M4HPT2ONE, BENZACETAL, 2-ethylhexyl octanoate (EHESTOA), 2-nonanol (NON2OL), propanoic acid (PPANOIC), 1-(2-furanyl)-ethanone (FURYLETONE), BMYRCNE, 3-methyl-2-pentanol (M2PT2OL), phoracanthol (PHOCATHOL), linalool (LINOL), 4-cyclopentene-1,3-dione (CYPT4E13DONE), 2-methyl-crotonal (M2CROTNAL), ethylene glycol butyl ether (ENGOLBETHR), M2BT2OL, 1-nonanol (NON1OL), pentanal (PTNAL), 5-methyl-2-hexanone (M5HX2AONE), trans-2-nonen-1-ol (TNON1E2OL), and TOCT1E2OL. All the 36 SC samples were classified at a 100% correct rate. Thus, the dimension of the matrix was reduced to 23 VOCs, corresponding to 8.8% of the original matrix of 260 VOCs.

The LDA 3D plot in Figure 13 (A) presented a high level of discrimination along the three CDFs between all cultivars. In CDF 1, a prominent discrimination was obtained between the CAN cultivar and the other southern cultivars. Also, in CDF1, an interesting discrimination was observed between two clusters, one formed by ROX and VER cultivars and the other formed by AMA, RAD, and VIO cultivars.

In CDF 2, a higher discrimination was observed to CAN and VIO cultivar from the other cultivars, where substantial discrimination was also verified between VER cultivar and other cultivars. Notably, in CDF3, an equilibrate and a reasonable discrimination between all cultivars under analysis were observed. According to the LDA results, discriminate was possible and all cultivar samples were classified correctly based only on selected 23 of 260 VOCs.

### *3.2.4. PLS and HCA*

A second PLS analysis was performed to verify the differentiation/correlation structure between all SC cultivars when only the 23 most predictive VOCs were used. The PLS information is summarized in Table S20. The loading results and VIP scores of PLS analysis for each one of 23 VOCs are summarized in Table 1. The PLS loading results of six cultivar centroids and the score results of all samples under analysis are described in Table S19. The PLS loadings line plots of all cultivars classified according to PLS1, PLS2, and PLS3 are shown in Figure S5 (A), (B) and (C), respectively. The PLS loading line plot of all 23 VOCs for PLS1, PLS2, and PLS3 are shown in Figure S5 (D), (E) and (F), respectively. The PLS loading 3D plots of the six cultivar centroids and 23 VOCs for PLS1, PLS2, and PLS3 are shown in Figure 14 (A) and (B), respectively.

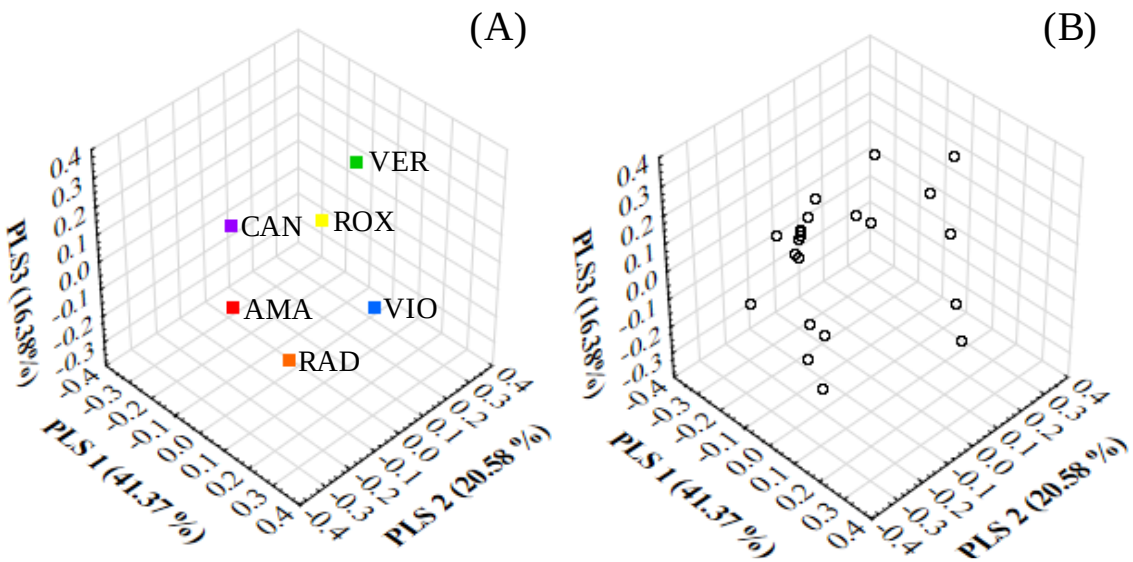


**Figure 14. The PLS loading 3D plot of all cultivar centroids (A) and the 23 most predictive VOCs (B) for the three main components.**

The PLS analysis based on PLS1, PLS2, and PLS3 explained 78.3% of TVA, where the sum of all 14 components explained 99.9%. As expected, the results presented in Figure 14 (A) demonstrate that the six cultivar centroids were undoubtedly separated from each other, presenting a high inter-cultivar variance for all cultivars. Moreover, the difference level of variance between cultivars was clearly higher than that obtained in the previous PLS (complete matrix). Throughout the individual analysis of PLS1 projection

(41.4%), it was possible to visualize a higher variance between CAN cultivar and the southern cultivars. In PLS2 projection (20.6%), a considerable variance among the five was observed as follows: AMA-RAD-ROX-VER-VIO. For PLS3 projection (16.4%), a high variance was observed between VIO and RAD cultivars from the other cultivars, principally from ROX and VER cultivars.

HCA was performed based on the previously selected 23 VOCs in order to determine the Euclidean linkage distances between all samples and complete an appropriate measure of distance and linkage criterion between the SC cultivars. The HCA dendrogram is presented in Figure 15.

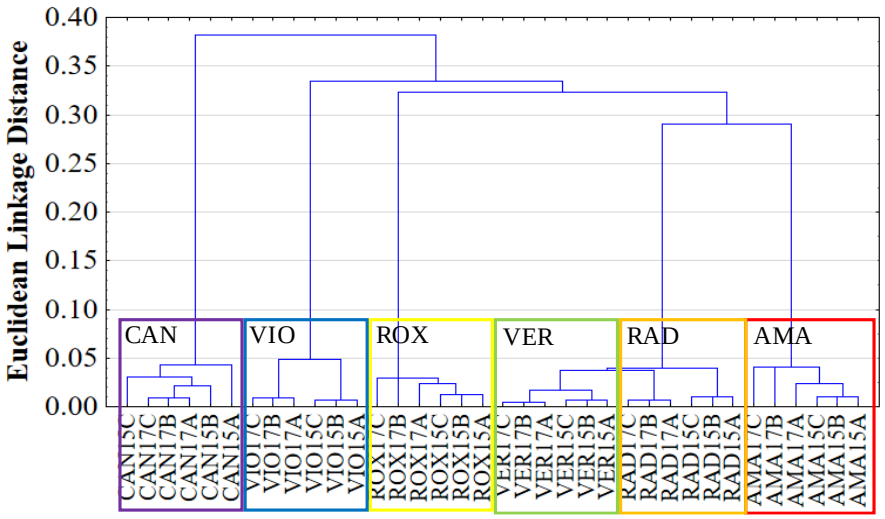


**Figure 15. The HCA dendrogram based on Euclidean linkage distances for all replicates from six SC cultivars during 2015 and 2017 harvest years.**

Once again, the higher distance was obtained between the CAN cultivar and southern cultivars. Among the southern cultivars, the linkage level decreases in the following order: VIO > ROX > AMA > VER > RAD. The samples from CAN, VIO, ROX, and AMA cultivars presented a high level of differentiation, being easily distinguished from all other regional cultivars. However, low distances were obtained for samples from RAD and VER cultivars, indicating the probable existence of a common pre-antecedent SC cultivar. The PLS projection, a supervised pattern recognition method, and HCA, an unsupervised pattern recognition method, presented similar results, allowing to infer that all cultivars can be well differentiated based only on the 23 most predictive VOCs.

## *4. Conclusions*

The present study represents the first application to differentiate molecularly the SC cultivars from Madeira Island, Portugal. The establishment of the volatile profile from all cultivars was performed by the HS-SPME/GC-MS method, recognizing a total of 260 different VOCs belonging to 15 different chemical classes, namely, ALC, ALD, BNZ, CAC, EST, ETH, FUR, HYD, KET, NPH, NIT, PHE, PYR, SUL, and

TER. Based on the chemometric analysis, we concluded that it was possible to establish an exclusive volatile profile for each one of the six different SC cultivars and consequently achieve a high level of differentiation between all cultivars. The CAN cultivar appears to be more molecularly different from the other regional cultivars. Interestingly, the CAN cultivar is empirically indicated by farmers as the oldest cultivar in Madeira Island, which is a potential cultivar originated from the group formed by the first cultivars introduced in the 14th century due to its agronomic isolation into a small cluster localized in the northern part of the island. Nevertheless, its volatile composition is also the result of its adaptation to the unique agronomic and climatic conditions of the north of the island. Among the southern cultivars, ROX and VIO cultivars presented a higher level of differentiation, followed by AMA cultivar, and in minor extension by VER and RAD cultivars. ROX cultivar is the most appreciated by regional farmers due to its high productivity when grown in areas with strong sunlight exposure and high-water availability, which is responsible for approximately 75% of the SC total production. Also, AMA and VER cultivars are commonly produced in areas with lower water availability, but with lower productivity. VIO and RAD cultivars were recently introduced in the regional SC production system due to its apparently high pest robustness.

In addition, some VOCs appear to have a specific correlation for a particular SC cultivar and can be recognized as a potential marker for those cultivars. The CAN cultivar was characterized by VOCs from KET, HYD, and TER chemical classes, such as M4PT2ONE, DM46HPT2ONE, M2HPTENE, DM24HPT1ENE, APHELDNE, and BPHELDNE. The ROX cultivar was influenced by VOCs from EST chemical class, such as EESTPA, M2EESTPA, PESTAA, M2PESTAA, and E2MESTPTA; the VIO cultivar was influenced by VOCs from KET and ALC, such as HPT2ONE, M5HX3E4ONE, OCT2OL, NON2OL, and CDEC5E1OL. The remaining regional cultivars were directly influenced by a few VOCs, namely, PTDONE and MALTOL for the AMA cultivar, M2FUR for the RAD cultivar, and DEC1OL for the VER cultivar. Furthermore, LDA, PLS, and HCA demonstrated that it is possible to differentiate all regional SC cultivars only based on the 23 most predictive VOC dataset, namely, MNTHOL, DM44PT2ONE, DM23HX2OL, E3M2HX13DENE, M4HPT2ONE, BENZACETAL, EHESTOA, NON2OL, PPANOIC, FURYLETONE, BMYRCNE, M2PT2OL, PHOCATHOL, LINOL, CYPT4E13DONE, M2CROTNAL, ENGOLBETHR, M2BT2OL, NON1OL, PTNAL, M5HX2AONE, TNON1E2OL, and TOCT1E2OL.

Finally, the information obtained in this study about the regional SC cultivars represents an important contribution for the maintenance of biodiversity and subsistence of the sugar industry not only in Madeira Island, Portugal, but also in Europe. Moreover, this study is also a fundamental input to establish the typicality of traditional SC-based products, such as SCH, and its submission to an EU certification.

## SECTION 3.3. VOLATILE FINGERPRINTING THROUGHOUT THE SUGARCANE HONEY PROCESSING

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# Effect of processing and storage on the volatile profile of sugarcane honey: a four-year study

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*Abstract*

SCH is a syrup from Madeira Island recognized by its unique and excellent aroma, associated to VOCs generated during the well-defined five stages of its traditional making process. The establishment of volatile profile throughout all SCH-making stages during four years, allowed the evaluation of the influence of each stage in the typical characteristics of SCH. One hundred eighty-seven VOCs were identified, being associated to several origins and formation pathways. VOCs formed during stage 1 and 2 were originate from raw material, and its oxidation (e.g. enzymatic browning) and thermal degradation (e.g. lipid oxidation, MLDRs, STKD). In stage 3 and 4, the caramelization and melanoidin degradation also occurred, while in stage 5, the thermal degradation continues, followed by microbial activity. Chemometric analysis allowed to identify 35 VOCs as potential markers for processing control by the producers and as guarantee of the typicality and authenticity of SCH. Based on the obtained results, we propose for the first time an innovative schematic diagram explaining the potential reactions and pathways for VOCs formation during the different steps of the SCH production.

Keywords: sugarcane honey; making process; storage; volatile profile; authenticity.

## 1. Introduction

The SCH, known as *"mel-de-cana"*, is a crystalline black syrup produced by thermal processing of the juice from SC stalks (*Saccharum officinarum L.*) cultivated under mild climate conditions in Madeira Island, Portugal. SCH is a regional product of excellence, worldwide recognized by its typical and unique aroma, being consumed in fresh or used as a main ingredient in traditional pastry and confectionery, as well in sauces for cooking meat, fish and salads or even for medicinal purposes. SCH is a syrup without any additive, colorant or preservative, being naturally rich in CBHs, minerals (Fe, Ca, Mg and Cu), vitamins (niacin, riboflavin and thiamin), antioxidants (flavonoids and non-flavonoids) and fibers [11,159].

The traditional making process of SCH is a true form of engineering and art, being based on five main stages: (i) S1 - starts with the placement of SC stalks in a grinder, where the juice, also known as *"guarapa"*, is extracted by mechanical pressing; (ii) S2 - the fresh juice is directly conducted to a first heated filtering process with a nylon membrane at 80 ºC; (iii) S3 - the filtered SC juice is heated up to 100 ºC for 24h into an evaporator to produce a primary and dark brown syrup, wherein is led to a second filtering process; (iv) S4 - the primary syrup is again placed into an evaporator for 10 hours with a temperature up to 120 ºC, to continue the thermal process and evaporation of the remaining water, being again filtered to ensure a flawless rigor of final product, a viscous and crystalline black syrup; (v) S5 - finally, the syrup is storage in a reservoir at 20ºC for 6 months, where it cools down naturally.

The typical and unique aroma of SCH is strongly influenced by the presence of VOCs that arise from its raw material, traditional processing and storage. Although some VOCs can be originated from the SC raw material, most are formed by a wide variety of reactions that occur during SCH making process, the well-known BRs [159]. BRs can be divided into two main types of reactions, EBRs and NEBRs. EBRs are caused by the activity of enzymes on the polyphenols in the SC juice during stalk pressing, where can promote the formation of VOCs in an indirect way through posterior reactions of its products, such as quinones, with AAs. However, the NEBRs are probably the main source of VOCs in thermal processed foods, encompassing a complex set of chemical reactions where a large number of food components (e.g. SGs, AAs, proteins, lipids, and vitamins) participate via multiple different pathways, originating a great diversity of VOCs [172,173]. Particularly, the VOCs responsible for the unique aroma of SCH are mainly formed by MLDRs, STKD and caramelization [159]. The high temperatures used during SCH processing and the large content of SGs in SC provide optimal conditions for these reactions. In addition, other NEBRs can also occur during SCH processing, namely the thermal degradation of lipids and L-ascorbic acid [159].

Moreover, some NEBRs can also occur during storage in products with high sugar and free AAs content, such as honey, jam and syrups [174]. Additionally, some enzymes can react with several components (e.g. fatty acids, ascorbic acid, due to the disruption of plant tissues that occurs throughout the harvesting, crushing and pressing of SC stalks. Finally, the microbial activity can occur naturally by bacteria, fungi or yeast on the SGs during the period of harvest and transportation of SC to the factory, and also in the storage of the SCH, leading to formation of several VOCs [175,176]. Nevertheless, the chemical complexity of VOCs formation can be valuable for establishment of its typicality and authenticity, which the standardization of processing and storage conditions, together with the exclusive use of SC cultivated on Madeira Island, can generate similarities in VOCs profile that potentially create a "fingerprint" of SCH.

Consequently, the control and monitoring of the chemical composition during the food processing stages is crucial to ensure the expected and typical organoleptic properties (e.g. aroma, flavor and texture) of a particular food product in order to guarantee its quality, typicality and authenticity, as well its compliance with national legislation, international standards and consumer safety rules. In this context, HS-SPME/GC-MS is, undoubtedly, the most popular method used for volatile profiling in Foodomics domain, being widely applied as an effective and useful tool for monitoring of VOCs during the processing of food products, such as wine [177], soy sauce [178], green tea [179], coffee [180], vinegars [181], among others.

The aim of the current study is the monitoring of volatile profile during the five main stages of SCH processing (S1, S2, S3, S4 and S5) in a certified producer through four years (2015, 2016, 2017 and 2018) using the HS-SPME/GC-MS method previously developed, optimized and fully validated in our previous study [159]. The chemometric analysis was performed according to the procedures developed in our previous studies [11,159], with some modifications. The data obtained from this study represents the first attempt to evaluate the volatile profile throughout all stages of SCH processing, providing a highly valuable information about the influence of raw material, effect of processing conditions (e.g. temperature, pH), impact of precursors (e.g. SGs, AAs, lipids) and complexity of reactions involved (e.g. BRs and microbial activity). Moreover, this information can be useful for an optimization of SCH processing and storage, where the importance of each stage was evaluated. Likewise, the identification of VOCs markers allows the strict control of key stages by producers in order to achieve the typical organoleptic proprieties expected by consumers. Finally, this data represents a powerful platform to guarantee the typicality and authenticity of SCH, supporting its EU certification of geographical origin, namely the PDO and PGI.

## 2. Materials and methods

### 2.1. Standards, Reagents, Materials and Software

Sodium chloride was acquired from Panreac (Barcelona, Spain). The internal standard (IS), 4-heptanone, was purchased from Sigma-Aldrich (Missouri, USA). SPME holder for the manual sampling of SPME fiber and the fiber divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) with 50/30 μm film thickness were purchased from Supelco (Pennsylvania, USA). Ultrapure deionized water ($H_2O^d$), purified with a Milli-Q ultra-pure water system from Millipore (Massachusetts, USA). The MAXI MIX Vortex Mixer was acquired from Thermo Scientific (Massachusetts, USA). All data analysis and statistical processing were performed using the STATSOFT STATISTICA 12.0 (2013) software (Tulsa, USA).

### 2.2. Samples

Samples from all stages (S1, S2, S3, S4 and S5) of processing and storage of SCH were provided by the traditional and certified producer FRS, Madeira Island, Portugal, in April 2015, 2016, 2017 and 2018, being stored under stable conditions (4 ºC, in the dark). Identification (ID) replicate number, ID replicate code, ID sample code, ID stage code, processing year, processing stage description and producer name are presented in Table S22.

### 2.3. SPME procedure

The SPME procedure used for VOCs extraction from SCH samples was based on our analytical method previously developed, optimized and validated [159]. Briefly, all samples were daily diluted in the ratio 3:2 (w/v), where 15 g of sample was added to 10 mL of $H_2O^d$ placed into a 50 mL PTFE centrifuge tube, being mechanical homogenized during 1 min and stored at 4 °C in aliquots of 5 ml. After, these aliquots were transferred to an 8 mL glass vial with 60 mg NaCl previously added, which was placed in a thermostatic bath at 30 °C for 5 min for sample temperature equilibrium. The SPME was performed in HS mode, where the fiber DVB/CAR/PDMS was attached to a manual SPME holder and exposed in the sample HS during 60 min at 30 ºC, under magnetic agitation (600 rpm). The VOCs extracted by SPME were thermally desorbed by the fiber direct insertion into GC injector at 250 °C, in splitless mode for 10 min. The fiber was daily conditioned for 15 min at 250 ºC into GC injector to avoid contamination by unwanted interferents. Triplicate experiments were performed for all samples under analysis. Blank experiments were performed before the analysis of each sample, where the fiber was directly placed into GC injector without being subjected to any SPME extraction procedure.

*2.4. GC-MS analysis*

The analysis of extracted VOCs was carried on Agilent Technologies 6890N Network GC system (California, USA) equipped with a BP-20 fused silica capillary column with 60 m × 0.25 mm I.D. × 0.25 µm film thickness (SGE, Dortmund, Germany), and interfaced with an Agilent 5975 quadrupole inert mass selective detector (California, USA). The employed protocol for column oven temperatures was: 40 ºC for 2 min, then was increased at 0.25 ºC $min^{-1}$ until 45 ºC with a 2 min hold, after was increased at 4 ºC $min^{-1}$ to 70 ºC with a 2 min hold, was increased again at 3 ºC $min^{-1}$ to 130 ºC with a 2 min hold, and finally, was increased at 3 ºC $min^{-1}$ to 220 ºC, this final temperature was maintained during 7 min, for a total GC run time of 91.25 min. Column flow was constant at 1 mL $min^{-1}$ using He carrier gas at a purity of 99.999% (Helium N60, Air Liquid, Portugal). The injection port was operated in the splitless mode and held at 250 ºC. For the 5975 MS system, the operating temperatures of the transfer line, quadrupole and ionization source were 270, 150 and 230 ºC respectively. Electron impact mass spectra was recorded at 70 eV ionization voltages and the ionization current was 10 µA. The electron multiplier was set to the auto tune procedure. The acquisitions were performed in scan mode (30-300 m/z). VOCs identification was based on visual interpretation of spectra through the Agilent MS ChemStation Software, and confirmed comparing each VOC mass spectra with the NIST14 Mass Spectral Library (2014), being successfully identified when a similarity threshold was higher than 75%. The TPA values were obtained by target ion quantification protocol. The results are presented as RPA, which were calculated by dividing the TPA value of each VOC by the TPA value of IS.

*2.5. Chemometric analysis*

The chemometric analysis procedure was performed according the previously developed procedures in our previous studies [11,159], being introduced some modifications based on the recommendations for analytical applications [160,182]. One-way ANOVA test was performed to determine the VOCs with statistically significant differences ($p < 0.05$) on its variance level between RPA values of samples obtained throughout all stages of SCH processing during 2015-2018 production years. Furthermore, individual One-way ANOVA tests were performed for S1-S2, S2-S3, S3-S4 and S4-S5 transitions. PCA and partial least squares (PLS) analysis were performed on RPA values of VOCs dataset to achieve the preview of correlation structure of samples from all stages, being constructed according to the samples variance, without and with stage classification, respectively. A 7-fold cross-validation was performed. LDA was used as supervised pattern recognition method for variable selection in order to obtain a matrix composed by the

lowest number of VOCs that lead to a correct classification of all samples for the group assignment (S1, S2, S3, S4 and S5). A backward selection method (p value of 0.05 to enter and remove) was used to determine the most predictive VOCs and remove the least predictive from analysis, being formed a classification structure according the CDFs. A leave-one-out CV was performed. LDA is commonly suggested as an efficient method to reduce the dimensionality of large dimension matrix into a lower dimension matrix by removal of less predictive variables preserving the interclass separation (classification structure) [160,182]. A matrix reduction procedure was applied prior to LDA, where the matrix was reduced to 20 % of initial dimension based on F-value from One-way ANOVA between all stage samples. Alternatively, a matrix reduction procedure based on the VIP scores from the PLS analysis was also applied. Thus, the 37 VOCs with higher F-Value and VIP score were selected, respectively. Finally, a second PLS analysis and HCA were applied on RPA values of the most predictive VOCs. PLS based on dataset from the reduced matrix was performed to confirm the correlation structure between all samples when classified according to stage of SCH processing, and compare with structure obtained from previous PLS performed with all 187 VOCs. HCA was performed in order to determine the Euclidean linkage distances between all samples and achieve a visual measure of distance and linkage criterion between stages throughout SCH processing based only in the most predictive VOCs.

## *3. Results and discussion*

### *3.1. Monitoring the volatile profile throughout the SCH processing*

For the first time, in a four-year study (2015-2018), the HS-SPME/GC-MS method was successfully applied to monitor the volatile profile during the traditional processing and storage of SCH. The ID number, RT, main ions (m/z), target ion, match percent, IUPAC name, NIST database, abbreviation, CAS number, molecular formula and main chemical class of identified VOCs are described in Table S23. The mean RPA values and respective % RSD of identified VOCs in samples during SCH processing stages from 2015-2018 production years are described in Table S24. The mean, minimum and maximum values of RPA for identified VOCs in each SCH processing stage are summarized in Table S25. The typical GC-MS chromatograms for S1, S2, S3, S4 and S5 of SCH processing are presented in Figure S6 (A), (B), (C), (D) and (E), respectively. Chemically, the volatile profile during SCH processing varies greatly from stage to stage, where can be observed a high diversity of the number, chemical classes and RPA values of identified VOCs for each stage.

### *3.1.1. Number of identified VOCs*

A total of 187 different VOCs were identified in samples from the five stages (S1-S5) of SCH processing between the years of 2015 and 2018. The number of identified VOCs for each stage were: 126 (S1), 136 (S2), 136 (S3), 136 (S4) and 149 (S5), wherein 93 VOCs (49.7%) are common to all stages. However, only 31 VOCs (16.6%) were identified in a specific stage: 11 (S1), 5 (S2) and 15 (S5). Curiously, only 51 (34.2%) of the 149 VOCs from S5, were identified on the SCH samples from the certified producer in our previous study [159]. The increase in the number of VOCs identified may be due to the database update (NIST05 to NIST14), and mainly, due to the identification procedure used, where all the 187 VOCs were searched in all samples based on a stage-by-stage follow-up strategy. Moreover, off the all 187 VOCs, 103 (52.3%) were previously identified in others SC based-products, namely: 30 in juice, 42 in brown sugar, 31 in molasses, 18 in treacle, 64 in syrup, 38 in rum, 6 in infusions, and 6 in alcoholic-fermented beverage described as "SC wine". This information and respective references are described in Table S26.

There, 92 VOCs (46.7%) have been previously identified in thermally processed SC products, such as syrups, molasses, treacle and brown sugar, wherein most of them were identified in S3, S4 and S5 of SCH processing. This is indicative of the influence of NEBRs in the volatile profile of SCH, particularly, the thermal degradation of SC components (e.g. SGs, AAs). On the other hand, only 30 VOCs (15.2%) were identified in unprocessed products based on SC juice, mainly identified in S1 and S2, being potentially from SC plant biochemistry, and also from enzyme and microbial action on SC components. Interestingly, 40 VOCs (20.3%) were previously identified in SC alcoholic-fermented beverages, such as spirits, rum, and wine, being mainly identified in final SCH product (S5), suggesting a potential action of microorganisms during its storage.

### *3.1.2. Main VOCs*

More than one hundred VOCs were identified for each stage of the SCH processing, where were obtained RPA (x $10^3$) values from 0.5 to 500000. Although the importance of each VOC to the volatile profile should not be measured only through its RPA value, this relative measure is vital to understand which are the main VOCs for each stage of SCH processing. The RPA values for the 20 main VOCs of S1, S2, S3, S4 and S5 are described in Figure 16 (A), (B), (C), (D) and (E), respectively.

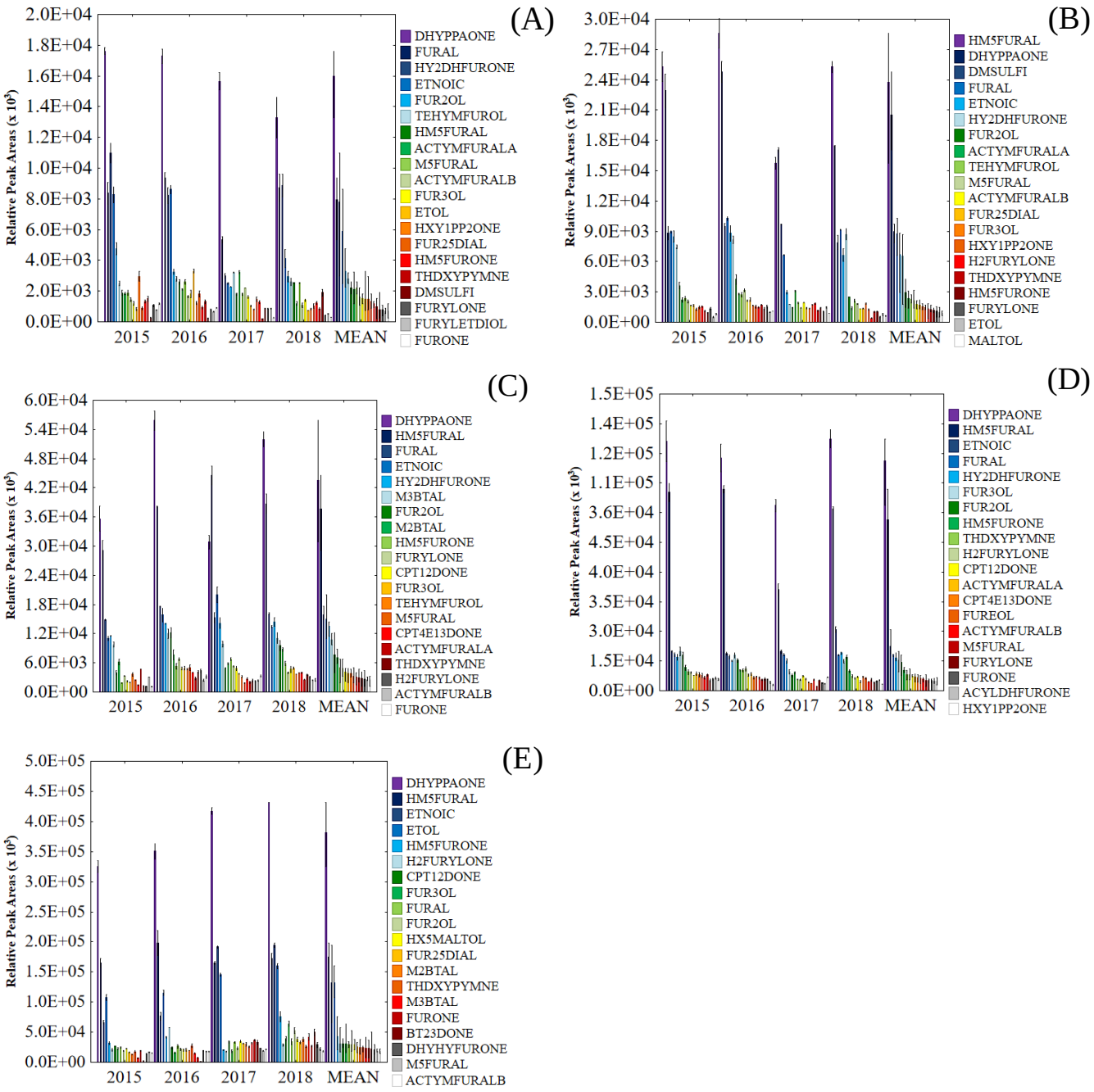


**Figure 16. The RPA values of the 20 main VOCs for stage 1 (A), stage 2 (B), stage 3 (C), stage 4 (D) and stage 5 (E) of SCH processing during 2015-2018 years.**

Through the analysis of the 20 main VOCs for each stage of SCH processing were found 32 different VOCs, where 10 were common to all stages, namely 1,3-dihydroxy-2-propanone (DHYPPAONE), furfural (FURAL), ethanoic acid (ETNOIC), 2-furanmethanol (FUR2OL), 5-(hydroxymethyl)-2-furfural (HM5FURAL), 5-methyl-furfural (M5FURAL), 5-acetoxymethyl-2-furfural B (ACTYMFURALB), 3-furanmethanol (FUR3OL), 5-(hydroxymethyl)-dihydro-2(3H)-furanone (HM5FURONE) and 2,4,6-trihydroxypyrimidine (THDXYPYMNE). On the contrary, eight were classified as main VOCs only in one stage, such as 1-(2-furanyl)-1,2-ethanediol (FURYLETDIOL) for S1, maltol (MALTOL) for S2, 5-Acetyl-Dihydro-2(3H)-Furanone (ACYLDHFURONE), furaneol (FUREOL) and 1-hydroxy-2-propanone

(HXY1PP2ONE) for S4, and 5-hydroxy-maltol (HX5MALTOL), 2,3-butanedione (BT23DONE) and 4-hydroxy-dihydro-2(3H)-furanone (DHYHYFURONE) for S5. Although not all of these VOCs have been classified as main contributors in all stages, 30 main VOCs were positively identified in all stages, with exception of BT23DONE (S2, S3, S4 and S5) and HY5MALTOL (S3, S4 and S5).

As expected, most of the main VOCs appears to be strongly linked to the NEBRs, such as DHYPPAONE (main contributor in S1, S3, S4 and S5), HM5FURAL (main contributor in S2), FURAL, M5FURAL and FUR2OL [11,183]. However, some high contributors VOCs commonly associated with NEBRs, such as ETNOIC and dimethyl sulfide (DMSULFI), can also be formed by action of microorganisms [161,184]. Remarkably, others main VOCs appear to be non-related to NEBRs. For example, ETOL has only high contribution in S1 and S5, where its formation in SCH is probably from enzyme or microbial activity [175,185].

### *3.1.3. Chemical Class Classification of VOCs*

Throughout the five stages of SCH processing was possible to recognize an enormous diversity of chemical classes, being fundamental its classification to characterize the volatile profile of each stage. The classification based on main chemical class of each VOC are described in Table S23. The summary of number of VOCs, RPA and TRPA values of main chemical classes identified in stage samples are summarized in Table S27. The contribution, RPA and % TRPA values, of each chemical class to volatile profile of all stages is presented in Figure 17 (A) and (B), respectively.

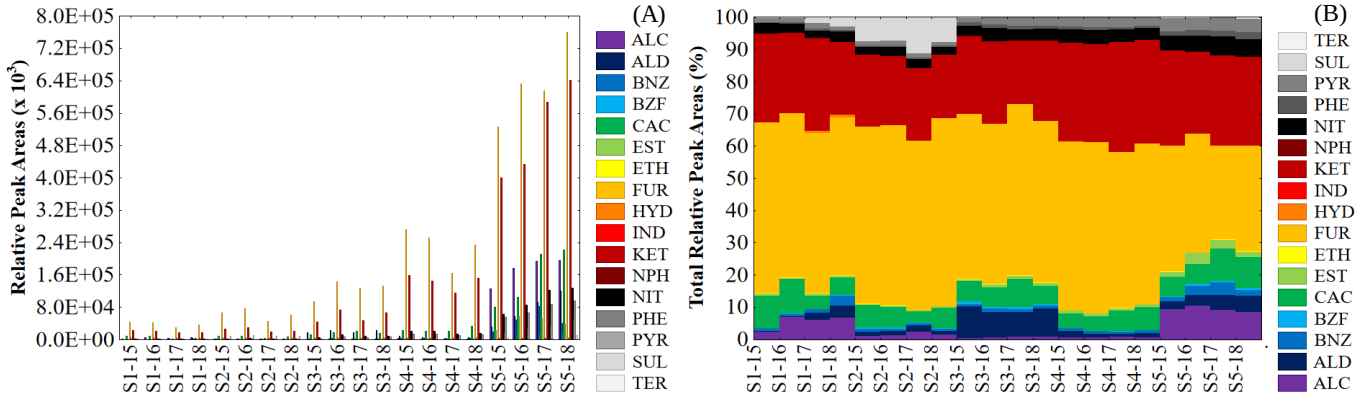


**Figure 17. The contribution, RPA (A) and TRPA (B) values, of each classification group assigned according to chemical class for all stages of SCH processing during 2015-2018 years.**

A total number of 17 chemical classes were identified, namely alcohol (ALC), aldehyde (ALD), benzene (BNZ), benzofuran (BZF), carboxylic acid (CAC), ester (EST), ether (ETH), furan (FUR),

hydrocarbon (HYD), indene (IND), ketone (KET), naphthalene (NPH), nitrogen (NIT), phenol (PHE), pyran (PYR), sulfur (SUL) and terpene/terpenoid (TER).

VOCs from 16 of 17 chemical classes were identified in all stages of SCH processing, the exception was IND group (identified only in S3, S4 and S5). Furthermore, for the first time, IND-VOCs were identified in SC-based products, being the only class where none VOC was identified in our previous study with certified SCH samples [159], and also in SC based-products described in Table S26. Undoubtedly, VOCs from KET and FUR were the main contributors to volatile profile throughout all stages of SCH processing, being always higher than 20%. FUR had the larger contribution and higher number of VOCs (44) in all stages, being about 50% in the S1, S2, S3 and S5. The VOCs with more influence in FUR contribution were HM5FURAL, HM5FURONE, FUR3OL, FUR2OL and FURAL. KET was the secondary main contributor in all stages, presenting a balanced contribution during SCH processing, between 20 and 35 %. 19 VOCs were assigned in KET, where the main contributor was DHYPPAONE, being followed by BT23DONE and 1,2-Cyclopentanedione (CPT12DONE). VOCs from ALD, CAC, NIT and PYR presented a reasonable contribution (> 1%) during all stages, being more expressive in the last three stages for PYR and NIT. Regarding the dimension, the number of VOCs assigned to each class was: NIT (16), ALD (14), CAC (8) and PYR (5). The contribution of NIT was mainly influenced by THDXYPYMNE and 2-acetylpyrrole (ACTLPYROLE), while for ALD was 2-methyl-butanal (M2BTAL), 3-methyl-butanal (M3BTAL) and 2-methyl-propanal (MPPAL). CAC contribution was explained by the presence of free fatty-acids, mainly by ETNOIC contribution. PYR contribution was principally influenced by MALTOL, and its derivatives, HX5MALTOL and 3-hydroxy-2,3-dihydro-maltol (HX3DH23MALTOL). VOCs from ALC, BNZ, EST, PHE and SUL were also identified in all stages, but only presented a considerable contribution (> 1%) at some stages. ALC and BNZ are characterized by its considerable dimension, 16 and 13 VOCs, respectively. On the contrary, EST, PHE and SUL are characterized by its small dimension, lower than 10 VOCs. ALC presented a reasonable contribution in S1, S2 and S5, being principally explained by ETOL, and in minor extension, by 2-cyclohexenol (CHEX2E1OL). Also, 1-penten-3-ol (PT1E3OL) and 1-hexanol (HX1OL) in S1, and the sugar-alcohol erythritol (ERYTOL) in S5, presented a considerable contribution. The higher contribution of BNZ was observed in S5, being highly influenced by benzeneacetaldehyde (BENZACETAL), 3-methoxy-1,2-benzenediol (M3BNZDIOL) and 2-methyl-1,4-benzenediol (M2BNZ14DIOL). A substantial contribution of SUL was observed in S2, influenced by DMSULFI, while the contribution of EST in S5 was explained by ethyl acetate (EESTAA), vinylene

carbonate (VYLESTCA) and 4,5-dimethyl vinylene carbonate (DM45VYLESTCA). The high contribution of PHE in S3, S4 and S5 was explicated by phloroglucinol (PHLOGLNOL), 4-amino-phenol (AMIPHEOL) and phenol (PHEOL). Although VOCs from BZF, ETH, HYD, NPH and TER were identified in all stages, its contribution were lower than 1% in all stages. In fact, these classes also presented small number of VOCs assigned, always lower than 5 VOCs.

There, the chemical classes highly related to NEBRs, such as FUR, BZF, PHE and PYR, and in minor extension, ALD, BNZ, KET and NIT, are responsible for 80% or more in S1 and S2, increasing to 90% in S3 and S4, and decreasing below 80% in S5. Recalling the existence of a sharp rise in temperature between S1 and S4 (40 to 120 ºC), it is evident the occurrence of some thermal reactions in these stages, such as MLDR, Streker degradation and caramelization. Nevertheless, some VOCs assigned in ALD, KET and NIT can be associated to others origins, being also formed in the raw material itself, or be products of enzymatic reactions and microbial activity that occurred in the raw material before being processed, or even during the storage of the SCH. VOCs from others chemical classes, namely ALC, CAC and EST, appears to be linked to action of enzymes (only in S1) and microorganisms due to its higher contribution in S1 and S5. On the other hand, VOCs from HYD and TER mainly found in S1, are probably from SC plant, being synthetized during several biochemical pathways. However, the origin of VOCs from IND, NPH and ETH are more difficult to explain. Due to the enormous diversity of VOCs within each chemical class, and also due to the complexity of their formation and origin, a chemometric analysis was used to obtain a more detailed view of each stage of SCH processing.

### *3.2. Chemometric analysis based on the volatile profile throughout the SCH processing*

Chemometric analysis was performed to comprehend the formation and origin of VOCs in each stage, and mainly, to recognize the pathways involved during processing and storage of SCH, allowing the optimization and control of conditions for each stage in order to establish the typicality and authenticity of final product.

#### *3.2.1. One-way ANOVA test*

One-way ANOVA was performed to determine the VOCs with statistically significant differences based on its variance level throughout the SCH processing, namely between all stages, and S1-S2, S2-S3, S3-S4 and S4-S5 transitions. The data obtained from ANOVA was valuable to understand the formation pathways

and origin of VOCs. The significance parameters, Probability (P) and Fischer (F) values, between all stages and for each transition are summarized in Table S28.

According with results from ANOVA test, all 187 VOCs presented statistically significant differences ($P < 0.05$) in RPA values between all stages (S1-S5), where 48 VOCs (25.7%) showed high differences (F values ≥ 100) between all five stages. Furthermore, 20 VOCs (10.7%) demonstrated very high significant differences (F values ≥ 200) throughout the SCH processing, namely DMSULFI, DHYPPAONE, 2,6-dimethyl-pyrazine (DM26PYZNE), ETOL, ACTYMFURALB, 2-ethyl-6-methyl-pyrazine (E6MPYZNE), octanal (OCTAL), HM5FURAL, HX3DH23MALTOL, FUREOL, MALTOL, 5-methyl-2(3H)-furanone (M5FURONE), M5FURAL, THDXYPYMNE, 1-(2-furanyl)-ethanone (FURYLONE), ACYLDHFURONE, C12PTDONE, pentanal (PTNAL), oxypurinol (OXYPUROL) and 4-cyclopentene-1,3-dione (CPT4E13DONE).

Likewise, the ANOVA results from each one of the four transitions between the stages during SCH processing (S1-S2, S2-S3, S3-S4 and S4-S5) showed that all 187 VOCs presented statistically significant differences in RPA values at least between one transition. Remarkably, 31 VOCs demonstrated significant differences throughout all transitions, namely DMSULFI, furan (FUR), 2-methyl-furan (M2FUR), 2-butanone (BT2ONE), M3BTAL, 5-butyl-dihydro-2(3H)-furanone (BDH2FURONE), m-cresol (MCREOL), 5-propyl-dihydro-2(3H)-furanone (PDH2FURONE), 2-methyl-dihydro-2(3H)-furanone (MDH2FURONE), M5FURONE, 1,3-dihydro-4-methyl-2H-imidazol-2-one (M4IMDZONE), furfuryl formate (FURYLFMTE), 2,2'-methylenebis[5-methyl-furan (MNEB5MFUR), CPT12DONE, 2,2-diethyl-3-methyl-oxazolidine (DEMOXZDNE), acrylamide (ACRYLMDE), 2,3-dimethyl-3-ppyrazolin-5-one (DM23PYZLONE), M2BNZ14DIOL, MALTOL, 2H-Pyran-2,6(3H)-Dione (PYR26DIONE), 1-(2-furanyl)-2-hydroxy-ethanone (H2FURYLONE), 1H-pyrrole-2-carboxaldehyde (PYRLE2AL), PHLOGLNOL, 2-furanpropionic acid (FURPPIONIC), DHYPPAONE, DM45VYLESTCA, 2-methoxy-4-vinyl-phenol (MXY2VYL4PHEOL), 4-pyridinol (PYRDINOL), HM5FURAL, FURYLETDIOL and DHYHYFURONE. Contrariwise, 36 VOCs presented statistically significant differences only for one specific transition. In S1-S2 transition, 76 VOCs presented significant differences, where 12 were specific from this transition, namely ethyl ether (EETHR), 3-pentanone (PT3ONE), methyl 2-ethylpentanoate (MESTPTA), 3-methyl-1-butanol (M3BT1OL), cis-2-pentenol (CPT1E2OL), 2-pentene (PT2ENE), 1-ethyl-1-methyl-cyclopentane (E1M1CYPTANE), 2-octanol (OCT2OL), trans-2-octenal (TOCT2EAL), 1-

octen-3-ol (OCT3E1OL), trans-2-octenol (TOCTE2OL) and diethylene glycol monobutyl ether (DETNGOLBTHR). Despite 146 VOCs showed significant differences from S2 to S3, only hexane (HXANE), 2-heptanone (HPT2ONE), 1-pentanol (PT1OL), 2,5-dimethyl-pyrazine (DM25PYZNE), 3-ethyl-2-methyl-1,3-hexadiene (E3M2HX13DENE), 1,4-butanediol (BT14DIOL), 2-ethyl-phenol (E2PHEOL) and benzophenone (BENZPONE) were found to be specific for S2-S3 transition. For S3-S4 transition, 112 VOCs were significantly different in terms of RPA values, which mesitylene (MESTLNE) and naphthalene (NPHNE) presented only for this transition. Finally, in the last transition S4-S5, where SCH was stored during 6 months at room temperature, 149 VOCs demonstrated significant differences in RPA values. Among these, the following 16 VOCs were specific for this transition, ethyl formate (EESTFA), ethyl propanoate (EESTPA), 1-propanol (P1POL), nonomethyl succinate (METESTBA), dimethyl disulfide (DMDSFD), 2-methyl-1-propanol (M2PP1OL), 1-butanol (BT1OL), 2-methyl-1-butanol (M2BT1OL), 5-methyl-2-furanmethanethiol (M2FURTHOL), decanal (DECAL), 2,3-Dihydro-1,1,4,6-tetramethyl-1H-indene (DHT1146MIDNE), phenylmethyl acetate (PMESTAA), 2-phenylethyl acetate (PEESTAA), ERYTOL, octanoic acid (OCTOIC) and undecanoic acid (UNDECOIC).

Interestingly, the results from ANOVA test confirmed some information mentioned before (in section 3.1.3). There, most of VOCs that showed significant differences between all transitions are related to NEBRs, such as M3BTAL, CPT12DONE, DHYPPAONE, HM5FURAL, M5FURONE and DHYHYFURONE. On the other hand, some specific VOCs from S1-S2 were originated from SC plant biochemistry, such as PT2ENE, CPT1E2OL, TOCTE2OL and PT3ONE, being probably degraded in S2. Furthermore, some specific VOCs from the transition S4-S5 are probable products of enzyme and microbial activity during SCH storage, such as EESTFA, EESTPA, P1POL and M2PP1OL.

### *3.2.2. PCA and PLS*

PCA and PLS analysis were applied on RPA values of VOCs dataset in order to obtain the preview of differentiation/correlation structure based on the variance of samples from all stages of SCH processing between 2015 and 2018, without classification and with classification according to the stage, respectively. The information of PCA and PLS analysis are summarized in Table S29.

The loading results and VIP scores of PCA and PLS analysis for each variable (VOCs) are described in Table S30, while the loading results of all stages samples (PCA) and five stages centroids (PLS) are described in Table S31. The PCA and PLS scores results of all samples under analysis are described in SM

Table 11. The PCA loadings line plot of all stages samples for PC1, PC2 and PC3 are showed in Figure S7 (A), (B) and (C), respectively. The PLS loadings line plot of five stages centroids for PLS1, PLS2 and PLS3 are showed in Figure S7 (D), (E) and (F), respectively. The PCA loading 3D plots of all stages samples and all variables for PC1, PC2 and PC3 are showed in Figure 18 (A) and (B), respectively. The PLS loading 3D plots of the five stages centroids and all variables for PLS1, PLS2 and PLS3 are showed in Figure 19 (A) and (B), respectively.

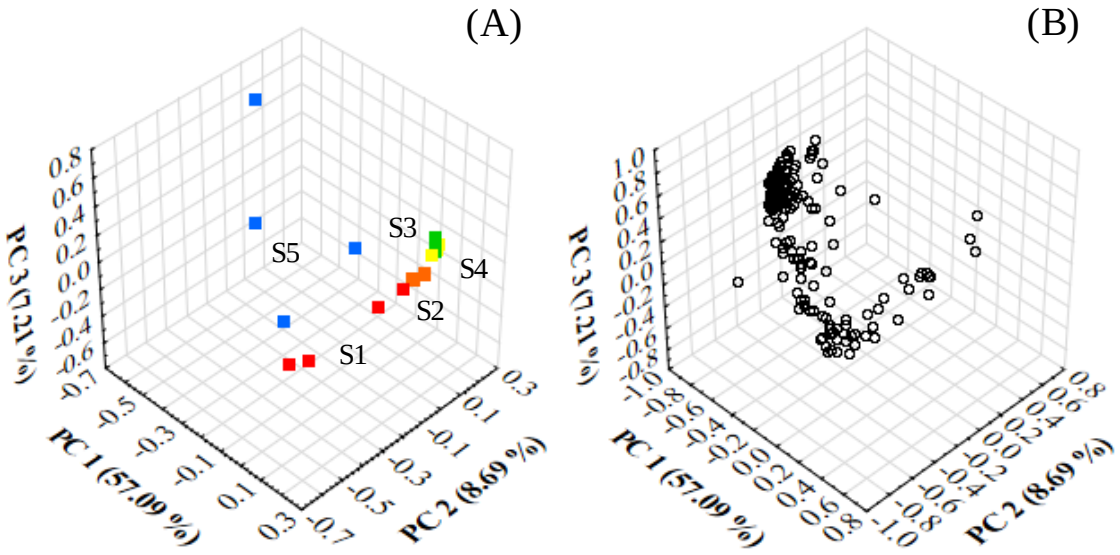


**Figure 19. The PCA loading 3D plot of all stages samples (A) and the selected 187 VOCs (B) for the three main components.**

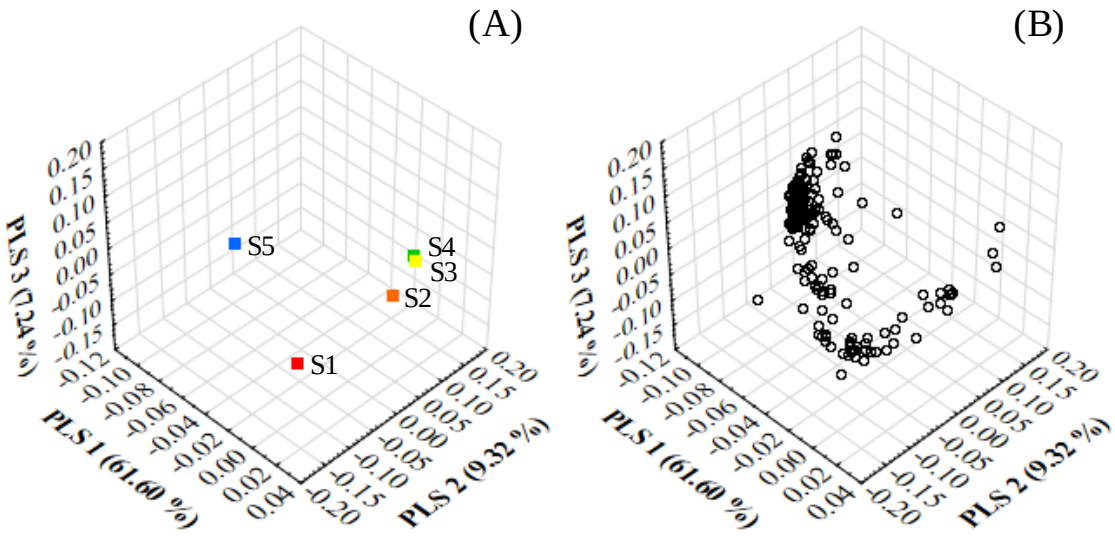


**Figure 18. The PLS loading 3D plot of all stages centroids (A) and the selected 187 VOCs (B) for the three main components.**

The PCA analysis based on PC1, PC2 and PC3 explained 72.99% of TVA, being that the sum of all 14 components explained 96.88%. Despite the existence of some intra-variability between samples from S5 in PC1 and PC3, and S1 in PC2, the projection of all samples based on PC1, PC2 and PC3 loading results

presented the formation of three well-defined groups according to SCH processing stage, namely the group formed by S1 samples, group formed by S5 samples, and a huge group formed by samples of intermediate stages, S2, S3 and S4. In PC1 projection (57.10% TVA), S5 samples demonstrated a high variance from the others samples stages. On the contrary, the projections of S1, S2, S3 and S4 samples in PC1 showed a low variance between stages, being observed a small but distinct difference between the projection of two group of samples, S1-S2 and S3-S4. Regarding the PC2 projection (8.70% TVA), S1 samples presented intra-variance among the four years of SCH production, mainly between 2015-2016 and 2017-2018. However, S1 samples also demonstrated high variance from S2, S3 and S4 samples, and in minor extension, from S5 samples. Also, the S3 and S4 samples presented a considerable variance from S1, S2 and S5 samples. According the PC3 projection (7.20% TVA) was observed a small variance between S1, S2, S3 and S4 samples. Nevertheless, a huge intra-variance was presented among the samples from S5. The projections of S5 in PC1 and PC3 indicate that the storage conditions should be more strictly controlled. Additionally, the period of time until the product sale could be a factor influencing the volatile profile of SCH. On the other hand, the stages associated to thermal processing (S2, S3 and S4) presented low intra-variance among the samples from the four years under study.

A PLS analysis was applied to confirm the variance between samples when classified according to stage of SCH processing, being classified as: centroid-S1 (CS1), centroid-S2 (CS2), centroid-S3 (CS3), centroid-S4 (CS4) and centroid-S5 (CS5). The three main PLSs (PLS1, PLS2 and PLS3) explained 78.16% of TVA, where the sum of all 20 components explained 99.96 %. As expected, an important variance was observed in projection of three main components between the CS1, CS5, and group formed by CS2, CS3 and CS4, being observed a slight variance between CS2 and CS3-CS4. In PLS1 projection (61.60% TVA), the CS5 presented a high variance from the others centroids. Even though in minor extension, the CS1, CS2, CS3 and C-S4 also demonstrated a good variance in PLS1 projection, principally between CS1-CS2 and CS3-CS4. In PLS2 (9.30% TVA), CS1, CS2, CS5, and CS3-CS4 centroids exhibited a substantial variance from the others, where the higher variance was verified for CS1. As PLS1, in PLS3 (7.20% TVA), the higher variance was also reached between CS5 and the others centroids.

Although the PLS model was constructed based on all 187 VOCs, each one influenced differently the projection of centroids, being possible to observe the contribution of each VOC for the projection of a centroid associated with a specific stage of SCH processing. On the main PLS projection (PLS1), the most

of VOCs influenced the CS5, where was highly influenced by 115 VOCs (61.50%), belonging a wide variety of chemical classes, which some can be highlighted due to their potential source or chemical pathway. Although some VOCs belong to chemical classes related to activity of microorganisms, namely ALC (e.g. ETOL), CACD (e.g. ETNOIC) and EST (e.g. PMESTAA and PEESTAA), most of VOCs belong to chemical classes associated a NEBRs, such as KET (e.g. 3-hydroxy-2-butanone (HXY3BT2ONE), HXY1PP2ONE and DHYPPAONE), PYR (e.g. MALTOL, HX3DH23MALTOL and HX5MALTOL), NIT (DM26PYZNE and E6MPYZNE), and FUR (e.g. FURAL, HM5FURAL, M5FURONE, DHYHYFURONE, H2FURYLONE and FUR2OL). The influence demonstrated by these VOCs in S5 indicate that is possible the occurrence of NEBRs during the storage period, at least in the first months. Interestingly, the projections of CS1 and CS2, and in minor extension, CS3 and CS4, were strongly influenced by 40 VOCs (21.39%), namely ALC (e.g. 2-methyl-3-buten-2-ol (M3BT2OL), 1-penten-3-ol (PT1E3OL), M3BT1OL, PT1OL, CPT1E2OL, 2-heptanol (HPT2OL), HX1OL, TOCTE2OL, 1-heptanol (HPT1OL), 1-octanol (OCT1OL), OCT2OL and BT14DIOL), KET (e.g. PT3ONE, 1-penten-3-one (PT1E3ONE), HPT2ONE, 3-octanone (OCT3ONE) and 2-nonen-4-one (NON2ONE)), ALD (e.g. PTNAL, hexanal (HXAL), heptanal (HPTAL), OCTAL, cis-2-heptanal (CH2PTAL), TOCT2EAL and (E,E)-2,4-heptadienal (TTHPT24DAL)) and HYD (e.g. 1,4-pentadiene (PT14DIENE), PT2ENE, E1M1CYPTANE and E3M2HX13DENE). There, VOCs are probably formed in SC plant, or later, by action of enzymes and microorganisms in SC raw material, or even in initial steps of NEBRs (e.g. MLDR).

### *3.2.3. LDA*

LDA was applied as supervised pattern recognition method in order to obtain classification rules for the group assignment (S1, S2, S3, S4 and S5) of all samples under analysis based only in the most predictive VOCs. A matrix reduction procedure was used due to the complexity of applying the LDA to a large number of variables. The LDA information of the selected 37 VOCs based on the VIP scores are summarized in Table S32. However, the procedure based on the VIP scores presented poor results on PLS and HCA analysis, showed in Figure S8, being ignored for further analysis. The CDF coefficients and highest probability classification results of all samples are summarized in Table S33. The LDA information and CDF coefficients of the most predictive VOCs based on F-Vale from one-way ANOVA test are summarized in Table 4.

**Table 4. Results of variables from LDA after matrix reduction method to 20% of original dimension according with higher F values obtained from One-way ANOVA test based on the RPA of the identified VOCs in samples from SCH processing stages during 2015-2018 production years.**

| Volatile Organic Compounds | Abbreviations | ANOVA | | | LDA | | | | | | PLS | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | CDF[4] | | | Loading Value | | | VIP[5] | |
| | | F[1] | W[2] | F[3] | 1 | 2 | 3 | 1 | 2 | 3 | Importance | Power (x 100) |
| Dimethyl Sulfide | DMSULFI | 562.68 | 5.05E-05 | 1.04E+05 | 0.00101 | 0.01304 | 0.02882 | 0.041 | -0.480 | -0.059 | 3.0 | 22.77 |
| 1,3-Dihydroxy-2-Propanone | DHYPPAONE | 549.57 | 2.07E-03 | 2.53E+03 | -0.00512 | -0.00305 | -0.00098 | -0.179 | 0.000 | -0.040 | 31 | 8.01 |
| 2,6-Dimethyl-Pyrazine | DM26PYZNE | 523.62 | 1.71E-03 | 3.06E+03 | -0.00494 | 0.00047 | 0.01127 | -0.171 | -0.002 | 0.153 | 13 | 16.50 |
| Ethanol | ETOL | 409.24 | 2.27E-04 | 2.32E+04 | -0.00445 | 0.00201 | -0.00198 | -0.176 | -0.061 | -0.014 | 34 | 7.84 |
| 5-Acetoxymethyl-2-Furfural B | ACTYMFURALB | 395.90 | 3.17E-04 | 1.66E+04 | -0.00436 | -0.00223 | -0.00144 | -0.178 | -0.005 | -0.044 | 12 | 16.59 |
| 2-Ethyl-6-Methyl-Pyrazine | E6MPYZNE | 369.28 | 1.10E-03 | 4.78E+03 | -0.00413 | 0.00048 | 0.00998 | -0.171 | -0.004 | 0.162 | 19 | 13.65 |
| Octanal | OCTAL | 343.03 | 1.33E-02 | 3.89E+02 | 0.00156 | 0.00337 | 0.05184 | 0.069 | -0.111 | 0.594 | 5 | 21.42 |
| 5-(Hydroxymethyl)-2-Furfural | HM5FURAL | 338.26 | 5.39E-04 | 9.73E+03 | -0.00380 | -0.00515 | 0.00578 | -0.167 | 0.015 | -0.023 | 10 | 18.77 |
| 3-Hydroxy-2,3-Dihydro-Maltol | HX3DH23MALTOL | 318.36 | 5.83E-03 | 8.95E+02 | -0.00389 | -0.00252 | -0.00060 | -0.178 | 0.004 | -0.036 | 21 | 10.74 |
| Furaneol | FUREOL | 315.94 | 9.31E-02 | 5.11E+01 | -0.00379 | -0.00412 | 0.00044 | -0.170 | 0.041 | -0.031 | 15 | 16.33 |
| Maltol | MALTOL | 261.99 | 5.44E-03 | 9.59E+02 | -0.00358 | 0.00002 | -0.00057 | -0.179 | -0.039 | -0.020 | 35 | 6.60 |
| 5-Methyl-2(3H)-Furanone | M5FURONE | 251.27 | 9.07E-02 | 5.26E+01 | -0.00134 | -0.00055 | 0.00002 | -0.161 | -0.005 | -0.017 | 4 | 21.87 |
| 5-Methyl-Furfural | M5FURAL | 248.78 | 1.28E-03 | 4.10E+03 | -0.00348 | -0.00115 | 0.00089 | -0.178 | -0.018 | -0.008 | 14 | 16.49 |
| 2,4,6-Trihydroxypyrimidine | THDXYPYMNE | 230.84 | 3.30E-03 | 1.59E+03 | -0.00330 | -0.00242 | -0.00078 | -0.176 | 0.007 | -0.046 | 18 | 14.29 |
| 1-(2-Furanyl)-Ethanone | FURYLONE | 225.90 | 3.70E-04 | 1.42E+04 | -0.00320 | -0.00302 | 0.00732 | -0.173 | 0.043 | 0.102 | 6 | 20.78 |
| 5-Acetyl-Dihydro-2(3H)-Furanone | ACYLDHFURONE | 224.75 | 2.12E-03 | 2.47E+03 | -0.00325 | -0.00265 | 0.00051 | -0.177 | 0.018 | -0.017 | 16 | 16.25 |
| 1,2-Cyclopentanedione | CPT12DONE | 220.79 | 1.43E-03 | 3.66E+03 | -0.00327 | -0.00155 | 0.00130 | -0.179 | -0.002 | 0.005 | 27 | 9.24 |
| Pentanal | PTNAL | 213.44 | | | Removed from analysis. | | | | | | | |
| Oxypurinol | OXYPUROL | 204.15 | 1.27E-03 | 4.12E+03 | -0.00316 | 0.00008 | -0.00142 | -0.179 | -0.036 | -0.026 | 28 | 9.22 |
| 4-Cyclopentene-1,3-dione | CPT4E13DONE | 200.16 | | | Removed from analysis. | | | | | | | |
| 4-(1-Methylpropyl)-Phenol | MPPYLPHEOL | 187.99 | 3.84E-03 | 1.36E+03 | 0.00097 | 0.00655 | 0.01898 | 0.062 | -0.455 | -0.040 | 2 | 24.56 |
| Octanoic Acid | OCTOIC | 183.47 | 8.26E-02 | 5.83E+01 | -0.00298 | 0.00132 | -0.00107 | -0.169 | -0.055 | -0.010 | 11 | 16.75 |
| 2-Methyl-Dihydro-2(3H)-Furanone | MDH2FURONE | 183.31 | 6.09E-02 | 8.09E+01 | -0.00299 | 0.00097 | 0.00085 | -0.176 | -0.049 | 0.028 | 25 | 9.63 |
| 3-Methyl-2(5H)-Furanone | M3FURONE | 177.33 | 3.00E-02 | 1.70E+02 | -0.00295 | 0.00007 | -0.00015 | -0.178 | -0.030 | 0.004 | 32 | 7.99 |
| 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | GLUPYROSE | 146.81 | 6.26E-04 | 8.38E+03 | -0.00268 | 0.00052 | -0.00004 | -0.175 | -0.049 | 0.000 | 23 | 10.34 |
| 2-Propenal | PPENAL | 139.12 | 1.66E-03 | 3.16E+03 | -0.00261 | 0.00041 | 0.00091 | -0.165 | -0.021 | 0.029 | 9 | 19.66 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Furfural | FURAL | 137.75 | 9.76E-04 | 5.37E+03 | -0.00239 | -0.00366 | 0.00665 | -0.168 | 0.066 | 0.103 | 7 | 20.36 |
| 5-Hydroxy-Maltol | HX5MALTOL | 136.53 | 9.92E-02 | 4.77E+01 | -0.00258 | -0.00048 | -0.00035 | -0.178 | -0.023 | -0.015 | 29 | 9.17 |
| 4-Pyridinol | PYRDINOL | 135.63 | 7.83E-04 | 6.70E+03 | -0.00258 | 0.00016 | -0.00014 | -0.178 | -0.042 | -0.007 | 30 | 8.28 |
| 1-(2-Furanyl)-1,2-Ethanediol | FURYLETDIOL | 134.76 | 2.51E-04 | 2.09E+04 | -0.00257 | -0.00042 | -0.00080 | -0.177 | -0.016 | -0.017 | 8 | 19.82 |
| 4-Hydroxy-Dihydro-2(3H)-Furanone | DHYHYFURONE | 132.15 | 1.35E-03 | 3.88E+03 | -0.00173 | 0.00409 | 0.00327 | -0.178 | -0.040 | -0.018 | 33 | 7.92 |
| 2-Acetylpyrrole | ACTLPYROLE | 129.05 | 2.03E-04 | 2.58E+04 | -0.00251 | -0.00010 | 0.00174 | -0.177 | -0.023 | 0.044 | 22 | 10.50 |
| 3-Methyl-2,4(3H,5H)-Furandione | M3FURDIONE | 128.42 | 3.24E-02 | 1.57E+02 | -0.00251 | 0.00010 | -0.00005 | -0.178 | -0.038 | -0.002 | 26 | 9.48 |
| Acrylamide | ACRYLMDE | 126.86 | 2.53E-04 | 2.07E+04 | -0.00249 | 0.00006 | 0.00003 | -0.176 | -0.044 | -0.013 | 24 | 10.17 |
| 2H-Pyran-2,6(3H)-Dione | PYR26DIONE | 121.86 | 2.84E-04 | 1.85E+04 | -0.00244 | -0.00005 | -0.00051 | -0.176 | -0.033 | -0.017 | 20 | 11.46 |
| 2-Nonen-4-one | NON2ONE | 121.21 | 5.71E-04 | 9.19E+03 | 0.00078 | 0.00526 | 0.01524 | 0.060 | -0.453 | -0.024 | 1 | 24.69 |
| 3-Methyl-Dihydro-2(3H)-Furanone | M3DHFURONE | 121.00 | 3.43E-04 | 1.53E+04 | -0.00244 | -0.00005 | 0.00019 | -0.175 | -0.027 | 0.003 | 17 | 14.57 |

[1]F - Fischer value from One-way ANOVA test.
[2]W - Wilks value from Linear Discriminant Analysis.
[3]F - Fischer value from Linear Discriminant Analysis.
[4]CDF - Canonical Discriminant Function Coefficients.

The LDA line plots of all stages classified according to CDF1, CDF2 and CDF3 are exposed in Figure S9 (A), (B) and (C), respectively. The LDA line plot of most predictive VOCs for CDF1, CDF2 and CDF3 are presented in Figure S9 (D), (E) and (F), respectively. The CDF coefficients 3D plots of the five stage centroids and most predictive VOCs for CDF1, CDF2 and CDF3 are presented in Figure 20 (A) and (B), respectively.

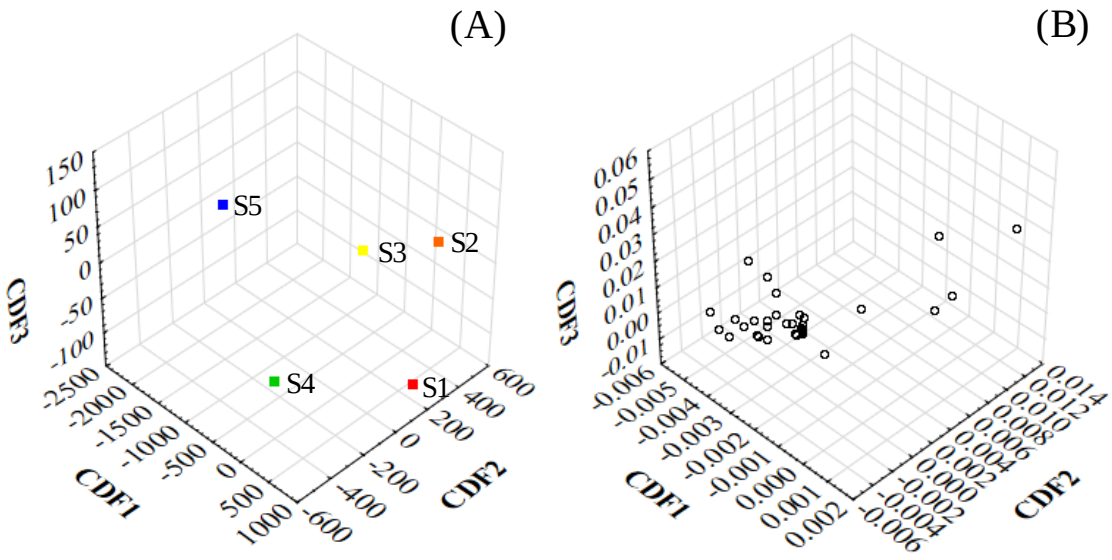


**Figure 20. The LDA loading 3D plot of all stages centroids (A) and the 35 most predictive VOCs (B) for the three main components.**

All samples under analysis were classified at 100% correct rate, being clustered according the five stages of SCH processing. Only two VOCs were removed from LDA analysis through 89 steps of the backward selection method ($p < 0.05$), PTNAL and CPT4E13DONE. Therefore, LDA analysis were only based on the 35 most predictive VOCs, namely DMSULFI, DHYPPAONE, DM26PYZNE, ETOL, ACTYMFURALB, E6MPYZNE, OCTAL, HM5FURAL, HX3DH23MALTOL, FUREOL, MALTOL, M5FURONE, M5FURAL, THDXYPYMNE, FURYLONE, ACYLDHFURONE, CPT12DONE, OXYPUROL, 4-(1-methylpropyl)-phenol (MPPYLPHEOL), OCTOIC, MDH2FURONE, 3-methyl-2(5H)-furanone (M3FURONE), 1,4:3,6-dianhydro-.alpha.-d-glucopyranose (GLUPYROSE), 2-propenal (PPENAL), FURAL, HX5MALTOL, PYRDINOL, FURYLETDIOL, DHYHYFURONE, ACTLPYROLE, 3-methyl-2,4(3H,5H)-furandione (M3FURDIONE), ACRYLMDE, PYR26DIONE, NON2ONE and 3-methyl-dihydro-2(3H)-furanone (M3DHFURONE). Remarkably, more than 80% of 35 most predictive VOCs are related to thermal degradation, while the remaining VOCs are mostly associated with enzyme and microbial activity.

The LDA results demonstrated a high level of discrimination along the three CDFs between the samples from the five stages. In CDF 1, a notable discrimination was obtained between the samples from S5 and others stages. For CDF 2, the higher discrimination was observed between samples of S4 and others stages. Also, in CDF2, a reasonable discrimination was observed between S1, S2, S3 and S5. For CDF3, a high discrimination level was observed in samples of S1 from the others samples, being also verified a considerable discrimination between others stages. LDA results proved that the is possible discriminate and classify correctly all samples from each one of the five stages of SCH processing based on the RPA values of the 35 most predictive VOCs, corresponding to 17.1% of the original matrix of 187 VOCs.

### *3.2.4. PLS and HCA*

An additional PLS analysis based only on the 35 most predictive VOCs were done to confirm the differentiation/correlation structure between all stages of SCH processing. The PLS information are summarized in Table S34. The loading results and VIP scores from PLS analysis of all 35 VOCs are summarized in Table 4. The PLS loading results of stages centroids and the scores results of all samples under analysis are described in Table S33. The PLS loadings line plots of all stages classified according to PLS1, PLS2 and PLS3 are showed in Figure 10 (A), (B) and (C), respectively. The PLS loadings line plot of the 35 most predictive VOCs for PLS1, PLS2 and PLS3 are showed in Figure 10 (D), (E) and (F), respectively. The PLS loading 3D plots of the five stages centroids and 35 most predictive VOCs for PLS1, PLS2 and PLS3 are showed in Figure 21 (A) and (B), respectively.

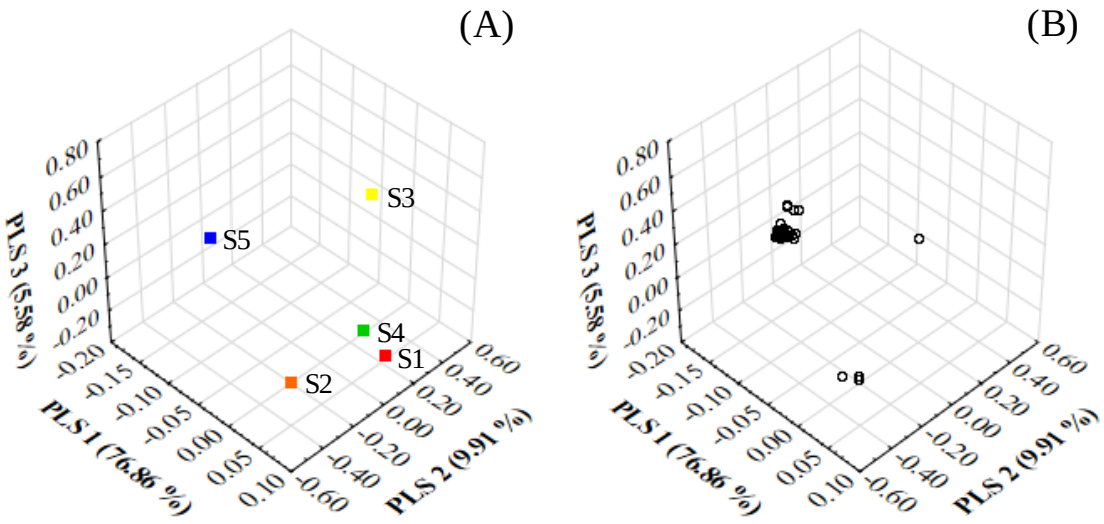


**Figure 21. The PLS loading 3D plot of all stages centroids (A) and the 35 most predictive VOCs (B) for the three main components.**

The PLS analysis based on PLS1, PLS2 and PLS3 explained 92.4% of TVA, where the sum of all 16 components explained 99.9%. There, a high inter-variance between was observed between all stages

centroids, even between CS2, CS3 and CS4. Expectably, in PLS1 (76.9%) the higher variance was verified between CS5 and others stages centroids, being also verified a considerable inter-variance between two groups of stages CS1-CS2 and CS3-CS4. Regarding the PLS2 projection (9.9%), a substantial variance was observed between CS2 and other stages centroids. Finally, in PLS3 projection (5.6%), a high variance was verified between S3 and other centroids. The projection of three main component from PLS based on the 35 most predictive VOCs presented a considerably higher differentiation between all stages centroid when compared to similar projection of the PLS performed with all 187 VOCs. In line with the previous results, through the analysis of the 35 most predictive VOCs in the projection of main component (PLS 1), it is possible to verify the influence of some VOCs with one or two specific stages of the processing of the SCH. There, close to 83% of most predictive VOCs influenced the projection of S5, where mainly are related to NEBRs, such as DHYPPAONE, DM26PYZNE, FURAL, HM5FURAL, FUREOL or MALTOL. Also, ETOL, a VOC that influenced highly the projection of S5, is a well-known product from alcoholic fermentation. On the contrary, only four VOCs, DMSULFI, OCTAL, MPPYLPHEOL and NON2ONE, influenced the projection of remaining stages. Despite this specific influence, all 35 most predictive VOCs can be considered as potential markers for control of SCH processing, which should be developed in further studies to achieve its quantification.

HCA was performed based on the RPA values of previously selected 35 VOCs in order to determine the linkage Euclidean distances between all samples and an appropriate measure of distance and linkage criterion between the five stages of SCH processing. The HCA dendrogram is presented in Figure 22.

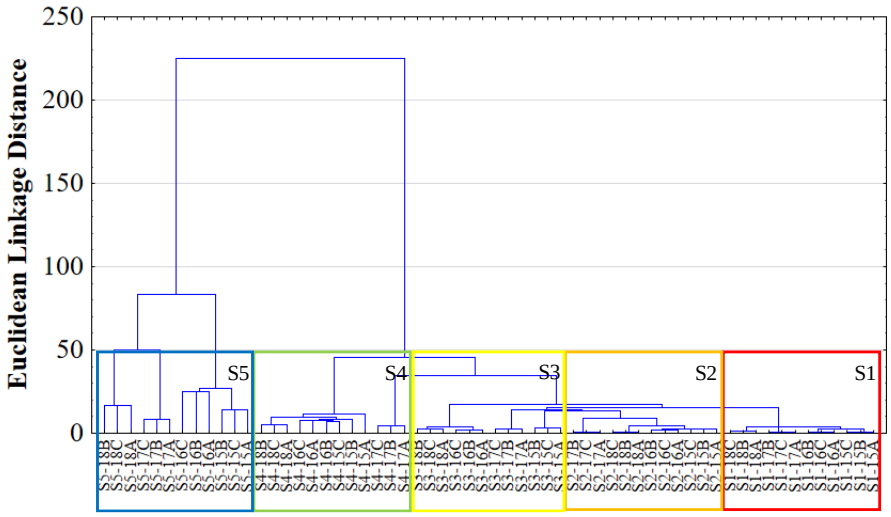


**Figure 22. The HCA dendrogram based on Euclidean linkage distances for all replicates from all stages of SCH processing during 2015-2018 years.**

As expected, the higher distance was achieved between the S5 and other stages, where the linkage level of samples decreases as follows: S5 > S4 > S3 > S2 > S1. The HCA results showed a perfect grouping of all samples according its stage of SCH processing. Moreover, low distances were obtained for samples of similar stage throughout the four years under study, demonstrating the high consistence of obtained results based on the most predictive VOCs. Thus, the results from second PLS and HCA confirm that is possible the establishment of typicality and authenticity of SCH through rigorous procedures and strict control of all stages during its traditional processing and storage based on the analysis of the 35 most predictive VOCs.

*3.3. Formation pathways model of volatile profile throughout the SCH processing*

Comprehensively, the origin and formation of VOCs from SCH is not simple to explain, where a wide and complex network of interconnecting chemical pathways can be involved throughout all stages. Nevertheless, based on the results previously described, and supported by the available information from the scientific literature, is possible to propose a preliminary model of VOCs formation pathways during all stages of SCH processing, being summarized in Figure 23.

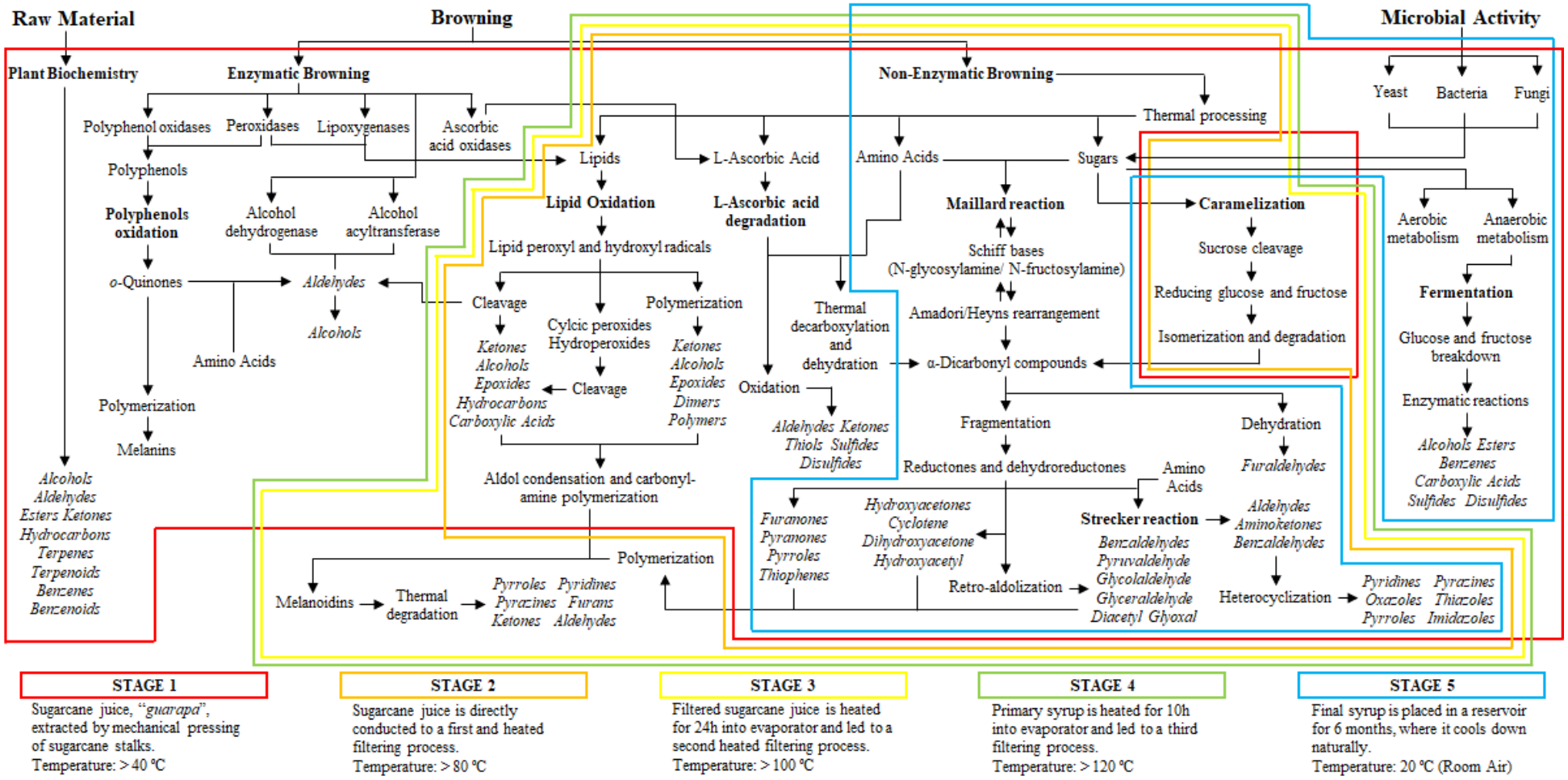


**Figure 23. The proposed model of VOCs formation pathways according the conditions at each stage of SCH processing.**

The proposed model of formation pathways was constructed according the conditions of processing at each stage (e.g. temperature, water content, atmosphere exposure) and the formerly recognized components of SC raw material (e.g. polyphenols, lipids, L-ascorbic acid, SGs and AAs), corresponding the main reactions or pathways that probably occur at each stage, and consequently, the chemical class of its products.

Firstly, some VOCs from BNZ, TER and HYD were found in higher quantities in S1 and S2, such as MESTLNE, p-cymene (PCYMNE) and PT2ENE, being VOCs linked to SC plant biochemistry, where play a key role in plant-environment interactions, abiotic stress response and microbial pathogens defense [163,186,187]. Likewise, a wide diversity of short-chain VOCs from ALC, ALD, EST and KET found in S1 and S2 were also found in various plant tissues, being formed *in vivo* by several enzymes [188]. In fact, these VOCs are probably formed during the crushing and pressing of SC stalks in S1, where the activity of enzymes is exponentially increased due to the disruption of plant tissues [189]. Lipoxygenase (LOX) and peroxidase (POX) can oxidize lipids (free fatty-acids) to form several VOCs from ALD and KET [190,191]. Polyphenol oxidase (PPO) and POX oxide the polyphenols into quinones, which in later reactions with AAs can generated ALD-VOCs [192]. Also, ascorbic acid oxidase (AAO), a copper-containing enzyme, catalyze the oxidation of vitamin C to originate ALD-VOCs [193]. Alcohol dehydrogenase (ADH) and alcohol acyltransferase (AAT) can react with previously formed aldehydes to produce short-chain ALC-VOCs [188]. Moreover, several VOCs from ALC, ALD, BNZ, CAC, EST, HYD, KET and SUL identified in S1 and S2, can also be naturally formed by bacteria, fungi or yeast during the period of harvest and transportation of stalks to the factory, the storage before entering into the processing line and even in S1 and S2 processing [175,176]. Here, we can highlight the microbial formation of three VOCs that were classified as the main contributors to volatile profile of S1 and S2, namely ETNOIC, DMSULFI and ETOL. ETNOIC can be formed by oxidation of SGs and alcohols during fermentation process by acetic acid bacteria group [161], DMSULFI can be produced by yeast-mediated mechanism during alcoholic fermentation [184], and ETOL can be easily produced by *Saccharomyces cerevisiae* in juice and syrups from SC [185]. Additionally, in S1, and principally in S2, some NEBRs are initiated. Several short-chain VOCs from ALD and KET can be generated by lipid oxidation, mainly due to high temperature (> 80 ºC) used in S2 [194]. Also, the temperatures used in S2 can promote the thermal degradation of L-ascorbic acid by reactions with some AAs, where are formed VOCs from ALD, FUR and NIT [195]. In addition, in S1 and S2 appear to occur the initial stages of MLDRs between AAs and SGs, where are formed a wide

diversity of VOCs, mainly belong to ALD, KET, FUR and NIT. Summarizing the contribution of most chemical classes in S1 and S2, these can arise from two different origins, raw material and SCH processing. ALC-VOCs, such as CPT1E2OL and TOCTE2OL, were probably generated in SC plant tissues, while PT1OL, HX1OL, HPT1OL and OCT1OL are generated by thermal reactions [166,196]. Similarly, VOCs from ALD and KET groups can be commonly found in various plant tissues, such as CH2PTAL and TOCT2EAL for ALD, and PT3ONE and OCT3ONE for KET [166]. However, its probable main route of formation occurs during the all stages of thermal processing by a wide diversity NEBRs. For example, KET-VOCs, such as DHYPPAONE, BT23DONE and CPT12DONE, and ALD-VOCs such as MPPAL, M2BTAL and M2BTAL, can be generated during any of the follow NEBRs, namely lipid oxidation, L-ascorbic acid degradation, MLDRs, caramelization and melanoidins degradation [117].

In S3 and S4, similar reactions to S2 occurred by thermal processing, where the caramelization process and melanoidins degradation can be added due to high temperatures used (up to 100 ºC), promoting the formation of a large number of FUR-VOCs, where some are main contributors in S2, S3 and S4, being well-established markers of MLDRs and caramelization, such as HM5FURAL, FURAL, HY2DHFURONE, HM5FURONE, FUR3OL [117,174]. Also, in S2, S3 and S4, a wide variety VOCs from ALD, KET, BZF, BNZ, NIT, PYR and PHE are formed. For example, NIT-VOCs, such as DM25PYZNE and ACTLPYROLE, are described as final products from MLDRs, STKD, caramelization and melanoidins degradation [117,166]. Likewise, PYR-VOCs, such as MALTOL and its derivatives, HX3DH23MALTOL and HX5MALTOL, are well-known products of last stages of MLDRs and caramelization that occurs during thermal degradation of sugary products [197]. In addition, BNZ-VOCs, such as benzaldehyde (BENZAL) and BENZACETAL, are common products of MLDRs, principally during the STKD [198,199]. Although BZF-VOCs can be found in natural sources (e.g. plants, marine, fungus and bacteria), the two VOCs identified in all stages of SCH processing, namely 2-methyl-benzofuran (M2BNZFUR) and 2,3-dihydro-benzofuran (DHBNZFUR), are commonly formed as products of the MLDRs [200,201].

Finally, in S5, certainly the most important stage for typicality of SCH, the thermal reactions continue to occur, at least for the first few weeks in storage, and from there, it is possible to verify a considerable microbiological activity, probably due to the action of yeasts associated with alcoholic fermentation, leading to formation of VOCs from ALC, ALD, CAC, BNZ, EST and SUL. A substantial contribution of EST-VOCs, such as EESTFA and EESTPA, was observed in S5, where were probably formed by

fermentation during SCH storage [202]. Also, ALC group demonstrated a high contribution in S5, being highly influenced by ETOL, and in minor extension, also by P1POL and M2PP1OL, where were apparently formed by action of microorganism during the SCH storage [185]. While the higher contribution of BNZ-VOCs in S5 indicated its presumable microorganism formation. For example, benzoic acid (BNZOIC) can be produced by microorganisms in food [203]. Moreover, some BNZ-VOCs can arise from degradation/conversion of BNZOIC, namely toluene (TOLNE) and benzenemethanol (BENZMTOL) [204]. Furthermore, some FUR-VOCs, such as FURYLFMTE, furfuryl acetate (FURYLACTE) and M2FURTHOL, had high RPA values only in the last stage, being probably also formed during the SCH storage by fermentation.

*4. Conclusions*

This study presents, for the first time, the monitoring of volatile profile throughout all stages (S1, S2, S3, S4 and S5) of SCH processing during four years (2015, 2016, 2017 and 2018) by a certified producer, in order to characterize the volatile profile developed in each stage, and consequently, establish the typicality and authenticity of SCH.

Based on obtained results, a preliminary model of VOCs formation pathways throughout the SCH processing is proposed, and consequently, contributed for the following conclusions. The volatile profile of S1 was influenced by EBRs, principally by enzymatic activity on the SC juice, and later, by NEBRs based on thermal degradation of L-ascorbic acid, lipid oxidation, MLDRs and STKD. In S2, S3 and S4, the thermal degradation reactions similar to S1 occurred at higher extension, where in S3 and S4 also occurred the caramelization and melanoidins degradation due to high temperatures used in these stages. Finally, in S5, the previously described thermal reactions continue to occur in first few weeks, being followed by microbial activity on the sugary components of SCH.

Thus, we conclude that is possible to establish a volatile profile for each stage of traditional SCH processing. Nevertheless, the volatile profile of SCH are strongly influenced by S5, where a strict and rigorous control is recommended in order to maintain the typicality and authenticity of SCH on the market. In this context, the 35 most predictive VOCs can be a valuables marker of SCH processing, being important its further quantification. Interestingly, the microbial activity that occurs naturally during the storage of SCH can give rise to new and differentiated products. For example, SCH can be marketed under controlled aging, following the example of liqueur wines, such as Madeira wine. Contrariwise, regarding the

optimization of SCH processing, the S3 and S4 can be combined in a single stage, due to its low level of differentiation. In conclusion, these obtained results are a promising and useful data in order to define the typicality and authenticity of SCH, promoting its EU certification and, consequently, avoiding potential frauds in the market. Additionally, the data obtained from this study about the VOCs formation can be valuable in order to comprehend the role and importance of BRs on food product, creating a preliminary database to support further studies in Foodomics domain.

## SECTION 3.4. VOLATILE FINGERPRINTING OF THE SUGARCANE HONEY

foods

MDPI

*Article*

# A predictive strategy based on volatile profile and chemometric analysis for traceability and authenticity of sugarcane honey on the global market

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*Abstract*

Food authenticity has become a global problem, increasing the importance of identification of markers to guarantee the food quality and consumer safety. SCH is a syrup produced at Madeira Island and recognized by its unique aroma which arise from VOCs generated during its traditional making process and storage. The purpose of this study was to establish the volatile profile of genuine SCH produced by a regional certified producer during seven years and compare it with syrups from non-certified regional producers and with producers from different geographical regions (Spain, Egypt, Brazil and Australia). Different volatile profiles were recognized for all samples, being identified 166 VOCs belonging to 17 chemical classes, such as furans, ketones, carboxylic acids, aldehydes and alcohols. Chemometric analysis allowed the differentiation between all syrups, being more pronounced between SCH and other syrups. Also, chemometric analysis identified 31 VOCs as potential markers for traceability and authenticity of SCH on the global market.

Keywords: sugarcane honey; syrup; volatile profile; authenticity; traceability; geographical origin

## 1. *Introduction*

Food authenticity has become a critical issue due to the high globalization of food trade, leading to an unprecedented diversity of food products on the market, and consequently, to an increasing occurrence of food fraud [205]. The food products with a high added-value, typically exclusive to certain regions or obtained from traditional processes, are the most desirable targets for counterfeiters [206]. In this context, the EU promotes three types of authenticity certification for regional or traditional food products: PDO, PGI and TSG. This type of certification is widely attractive to both producers and consumers. On the one hand, it guarantees a greater appreciation of the product on the market, increasing profitability for producers. On the other hand, it is a guarantee of the quality expected by consumers, and mainly, a guarantee of food security. However, the application process for any of these three types of EU certification is long, time-consuming and exhaustive, which every step of the regulatory framework (Regulation N° 1151/2012) must be meticulously followed, being submitted to the EC in order to guarantee the right to use the respective label of certification [206–208]. To date, hundreds of EU certification applications have been accepted, where several food products have been authorized to use their respective authenticity labelling (e.g. wine, vinegar, olive oil, cheese, among others), protecting the local producers and traditional practices.

Recently, the government of Madeira Island, Portugal, has started the process of authentication to protect one of its most valuable traditional food products, the SCH, locally known as *"mel-de-cana"*. The SCH is a crystalline black syrup produced from stalks of fresh SC (*Saccharum officinarum L.*) cultivated under mild climate conditions of the Atlantic region, worldwide recognized for its excellent quality and sui generis organoleptic properties, being consumed fresh and used as the main ingredient in traditional pastry and confectionery. The distinctive and unique properties of SCH arise from the use of SC cultivars grown in the region, and principally, from secular and traditional processing and storage conditions in addition to terroir (climatic conditions and cultivation treatments). To distinguish the SCH from other syrups, molasses and treacle's, the government created a regional production certification brand. Nevertheless, its importance and economic value have led to the emerging adulterated SCH with low-quality SC-derived products from different geographical origins, affecting its notoriety [11,159]. Thus, it becomes essential the identification of potential molecular markers to guarantee its typicality and authenticity, and consequently, the traceability on the market, promoting a potential application to EU certification.

One of the most recent and promising developments in the food authentication domain is Foodomics, which appears as a new approach supported by high resolution- and MS-based techniques to solve some of the new challenges from global food safety [111–113]. This approach is based on the establishment of the volatile profile, which a wide and complex network of VOCs arise from a specific food product, being each identified VOC based on its unique mass fragments spectrum [209]. In SCH, the chemical complexity of VOCs formation and origin can be valuable for the establishment of its typicality and authenticity. The traditional conditions of processing and storage, together with the exclusive use of SCs, from authorized varieties, cultivated on Madeira Island, can generate a specific "fingerprint" of volatile pattern. Furthermore, this approach has been used for EU certification of several food products, such as Modena Balsamic Vinegar from Italy [124], "*La Rioja*" Olive Oil from Spain [210], "*Corsica*" Honey from France [211] and Madeira Wine from Portugal [212].

The purpose of this study was to establish the volatile profile of genuine SCH produced by a regional certified producer analyzing seven processing years (2007, and 2013 to 2018) to define its typicality and authenticity. Also, the volatile profile of SC-based syrups from non-certified regional producers and from different geographic regions (Spain, Egypt, Brazil and Australia), was established. Subsequently, chemometric analysis was applied to the obtained data allowing the identification of a set of predictive VOCs as potential traceability markers of genuine SCH on the market. The predictive strategies based on MS techniques combined with chemometric analysis have been widely recognized as a successful tool in traceability of food products [209,213,214]. HS-SPME/GC-MS methodology, previously developed, optimized and fully validated in our previous study [159], was used to establish the volatile profile of all samples. The chemometric analysis was based on procedures used in our previous studies [11,159], with some modifications. The predictive strategy, based on volatile profile and chemometric analysis, will represents a valuable tool to guarantee the traceability of genuine SCH, and to support on a potential application to EU certification of geographical origin.

## *2. Materials and methods*

### *2.1. Standards, Reagents, Materials and Software*

IS, 4-heptanone, was purchased from Sigma-Aldrich (Missouri, USA). Sodium chloride was acquired from Panreac (Barcelona, Spain). SPME holder for the manual sampling of SPME fiber and the fiber DVB/CAR/PDMS with 50/30 μm film thickness were purchased from Supelco (Pennsylvania, USA). The

BP-20 fused silica capillary column with 60 m × 0.25 mm I.D. × 0.25 µm film thickness was purchased from SGE (Dortmund, Germany). Ultrapure deionized water ($H_2O^d$) was purified with a Milli-Q ultra-pure water system from Millipore (Massachusetts, USA). The MAXI MIX Vortex Mixer was purchased from Thermo Scientific (Massachusetts, USA). All data analysis and statistical processing were performed using the STATSOFT STATISTICA 12.0 (2013) software (Tulsa, USA).

*2.2. Samples*

Samples from the traditional and certified producer FRS, Madeira Island, Portugal, were collected from lots subsequently placed on the market in 2007 (FRS07), 2013 (FRS13), 2014 (FRS14), 2015 (FRS15), 2016 (FRS16), 2017 (FRS17) and 2018 (FRS18). All other SC-based syrups samples were purchased on the regional market between 2014 and 2018, while the samples from the non-certified regional producers (ECAL14 and NCAL14) and regional homemade producer (GLA14), were obtained in 2014. Samples from Brazil (MDBR14 and MCBR14) were from 2014 harvest, whereas the samples from Spain (ESP16), Egypt (EGPA16, EGPB16, EGPC16 and EGP17) and Australia (AUS17) were from in 2016 and 2017, respectively. All samples were stored under stable conditions (4 ºC, in the dark). Identification (ID) replicate number, ID replicate code, ID sample code, ID group code, processing year, processing type, geographic origin and regional certification are described in Table S35.

*2.3. SPME procedure*

VOCs extraction from SCH samples was based on the SPME procedure previously developed, optimized and validated [159]. All samples were daily prepared in the ratio 3:2 (w/v), where the sample (15 g) was diluted with $H_2O^d$ (10 mL) into a 50 mL PTFE centrifuge tube, being homogenized for 1 min and stored at 4 °C in aliquots (5 mL). Subsequently, the aliquots were transferred to a glass vial (8 mL) containing NaCl (60 mg), being placed in a thermostatic bath at 30 °C for 5 min for sample temperature equilibrium. The SPME was performed in HS, where the fiber DVB/CAR/PDMS was exposed in sample HS for 60 min at 30 ºC, under magnetic agitation (600 rpm). The VOCs extracted by SPME were thermally desorbed by the fiber direct insertion into GC injector at 250 °C, in splitless mode for 10 min. The fiber was daily conditioned for 15 min at 250 ºC into GC injector to avoid contamination by unwanted interferents. Triplicate experiments were performed for all samples under analysis. Blank experiments were performed before the analysis of each sample, where the fiber was directly placed into GC injector without the application of SPME extraction procedure.

*2.4. GC-MS analysis*

The analysis of extracted VOCs was carried on Agilent Technologies 6890N Network GC system (California, USA) equipped with a BP-20 fused silica capillary column, and interfaced with an Agilent 5975 quadrupole inert mass selective detector (California, USA). The temperature protocol for column oven was: 40 ºC for 2 min, then was increased at 0.25 ºC $min^{-1}$ until 45 ºC with a 2 min hold, after was increased at 4 ºC $min^{-1}$ to 70 ºC with a 2 min hold, was increased again at 3 ºC $min^{-1}$ to 130 ºC with a 2 min hold, and finally, was increased at 3 ºC $min^{-1}$ to 220 ºC, this final temperature was continued during 7 min, resulting in a run time of 91.25 min. The column flow was constant at 1 mL $min^{-1}$ using helium (He) carrier gas at a purity of 99.999% (He N60, Air Liquid, Portugal). The injection port was operated in the splitless mode and held at 250 ºC. For the 5975 MS system, the operating temperatures of the transfer line, quadrupole and ionization source were 270, 150 and 230 ºC, respectively. Electron impact mass spectra was recorded at 70 eV ionization voltage and the ionization current was 10 µA. The electron multiplier was set to the autotune procedure. The acquisitions were performed in scan mode (30-300 m/z). VOCs identification was based on visual interpretation of spectra through the Agilent MS ChemStation Software, and confirmed comparing each VOC mass spectra with the NIST14 Mass Spectral Library (2014), being successfully identified when a similarity threshold was higher than 75%. The TPA values were obtained by target ion quantification protocol. The results are presented as RPA, which were calculated by dividing the TPA value of each VOC by the TPA value of IS.

*2.5. Chemometric analysis*

The chemometric analysis procedure was completed according to the developed procedures in our previous studies [11,159], being introduced some modifications based on the recommendations for analytical applications [160,182]. All samples were grouped in one of four groups formed according to the geographic origin. The FRS07, FRS13, FRS14, FRS15, FRS16, FRS17 and FRS18 samples are classified into the regional certified producer group (CERT), ECAL14, NCAL14 and GLA14 samples into the regional non-certified producers group (NCERT), ESP16, EGP17, EGPA16, EGPB16 and EGPC16 samples into the Mediterranean region producers group (MED), and MDBR14, MCBR14 and AUS17 samples into the southern hemisphere region producers group (STH). One-way ANOVA was achieved to determine the VOCs with statistically significant differences ($p < 0.05$) based on its variance level between RPA values of all samples. Also, the Tukey post-hoc test was done to confirm the VOCs with statistically significant differences ($p < 0.05$) between two pairs of groups (CERT, NCERT, MED and STH). The VOCs

without statistically significant differences between all samples were removed from further analysis. PCA and PLS analysis were applied on RPA values of VOCs dataset in order to obtain the preview of differentiation/correlation structure based on the variance of all samples, without classification and with classification according to the group, respectively. A V-fold with a V-value fixed in 7 was used for cross-validation. LDA was applied as supervised pattern recognition method for variable selection in order to achieve a matrix composed by the most predictive VOCs that permits the correct classification of all samples for the group assignment. A backward selection method (p value of 0.05 to enter/remove) was used to select the most predictive VOCs, removing the least predictive from analysis, being obtained a classification structure based in CDFs. A V-fold with leave-one-out strategy was applied for CV. A matrix reduction procedure was applied prior to LDA, where the matrix was reduced to 20% of initial dimension based on F-value from One-way ANOVA between all samples. Alternatively, a matrix reduction procedure based on the VIP scores from the PLS analysis was also applied. Therefore, the 32 VOCs with higher F-Value and VIP score were selected, respectively. Finally, a second PLS analysis and HCA were applied on RPA values of the most predictive VOCs. PLS based on dataset from the reduced matrix was performed to verify the differentiation/correlation structure between all samples when classified. HCA was performed in order to determine the Euclidean linkage distances between all samples and complete an appropriate and visual measure of distance and linkage criterion based only in the most predictive VOCs.

## *3. Results and discussion*

### *3.1. Establishment of the volatile profile from SC-based syrups*

The establishment of the volatile profile of 18 SC-based syrups from different geographical origins was successfully achieved by HS-SPME/GC-MS method, where FRS07, FRS13, FRS14, FRS15, FRS16, FRS17 and FRS18 samples come from a regional certified producer, ECAL14 and NCAL14 from regional non-certified producers, GLA14 from a regional homemade producer, ESP16 from Spanish producer, EGPA16, EGPB16, EGPC16 and EGP17 from Egyptian producers, MDBR14 and MCBR14 from Brazilian producers, and AUS17 from Australian producer. The ID number, RT, main ions (m/z), target ion, match percent, IUPAC name, NIST database, abbreviation, CAS number, molecular formula and main chemical class of identified VOCs are described in Table S36. The mean RPA values and respective % RSD of identified VOCs are described in Table S37 (A), (B), (C) and (D). The mean, minimum and maximum values of RPA for identified VOCs are summarized in Table S38. The typical GC-MS chromatograms for each sample under analysis is presented in Figure S11.

### *3.1.1. Number of identified VOCs*

The analysis of the volatile profile of all samples allowed the identification and semi-quantitation of 166 VOCs from a wide diversity of chemical classes. The number of identified VOCs for each sample was: 150 (FRS07), 149 (FRS13), 149 (FRS14), 149 (FRS15), 149 (FRS16), 149 (FRS17), 141 (FRS18), 143 (ECAL14), 136 (NCAL14), 147 (GLA14), 137 (ESP16), 136 (EGP17), 135 (EGPA16), 142 (EGPB16), 138 (EGPC16), 142 (MDBR14), 143 (MCBR14), and 137 (AUS17). There, 119 VOCs (71.69%) were identified in all samples under analysis. On the contrary, only six VOCs (3.61%) were identified in one specific sample, namely: 2-heptanone (HPT2ONE) in ECAL14; ethyl hexanoate (EESTHA), ethyl octanoate (EESTOA), and ethyl decanoate (EESTDA) in GLA14; 2-ethyl-5-methyl-pyrazine (E5MPYZNE), and trimethyl-pyrazine (TMPYZNE) in AUS17. As expected, 54 VOCs (32.53%) were also identified in our previous study [159]. Interestingly, 48 VOCs (28.92%) were also previously identified in SC-based syrups from other geographical origins in six previous studies, namely 17 VOCs in syrup from Egypt, [118], 14 VOCs in syrup from USA [120], 12 VOCs in syrup from Dominican Republic [215], 11 VOCs in syrup from China [216], and 15 VOCs in syrups from Japan [142,217]. This information is described in Table S39.

### *3.1.2. Main VOCs*

Although the contribution of each of the 166 VOCs was important to establish the volatile profile of samples under analysis, their RPA (x $10^3$) values vary between 0.5 and 1000000. The 20 main VOCs with higher contribution for the volatile profile for samples from the regional certified producer (FRS07, FRS13, FRS14, FRS15, FRS16, FRS17 and FRS18), others regional producers (ECAL14, NCAL14 and GLA14), Mediterranean region (ESP16, EGP17, EGPA16, EGPB16 and EGPC16) and southern hemisphere region (MDBR14, MCBR14 and AUS17), are described in Figure 24 (A), (B), (C) and (D), respectively.

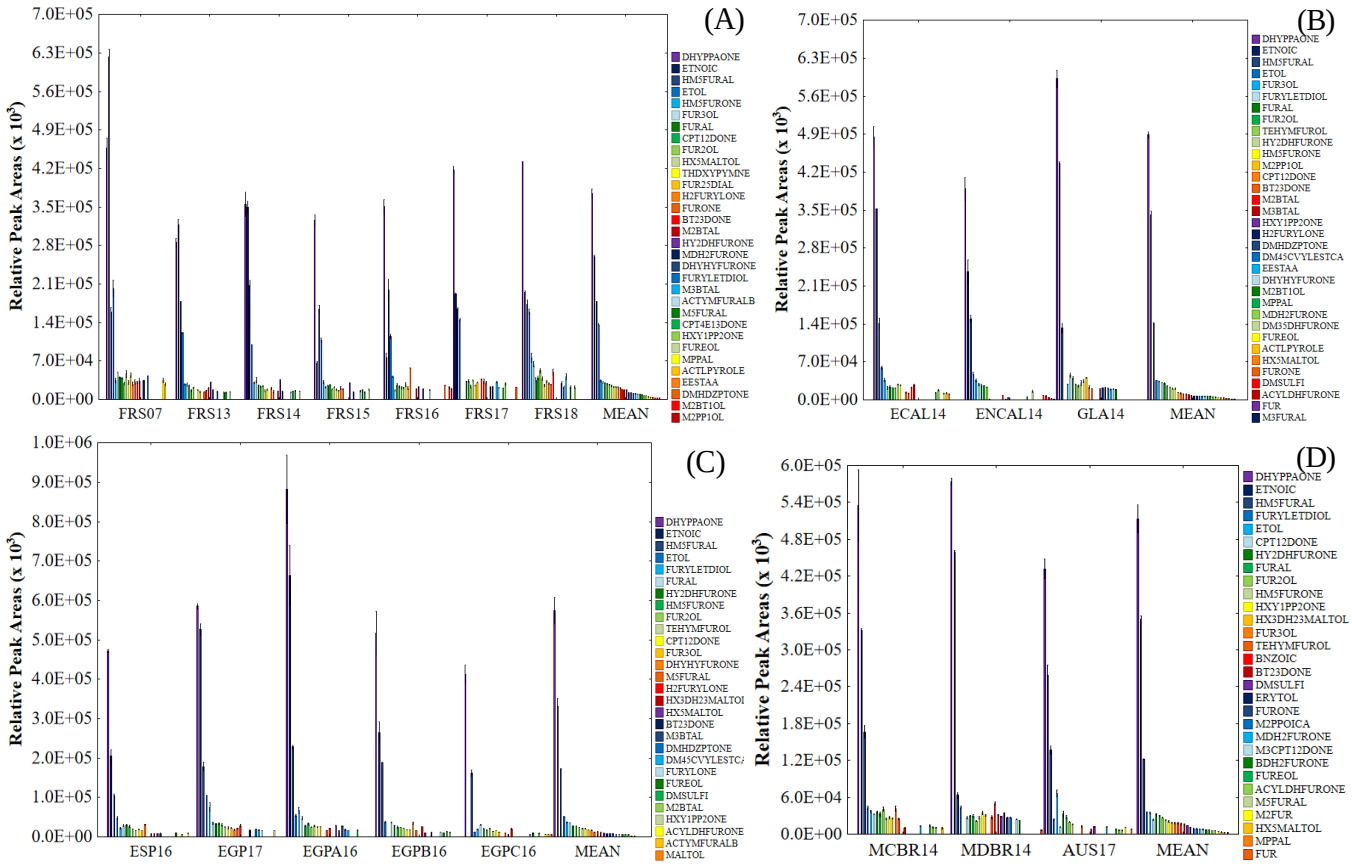


**Figure 24. The RPA values of the 20 main VOCs for samples of SC-based syrups from CERT (A), NCERT (B), MED (C) and STH (D) groups.**

A total of 48 VOCs were selected as one of the 20 main contributors to the volatile profile at least for one sample under analysis, where 1,3-dihydroxy-2-propanone (DHYPPAONE), 5-(hydroxymethyl)-2-furfural (HM5FURAL), furfural (FURAL) and 2-furanmethanol (FUR2OL) were common to all samples. Furthermore, DHYPPAONE was the main contributor for the volatile profile of 17 samples, being the second main contributor only for FRS07. Similarly, HM5FURAL was the second or third main contributor for the most of samples, where the exception was the FRS07. The high contribution of these two VOCs is expected because both are strongly linked to the thermal processing of food components (e.g. SGs, AAs), being well-known markers of occurrence of NEBRs, such as MLDRs, STKD and caramelization [11,183]. Contrariwise, nine VOCs were one of the 20 main contributors only for a specific sample, namely: 3,5-dimethyl-dihydro-2-furanone (DM35DHFURONE) and 3-methyl-furfural (M3FURAL) for ENCAL14; maltol (MALTOL), benzoic acid (BNZOIC), erythritol (ERYTOL), 2-methyl-propanoic acid (M2PPOICA), 3-methyl-1,2-cyclopentanedione (M3CPT12DONE), and 5-butyl-dihydro-2(3H)-furanone (BDH2FURONE) for MDBR14; and 2-methyl-furan (M2FUR) for AUS17. In fact, most of the VOCs classified as main contributors to volatile profile are commonly linked to high temperatures used in the processing of SC-based syrups, indicating that processing is critical for the establishment of its volatile profile.

### *3.1.3. Chemical Class Classification of VOCs*

During the analysis of volatile profile of SC-based syrups, it was recognized a wide diversity of chemical structures and functional groups, where each one of 166 VOCs was classified into a chemical class according to its chemical proprieties. The classification of each VOC according to its main chemical class is described in Table S36. The number of VOCs, RPA and TRPA values of main chemical classes identified in samples from the regional certified producer (FRS07, FRS13, FRS14, FRS15, FRS16, FRS17 and FRS18), others regional producers (ECAL14, NCAL14 and GLA14), Mediterranean region (ESP16, EGP17, EGPA16, EGPB16 and EGPC16) and southern hemisphere region (MDBR14, MCBR14 and AUS17), are summarized in Table S40 (A), (B), (C) and (D), respectively. The contribution, RPA and % TRPA values, of each chemical class to the volatile profile of all samples are presented in Figure 25 (A) and (B), respectively.

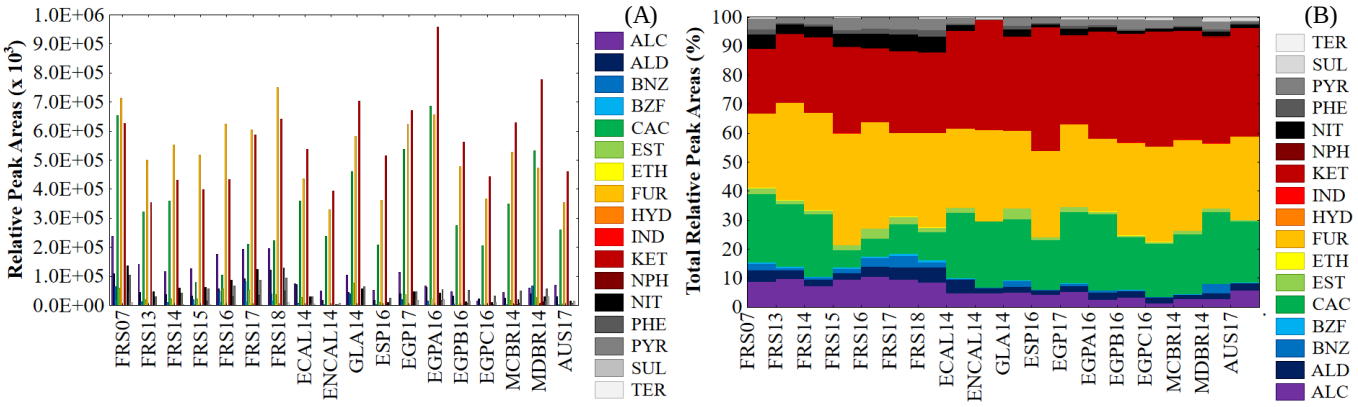


**Figure 25. The contribution, RPA (A) and TRPA (B) values, of each classification group assigned according to chemical class for all samples SC-based syrups.**

There, 17 chemical classes were recognized in the volatile profile of all samples, namely alcohol (ALC), aldehyde (ALD), benzene (BNZ), benzofuran (BZF), carboxylic acid (CAC), ester (EST), ether (ETH), furan (FUR), hydrocarbon (HYD), indene (IND), ketone (KET), naphthalene (NPH), nitrogen (NIT), phenol (PHE), pyran (PYR), sulfur (SUL) and terpene/terpenoid (TER). VOCs from all chemical classes were identified in all SC-based syrups. Interestingly, FUR was the chemical class with more contribution to volatile profile only for samples of genuine SCH obtained by the certified producer, which its contribution was always higher than 25%. For the remaining samples, FUR was the second main class for ECAL14, NCAL14, GLA14, ESP16, EGP17, EGPB16, EGPC16, MCBR14 and AUS17, being the third main class for EGPA16 and MDBR14, where its contribution was continuously higher than 22%. Also, FUR was the class with the higher number of VOCs, where 44 VOCs were assigned. Indubitably, HM5FURAL was the VOC with more influence in FUR contribution for all samples, being followed by

FURAL, FUR2OL and 3-furanmethanol (FUR3OL). On the contrary, KET was the main class for most of the samples under analysis, where its contribution was higher than 30%, being the second main contributor only for samples from the certified producer, with the exception of the FRS07 sample where was the third main contributor. Although the KET class comprises 16 VOCs, DHYPPAONE is undoubtedly the largest contributor from KET class, being responsible for more than 50% of the total contribution of this chemical class for the volatile profile. Also, 1-hydroxy-2-propanone (HXY1PP2ONE), 1,2-cyclopentanedione (CPT12DONE) and 2,3-butanedione (BT23DONE) have a significant contribution to KET class, but to a minor level. CAC was another chemical class with a high contribution to the volatile profile of all samples, which its contribution varies between 5.97% (FRS15) and 26.26% (EGP16A). Among the nine VOCs classified in CAC class, ethanoic acid (ETNOIC) was responsible for more than 90% of its contribution for most of the samples. In fact, FUR, KET and CAC classes comprise a large part of the volatile profile of all samples analyzed, where the sum of the contribution of these three classes ranges from 66.92% (FRS17) to 92.07% (ENCAL14). ALC and NIT classes also had a substantial contribution to the volatile profile of all samples, being more pronounced in samples from the certified producer. The contributions of ALC and NIT for certified samples varies between 7.14-10.39% and 3.18-5.88%, respectively. For remaining samples, the contributions of ALC and NIT range between 1.27-5.67% and 0.17-2.59%, respectively. Of the nine VOCs of ALC class, ethanol (ETOL) was the highest contributor, being followed by 2-methyl-1-propanol (M2PP1OL) and 2-cyclohexenol (CHEX2E1OL). Among the 16 VOCs assigned in NIT class, 2,4,6-trihydroxypyrimidine (THDXYPYMNE), 2-acetylpyrrole (ACTLPYROLE) and 4-pyridinol (PYRDINOL) were the VOCs with more contribution. Likewise, ALD, EST and PYR classes had a reasonable contribution (> 1%) for all samples from the certified producer, being less expressive for most of the other samples. Typically, BNZ and PHE classes also presented a higher contribution for the volatile profile of certified samples compared to non-certified samples. The number of VOCs classified into each of these chemical classes were: ALD (9), EST (11), PYR (5), BNZ (13) and PHE (8). ALD contribution was mainly explained by 2-methyl-propanal (MPPAL), 2-methyl-butanal (M2BTAL) and 3-methyl-butanal (M3BTAL), while EST contribution was mostly influenced by vinylene carbonate (VYLESTCA), 4,5-dimethyl vinylene carbonate (DM45CVYLESTCA) and ethyl acetate (EESTAA). PYR contribution was predominantly influenced by MALTOL, and its derivatives, 5-hydroxy-maltol (HX5MALTOL) and 3-hydroxy-2,3-dihydro-maltol (HX3DH23MALTOL). BNZ and PHE contributions were highly influenced by benzeneacetaldehyde (BENZACETAL) and 3-methoxy-1,2-benzenediol (M3BNZDIOL);

phloroglucinol (PHLOGLNOL) and phenol (PHEOL), respectively. VOCs from BZF, ETH, HYD, NPH, SUL and TER were identified in all samples, but their contribution was normally lower than 1% and the number of VOCs assigned was always lower than 5.

As expected, most of the chemical classes found in volatile profile of SC-based syrups, such as FUR, BZF, PHE and PYR, and in minor extension, ALD, BNZ, KET, NPH and NIT, are highly related to thermal reactions (e.g. MLDR, STKD and caramelization) that occurs during the processing of SC until the formation of the syrup [117,167,218]. Alternatively, ALD, KET and NIT classes can also be originated from enzymatic reactions and microbial activity in the SC before the processing or during the syrups storage. Also, ALC, CAC, EST and SUL classes are commonly associated to activity of enzymes and microorganisms [164–166]. Other classes, namely HYD and TER, probably are products from biochemistry pathways that occur in SC plant [163]. The formation and origin of VOCs from IND and ETH classes are more difficult to establish, being probably result of crop contamination by biomass burning, plastic residues combustion and pesticide application [168,219].

### *3.2. Chemometric analysis based on the volatile profile of SC-based syrups*

Chemometric analysis was applied to the dataset obtained from the establishment of volatile profiles of 18 samples under study in order to obtain a predictive strategy that guarantees the traceability of genuine SCH on the global market. Similar predictive strategies have been successfully applied for the traceability of food products, such as olive oil [220], coffee [221] and cider [222].

#### *3.2.1. One-way ANOVA test*

One-way ANOVA was done to determine the VOCs with statistically significant differences based on its variance level between RPA values from all syrup samples under analysis. The post-hoc Tukey test was done to determine the statistically significant differences between RPA values of groups (CERT, NCERT, MED and STH). The assigned group for each sample was described in Table S35. One-way ANOVA with post-hoc Tukey test results, namely Probability (P) and Fischer (F) values, between all samples and for each pair of groups are summarized in Table S41.

There, 144 VOCs (86.75%) presented statistically significant differences ($P < 0.05$) in RPA values between all 18 samples under analysis. Moreover, 53 VOCs (31.93%) showed high differences (F values ≥ 10) between all samples, and among these, 19 VOCs (11.45%) demonstrated very high significant differences (F values ≥ 20), namely pentane (PTANE), 1,4-pentadiene (PT14DIENE), ETOL, 2-methyl-

dihydro-2(3H)-furanone (MDH2FURONE), 5-methyl-2(3H)-furanone (M5FURONE), furfuryl acetate (FURYLACTE), 4-cyclopentene-1,3-dione (CPT4E13DONE), 2-methyl-benzofuran (M2BNZFUR), 2-(2-furanylmethyl)-5-methyl-furan (FURYLMFUR), 2,2'-methylenebis[5-methyl-furan (MNEB5MFUR), CHEX2E1OL, THDXYPYMNE, oxypurinol (OXYPUROL), furfural acetone (FURALTONE), 2,5-furandicarboxaldehyde (FUR25DIAL), 5-acetoxymethyl-2-furfural B (ACTYMFURALB), 3-methyl-2,4(3H,5H)-furandione (M3FURDIONE), PYRDINOL and M3BNZDIOL.

The post-hoc Tukey test results demonstrated a high level of dissimilarity in volatile profiles between all groups. CERT group showed the higher dissimilarity from the other groups, which presented 47 VOCs (28.31%) with statistically significant differences for NCERT, MED and STH groups, simultaneously. In a minor level of dissimilarity, STH group presented 22 VOCs (13.25%), followed by NCERT group with 12 VOCs (7.23%), and MED group only with 2 VOCs (1.20%). Interestingly, most of these VOCs only presented significant differences for one specific group and it respective all combinations with other groups. The exceptions were the PTANE (MED vs CERT, MED vs NCERT, STH vs CERT, STH vs NCERT, and MED vs STH) and 5-acetoxymethyl-2-furfural A (ACTYMFURALA) (CERT vs NCERT, CERT vs MED, CERT vs STH, and MED vs STH). On the contrary, none of the VOCs demonstrated statistically significant differences for all combinations of pairs between the four groups.

### *3.2.2. PCA and PLS*

PCA and PLS analysis were performed to preview the differentiation/correlation structure based on the variance of all syrup samples, without classification and with classification according to the group previously assigned, respectively. The PCA and PLS information are summarized in Table S42. The loading results and VIP scores of PCA and PLS analysis for each variable (VOCs) are described in Table S43. The loading results of all 18 syrup samples (PCA) and four centroids (PLS) are described in Table S44. The PCA and PLS scores results of all samples are summarized in Table S45. The PCA loadings line plot of all syrups samples for PC1, PC2 and PC3 are presented in Figure S12 (A), (B) and (C), respectively. The PLS loadings line plot of four centroids for PLS1, PLS2 and PLS3 are showed in Figure S12 (D), (E) and (F), respectively. The PCA loading 3D plots of all syrup samples and all VOCs for PC1, PC2 and PC3 are showed in Figure 26 (A) and (B), respectively. The PLS loading 3D plots of the four centroids and all variables for PLS1, PLS2 and PLS3 are showed in Figure 27 (A) and (B), respectively.

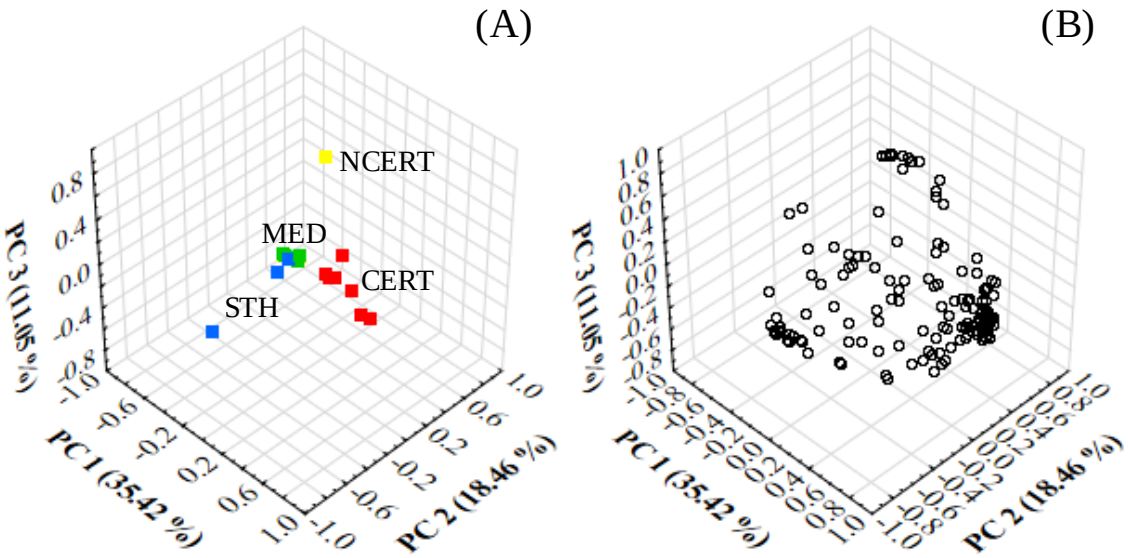


**Figure 27. The PCA loading 3D plot of all centroids (A) and the selected 144 VOCs (B) for the three main components.**

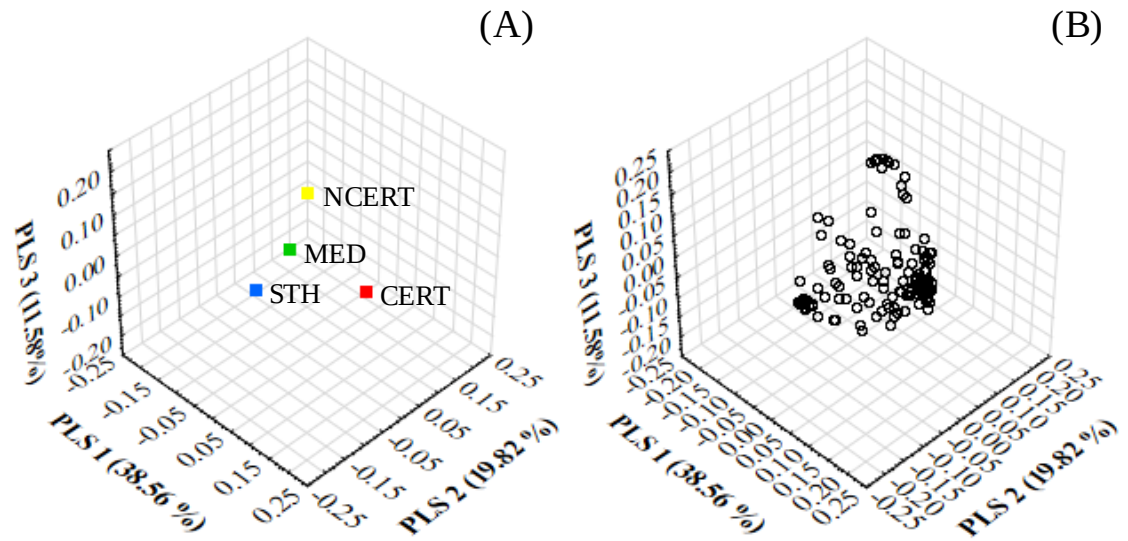


**Figure 26. The PLS loading 3D plot of all samples (A) and the selected 144 VOCs (B) for the three main components.**

The three main components of PCA analysis (PC1, PC2 and PC3) explained 64.92% of TVA, being that the sum of all six components explained 78.85%. The projection of structure based on loading results from three main components demonstrated a clear differentiation between the samples from the certified producer and samples from the other producers. In PC1 projection (35.42% TVA), all samples from certified producer cultivar demonstrated a high variance from the remaining samples under analysis. In PC2 projection (18.46%), the samples from Madeira Island, including certified and non-certified producers, presented a slight variance from other geographical regions samples. Also, in PC2 projection, the MDBR14 sample showed a high variance from all remaining samples. Finally, in PC3 projection (11.05%), a high variance was observed between the sample from the homemade producer (GLA14) and all other samples.

A PLS analysis was achieved in order to evaluate the variance between samples when classified according to the type of producer and geographical localization, being classified as: centroid-CERT (C-CERT), centroid-NCERT (C-NCERT), centroid-MED (C-MED) and centroid-STH (C-STH). The three main components of PLS analysis (PLS1, PLS2 and PLS3) were responsible for 69.96% of TVA, being that the sum of all 18 components explained 99.66%. Interestingly, the projection of structure based on PLS1, PLS2 and PLS3 demonstrated that all group centroids were clearly separated. In PLS1 projection (38.56%), a high variance was obtained between C-CERT and the other centroids. For PLS2 projection (19.82%) a substantial and equitable differentiation was observed between all centroids. In PLS3 projection (11.58%), a higher variance was observed between C-NCERT and the other centroids.

Both PCA and PLS projections were based on 144 VOCs, where each one influenced differently the projection of samples and centroids, respectively. In the case of PLS projection, was possible to recognize the individual contribution of each VOC for the projection structure. The 3D plot constructed with PLS loading results for all VOCs under analysis showed that a high number of VOCs influenced the projection of C-CERT, mainly belonging to ALD, ALC, FUR and NIT chemical classes, where can be highlighted MPPAL, M2BTAL, M3BTAL, decanal (DECAL), ETOL, CHEX2E1OL, MDH2FURONE, FURYLMFUR, 2-furanpropionic acid (FURPPIONIC), THDXYPYMNE and PYRDINOL. The projection of NCERT was very influenced by VOCs from EST and BNZ classes, such as EESTOA, EESTDA, ethyl undecanoate (EESTUNDA), benzyl acetate (PMESTAA) and benzeneethanol (BENZETOL), while the projection of STH was influenced principally by VOCs from CAC, IND and NPH, such as heptanoic acid (HPTOIC), octanoic acid (OCTOIC), decanoic acid (DECOIC), 2,3-dihydro-1,1,4,6-tetramethyl-1H-indene (DHT1146MIDNE), 2,3-dihydro-1,1,5,6-tetramethyl-1H-indene (DHT1156MIDNE), 1,2,3,4-tetrahydro-1,1,6-trimethyl-naphthalene (T116TNP) and 1,2,3,4-tetrahydro-1,6,8-trimethyl-naphthalene (T168TNP). Lastly, the projection of C-MED was influenced by a smaller number of VOCs than the other three centroids, where can be referred dimethyl disulfide (DMDSFD), HPT2ONE, E5MPYZNE, TMPYZNE and M3FURAL.

### *3.2.3. LDA*

The supervised pattern recognition method LDA was performed to determine classification rules for the group assignment of all syrups samples based only on the most predictive VOCs. The matrix reduction procedure based on the VIP scores presented unsatisfactory results to PLS and HCA analysis, not being

used for further analysis. The LDA information and respective PLS and HCA plots constructed according to the selected VOCs based on the VIP scores are summarized in Table S46 and Figure S13 (A) and (B), respectively. The LDA information and CDF coefficients of the selected 32 VOCs based on F-Value from one-way ANOVA test are summarized in Table 5. The CDF coefficients and highest probability classification results of all syrups samples are described in Table S47.

**Table 5. Results of variables from LDA after matrix reduction method to 20% of original dimension according with higher F values obtained from One-way ANOVA test based on the RPA of the identified VOCs in SC-based syrups samples.**

| Volatile Organic Compounds | Abbreviations | ANOVA | | | LDA | | | PLS | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | CDF[4] | | | Loading Value | | | VIP[5] | |
| | | F[1] | W[2] | F[3] | 1 | 2 | 3 | 1 | 2 | 3 | Importance | Power (x 100) |
| 2,4,6-Trihydroxypyrimidine | THDXYPYMNE | 180.09 | 4.62E-02 | 130.62 | -70.540 | -8.258 | 14.822 | -0.107 | -0.339 | -0.167 | 2 | 22.49 |
| 1,4-Pentadiene | PT14DIENE | 49.98 | 2.70E-01 | 17.12 | 26.030 | -39.002 | 1.486 | -0.063 | -0.420 | 0.200 | 17 | 15.85 |
| Pentane | PTANE | 48.69 | 1.96E-01 | 25.97 | -34.120 | 12.658 | -10.012 | 0.187 | 0.035 | 0.091 | 16 | 15.91 |
| 4-Pyridinol | PYRDINOL | 45.77 | 1.73E-01 | 30.19 | -162.900 | 51.083 | -51.729 | 0.181 | 0.065 | -0.015 | 5 | 21.08 |
| 4-Cyclopentene-1,3-dione | CPT4E13DONE | 42.70 | 5.21E-01 | 5.82 | -4.580 | -17.467 | 10.460 | 0.188 | -0.016 | 0.007 | 20 | 15.15 |
| Ethanol | ETOL | 38.57 | 2.63E-01 | 17.70 | -15.990 | -9.449 | -3.794 | 0.167 | 0.007 | 0.188 | 13 | 16.76 |
| 2,5-Furandicarboxaldehyde | FUR25DIAL | 30.06 | 3.12E-01 | 13.95 | 71.890 | -55.246 | -11.369 | 0.179 | -0.069 | 0.049 | 10 | 17.99 |
| 5-Methyl-2(3H)-Furanone | M5FURONE | 29.65 | 1.88E-01 | 27.32 | -9.110 | -61.784 | 18.575 | 0.197 | -0.085 | 0.005 | 25 | 12.42 |
| 2-(2-Furanylmethyl)-5-Methyl-Furan | FURYLMFUR | 28.08 | 1.36E-01 | 40.21 | 88.730 | -8.719 | 24.338 | -0.008 | 0.187 | 0.392 | 4 | 22.12 |
| 2-Methyl-Benzofuran | M2BNZFUR | 27.39 | 6.90E-02 | 85.49 | -185.440 | 48.514 | -37.864 | 0.179 | -0.041 | -0.087 | 8 | 18.11 |
| 2,2'-Methylenebis[5-Methyl-Furan | MNEB5MFUR | 24.37 | 1.02E-01 | 55.62 | 105.390 | 46.353 | 2.323 | 0.189 | -0.029 | 0.012 | 9 | 18.10 |
| Oxypurinol | OXYPUROL | 23.80 | 2.85E-01 | 15.90 | 29.440 | -11.140 | -8.239 | 0.188 | -0.126 | 0.032 | 18 | 15.48 |
| 2-Cyclohexenol | CHEX2E1OL | 23.74 | 1.88E-01 | 27.37 | 122.070 | -26.365 | 46.694 | 0.197 | 0.023 | 0.067 | 19 | 15.46 |
| 2-Methyl-Dihydro-2(3H)-Furanone | MDH2FURONE | 23.37 | 5.09E-02 | 118.02 | 87.910 | -10.980 | 6.705 | -0.041 | -0.436 | 0.141 | 12 | 17.01 |
| 5-Acetoxymethyl-2-Furfural B | ACTYMFURALB | 22.74 | 3.75E-02 | 162.39 | -220.540 | 45.621 | -33.535 | -0.043 | -0.443 | 0.068 | 11 | 17.51 |
| Furfural Acetone | FURALTONE | 22.71 | 1.14E-01 | 49.18 | -279.810 | 36.381 | -44.076 | 0.198 | -0.013 | -0.001 | 21 | 14.86 |
| 3-Methyl-2,4(3H,5H)-Furandione | M3FURDIONE | 22.67 | 6.43E-02 | 92.12 | 287.950 | -18.438 | 49.078 | 0.190 | -0.022 | 0.027 | 6 | 19.74 |
| 3-Methoxy-1,2-Benzenediol | M3BNZDIOL | 22.36 | 6.43E-02 | 92.12 | -206.700 | 126.409 | -33.892 | 0.203 | -0.072 | -0.031 | 32 | 9.20 |
| Furfuryl Acetate | FURYLACTE | 20.88 | | | Removed from analysis. | | | | | | | |
| 2-Furanpropionic Acid | FURPPIONIC | 19.07 | 6.24E-02 | 95.17 | 303.870 | -13.701 | 39.789 | -0.079 | -0.128 | -0.415 | 1 | 23.54 |
| 3-Methyl-Pyridazine | M3PYRDZNE | 17.95 | 1.32E-01 | 41.58 | 131.650 | -2.761 | -0.685 | 0.197 | 0.016 | 0.011 | 24 | 12.79 |
| 2-Methyl-Butanal | M2BTAL | 17.62 | 3.43E-01 | 12.13 | 0.060 | -23.095 | 7.286 | 0.199 | -0.047 | -0.097 | 14 | 16.51 |
| Cyclotene | CYTENE | 17.59 | 3.19E-01 | 13.49 | -83.600 | -28.243 | 12.252 | 0.201 | -0.091 | 0.002 | 31 | 10.46 |
| 2-Acetylpyrrole | ACTLPYROLE | 17.38 | 9.14E-02 | 62.99 | -90.260 | 55.198 | -30.992 | 0.188 | -0.146 | -0.003 | 27 | 11.84 |
| Furfuryl Formate | FURYLFMTE | 17.23 | 6.55E-01 | 3.33 | -17.910 | 7.134 | -37.968 | 0.185 | -0.001 | -0.129 | 15 | 16.08 |
| 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | DHT1146MIDNE | 17.05 | 4.92E-01 | 6.53 | 36.680 | 0.135 | 3.888 | 0.179 | 0.075 | 0.090 | 23 | 13.62 |
| 3-Methyl-Furfural | M3FURAL | 16.94 | 2.36E-01 | 20.52 | 23.630 | -29.167 | 15.070 | 0.201 | 0.001 | -0.083 | 30 | 11.26 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Ethyl-Hexanoic Acid | E2HXNOIC | 16.91 | 1.10E-01 | 51.37 | 36.630 | -16.971 | 11.398 | 0.196 | -0.022 | -0.128 | 22 | 14.73 |
| Maltol | MALTOL | 15.39 | 2.29E-01 | 21.26 | 53.870 | 3.310 | 19.627 | -0.123 | -0.085 | -0.066 | 3 | 22.20 |
| Tetrahydro-5-Methyl-2-Furanmethanol | TEHYMFUROL | 15.38 | 6.09E-02 | 97.61 | -46.990 | 11.888 | 1.765 | 0.177 | -0.003 | -0.206 | 7 | 18.33 |
| 3,5-Xylenol | XYL35NOL | 15.25 | 7.90E-02 | 73.85 | -137.460 | -96.967 | -1.898 | 0.201 | -0.088 | -0.018 | 29 | 11.29 |
| 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | DHT1156MIDNE | 14.77 | 6.28E-01 | 3.76 | -4.680 | 56.537 | -28.156 | 0.204 | -0.007 | -0.004 | 28 | 11.42 |
| Decanal | DECAL | 14.47 | 3.55E-02 | 172.01 | 125.780 | -31.467 | 30.132 | 0.195 | -0.030 | -0.020 | 26 | 11.95 |

[1]F - Fischer value from One-way ANOVA test.
[2]W - Wilks value from Linear Discriminant Analysis.
[3]F - Fischer value from Linear Discriminant Analysis.
[4]CDF - Canonical Discriminant Function Coefficients.

The LDA line plots of all stages classified according to CDF1, CDF2 and CDF3 are exposed in Figure S14 (A), (B) and (C), respectively. The LDA line plot of most predictive VOCs for CDF1, CDF2 and CDF3 are presented in Figure S14 (D), (E) and (F), respectively. The CDF coefficients 3D plots of the four groups centroids and selected VOCs for CDF1, CDF2 and CDF3 are presented in Figure 28 (A) and (B), respectively.

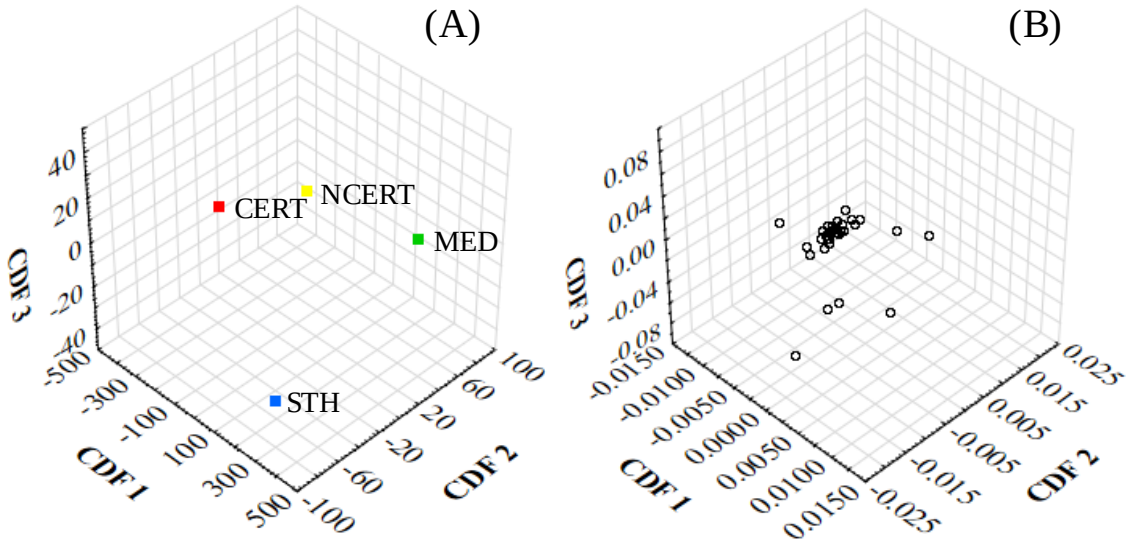


**Figure 28. The LDA loading 3D plot of all centroids (A) and the 31 most predictive VOCs (B) for the three main components.**

Only furfuryl acetate was removed from LDA analysis throughout all 22 steps of the backward selection method ($p < 0.05$). Thus, LDA analysis results were based on 31 VOCs (18.67%), is described in Table 5. All 54 replicates obtained from 18 syrups samples were classified at a 100% correct rate.

The projection of LDA results based on the three main CDFs presented in Figure 28 (A) demonstrated a high level of discrimination between all four centroids. In CDF 1, a huge discrimination was verified between the C-CERT and the other centroids. In CDF 2, a higher discrimination was observed between all centroids, where was verified a proximity between the centroids based on syrups from Madeira Island (C-CERT and C-NCERT) compared to centroids formed with samples from foreign syrups (C-MED and C-STH). Likewise, in CDF3 was observed a higher discrimination among the four centroids, being more prominent between the C-NCERT and the remaining three centroids. The LDA results evidenced that was possible to discriminate and classify correctly all syrups samples based only on the selected 31 VOCs.

### *3.2.4. PLS and HCA*

An additional PLS analysis was completed to validate the differentiation/correlation structure between all syrups samples based only on 31 most predictive VOCs. The PLS information is summarized in Table S48. The loading results and VIP scores of PLS analysis for each VOC are described in Table 5. The PLS loading results of four centroids and the scores results of all 18 samples are described in Table S46. The PLS loadings line plots of four centroids classified according to PLS1, PLS2 and PLS3 are showed in Figure S15 (A), (B) and (C), respectively. The PLS loadings line plot of previously selected 31 VOCs for PLS1, PLS2 and PLS3 are presented in Figure S15 (D), (E) and (F), respectively. The PLS loading 3D plots of the four centroids and 31 VOCs for PLS1, PLS2 and PLS3 are presented in Figure 29 (A) and (B), respectively.

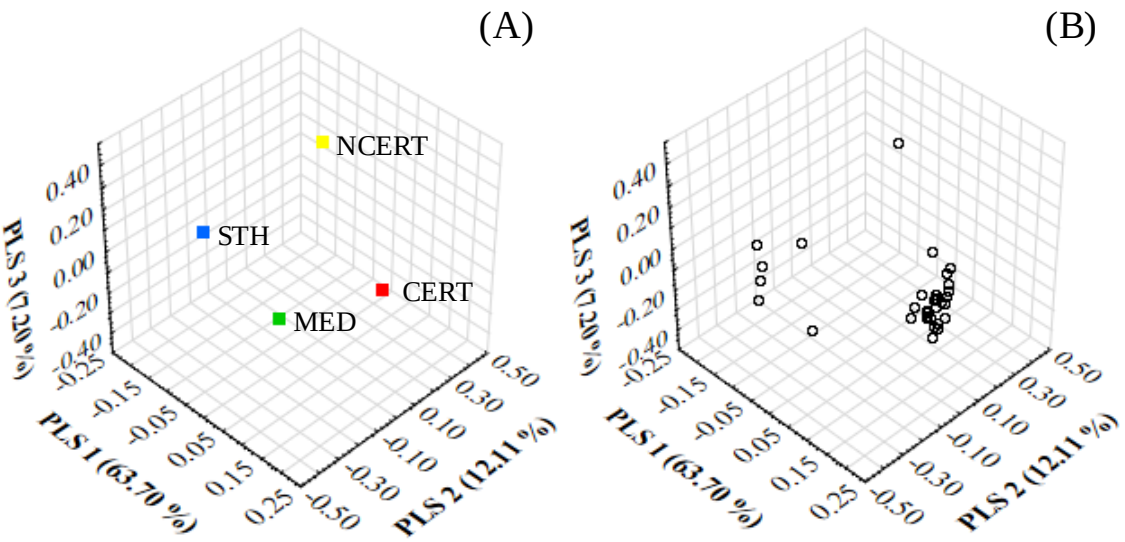


**Figure 29. The PLS loading 3D plot of all centroids (A) and the 31 most predictive VOCs (B) for the three main components.**

The PLS analysis performed according to the three main components explained 83.00% of TVA, where the sum of all 18 components described 99.88%. As predicted, the results presented in the PLS loading 3D plot reveal that the four centroids were categorically separated, where a higher and equitable variance between all centroids was verified. Likewise to CDF1, the projection of PLS1 (63.70%) showed a higher variance between the C-CERT and the other three centroids. In PLS2 projection (12.11 %), a high variance was verified between the C-STH and the remaining centroids. Finally, in PLS3 projection (7.20%), a high variance was observed between the C-MED and the other centroids.

HCA was completed based on the previously selected 31 VOCs to determine the Euclidean linkage distances between all 18 syrups samples and complete a suitable and visual measure of distance and linkage criterion between all 54 replicates. The HCA dendrogram is presented in Figure 30.

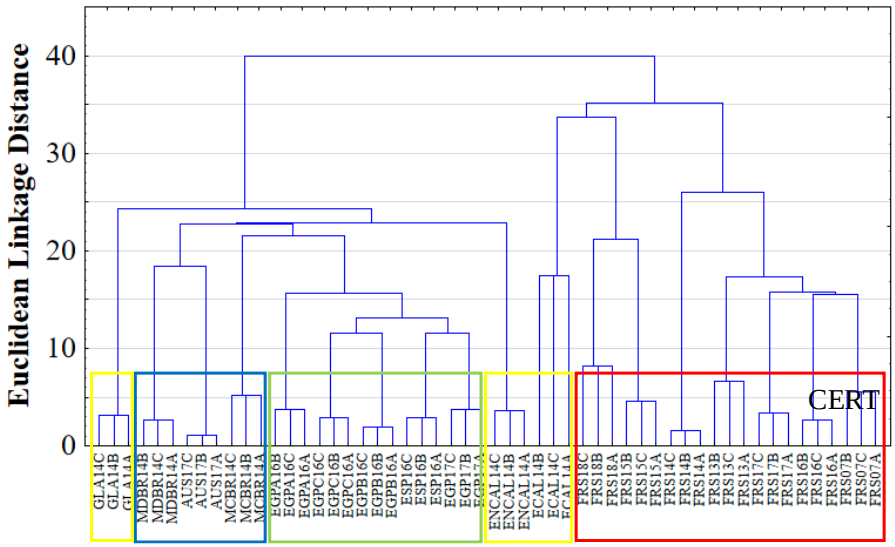


**Figure 30. The HCA dendrogram based on Euclidean linkage distances for all replicates from all samples of SC-based syrups.**

Predictably, the higher Euclidean distance was verified between the samples from the certified producer and the remaining syrups samples. There, the ECAL14 sample from non-certified regional producers presented a substantial proximity with samples from certified producer. On the contrary, the other syrups samples from non-certified regional producers, GLA14 and ENCAL14, presented a higher distance from samples of certified producer, and also among themselves. Another interesting fact is the proximity between the various syrups samples from the Mediterranean region (Spain and Egypt). The PLS projection and HCA results confirmed that is possible to differentiate the genuine SCH from other syrups based only on the 31 most predictive VOCs, proving its potential as useful markers for traceability and authenticity of SCH on the global market.

## *4. Conclusions*

The HS-SPME/GC-MS method was successfully applied for the establishment of the volatile profile from all 18 syrups under analysis. A total of 166 different VOCs were recognized, where 119 VOCs were identified in all samples under analysis, being classified into 17 different chemical classes, namely ALC, ALD, BNZ, BZF, CAC, EST, ETH, FUR, HYD, IND, KET, NPH, NIT, PHE, PYR, SUL and TER. The three main chemical classes were FUR, KET and CAC, being responsible for a large part of the volatile profile in the number of VOCs and RPA value, where HM5FURAL, DHYPPAONE and ETNOIC are the main VOCs for each one of these chemical classes, respectively. Interestingly, FUR was the main class for all samples from the certified regional producer, where KET was the main class for the other syrups samples.

The ANOVA test showed that 144 VOCs showed statistically significant differences between all syrups. PCA and PLS with complete matrix demonstrate that the higher level of differentiation was verified between samples from certified producers and other syrups samples. The selection of 31 most predictive VOCs based on the LDA proved its high predictive capacity by PLS and HCA, where a high level of differentiation was reached between samples from the regional certified producer, regional non-certified producers, Mediterranean producers (Spain and Egypt), and south hemisphere producers (Brazil and Australia). Once again, the higher differentiation level was verified between samples from the certified producer and other syrups samples.

In accordance with the results obtained from the chemometric analysis, we concluded that the establishment of a volatile profile can be a promising strategy to differentiate the genuine SCH from other syrups on the market, and also to discriminate the syrups based on its geographical origin. Furthermore, the specificity of some VOCs for a group of syrup samples could signify a potential marker. Additionally, the information obtained in this study is fundamental to guarantee the traceability and authenticity of SCH on the global market, and consequently, to support its submission process to an EU certification.

# CHAPTER 4. FURAN DERIVATIVES

# PROFILE

# SECTION 4.1. DEVELOPMENT OF METHODOLOGY FOR FURAN DERIVATIVES FINGERPRINTING

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## A useful strategy based on chromatographic data combined with quality-by-design approach for food analysis applications. The case study of furanic derivatives in sugarcane honey☆

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*Abstract*

SCH is one of the Madeira Island products par excellence and it is now popular worldwide. Its sui generis and peculiar sensory properties, explained by a variety of volatile compounds including FDs, arise mainly from manufacturing and storage conditions. A simple high-throughput approach based on MEPS/UHPLC was developed and validated for identification and quantification of target FDs in SCH. A Quality-by-Design (QbD) approach was used as a powerful strategy to optimize analytical conditions for high throughput analysis of FDs in complex sugar-rich food matrices. The optimum point into MEPS-Method Operable Design Region (MODR) was obtained with R-CX sorbent, acetonitrile (ACN) as elution solvent, three loading cycles and 500 µL of sample volume. The optimum point into UHPLC-MODR was obtained with a CORTECS column operating at a temperature of 50 °C, ACN as eluent and a flow rate of 125 µL $min^{-1}$. The robustness was demonstrated by Monte Carlo simulation and capability analysis for estimation of residual errors. The concentration-response relationship for all FDs were described by polynomial function models, being confirmed by Fisher variance (F-test). The % recoveries were in a range of 91.9-112.1%. Good method precision was observed, yielding % RSD less than 4.9% for repeatability and 8.8% for intermediate precision. The limits of quantitation for the analytes ranged from 30.6 to 737.7 µg $kg^{-1}$. The $MEPS_{R-CX}$/$UHPLC_{CORTECS}$-PDA method revealed an effective and potential analytical tool for SCH authenticity control based on target analysis of FDs allowing a strict control and differentiation from other similar or adulterated products.

Keywords: Sugarcane honey, Furanic derivatives, Quality-by-design, MEPS, UHPLC-PDA

*1. Introduction*

SCH is a black syrup produced by thermal processing of SC (*Saccharum officinarum L.*) juice, widely recognized by sui generis organoleptic properties. SCH is constituted of a complex matrix rich in minerals, CBHs, proteins, minerals (calcium, magnesium and iron), vitamins and antioxidants (flavonoids and non-flavonoids) [159]. Its peculiar flavor and distinct aroma arise mainly from aroma-active compounds, belonging to different chemical families including higher alcohols, esters, carbonyl compounds and especially FDs, produced during traditional manufacturing and storage procedures. Although, FDs can be produced by fermentation process during storage, the most important pathway is through NEBRs that occur during heat processing. These reactions are based in thermal degradation of several food components, such as caramelization of carbohydrates, MLDRs and STKD of reducing SGs with AAs, oxidation of lipids or decomposition of ascorbic acid [223,224]. Commonly, FDs are found in coffee, wine, balsamic vinegar, roasted cereals, fruit juices and milk, and in large amounts in heat-processed matrices with high sugar-content, such as honey, syrup and molasses [118,225–227]. The sugary-products have excellent conditions for the formation of FDs: high SGs and organic acids concentration, acidic pH and low water activity [228]. FDs have great importance in food industry, because their presence even in small amounts affects strongly the nutritional, sensory and organoleptic properties of products [229,230]. Moreover, recent investigations have been demonstrated that FDs can exhibit antioxidant and antiproliferative activities [231,232]. FDs profiling can be a promising strategy to solve new demands of food analysis science, namely in product traceability for the quality management, authenticity assessment and safety control [233–236].

Current analytical methods for FDs quantification are based mainly, on LC combined with UV-VIS or MS, and usually involve a previous extraction procedure to avoid the matrix interferences Table S49. Despite the results, these methods present some drawbacks in food analysis, including: (i) high sample dilution, making the quantification very difficult; (ii) direct injection without cleaning step, leading to unsatisfactory sensitivity results; (iii) extraction procedures as (LLE or SPE to sample clean-up, resulting in high solvent consumption [234–236]. Nowadays, food research have focused on cost-effective, sustainable and miniaturized approaches [236,237]. In this context, MEPS has been successful applied for food analysis, such as isolation of phenolic acids [236], lactones [34] and resveratrol [238] from wines, prenylflavonoids [239] from beers and ascorbic acid [237] from beverages. MEPS combines the sample extraction, pre-concentration and clean-up in a single device based in a miniaturization of SPE suitable for semi or full automation, providing high extraction speed, low operational costs, suitable precision,

sensitivity and selectivity [36,240,241]. Despite the development of food analysis domain in the last decades, the lack of control, transfer and harmonization of analytical methods hampers the quality and risk management of processing, safety and traceability of food products. QbD approach has been widely applied by pharmaceutical industry in drug development to promote the process and product quality [242–245], being defined by International Conference on Harmonization (ICH) in Guideline ICHQ8(R2) [246] as "a systematic approach to development that begins with predefined objectives and emphasizes product and process understanding and process control, based on sound science and quality risk management". Recently, the European Medicines Agency (EMA) and FDA regulators recognized through a pilot program that the application of QbD elements in development of analytical methods is useful as "a qualifier of the expected method performance" [247]. A QbD approach applied to analytical method development is based on a few key steps starting with the analytical target profile (ATP) and resulting in the definition of a MODR (a term coined by regulators [247] used to describe the analytical method design space). A QbD approach includes the use of risk assessment and multivariate statistics which leads to comprehensive method understanding and guaranteed data quality [248–251]. Therefore, the introduction of QbD concept in food analysis seems to be a promising strategy to provide assurance of quality of the analytical data and harmonization of methods.

In this paper, the development of an effective and time-saving approach based on semi-automated digitally eVol MEPS/UHPLC-PDA detection system for the simultaneous analysis of target FDs in SCH, is presented, following QbD principles according to Borman et al. [248] which are aligned with ICHQ8(R2) guideline [246]. To the best of our knowledge the QbD principles were used for the first time as useful strategy in food analysis. Several extraction- and analysis-influencing parameters, including sorbent type, number of loading cycles, elution solvent and sample volume of MEPS, and column type, mobile phase, flow rate of UHPLC analysis, were investigated and optimized. The method was fully validated (selectivity, calibration function, linearity, precision, accuracy, matrix effect, LOD and LOQ) and applied on FDs profiling of SCH to provide a useful tool for its differentiation and authentication.

## *2. Materials and methods*

### *2.1. Samples, standards, reagents and materials*

Commercial SCH and SC juice samples were supplied by the traditional producer FMCRS in April 2015, Madeira Island, Portugal, and stored under stable conditions (4 °C, in the dark). FDs standards, 5-

hydroxymethyl-2-furaldehyde (5HMF), 2-furaldehyde (FURL), 2-furylmethanol (FAL), 2-furyl methyl ketone (2FMK) and 5-methyl-2-furaldehyde (5MF), and the solvents/eluents formic acid (FA), ACN and methanol (MeOH), were purchased from Sigma-Aldrich (St. Louis, USA). Ultrapure deionized water ($H_2O^d$), purified with a Milli-Q ultra-pure water system from Millipore (Massachusetts, USA), was used throughout the study. All solvents and samples were filtered through 0.22 μm membrane filters from Millipore (Massachusetts, USA), before analysis. MEPS sorbents, C2 (ethyl-silica), C8 (octyl-silica), C18 (octadecyl-silica), SIL (unmodified silica), M1 (mixed sorbent containing C8 (80%) and strong cationic exchange (20%)), were purchased from SGE Analytical Science (Melbourne, Australia), whereas PGC (HyperSep Hypercarb porous graphitized carbon), RC-X (HyperSep retain cationic exchange), RA-X (HyperSep retain anionic exchange) and PEP (HyperSep retain polar enhanced polymer),were obtained from Thermo Fisher Scientific (Massachusetts, EUA). UHPLC analytical columns, CORTECS C18 (1.6 μm, 2.1 × 100 mm), ACQUITY BEH C18 (1.7 μm, 2.1 × 50 mm), ACQUITY HSS T3 (1.8 μm, 2.1 × 100 mm) and the VANGUARD pre-column (1.6 μm, 2.1 × 5 mm) were acquired from Waters Corporation (Massachusetts, EUA), while the KINETEX HILIC (1.7 μm, 2.1 × 100 mm) column was from Phenomenex (California, EUA).

*2.2. Samples and standards solutions preparation*

Samples were prepared using 10 g of SCH in 20 mL of $H_2O^d$:MeOH (95:5% v/v) acidified with 0.1% FA and stored (4 °C, in the dark). FDs standard stock solutions (1000 mg L−1) were prepared by dissolving appropriate amounts of the compounds in MeOH, and stored at -20 °C, in the dark, till analysis. Under these conditions, the solutions are stable for at least 3 months. Working solutions of lower concentration with all FDs standards were daily prepared, by appropriate dilution, with $H_2O^d$:MeOH (95:5% v/v) solution acidified with 0.1% FA.

*2.3. MEPS procedure*

MEPS procedure was performed using an eVol digital semi-automated syringe equipped with a 500 μL gas-tight syringe and removable needles containing the sorbent BINs, and following the recommended extraction protocol steps by M. Abdel-Rehim [240]: sorbent conditioning, sample loading, sorbent washing and analytes elution. The samples and operation solutions for each step (conditioning, washing and elution) were loaded and discarded through the BINs under constant flow (20 μL per second) controlled by eVol, minimizing the cavitation events and experimental errors. The sorbent conditioning was achieved with 250

μL of MeOH and 250 μL of $H_2O^d$ acidified with 0.1% FA to activate the sorbent and guarantee reproducible retention of FDs. The sample loading was performed through a three loading/discharge cycles for 500 μL of sample through the R-CX sorbent. The washing was done by 100 μL of MeOH, whereas the elution was performed in two steps: initially with 100 μL of $H_2O^d$:MeOH (95:5% v/v) acidified with 0.1% FA and after with 100 μL of $H_2O^d$ acidified with 0.1% FA, to ensure the complete elution of FDs and avoid memory effects (carry-over). All MEPS procedures were carried out in triplicate. All the extracts were filtered before injection into the UHPLC-PDA system.

*2.4. UHPLC-PDA conditions*

The separation and identification of FDs was carried out on a UHPLC-PDA ACQUITY system acquired from Waters (Massachusetts, EUA) equipped with an H-Class ultra-pressure liquid chromatography system, quaternary solvent manager, sample manager, column heater, degassing system and a 2996 PDA detector. The configuration was driven by Empower software version 2.0 also from Waters (Massachusetts, EUA). The chromatographic separation was achieved with a CORTECS UHPLC C18 column (1.7 μm, 50 mm × 4.6 mm i.d.). The binary mobile phase was composed by acidified $H_2Od$ (0.1% FA, eluent A) and ACN (eluent B), with a constant flow rate at 125 μL $min^{-1}$. The 15 min gradient was as follows: 95% A (0 min); 80% A (1 min); 75% A (2 min); 70% A (5 min); 20% A (8 min); and 95% A (15 min). The column temperature was kept at 50 °C and the sample manager at 20 °C. The injection volume was set at 10 μL. and the detection wavelength was set at 275 nm. For quantification purposes, the PDA detection was carried out by different channels according with to the maximum absorbance wavelength of each FDs (Table 6). The identification was based on the comparison of RTs and maximum absorbance wavelengths of pure standards, and quantified by the standard addition method.

*2.5. Statistical software*

All data analysis and modelling processing were performed using the STATSOFT STATISTICA 12.0 (2013) software (Tulsa, USA).

## *3. Results and discussion*

The development of the proposed analytical method was based on QbD approach according with ICHQ8(R2) [246] guideline described by Borman et al. [248], Schweitzer et al. [249], Hanna-Brown et al. [250] and Martin et al. [252], and adapted according to recommendations for chromatography applications

from Pasquini et al. [242], Orlandini et al. [243], Oliva et al. [244] and Tol et al. [245]. The workflow chart for QbD approach-based analytical method are summarized in Figure S16.

*3.1. ATP, CMAs and method scouting*

In our study, analytical target profile (ATP) was defined by the separation, identification and quantification of selected FDs in complex sugary-products (SCH sample) through MEPS/UHPLC-PDA analytical method. FDs standards were selected to encompass the main functional groups on the furan ring, such as aldehydes (5HMF, FURL and 5MF), alcohols (FAL) and ketones (2FMK). The selection of critical method attributes (CMAs) for MEPS technique were based on the extraction efficiency, being selected the number of FDs standards extracted, their TPA and intermediate precision (IP). For UHPLC analysis were the TPA and peak resolution (PR). The requirements for CMAs were set as the following: the FDs under analysis must be identified, the TPA value was defined by the maximum that can be reached and PR values greater than 1.5 For IP, the RSD values were the lower at possible, being considered acceptable when not higher than 15% [130]. The scouting of analytical method was based on preliminary results obtained by study previously developed by our laboratory, which were quantified the 5HMF, 5MF, FURL and 2FMK in fortified wine through MEPS/UHPLC-PDA analysis [253]. However, some procedures were adjusted to complexity of SCH samples. The sample dilution ratio (2:3, 1:1 and 1:2 (w/v)) was investigated to avoid problems related with sample viscosity, wherein the ratio 1:2 was demonstrated to be the most suitable for the extraction of FDs by MEPS (data not shown). Another adjustment was performed on MEPS procedure, which a further step has been added in the elution step to ensure the complete elution of FDs and avoid memory effects.

*3.2. QRA and CMPs*

The selection of parameters by quality risk assessment (QRA) was performed through Ishikawa diagram based on scouting phase results, which are shown in Figure S17. The selected CMPs for MEPS were sorbent type, elution solvent, loading cycles and loading sample volume, while for UHPLC-PDA were column type, organic eluent, column flow and column temperature. The non-investigated parameters were fixed during method development. The critical method parameters (CMPs) were investigated based on extraction efficiency of MEPS and separation performance of UHPLC. The main parameter regarding to MEPS effectiveness is the sorbent, which its selection is based on the sorptive material selectivity to the target analytes. The additionally critical parameters are the elution solvent, number cycles, flow rate and sample

volume used for loading step [36,241]. In LC methods, the type of column is the most important parameter for separation performance, being optimized according its stationary phase chemistry, functional groups and bonding type. The other relevant parameters that can be adjusted are the eluent composition (organic eluent, pH and gradient), chromatographic operational conditions (column flow, column temperature and injection volume) and detector (detection wavelength) [254,255].

*3.3. KS*

The MEPS/UHPLC-PDA methods previously developed by our laboratory are an excellent way for the prior investigation of knowledge space (KS), providing valuable knowledge for definition of influencing CMPs range [34,236,239,253]. A Full Factorial Design (FFD) based on 32-level and 19-level factors model was applied as design of experiment (DoE) experiment for MEPS-KS screening, being evaluated the following parameters: elution solvent (ACN and MeOH), loading cycles (3 and 5 ×) and loading sample volume (250 and 500 µL) for each sorbent (C2, C8, C18, SIL, M1, PGC, RC-X, RA-X and PEP). The CMAs response results, CMPs and respective range values for MEPS-KS FFD screening model are summarized in Table S50. The TPA and IP results for each sorbent at optimal extraction conditions are showed in Figure 31 (A) and (B), respectively.

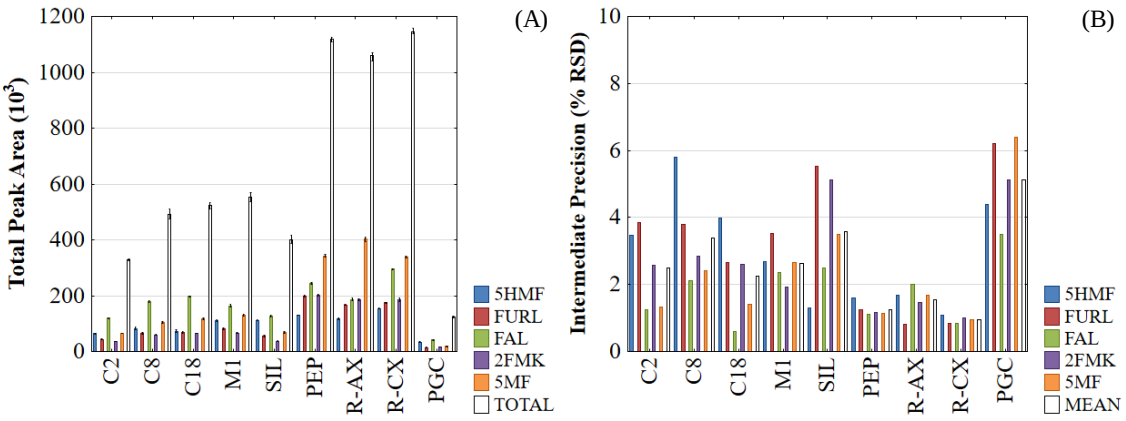


**Figure 31. The bar plot of screening of MEPS-KS regarding the TPA (A) and IP (B) results for each sorbent with optimal conditions.**

According to the results, all sorbents were suitable to extract all FDs under study. However, sorbents showed high variability in extraction efficiency, wherein the TPA decreased in the following order: R-CX > PEP > R-AX > M1 > C18 > C8 > SIL > C2 > PGC, and IP increased in this order: R-CX < PEP < R-AX < C18 < C2 < M1 < C8 < SIL < PGC. Interestingly, the mixed-sorbents with highly porous polystyrene DVB material (R-CX, PEP and R-AX) showed the highest TPA and lowest IP values, followed by silica-based sorbents (M1, C18, C8, SIL and C2) and carbon-based sorbent (PGC). The high extraction efficiency of mixed-sorbents may be due to the fact that they are specific for retention of low polarity compounds in

water-soluble matrices. Despite these similarities, different TPA values were obtained, where R-CX showed higher efficiency for 5HMF and FAL, PEP for FURL and 2FMK, and R-AX for 5MF. For IP results, R-CX showed lower RSD values for most of FDs, with exception of FURL. This specificity of each sorbent on FDs extraction may be due to the modification on the surface of sorptive material with different functional groups, namely sulfonic acid (R-CX), urea (PEP) and quaternary amine (R-AX). Nevertheless, the CMAs responses confirmed that R-CX was the most suitable sorbent for a comprehensive extraction of FDs via MEPS technique in complex sugary-matrices. Surprisingly, it was the first time that R-CX was selected as the best sorbent for food analysis. Moreover, this selection is contrary to the results obtained in our previous studies, wherein C8 and PEP sorbents were selected trough univariate optimization for the extraction of FDs [253] and sotolon (compound based on a furan ring) [34] in wines, respectively.

The FFD for UHPLC-KS screening was based on 12-level, 23-level and 14-level factors model, being evaluated the organic eluent (MeOH and ACN), column flow (125, 250 and 375 µL $min^{-1}$) and column temperature (30, 40 and 50 °C) for each column under study, namely the CORTECS, BEH, HSS and HILIC. The CMAs (TPA and PR) results, CMPs and respective range values of UHPLC-KS FFD screening model are summarized in Table S51 and Table S52, respectively. The TPA and PR for each column at optimal separation conditions are showed in Figure 32 (A) and (B).

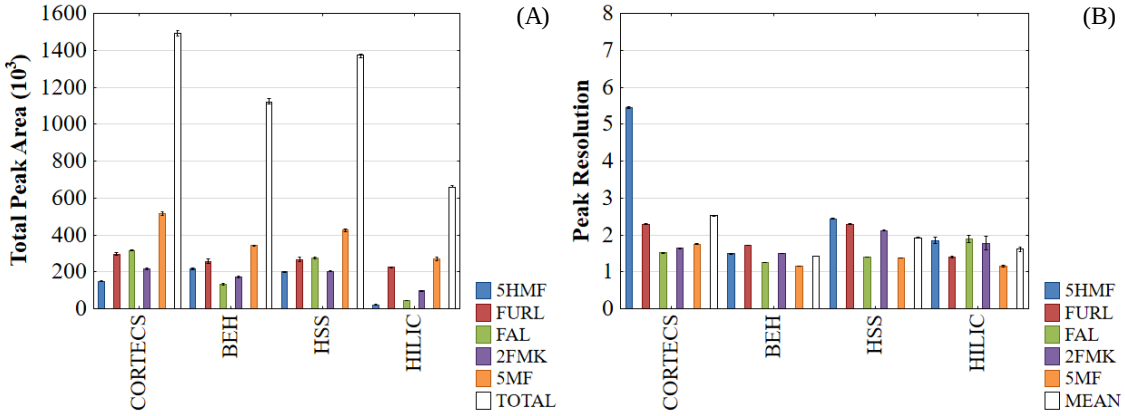


**Figure 32. The bar plot of screening of UHPLC-KS regarding the TPA (A) and PR (B) results for each column with optimal conditions.**

Although all columns were capable of separating the FDs under study, the chromatographic efficiency differed greatly depending on column type. The TPA values decreased in the following order: CORTECS > HSS > BEH > HILIC, and PR values decreased in this order: CORTECS > HSS > HILIC > BEH. As expected, HILIC presented poor TPA results, since it was a silica phase column used under hydrophilic interaction to provide the retention of high polar compounds. On the other hand, HILIC showed reasonable PR for most of FDs, presenting the higher PR value for FAL. Although the chromatographic separation of

CORTECS, BEH and HSS were based on reversed-phase through C18 surface, CORTECS showed higher TPA values for FDs under study (except for 5HMF). Regarding the PR values, CORTECS demonstrated greatest PR values for 5HMF, 5MF and FURL (similar to HSS), HSS for 2FMK and HILIC for FAL. The high efficiency of CORTECS its explained by small particle core-shell diameter (1.6 μm) than BEH and HSS (1.7 μm), increasing the surface absorption and higher retention of analytes. These results confirm the excellent performance of CORTECS for separation of compounds based on the furan ring, previously demonstrated in the separation of FDs [253] and sotolon [34] in wines. Chebrolu et al. [256] reported that CORTECS present better performance than Kinetex C18 for analysis of carotenoids, chlorophylls and tocopherol in broccoli, and Wang et al. [257] demonstrated that CORTECS showed a better performance for analysis of mycotoxins in fruit matrices than BEH C18.

*3.4. MODR*

A MODR was defined for MEPS and for UHPLC with the objective to define a space where each one will be fit for purpose. The $MEPS_{R\text{-}CX}$-MODR definition was performed based on CMAs responses from interactions of elution solvent, loading cycles and loading sample volume. The Pareto ranking analysis (PRA) for TPA and IP are showed in Figure S18 (A) and (B), respectively. The only CMPs that demonstrated a significant effect on the TPA results was the type of elution solvent, while none CPP significantly influenced the IP of R-CX. This first step for MEPS-MODR definition was the selection of discontinuous CPP, the elution solvent. The TPA and IP results for each elution solvent are showed in Figure S19 (A) and (B), respectively. The results indicate that ACN was clearly a better elution solvent than MeOH, where showed higher TPA values for all FDs. Although, any parameter significantly affected the IP, the ACN showed lower RSD values for most FDs, with the exception of FURL. Thus, ACN was selected for the definition of $MEPS_{R\text{-}CX}$-MODR. The RSM plots of effect between loading cycles number and loading sample volume on the TPA and IP responses are showed in Figure 33 (A) and (B), respectively.

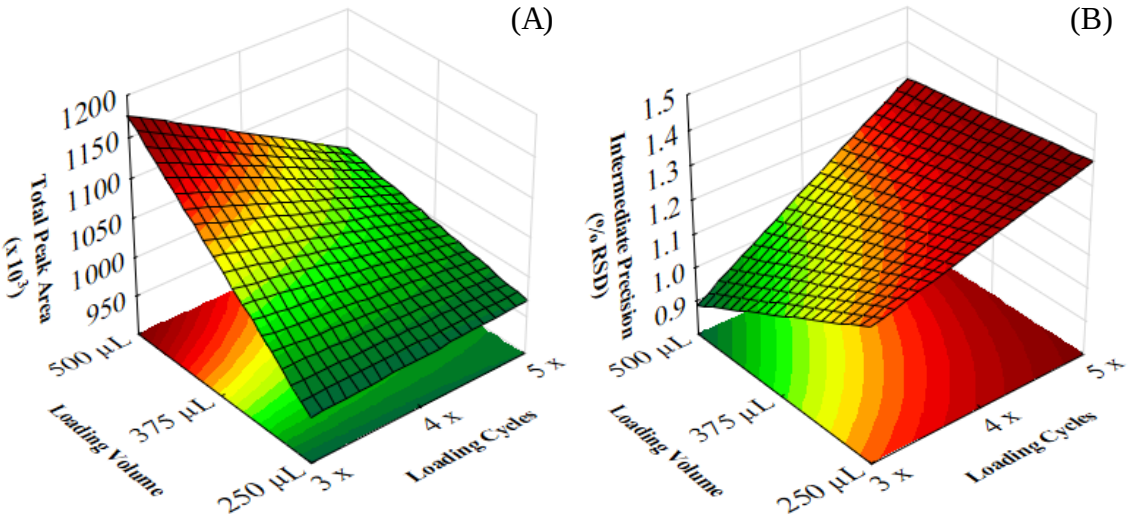


**Figure 34. The RSM plot of evaluation of continuous CMPs for definition of MEPS$_{R\text{-}CX}$-MODR regarding the TPA (A) and IP (B) results.**

Based on the results, it was found that the highest TPA values were obtained on the interaction space between 3 × and 4 × loading cycles with sample volumes of 375-500 µL, which decreased dramatically outside this space. Interestingly, the lowest RSD values were also obtained in the same space of interaction between the two CMPs. In order to define the MEPS$_{R\text{-}CX}$-MODR, a desirability analysis (DA) was performed by overlay of CMAs responses (TPA and IP) and selection of respective desirable (optimum) values. For TPA response was defined the highest as desirable (1146.6), mean as acceptable (1031.6) and lowest as unacceptable (974.4) values, while the values for IP were defined as: desirable (0.9), acceptable (1.2) and unacceptable (1.4). The DA plot is shown in Figure 34.

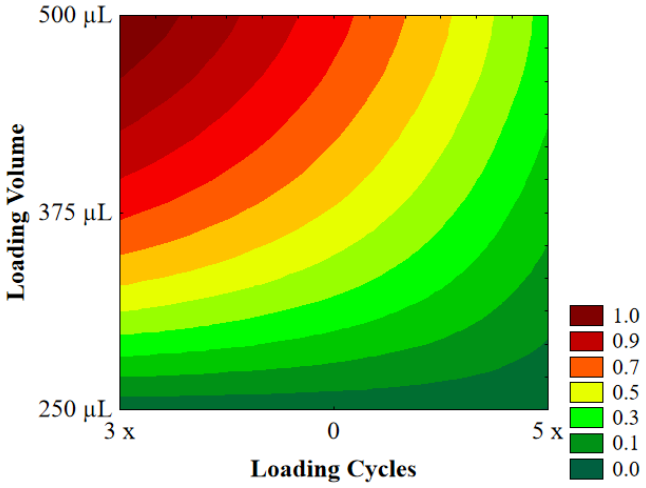


**Figure 33. The DA index plot for definition of MEPS$_{R\text{-}CX}$.**

As expected, the highest DA index was found in the interaction space (dark red zone) between 3× loading cycles and a sample volume of 500 µL, which was defined as MEPS$_{R\text{-}CX}$-MODR. The data verification was performed through analysis of agreement between the predicted and observed values, which are described in Table S53. According to the results, it was found that all the values observed for the

experiments were very close to predicted values, wherein all were within the 95% confidence interval. Thus, it can be stated with a high level of confidence that the optimal conditions of MEPS technique for the extraction of FDs from sugary-complex matrices was carried out through the R-CX sorbent with ACN as elution solvent, with 3× loading cycles and 500 µL of sample volume.

The UHPLC$_{CORTECS}$-MODR definition was performed based on CMAs responses from interactions of organic eluent, column flow and column temperature. The PRA for TPA and PR are showed in Figure S18 (C) and (D), respectively. The only CPP with significant influence on the TPA response was the column flow and its interaction with the organic eluent. On the other hand, PR response was significantly influenced by all CMPs. The organic eluent is the only CPP classified as discontinuous variable, and its selection was the first step in UHPLC$_{CORTECS}$-MODR definition. The TPA and PR results for each organic eluent are presented in Figure 19 (C) and (D), respectively. The results demonstrated that ACN obtained a higher TPA values than MEOH, which it showed superior values for FURL, FAL and 5MF, and no differences were found for 5HMF and 2FMK. Regarding the PR, ACN also obtained higher mean value, where it had higher values for all FDs, with the exception of 2FMK. Thus, ACN proved to be a better option as organic eluent than MeOH, being selected for UHPLC$_{CORTECS}$-MODR definition. The RSM plots of interaction between the change level of continuous CMPs (column flow and column temperature) on TPA and PR responses are showed in Figure 35 (A) and (B), respectively.

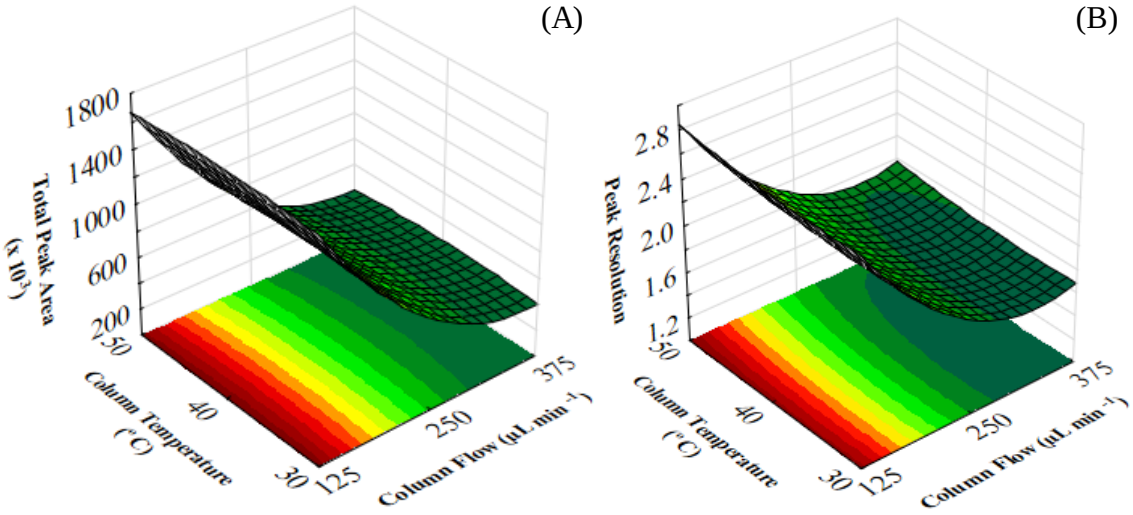


**Figure 35. The RSM plot of evaluation of continuous CMPs for definition of UHPLC$_{CORTECS}$-MODR regarding the TPA (A) and PR (B) results.**

From the results, it was possible to verify that the higher TPA and PR values were clearly influenced by column flow rate, where the better results were obtained with 125 µL min$^{-1}$, with the flow rates above causing a sharp decrease on CMAs values. However, no remarkable differences were observed for TPA

and PR values in the range of column temperatures used at a flow of 125 µL min$^{-1}$. For UHPLC$_{CORTECS}$-MODR definition a DA was performed through overlay of CMAs responses. The values for TPA and PR were defined as: desirable (1492 and 2.59), acceptable (863 and 2.02) and unacceptable (392 and 1.59). The DA analysis plot is presented in Figure 36.

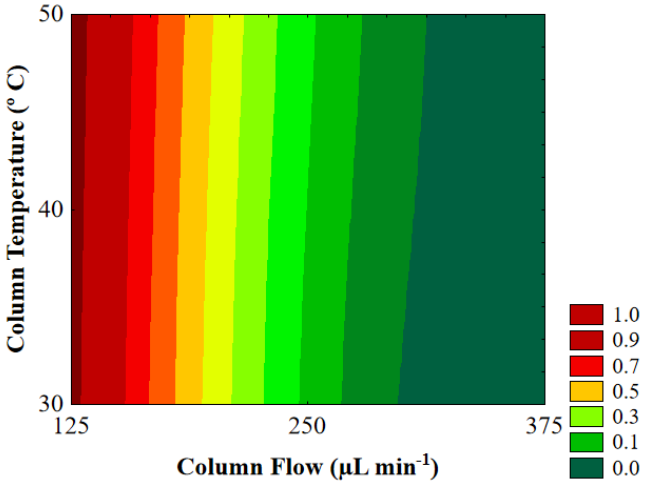


**Figure 36. The DA index plot for definition of UHPLC$_{CORTECS}$-MODR.**

The highest DA index was obtained with a flow rate close to 125 µL min$^{-1}$ and a column temperature between 30 and 50° C, being that this space of interaction was defined as UHPLC$_{CORTECS}$-MODR. Although, the temperature was not determinant for the definition of MODR, small differences were observed between the temperatures studied, with the temperature 50 °C showing a slightly superior DA index. Thus, the optimum point into UHPLC$_{CORTECS}$-MODR was obtained with ACN as organic eluent, flow rate of 125 µL min$^{-1}$ at a temperature of 50 °C. The data verification was performed through the analysis of agreement between the predicted and observed values at optimum point, which are described in Table S54. The results showed slight differences between the observed and predicted values in CMAs responses for all FDs. These differences may be due to the fact that the range of values for the CMPs were relatively large, and small variations at the optimum point produce variability in the CMAs responses. Thus, in order to guarantee a more restricted control of UHPLC$_{CORTECS}$-PDA analysis, this point was analyzed in more detail through a robustness study.

*3.5. Robustness and method control*

Robustness was evaluated at the optimum point (set as the nominal conditions) in the MODR using a new DoE based on continuous CMPs with range values around this point. The Fractional Factorial Design for robustness screening was based on 23-level factors model, being evaluated the flow column (115, 125 and 135 µL min$^{-1}$) and temperature column (48, 50 and 52 °C). The CMAs response results, CMPs and

respective range values for robustness screening model are described in Table S55. DA was performed through overlaying of all CMAs responses with a previously predefined optimum values for method control. The selection of DA values was based on % RSD from TPA and PR results at optimum point, where 0% was defined as desirable (1480 and 2.590), 0.5% as acceptable (1465 and 2.564) and 1.0% as unacceptable (1450 and 2.538). The DA plot is presented in Figure 37.

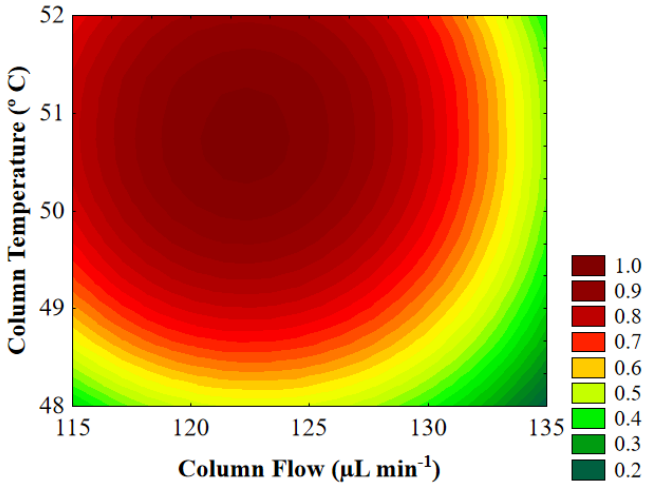


**Figure 37. The DA index plot for evaluation of robustness at optimum point into UHPLC$_{CORTECS}$-MODR.**

The highest DA index was reached with flow rates between 120 and 125 µL min$^{-1}$ at temperatures of 50–51 °C, where %RSD values were above of 0.1%. The robustness data verification was performed through analysis of agreement between the predicted and observed values at working point, which are described in Table S56. The results showed that all observed values were very close to predicted values, where for most of FDs were within the 95% confidence interval, with the exception for TPA values from one experiment of 5HMF and FURL. Apparently, our method presents an excellent robustness, in which all experiments performed have % RSD values below 0.8%. However, robustness is strongly dependent on the sensitivity of CMPs, being necessary the establishment of system suitability limits. The method control was performed by generating large amount of data (100 cases) through the Monte Carlo bootstrapping simulation at CMPs range with highest DA index, where was applied the capability analysis on this large data for estimation of residual errors from CMAs responses. The capability analysis for TPA and PR are presented in Figure 38 (A) and (B), respectively.

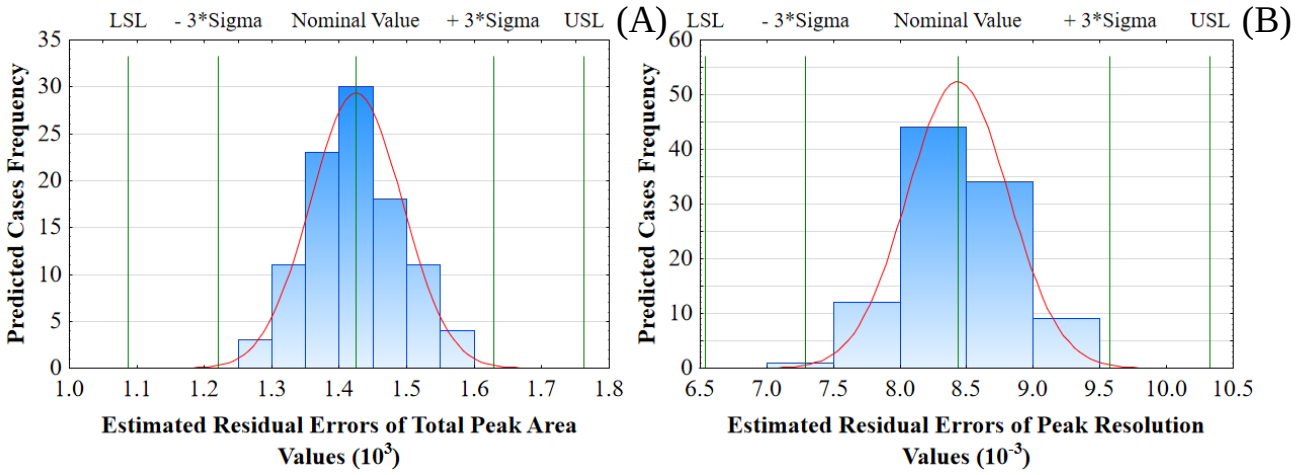


**Figure 38. The capability analysis plot regarding the TPA (A) and PR (B) residual error results.**

All cases were within the limits defined for residual error values of TPA (RSD below 0.1%), namely between the lower specification limit (1.09) and upper specification limit (1.76), which was obtained a process capability index (Cpk) of 1.62. Similarly, the residuals errors values of PR were within both specification limits (0.0065-0.0084), where Cpk was 1.65. Based on this analysis, it can be concluded with high level of confidence that our analytical method is highly robust, since both CpK values were above the reference value of 1.33, which is a minimum value for a method to be considered robust [245].

### *3.6. Validation of the analytical method*

The analytical method was validated according to ICHQ2(R1) guidelines [246], and based on validation procedure developed in our previous study [159]. Selectivity was evaluated through analysis of peak shape, PR, RT and chromatographic purity of the spectrum to avoid interferences. The RTs and maximum absorbance wavelength are presented in Table 6.

**Table 6. Calibration function and linearity results of FDs in SC-based syrups.**

| Furanic Derivatives | RT (min)[a] | λ max (nm)[b] | Concentration range (mg $L^{-1}$) | Linear | | | | | Polinominal | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Regression equation | Correlation coefficient ($r^2$) | $F_{exp}$ Value[c1] | Diference[d1] $F_{theo}/F_{exp}$ | Function Suitability[e] | Regression equation | Correlation coefficient ($r^2$) | $F_{exp}$ Value[c2] | Diference[d2] $F_{theo}/F_{exp}$ | Function Suitability[e] |
| 5HMF | 4.4 | 283 | 0.13 - 17.8 | y = 1.0779× + 0.2759 | 0.9989 | 3.26 | 0.84 | no | y = -0.0075$×^2$ + 1.2054× + 0.0674 | 0.9999 | 0.08 | 37.53 | Yes |
| FURL | 5.2 | 278 | 0.12 - 15.9 | y = 4.5075× + 1.1292 | 0.9982 | 152.91 | 0.02 | no | y = -0.0457$×^2$ + 5.1996× + 0.1179 | 0.9998 | 2.28 | 1.25 | Yes |
| FAL | 5.0 | 216 | 0.53 - 72.3 | y = 0.5713× + 1.1888 | 0.9985 | 5.90 | 0.46 | no | y = -0.001$×^2$ + 0.6421× + 0.7192 | 0.9996 | 0.26 | 11.05 | Yes |
| 2FMK | 6.3 | 274 | 0.10 - 13.1 | y = 3.3863× + 1.401 | 0.9950 | 418.35 | 0.01 | no | y = -0.0719$×^2$ + 4.2799× + 0.3299 | 0.9998 | 1.05 | 2.71 | Yes |
| 5MF | 7.0 | 291 | 0.10 - 13.4 | y = 6.4458× + 0.8533 | 0.9992 | 13.62 | 0.20 | no | y = -0.0505$×^2$ + 7.0872× + 0.067 | 0.9999 | 0.27 | 10.57 | Yes |

[a] Retention time.

[b] Maximum absorbance values obtained in the PDA system detection.

[c1] The Fisher value calculated experimentally with 16 degrees of freedom of experimental error and 6 degrees of freedom of lack of fit of function.

[c2] The Fisher value calculated experimentally with 16 degrees of freedom of experimental error and 5 degrees of freedom of lack of fit of function.

[d1] The Fisher value calculated experimentally is compared against the critical value of Fisher theoretical at the 95% with 16 degrees and 6 of freedom degrees. If the experimental data set describes a proposed function calibration of the form given then the condition Ftheo. > Fexp must be fulfilled.

[d2] The Fisher value calculated experimentally is compared against the critical value of Fisher theoretical at the 95% with 16 degrees and 5 of freedom degrees. If the experimental data set describes a proposed function calibration of the form given then the condition Ftheo. > Fexp must be fulfilled.

[e] The suitability of proposed function model to describe the observed data due to some significant lack of fit.

The chromatograms with optimum conditions are presented in Figure 39, where it is possible to verify that all FDs were clearly well separated in all samples matrices. The method showed high selectivity with all PR values above 1.5, varying between 1.5 (FAL) and 5.4 (5HMF).

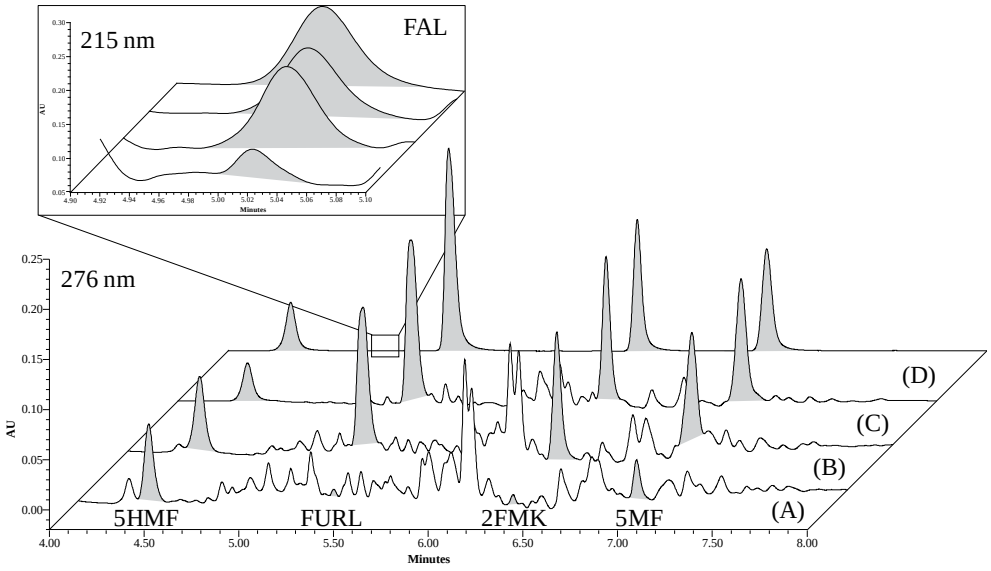


**Figure 39. The experimental MEPS$_{R\text{-}CX}$/UHPLC$_{CORTECS}$-PDA chromatograms of FDs for SCH (A), SCH spiked with FDs (B), SC juice spiked with FDs (C) and solvent-based matrix spiked with FDs (D).**

Calibration function was performed through the standard calibration curves prepared with six different concentrations of FDs in SC juice (similar interferents to SCH) plotted as TPAs vs concentration. Linearity was evaluated checking the suitability of function model by estimation of Fisher variance (F-test). The results are summarized in Table 6. Although, the correlation coefficients of curves for all FDs have values above 0.99 in linear function model, the F-test results showed that linear function model was not suitable ($F_{theo}/F_{exp} < 1$). Alternatively, a polynomial function model is proposed. The F-test indicates that the polynomial function was suitable to describe the concentration-response relationship for all FDs, where the ratio $F_{theo}/F_{exp}$ was always greater than 1.

The precision, accuracy, matrix effect, LOD and LOQ concentration ranges and results are summarized in Table 7.

**Table 7. Accuracy, precision, matrix effect, LOD and LOQ results of FDs in SC-based syrups.**

| Furanic Derivatives | Concentration range (mg $L^{-1}$) | Accuracy | | Precision | | Matrix Effect | | LOD (µg $kg^{-1}$ SCH) | LOQ (µg $kg^{-1}$ SCH) |
|---|---|---|---|---|---|---|---|---|---|
| | | Recovery (%) | (% RSD) | Repeatability (% RSD) | Intermediate Precision (% RSD) | Variation Effect (%) | Significance[a] (p value < 0.05) | | |
| 5HMF | 15.3[LL] | 112.1 | 0.8 | 3.0 | 9.8 | 113.4 | 0.235 | 19.9 | 60.2 |
| | 7.7[ML] | 106.6 | 1.7 | 3.9 | 1.4 | | | | |
| | 3.8[HL] | 104.5 | 3.0 | 5.6 | 0.3 | | | | |
| FURL | 13.7 | 95.5 | 0.6 | 2.4 | 8.6 | 95.4 | 0.549 | 78.7 | 238.5 |
| | 6.8 | 94.0 | 0.8 | 3.0 | 9.0 | | | | |
| | 3.4 | 91.9 | 0.8 | 4.2 | 3.0 | | | | |
| FAL | 62.1 | 98.8 | 2.7 | 2.5 | 5.2 | 91.7 | 0.155 | 243.4 | 737.7 |
| | 31.1 | 95.7 | 1.3 | 4.1 | 4.2 | | | | |
| | 15.5 | 95.1 | 2.6 | 4.5 | 4.0 | | | | |
| 2FMK | 11.2 | 102.5 | 1.0 | 2.4 | 8.2 | 105.7 | 0.477 | 61.4 | 185.9 |
| | 5.6 | 101.3 | 0.8 | 3.4 | 8.8 | | | | |
| | 2.8 | 97.6 | 0.5 | 4.9 | 1.6 | | | | |
| 5MF | 11.5 | 104.3 | 1.1 | 2.1 | 6.1 | 103.0 | 0.719 | 10.1 | 30.6 |
| | 5.7 | 109.0 | 0.9 | 3.1 | 7.8 | | | | |
| | 2.8 | 107.2 | 1.1 | 4.1 | 2.2 | | | | |

[LL] Low level concentration of FD.

[ML] Medium level concentration of FD.

[HL] Hihg level concentration of FD.

[a] The *p* value calculated experimentally through t-student test between slopes obtained by calibration curves of FDs in SCH and SCJ samples. If the obtained $p_{value} \geq 0.05$, no significant matrix effect was observed.

The accuracy was determined through % recovery, wherein the values were within acceptable limits from guidelines (70-125%), ranging between 91.9 (FURL) and 112.1% (5HMF). The precision was determined by repeatability and IP, measuring the inter- and intraday variation, respectively. All obtained values were below the maximum described in guidelines (%RSD < 15), where repeatability values ranged between 2.1 (5MF) and 5.6% (5HMF) and the IP values from 0.3 to 9.8% (5HMF). The matrix effect was evaluated by applying the method of "standard additions", where values ranging between 91.7 (FAL) and 113.4% (5HMF). The significance of results was confirmed through t-student test, which was possible verified that the matrix effect was not significant. The LOD and LOQ determination was based on the standard deviation (s) of calibration curve interception and the slope of a regression curve, which were calculated using the following equations: LOD = 3.3 × σ/slope and LOD = 10 × σ/slope. The lowest LOD and LOQ were obtained for 5MF presenting values of 10.1 and 30.6 μg $kg^{-1}$ SCH, respectively. On the other hand, the highest LOD and LOQ values obtained were 243.4 and 737.7 μg $kg^{-1}$ SCH for FAL. Interestingly, the LOD (19.9 μg $kg^{-1}$ SCH) and LOQ (60.2 μg $kg^{-1}$ SCH) obtained in our study for 5HMF were lower than those obtained in the study conducted by Andrade et al. [226] in cane syrups by HPLC-PDA, which were approximately 45.0 μg $kg^{-1}$ and 130.0 μg $kg^{-1}$, respectively.

### *3.7. Application of the analytical method*

The $MEPS_{R\text{-}CX}$/$UHPLC_{CORTECS}$-PDA method was applied for FDs profiling of real SCH sample. The analytical procedure was performed in triplicate and the FDs were quantified being obtained the following values: 5HMF (21.9 mg $kg^{-1}$, 3.0% RSD), FURL (1.5 mg $kg^{-1}$, 3.0% RSD), FAL (9.3 mg $kg^{-1}$, 3.9% RSD), 2FMK (0.3 mg $kg^{-1}$, 3.6% RSD) and 5MF (1.6 mg $kg^{-1}$, 3.0% RSD). By the results obtained in the analysis of a real sample of SCH, it is possible to verify that the concentrations obtained for all FDs were above the LODs and LOQs obtained in the validation procedure. Moreover, the results also demonstrated that the developed methodology presents excellent repeatability when applied in real samples. Thus, the $MEPS_{R\text{-}CX}$/$UHPLC_{CORTECS}$-PDA method proved to be a potential analytical tool for the quantification of FDs in SCH and similar products.

## *4. Conclusions*

In this work an ultrafast and robust $MEPS_{R\text{-}CX}$/$UHPLC_{CORTECS}$-PDA analytical method combined with QbD approach for FDs profiling in complex sugary matrices was successfully developed. Moreover, for the first time, an analytical method for food analysis applications was developed following each step of the

QbD approach. After development of the method, we can conclude that the most efficient MEPS procedure was obtained with R-CX sorbent, ACN as elution solvent, three loading cycles and 500 μL of sample volume. Similarly, the optimal conditions for UHPLC-PDA analysis was obtained with a CORTECS column operating at a temperature of 50 °C, ACN as organic eluent and a flow rate of 125 μL $min^{-1}$. Through Monte Carlo simulation and the capability analysis was possible concluded that the method demonstrated high robustness. The validation procedure proved that the method is selective, precise and accurate, demonstrating no significant matrix effect and good LOD and LOQ values. The performance of the method was demonstrated by its application to SCH real samples providing an effective analytical tool for differentiation of SCH from others similar products and as a powerful platform for its authenticity control. Compared with conventional extraction techniques, MEPS was simpler, faster, efficient and an environmental-friendly procedure as it requires small amounts of organic solvents.

## SECTION 4.2. FURAN DERIVATIVES FINGERPRINTING OF THE SUGARCANE HONEY

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# Fingerprint targeted compounds in authenticity of sugarcane honey - An approach based on chromatographic and statistical data

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*Abstract*

SCH is a black syrup recognized by its excellent quality, being produced in Madeira Island using the regional SC cultivars and following a traditional and peculiar manufacturing and storage processes. However, some low-quality commercial products have been labelled as SCH but do not respect its criteria, revealing the need of develop powerful strategies in order to detect and prevent adulterations. The knowledge of FDs profile, produced during BRs that occurs during food processing and storage, emerged as a promising strategy in food quality and fraud prevention. Therefore, the aim of this study was to establish the FDs profiling of typical SCH produced by certified and non-certified producers, in different geographical regions (Madeira and Brazil), based on MEPS/UHPLC-PDA as a useful approach to define its typicality and authenticity. These parameters are defined through the differentiation and discrimination of FDs profiles among other SC-derived products using multivariate statistical analysis (ANOVA with post-hoc Tukey, PCA, PLS, LDA and HCA). The results demonstrated that SCH samples from non-certified producers present the highest levels of FDs. In addition, SCH samples from Brazil present higher levels of FDs than samples from Madeira Island. The obtained results revealed that the proposed approach is a valuable strategy to establish the typicality of SCH, ensuring its quality, authenticity, safety control and a useful support regarding the application of SCH from Madeira Island to EU certification.

Keywords: Sugarcane honey, authenticity, furanic derivatives, MEPS, UHPLC-PDA

## 1. Introduction

The SCH, known as *"mel-de-cana"*, is a black syrup produced from fresh SCs (*Saccharum officinarum L.*) in Madeira Island, Portugal, being consumed fresh and used as a main ingredient in traditional pastry and confectionery, as well in sauces for cooking meat, fish and salads or even for medicinal purposes. SCH is a syrup with no additives, coloring or preservatives, rich in CBHs, proteins, minerals (Fe, Ca, Mg and Cu), vitamins (niacin, riboflavin and thiamin), antioxidants (flavonoids and non-flavonoids) and fibers. Its unique widely recognized organoleptic properties arise from the use of regional SC cultivars and, mainly, from specific manufacturing and storage processes, based on three main steps: (i) cold mechanical pressing of SC stalks; (ii) filtering and heating procedures of juice that ensures a flawless rigor in order to produce a dark greenish syrup; and (iii) new heating and filtration of syrup until obtain a viscous and crystalline black syrup, which is placed in a reservoir where it cools down naturally under strictly controlled conditions [159].

Although, there are other SC-derived products (syrups, molasses and treacles) produced in Europe, Caribbean and South America regions, their physical-chemical and sensory characteristics differ greatly from those found in SCH. Moreover, unlike SCH, most of SC-derived products are low-quality products obtained as residuals from the industries of sugar refining, alcoholic beverages and biofuel production. Nevertheless, the organoleptic qualities of SC-derived products are strongly influenced by many factors, namely the SC crops (SC cultivars, agricultural treatments, soil and climatic conditions), manufacturing process (temperature, pressure and duration) and product storage (outdoor humidity, light and packing) [104,105,258]. In order to distinguish the SCH from other SC-derived products, the local government created a regional production certification brand. However, recently it has been detected some situations that affects its notoriety by the introduction of several low-quality products on the market labelled as SCH that do not use the regional cultivars and/or not respect the traditional manufacturing and storage processes. Fortunately, the EU introduced legislation that protects and ensure the authenticity of agro-food products from specific geographical origin and produced under traditional processes, wherein can be assigned three types of certification: PDO, PGI and TSG [107,109]. However, the lack of a deep and comprehensive characterization of SCH typicality, namely its physical-chemical and organoleptic proprieties, hampers its potential application for EU certification. In addition, is also necessary to establish the traceability of SCH, allowing its differentiation from others similar SC-derived products. Therefore, it is of utmost importance

to develop tools that allow the fulfilment of all the mandatory requirements by the EU, providing a stricter control of SCH authenticity on the market.

The establishment of FDs profiling can be a promising strategy in the product traceability for typicality definition, quality management, authenticity assessment and safety control. FDs are a class of heterocyclic organic compounds with a molecular structure based on the furan unit that are not naturally found in animal or vegetable-derived products. Its formation occurs during food processing and is highly dependent on the raw material, manufacturing process and storage conditions, being formed through so-called BRs. These reactions can occur via two pathways: (i) NEBRs by caramelization of CBHs, MLDRs and STKD of reducing SGs with AAs, oxidation of lipids or decomposition of ascorbic acid during high temperatures used in manufacturing proceedings, and (ii) EBRs by microbial activity on the sugary components during storage [223,224]. Although, FDs can be found in coffee, wine, balsamic vinegar, roasted cereals, fruit juices and milk, highest contents are found in heat-processed products with high SGs-content, such as honey, syrup, treacle and molasses [118,225–227]. SC-derived products have favorable conditions for the formation of FDs: high concentrations of SGs and organic acids under acidic pH and low water activity. Recently, FDs have received great attention from the food industry, because even in small amounts can promote changes in nutritional, sensory and organoleptic proprieties [229,230]. Furthermore, FDs are already used as food markers, namely for evaluation of quality [230], safety [259], geographical origin [225] and authenticity [260] of food products. In this context, FDs have potential as analytical tool for definition of typicality and traceability of SCH, because the use of regional SC cultivars associated with traditional manufacturing process and storage conditions established by government entities, may give rise to similarities in formation of FDs that create a SCH “fingerprint”, allowing the differentiation from other SC-derived products.

Currently, the analytical methods for quantification of FDs are based on GC or LC and usually involves an extraction technique to sample clean-up and selective analysis, such as SPME, LLE or SPE. However, these techniques present some disadvantages in food analysis applications. Special attention should be taken concerning SPME to avoid artefact formation on fiber when performing trace analysis of thermally generated volatiles. On the other hand, LLE and SPE requires large sample volume, high time preparation, huge solvents amount and have difficulty in automating the extraction processes [234,236]. Alternatively, MEPS has been successful applied for quantification of several food components, such as phenolic acids

[236], lactones [34], resveratrol [238], prenylflavonoids [239] and ascorbic acid [237]. In addition, a work carried out by our group developed successfully an analytical method based on the MEPS for the quantification of FDs in Madeira wine [253]. MEPS is based on miniaturization of SPE that combines the sample extraction, pre-concentration and clean-up in a single step, providing high extraction speed, low operational costs, suitable precision, sensitivity and selectivity [240].

Thus, the aim of this study was to establish, for the first time, the FDs profile of SCH samples produced by a certified producer in order to define its typicality. Likewise, the FDs profiles of products labelled as SCH from industrials and homemade regional non-certified producers, as well the syrups from Brazilian producers, were established. Afterwards, the traceability of genuine SCH was performed through differentiation and discrimination of the FDs profiles using multivariate statistical analysis, as valuable strategy to ensure its authenticity and safety, preventing the product fraud and adulteration. The FDs profiling was performed using MEPS/UHPLC-PDA analytical method previously developed according with QbD approach guidelines [33]. The statistically significant differences between producers were assessed by one-way ANOVA with post-hoc Tukey test. The differentiation and discrimination profiling between FDs profiles from certified, non-certified and Brazilian producers were performed by PCA, PLS and LDA, respectively. HCA was performed based on linkage Euclidean distances of samples to determine the distance and linkage criterion between all producers.

## *2. Materials and methods*

### *2.1. Samples*

Commercial SCH samples were collected from the traditional and certified producer (FRS) in April 2013, 2014 and 2015, at Madeira Island, Portugal. Commercial samples of products labelled as SCH from non-certified producers were purchased in May 2015, while samples from homemade producers were purchased in April 2015. Commercial syrup samples from Brazilian producers were purchased in February 2015. All samples were stored under stable conditions (4 °C, in the dark) until further analysis. Sample name, replicate number, producer, production type, production year, geographical area and authenticity certification are presented in Table S57.

*2.2. Standards, reagents and materials*

FDs standards, 5-hydroxymethyl-2-furaldehyde (5HMF), 2-furaldehyde (FURL), 2-furylmethanol (FAL), 2-furyl methyl ketone (2FMK) and 5-methyl-2-furaldehyde (5 MF) were purchased from Sigma-Aldrich (St. Louis, USA). IS, Trolox, was purchased from Sigma-Aldrich (St. Louis, USA). FA, ACN, MeOH were purchased from Sigma-Aldrich (St. Louis, USA). Ultrapure deionized water ($H_2O^d$) was purified with a Milli-Q ultra-pure water system from Millipore (Massachusetts, USA). All solvents and samples were filtered through 0.22 μm membrane filters from Millipore (Massachusetts, USA), before use. Sorbent BIN RC-X (HyperSep retain cationic exchange) was purchased from Thermo Fisher Scientific (Massachusetts, EUA). UHPLC analytical column CORTECS C18 (1.6 μm, 2.1 × 100 mm) was acquired from Waters Corporation (Massachusetts, EUA).

*2.3. Samples and standards solutions preparation*

Regional samples (FRS15, FRS14, FRS13, NCAL14, CAL14 and GLA14) were prepared daily using 10 g SCH in 20 mL $H_2O^d$:MeOH (95:5% v/v) acidified with 0.1% FA, while the Brazilian samples (MDBR14 and MCBR14) were prepared using 10 g SCH in 40 mL $H_2O^d$:MeOH (95:5% v/v) acidified with 0.1% FA. FDs and IS standards (1 g $L^{-1}$) were prepared individually in MeOH and stored at - 20 °C. Under these conditions, they were stable for at least 3 months (confirmed by UHPLC). Working solutions with all FDs and IS standards were prepared daily in $H_2O$d:MeOH (95:5% v/v) acidified with 0.1% FA and used to spike the samples in order to perform the assays for method development. Calibration function for each FD standard was performed through the standard calibration curves prepared with six different concentrations in SC juice (similar interferents to SCH) plotted as relative peak area vs concentration (Table S58).

*2.4. MEPS procedure*

MEPS procedure was performed using a digital semi-automated syringe eVol® from SGE Analytical Science (Melbourne, Australia) equipped with a 500 μL gas-tight syringe and removable needles containing the sorbent BIN, and following the recommended extraction protocol steps by M. Abdel-Rehim [240]: sorbent conditioning, sample loading, sorbent washing and elution. The samples and standard solutions for each step were loaded and discarded through the BIN under constant flow (20 μL per second) controlled by eVol®, minimizing the cavitation events and experimental errors. Before each extraction, the R-CX sorbent conditioning was achieved with 250 μL MeOH and 250 μL $H_2O$d acidified with 0.1% FA. The sample loading was performed through a three loading/discharge cycles for 500 μL of sample through the R-CX

sorbent. The washing sorbent was done by 100 µL MeOH. The elution was performed in two steps, the first was done with 100 µL of elution solution composed by $H_2O^d$:MeOH (95:5% v/v) acidified with 0.1% FA and the second with 100 µL $H_2O^d$ acidified with 0.1% FA to ensure the complete elution of FDs and avoid memory effects (carry-over). All MEPS procedures were carried out in triplicate. The extracts were then filtered and injected in triplicate into the UHPLC-PDA system.

*2.5. UHPLC-PDA conditions*

The analysis of FDs was carried out on a ACQUITY UHPLC-PDA system acquired from Waters (Massachusetts, EUA) including an H-Class UHPLC system, quaternary solvent manager, sample manager, column heater, degassing system and a 2996 PDA detector. The configuration was driven by Empower software version 2.0 also from Waters (Massachusetts, EUA). The injection was performed with a sample volume of 10 µL. Every injection was preceded by a seal wash period of 2 min. The chromatographic separation was achieved on a CORTECS® UHPLC C18 column coupled with VANGUARD pre-column. The binary mobile phase was composed by acidified $H_2O^d$ (0.1% FA, eluent A) and ACN (eluent B), with a constant flow rate at 125 µL $min^{-1}$. The 15 min gradient was as follows: 95% A (0 min); 80% A (1 min); 75% A (2 min); 70% A (5 min); 20% A (8 min); and 95% A (15 min). The separation was performed with a column temperature of 50 °C and the sample manager was kept at 20 °C. All eluents were filtered before use. For quantification purposes, the PDA detection was carried out by different channels according with to the maximum absorbance wavelength of FDs (Table S58), which have been identified based on the comparison of RTs and maximum absorbance wavelengths of pure standards and quantified by the standard addition method.

*2.6. Statistical software*

All statistical analysis and modeling processing were performed using the STATSOFT STATISTICA 12.0 (2013) software (Tulsa, USA). The statistically significant differences between producers were assessed by one-way ANOVA with post-hoc Tukey test. PCA, PLS and LDA were carried out to establish the differentiation and discrimination between FDs profiles from certified, non-certified and Brazilian producers. HCA was performed based on linkage Euclidean distances of samples to determine the distance and linkage criterion between all producers.

## 3. *Results and discussion*

### *3.1. Establishment of FDs profile*

The application of $MEPS_{R\text{-}CX}$/$UHPLC_{CORTECS}$-PDA analytical method for establishment of FDs profile allowed the quantification of 5HMF, FURL, FAL, 2FMK and 5 MF in all investigated samples. Typical UHPLC-PDA chromatograms of FDs are showed in Figure S20. The average concentration of FDs for each sample are listed in Table 8.

**Table 8. Mean concentrations and one-way ANOVA results based on the concentration values of FDs in SC-based syrups.**

| Samples | Code | 5HMF | | | FURL | | | FAL | | | 2FMK | | | 5MF | | | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Conc. Mean[a] (mg $kg^{-1}$) | RSD (%) | Tukey Test[b] ($p < 0.05$) | Conc. Mean[a] (mg $Kg^{-1}$) | RSD (%) | Tukey Test[b] ($p < 0.05$) | Conc. Mean[a] (mg $kg^{-1}$) | RSD (%) | Tukey Test[b] ($p < 0.05$) | Conc. Mean[a] (mg $kg^{-1}$) | RSD (%) | Tukey Test[b] ($p < 0.05$) | Conc. Mean[a] (mg $kg^{-1}$) | RSD (%) | Tukey Test[b] ($p < 0.05$) | Conc. (mg $kg^{-1}$) |
| FRS15 | A | 21.9 | 3.0 | B/D/E/F/G/H | 1.5 | 3.0 | C/D/E/F/G/H | 9.3 | 3.9 | D/E/F/G/H | 0.3 | 3.6 | D/E/F/G/H | 1.6 | 3.0 | D/E/F/G | 34.6 |
| FRS14 | B | 17.6 | 3.5 | A/C/D/E/G/H | 1.4 | 4.4 | C/D/E/F/G/H | 8.8 | 3.6 | D/E/F/G/H | 0.3 | 4.6 | D/E/F/G/H | 1.5 | 1.4 | D/E/F/G | 29.6 |
| FRS13 | C | 23.0 | 4.3 | B/D/E/F/G/H | 1.2 | 5.5 | A/B/D/E/F/G/H | 8.3 | 1.9 | D/E/F/G/H | 0.3 | 1.4 | D/E/F/G/H | 1.7 | 1.3 | D/E/F/G | 34.4 |
| NCAL14 | D | 5.5 | 0.9 | A/B/C/E/F/G/H | 0.9 | 1.4 | A/B/C/F/G | 24.2 | 1.4 | A/B/C/E/F/G/H | 0.4 | 5.2 | A/B/C/E/F/G/H | 1.9 | 0.9 | A/B/C/E/F/G/H | 32.9 |
| CAL14 | E | 47.3 | 2.7 | A/B/C/D/F/G/H | 0.8 | 3.7 | A/B/C/F/G | 4.7 | 3.9 | A/B/C/D/F/G | 1.3 | 1.2 | A/B/C/D/F/G/H | 3.4 | 1.3 | A/B/C/D/G/H | 57.6 |
| MCBR14 | F | 16.3 | 2.5 | A/C/D/E/G/H | 1.8 | 3.5 | A/B/C/D/E/H | 53.7 | 2.8 | A/B/C/D/E/G/H | 0.2 | 1.2 | A/B/C/D/E/G | 3.2 | 3.7 | A/B/C/D/G/H | 75.3 |
| MDBR14 | G | 87.3 | 1.5 | A/B/C/D/E/F/H | 1.9 | 4.7 | A/B/C/D/E/H | 13.6 | 4.5 | A/B/C/D/E/F/H | 0.5 | 4.2 | A/B/C/D/E/F/H | 0.6 | 3.6 | A/B/C/D/E/F/H | 104.0 |
| GLA14 | H | 2.5 | 1.3 | A/B/C/D/E/F/G | 0.9 | 1.5 | A/B/C/F/G | 6.8 | 1.9 | A/D/F/G | 0.2 | 4.4 | A/B/C/D/E/G | 1.6 | 2.4 | D/E/F/G | 12.0 |

[a] Concentration mean values ($n = 3$; RSD<8%.

[b] Samples with concentration values statistically significant determined by one-way ANOVA with Post-hoc Tukey test ($p < 0.05$).

Different FDs profiles were achieved according to producer and geographical region, being showed in Figure 40.

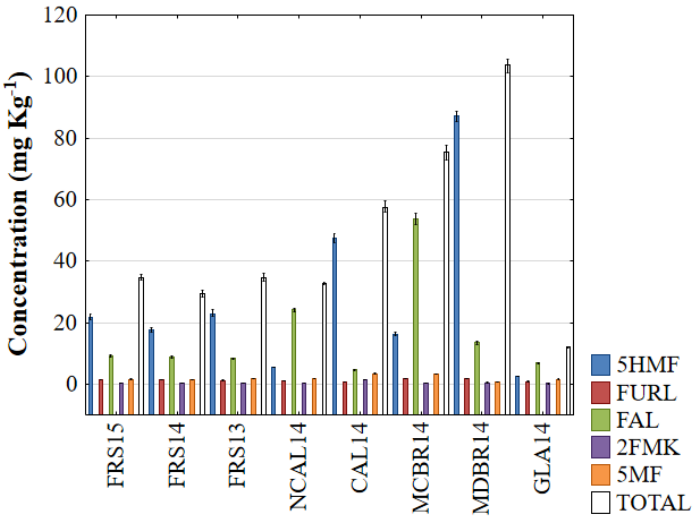


**Figure 40. The mean concentration values of FDs obtained by MEPS$_{R\text{-}CX}$/UPLC$_{CORTECS}$-PDA analytical method for the SC-based syrups samples.**

The FDs of samples from certified producer (FRS13, FRS14 and FRS15) present a very similar profile. 5HMF presented the higher concentration (17.6-23.0 mg kg$^{-1}$), followed by FAL (8.3-9.3 mg kg$^{-1}$), 5 MF (1.5-1.7 mg kg$^{-1}$), FURL (1.2-1.5 mg kg$^{-1}$) and 2FMK (0.3 mg kg$^{-1}$). On the other hand, samples from regional non-certified (Madeira Island) and Brazilian producers showed great variability in FDs pattern among themselves and also in comparison with the certified producer, namely for 5HMF and FAL. Interestingly, 5HMF was the major FD for FRS15, FRS14, FRS13, CAL14 and MDBR14 samples, while the FAL was the major FD for NCAL14, MCBR14 and GLA14 samples. The highest content of 5HMF was found in MDBR14 (87.3 mg kg$^{-1}$) from Brazil, followed by CAL14 (47.3 mg kg$^{-1}$) from a non-certified regional (Madeira Island) producer. On opposite, the lowest concentration of 5HMF was found in GLA14 (2.5 mg kg$^{-1}$) from a home-made producer. The formation of 5HMF is based on two main pathways: as an intermediate of MLRs produced during heat treatment of SCH containing reducing SGs (hexoses) and AAs, or, alternatively, as a product of caramelization formed during dehydration of SGs under acidic conditions [232,261,262]. Although, there are no legal concentration limits for 5HMF, the EU recommended a maximum quality level of 40 mg kg$^{-1}$ in honey [263]. According to the obtained results two samples, MDBR14 and CAL14, exceed the maximum level recommended by EU. The high concentrations of 5HMF in some of the investigated samples may be explained by the presence of hexoses, such as GLU and FRU, both constituents of SUC, the major sugar of SC (Arruda, 2012), and by the heating process during its production in addition to storage conditions. Furthermore, high levels of 5HMF were found in SC-derived

products similar to SCH, namely in syrups (100-300 mg $kg^{-1}$) and molasses (100 mg $kg^{-1}$) from Spain [104], syrups (100-893 mg kg−1) from Brazil [226] and treacle (66.1–179 mg $kg^{-1}$) from Egypt [118]. Also, 5HMF has also been previously quantified in other SC-based products, such as distilled beverage "cachaça" (0.13-3.9 mg $L^{-1}$) [264,265], brown SGs (0.01-0.1 mg $kg^{-1}$) [143] and dry bagasse (170-2600 mg $kg^{-1}$) [266]. Its presence and formation in foods and food-based products has been the topic of several studies since HMF is regarded as being potentially carcinogenic to humans [232].

FAL is also one of the most dominant FDs found in the investigated samples. Its highest concentration was found in MCBR14 SCH (53.7 mg $kg^{-1}$) and the lowest in CAL14 sample (4.7 mg $kg^{-1}$). FAL can be formed through the degradation of 1,2-enediols during thermal food processing, where in acidic conditions it is able to polymerize and form aliphatic polymers that contribute to the formation of the brown color in heated foods [267]. In addition, FAL can be also formed as a result of enzymatic or chemical reduction of furfural during storage [268]. FAL has already been identified in the volatile profile of SCH [159], treacle [118] and blackstrap molasses [120]. Unlike 5HMF, there are few studies on the quantification of FAL in SC-derived products. Of the few available, both were performed in natural sweetener beverages obtained by evaporation under heat of SC juice, namely the "panela" (0.03-0.16 mg $kg^{-1}$) from Spain [269] and "kokuto" (0.20-0.35 mg $kg^{-1}$) from Japan [270]. Although FURL and 5 MF are not the dominant FD compounds, both were found in considerable amounts in all studied SCH samples. The highest concentrations of FURL were found in MDBR14 (1.9 mg $kg^{-1}$) and MCBR14 (1.8 mg $kg^{-1}$) samples from Brazil, while the highest levels of 5 MF were found in regional producer CAL14 (3.4 mg $kg^{-1}$) and MCBR14 (3.2 mg $kg^{-1}$). The lowest concentration of FURL was found in samples from non-certified regional producers, namely CAL14 (0.8 mg $kg^{-1}$), NCAL (0.9 mg $kg^{-1}$) e GLA (0.9 mg $kg^{-1}$), whereas the lowest amount of 5 MF was found in MDBR14 (0.6 mg $kg^{-1}$). Likewise to 5HMF, the main pathway for FURL and 5 MF formation is through MRs that occurs between reducing SGs and proteins during processing and storage of food products [262]. However, 5 MF derived preferably from deoxyhexoses, such as rhamnose (RHA), while FURL is derived from pentoses, such as arabinose, ribose and xylose (XYL), which are minority or residual in SC-based products. Alternatively, FURL also can be formed through hydrolysis of cellulose at high temperatures used in manufacturing process or via decomposition of ascorbic acid during storage [268]. FURL and 5MF have already been identified in volatile composition of SCH [159] and treacle [118]. However, there are no reports on its concentrations in SCH-related products, such as syrups,

molasses and treacle. FURL was only quantified in "cachaça" (0.24-14.4 mg $L^{-1}$) [264] and dry bagasse (70-18870 mg $kg^{-1}$) [266], whereas 5 MF has never been quantified in SC-based products.

2FMK was the FD quantified in lowest concentration for most of analyzed samples, ranging from 0.2 (MCBR14 and GLA14) to 1.3 mg $kg^{-1}$ (CAL14). The main pathway for 2FMK formation also occurs through MRs, mainly between hexoses and AAs via cyclisation of 1,4-dideoxyosone by dehydration [271]. 2FMK was identified in the volatile profile of SCH [159] and treacle [118]. However, it has never been previously quantified in SC-derived products. According to the obtained results, it was possible the establishment of FDs profile for each sample under study based on quantification of 5HMF, FAL, FURL, 5 MF and 2FMK. Moreover, for the first time, FAL, FURL, 5 MF and 2FMK were quantified in complex matrices derived from SC.

### *3.1. Chemometric analysis based on the FDs profile of SC-based syrups*

The definition of SCH typicality was based on similarity between FDs profiles of samples from certified produced (FRS13, FRS14 and FRS15). On the contrary, the distinction between samples according with the type of producer was carried out considering the dissimilarity of FDs profiles.

#### *3.1.1. One-way ANOVA test*

The analysis of similarity/dissimilarity was based on statistically significant differences based on concentrations of selected FDs by one-way ANOVA with post-hoc Tukey test ($p < 0.05$), being described in Table 8. The ratio plot of statistically significant differences ($p_{tukey}$ values) is showed in Figure 41.

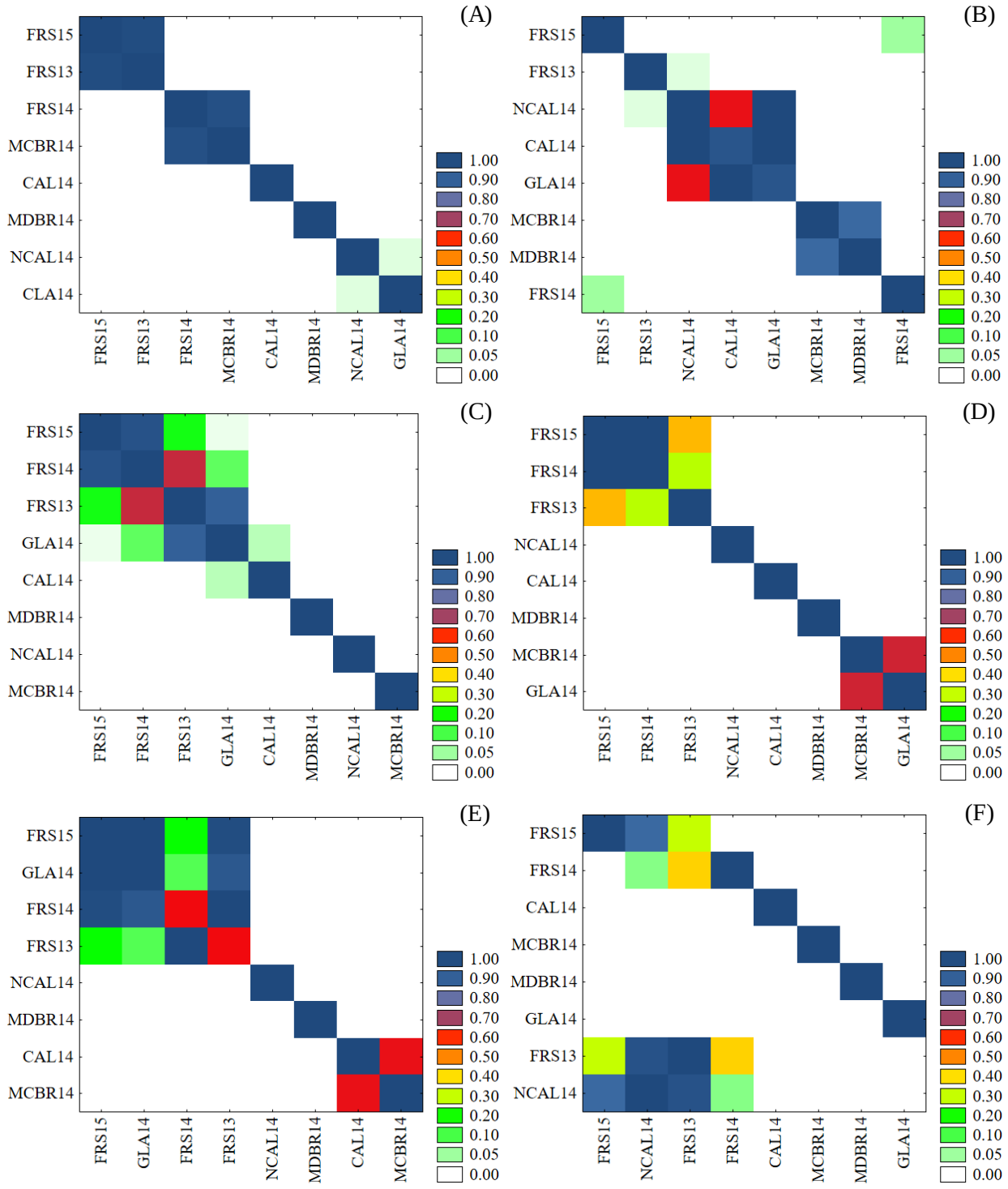


**Figure 41. The ratio plot of statistically significantly differences based on the concentration values of 5HMF (A), FURAL (B), FAL (C), 2FMK (D), 5MF (E) and TOTAL (F) in SC-based syrups samples.**

The samples from certified producer present high levels of similarity for FAL ($p_{tukey} > 0.2$), 2FMK ($p_{tukey} > 0.3$) and 5 MF ($p_{tukey} > 0.1$). Moreover, the levels of similarity for FDs between FRS14 and FRS15 samples were always higher than 0.9. However, significant differences were found between FRS15/FRS13 and FRS14 samples for 5HMF, and between FRS15/FRS14 and FRS13 for FURL. On the other hand, the similarity between FRS15 and FRS13 for 5HMF was higher than 0.9, and between FRS15 and FRS14 was higher than 0.05. Despite the significant differences in both cases, the samples from certified producer

always presented similarities among themselves in at least four FDs, demonstrating that is possible to define the SCH typicality through the FDs profile. Furthermore, high dissimilarity was found in FDs profiles between the certified producer and non-certified producers, particularly in the case of 2FMK, where the concentration found in samples of certified producer were significantly different from those quantified in all other producers. Likewise, significant differences were found in 5HMF, FURL, FAL and 5 MF concentrations between the samples of certified producer and the most of other producers. However, some level of similarity was found between FRS14 and MCBR14 for 5HMF, FRS13 and NCAL14 for FURL, and FRS13/FRS14/FRS15 and GLA14 for FAL and 5 MF. In general, the similarity/dissimilarity analysis showed that it is possible to define the typicality and traceability of genuine SCH among several SC-derived products based on FD profile.

### *3.1.2. PCA and PLS*

The PCA and PLS were applied on FDs profile dataset in order to obtain the preview of variance/covariance structure of samples under investigation without classification and with classification according to the type of producer, respectively. For CV, a V-fold with leave-one-out strategy was used. The PCA and PLS data analysis and variables information are summarized in Table S59 and Table S60, respectively. The PCA loading scatter plot of samples and variables is showed in Figure 42 (A). The PLS loading scatter plot of centroids corresponding to the assigned classification groups and variables is showed in Figure 42 (B).

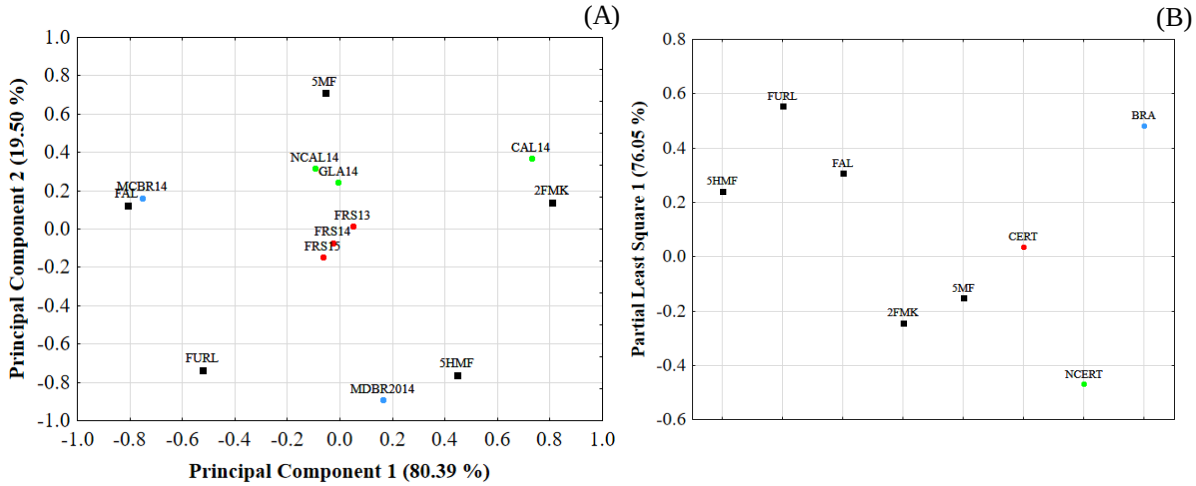


**Figure 42. The PCA (A) and PLS (B) loading scatter plot based on FDs profiles of all SC-based syrups samples.**

Although, the samples have not been classified according to the producer, the PCA loading scatter plot showed an excellent separation between samples from certified producer and non-certified producers, generated by two principal components (PC1 and PC2) that explain 99.8% of TVA. Moreover, the PCA

showed that the variance among samples of certified producer (FRS13, FRS14 and FRS15) was very low. On the other side, a high variance was found between certified samples and samples from SC-related products, mainly for CAL14, MCBR14 and MDBR14. Interestingly, it is possible to observe that the variance between samples along the two first components was influenced differently by the FDs concentrations, where the high variance of CAL14, MCBR14 and MDBR14 relative to the samples from certified producer was highly influenced by 2FMK, FAL and 5HMF, respectively. To confirm the variance/covariance of samples according to type of production (certified or non-certified) and origin (regional or Brazilian), the samples were classified as follows: CERT (FRS13, FRS14 and FRS14), NCERT (CAL14, NCAL14 and GLA14) and BRA (MCBR14 and MDBR14).

As expected, a high variance was observed between the three centroids of classified groups along the only significant partial least square (76.05% of TVA). The variance between CERT and NCERT groups was mainly explained by 2FMK and 5 MF concentrations, while the variance among CERT and BRA groups was influenced by 5HMF, FURL and FAL amounts. Regarding the covariance of samples within each assigned group, it is relatively low within the CERT and BRA groups. However, a slight covariance was observed between samples classified into NCERT group, mainly between NCAL14/GLA14 and CAL14. The PLS analysis showed that the samples of different producers can be grouped according to the type of production and origin, forming three well-defined clusters belonging to CERT, NCERT and BRA groups.

### *3.1.3. LDA*

LDA, a supervised pattern recognition method, was applied to develop classification rules for the group assignment of samples (CERT, NCERT and BRA). A discriminant function was calculated (Wilk's Lambda = 0.003, $p < 0.0000001$) after backward removal of variables (p value of 0.05 to enter and 0.05 to remove). For CV, a V-fold with leave-one-out strategy was used. Recognition ability, calculated as the percentage of members of the training set that were correctly classified, and prediction ability, calculated as the percentage of members that were correctly classified, were 100% in both cases. All variables (5HMF, FURL, FAL, 2FMK and 5 MF) were selected by the method for prediction of group membership. The variables information is summarized in Table S60. The scatter plot of samples classified according to the CDFs is showed in Figure 43.

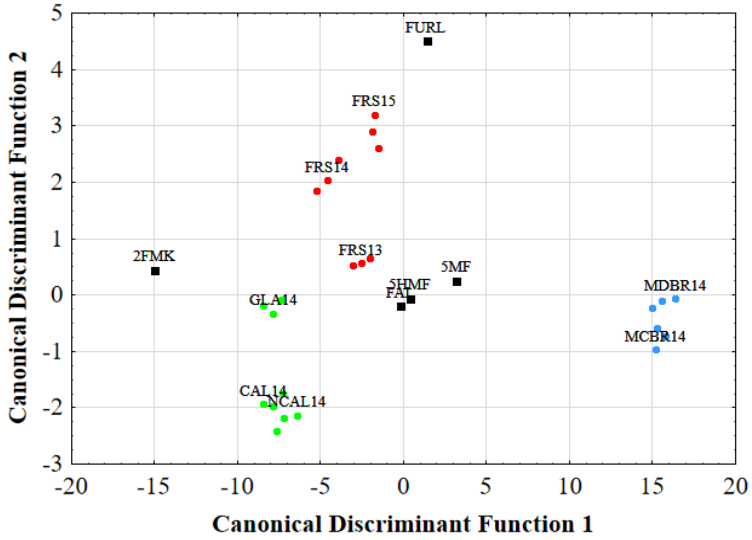


**Figure 43. The LDA scatter plot based on FDs profiles of all SC-based syrups samples.**

The samples from certified producer, non-certified producers and Brazilian producers form three clearly defined clusters with a correct classification rate of 100%, being introduced in CERT, NCERT and BRA groups, respectively. The discrimination between the three groups was very high along the two CDFs. For CDF 1, high level of discrimination was obtained between the samples from regional producers (CERT/NCERT) and samples from Brazil (BRA). On the other hand, for CDF 2, the higher discrimination was observed between samples of certified producer (CERT) and all non-certified producers (NCERT/BRA). LDA results proved that the FDs profiling is an efficient strategy for discrimination of SC-derived products according with type of production and origin.

### *3.1.4. HCA*

HCA was performed based on linkage Euclidean distances of samples to achieve a measure of distance and linkage criterion between producers. The HCA dendrogram is showed in Figure 44.

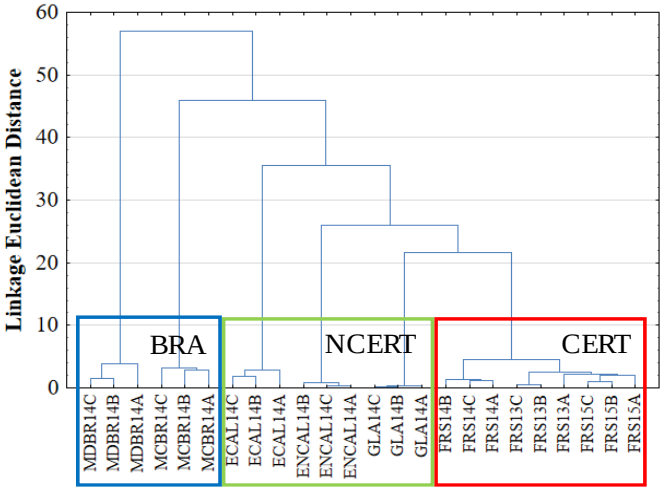


**Figure 44. The HCA dendrogram based on FDs profiles of all SC-based syrups samples.**

Low distances were obtained for samples from certified producer, demonstrating the great resemblance of genuine SCH over the years. Conversely, high distances were achieved between the genuine SCH and other SC-derived products, where the linkage level of certified producer with other producers decreases as follows: FRS > GLA > NCAL > CAL > MCBR > MDBR. Interestingly, the largest distance from the certified producer was obtained by the Brazilian producers, followed by the non-certified regional industrial producers and, finally, the non-certified home-made producer. Although, some regional producers may adulterate their products with residual raw material from the production of other products (regional alcoholic beverage, called *"aguardente"*), or even with products from other regions, the differences between certified producer and regional non-certified producers are normally due to the manufacturing and storage processes. However, the distances between samples from regional producers and Brazilian producers may also be due to the differences in the chemical composition of SC plant, since the cultivars, agricultural treatments, soil and climatic conditions are completely different in both regions.

## *4. Conclusions*

An analytical method based on $MEPS_{R\text{-}CX}$/$UHPLC_{CORTECS}$-PDA was successfully applied for FDs profiling - 5HMF, FURL, FAL, 2FMK and 5 MF, in complex SC-derived products. This study represents the first application for establishment the FDs profile of genuine SCH produced at Madeira Island. In addition, it was possible to quantify, for the first time, FAL, FURL, 5 MF and 2FMK in complex matrices derived from SC. The results obtained from our study suggested that the formation of FDs in SC-derived products is strongly influenced by chemical composition of SC raw materials (SGs, AAs and ascorbic acid amounts), type of manufacturing process (temperature, pressure and duration) and conditions of product storage (outdoor humidity, light and packing), and even slight differences in these variables of SC-derived products processing will result in different FDs profiles, allowing to establish the typicality of the final product. Thus, our strategy based on FDs profiling can be a valuable, suitable and effective tool for the definition of SCH typicality, as well its traceability between several similar products, promoting its authenticity and safety. Similarly, the results are very promising to support its application to EU certification.

# CHAPTER 5. SUGARS PROFILE

## SECTION 5.1. DEVELOPMENT OF METHODOLOGY FOR SUGARS FINGERPRINTING

Food Analytical Methods
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# Application of Quality-by-Design Approach in the Analytical Method Development for Quantification of Sugars in Sugarcane Honey by Reversed-Phase Liquid Chromatography

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*Abstract*

Produced in Madeira Island from regional SC cultivars through a traditional manufacturing and storage process, SCH is a black syrup recognized by its excellent quality. Its economic value has led to the emergence of adulterated SCH, whereby the identification of molecular markers became an essential task in order to overcome the fraudulent activities, protect its authenticity, and guarantee the consumer safety. In the present study, an analytical strategy based on ultrasound-assisted liquid-liquid extraction (USA-LLE) followed by reversed-phase HPLC with a refractive index detector (RI) was developed for the determination of SGs (GLU, FRU, SUC, XYL, and mannose (MAN)) in SCH samples from certified producers, supported on analytical QbD approach, as a useful tool to establish its typicality. The application of QbD was based on analytical risk assessment, multivariate statistics and quality control procedures for definition of the MODR. The optimal conditions into MODR were accomplished using BEH Amide column operating at a temperature of 80 °C and a flow rate of 300 μL $min^{-1}$, with a mobile phase composed by acetone and water (85:15, v/v) at a flow rate of 1.0 mL $min^{-1}$. The robustness was determined by Monte Carlo simulation and capability analysis. The concentration-response function for all SGs was described by polynomial models. Accuracy was presented by recovery values between 98.2 and 119.5%. The analytical figures of merit validated the utility of QbD in the systematic design of a HPLC-RI method with fine sensitivity for sugar analysis in SCH.

Keywords: sugarcane honey; sugars, typicality, quality-by-design, USA-LLE, LC-RI

## 1. *Introduction*

Food authenticity has become a global problem, increasing the importance of the establishment of typicality markers to guarantee the authenticity of products and consumer safety. The SCH, known as "mel-de-cana," is a black syrup produced in Madeira Island, Portugal, commonly used as a main ingredient in regional pastry and confectionery, being also consumed fresh and in traditional sauces for meat, fish and salads [11,159]. The manufacturing process of SCH was developed for more than a century, which started in late years of XIX century, since then, it has become a part of the historical and cultural patrimony of the region. This manufacturing process is based only in thermal treatment and filtering procedures of juice obtained by mechanical pressing of fresh stalks from regional SC (*Saccharum officinarum L.*) cultivars, originating the worldwide recognized quality and unique organoleptic properties of SCH [33]. However, recently some low-quality products have been introduced in the market labeled as SCH that not respect the traditional manufacturing process or the use of regional cultivars. Many of these low-quality products are obtained as by-products from the SGs refining, alcoholic beverages and biofuel production industries, where refined SGs, corn syrups, invert syrups, or other low-cost syrups are also often added to reduce production costs [11,159]. These cases of product adulteration are threatening significantly the notoriety of SCH. Thus, it is imperative to develop strategies for establishment of typicality of SCH to guarantee its authenticity.

SGs are the most abundant compounds found in nature, being widely used as molecular markers in food analysis domain for determination of geographical origin [272–274], typicity [275–277] and authenticity [278–280] of several food products. The sugar profile influences strongly the nutritional, sensory, and organoleptic properties of the final product, such as sweetness, viscosity, crystallization, granulation, and energy value [281,282]. Moreover, several important active aroma and taste compounds are formed by thermal degradation (e.g., MLDRs, STKD, caramelization) and microbial activity (e.g., bacterial, yeast activity) on SGs during manufacturing and storage processes [33,282]. Although SUC, GLU, and FRU are normally the main components of thermal processed sugary-products, such as agave syrup [279,283], yacon syrup [284], date syrup [285], maple syrup [276], raspberry syrup [286], beet molasse [287], cane honey [288], SC molasse [289], and inverted sugar syrup [278], its profile varies depending on raw materials, manufacturing process, and storage. In this context, the establishment of SGs profile of SCH from certified producers can be a valuable strategy to define its typicality.

Recently, a wide variety of analytical methods have been proposed for SGs analysis of food products, synthesized in Table S61. Although some alternative analytical methods have been developed for the SGs analysis, such as GC-MS [290,291] or GC-FID [279,292], NMR [293], high performance thin layer chromatography (HPTLC) [287,294], CE [295,296] and Raman spectroscopy [281]. High performance anion exchange liquid chromatography (HPAEC) with pulsed amperometry detector (PAD) [276,278,288,297] and HPLC-RI [283–285,289] or evaporating light scattering detector (ELSD) [277,298,299] are the most widely applied methods for SGs profile of food products. Other types of detection are also used in combination with HPLC, namely MS [275,282], fluorescence (FLD) [300], ultraviolet (UV) [301], and charged aerosol detector (CAD) [286]. However, FLD and UV detections require a time-consuming derivatization step before analysis, while MS and CAD detectors are too expensive for routine analysis [302,303]. Although the HPAEC has been successfully applied to SGs profiling of some food products, the high-pH eluents that are required can generate interferents by epimerization or degradation of food components. In addition, poor resolution of SUC is normally obtained in HPAEC-PAD analysis [300,303]. On the other hand, HPLC-ELSD and HPLC-IR are two popular methods for determination of underivatized SGs analysis without the use of high-pH eluents. However, HPLC-ELSD requires high amount of expensive nebulizer gas and presents low reproducibility and sensitivity in analysis of low molecular weight SGs [298,304]. Alternatively, HPLC-IR is a simple, fast and economical method that does not require additional gas or complex eluent gradient, being successfully used to sugar profiling of various food products, such as milk [305], juice [272], wine [273], fruits [306,307], honey [274,280], syrups [283–285], molasses [289], among others.

The lack of harmonization and quality processes in development of these analytical methods for sugar profiling hampers its application as a routine and precise tool in determination of typicity of food products. For example, during the development of most methods described in Table S61, an optimization of the parameters that affect its performance is not performed, and when performed, is based on the univariate strategy. Likewise, usually an appropriate method validation procedure is not applicated. Thus, the applicability of analytical information obtained by these described methods in other food products is complicated, being imperative the implementation of quality and harmonized procedures in development of analytical methods.

Analytical QbD is an effective and successful approach for quality assurance in the development of an analytical method based on risk assessment, multivariate statistics, and control quality procedures, being recognized by EMA and FDA regulators as a performance qualifier of analytical methods [33,247]. The ICH in Guideline ICHQ8(R2) [246] define QbD as "a systematic approach to development that begins with predefined objectives and emphasizes product and process understanding and process control, based on sound science and quality risk management." Normally, the workflow of QbD for development of an analytical method is based on the follow key stages: (i) selection of ATP, where the analytes, extraction technique, and analysis equipment are selected according the purpose of study; (ii) definition of critical CMAs, which are representative of the analytical performance of method, such as peak area, peak resolution, peak asymmetry (ASY) and RT; (iii) method scouting through preliminary studies, where are evaluated which parameters have the potential to influence the CMAs; (iv) selection of parameters by QRA based on the Ishikawa diagram according scouting phase results; (v) determination of CMPs, where the parameters that significantly affect the analytical performance of method are defined; (vi) definition of KS by DoE screening to explore the effects of the CMPs on the CMAs; (vii) definition of MODR through statistical analysis of method responses based on the interactions between the CMPs and CMAs, such as PRA, response surface methodology (RSA) and DA; (viii) evaluation of method robustness by its capacity to remain unaffected by small deliberate variations on the MODR; (ix) method control by establishment of system suitability limits on the MODR; (x) validation of method by determination of selectivity, calibration function, linearity, precision, accuracy, matrix effect, LOD and LOQ; (xi) applicability of method to real samples [33,248,250,308,309]. Although the QbD approach has been widely applied in the pharmaceutical industry, only in last years has started to be introduced in food analysis. The first application of QbD approach in development of an analytical method for food analysis was described in our previously study, where QbD procedures was applied for identification and quantification of furan derivatives in authenticity of SCH samples [11,33]. Recently, other two studies were published, where the analytical methods were developed based on QbD framework for determination of polyphenols in diospyros fruit [309] and cereals [310]. The application of QbD principles is a promising strategy to improve the confidence, control and harmonization of analytical methods and facilitate the exchange of analytical information in food analysis.

The objective of the present study was to develop a robust and precise strategy based on USA-LLE combined with reversed phase HPLC-RI, employing QbD approach, for quantification of SGs (GLU, FRU,

SUC, XYL and MAN) in SCH samples from a certified producer during three consecutive production years (2016, 2017 and 2018), as a powerful strategy to define its typicality.

## *2. Materials and Methods*

### *2.1. Samples, Standards, Reagents, and Materials*

SCH samples were provided by the certified producer FRS in April 2016 (FRS16), 2017 (FRS17), and 2018 (FRS18) (Madeira Island, Portugal), and stored under stable conditions (4 °C, in the dark). SGs standards, GLU, FRU, SUC, XYL, MAN and RHA were purchased from Sigma-Aldrich (St. Louis, USA). Acetone (ACT), ACN, ethanol (EtOH), MeOH, and triethylamine (TEA) were purchased from Sigma-Aldrich (St. Louis, USA). Ultrapure deionized water ($H_2O^d$), purified with a Milli-Q ultra-pure water system from Millipore (Massachusetts, USA). All solvents and samples were filtered through 0.22 μm membrane filters from Millipore (Massachusetts, USA), before analysis.

### *2.2. Sugar Standard Solution Preparation*

Sugar standard stock solutions (100 g $L^{-1}$) were prepared by 500 mg of each standard in 5 mL $H_2O^d$:EtOH (50:50%, v/v), and stored at - 20 °C. Under these conditions, the standards solutions are stable for at least 3 months. Working solutions of lower concentrations with all SGs standards were daily prepared by appropriate dilution with $H_2O^d$:ACT (50:50%, v/v).

### *2.3. USA-LLE*

USA-LLE procedure was performed adding 2.5 g SCH and 7.5 mL $H_2O^d$:ACT (50:50%, v/v) into a 50 mL PTFE centrifuge tube, followed by homogenization (MAXI MIX Vortex Mixer, from Thermo Scientific, Massachusetts, USA) for 2 min and ultrasonication (BRANSON 2510 ultrasonic cleaner, from Bransonic, CT, USA) for 10 min. After this, the extraction solution was centrifuged (ROTOFIX 32A, from Hettich, Kirchlengern, Germany) at 4000 rpm for 15 min. A 2 mL aliquot from the upper part of the extraction solution (ACT phase) was transferred into an 8 mL glass flask. Before injection into the HPLC-RI system, all extracts were filtered through 0.22 μm membrane filters and transferred to HPLC vials.

### *2.4. HPLC-RI Conditions*

The sugar analysis was performed on a HPLC ULTIMATE 3000 series system acquired from Dionex (California, USA), equipped with a binary pump, an autosampler and a column compartment, coupled to a refractive index detector SHODEX R1-101 from Thermo Scientific (Massachusetts, USA). The instrument configuration and analysis were achieved with Chromeleon™ Chromatography Data System Software from

Thermo Scientific (Massachusetts, USA). The chromatographic separation of SGs was carried on a X-Bridge BEH Amide XP (2.5 μm, 4.6 × 100 mm) column acquired from Waters Corporation (Massachusetts, USA). The binary mobile phase was composed by $H_2O^d$ with 0.05% TEA (eluent A) and ACT (eluent B), with an isocratic gradient (15% A and 85% B) at a constant flow rate at 300 μL $min^{-1}$. The temperatures were strictly controlled, and the column was kept at 80 °C, sample manager at 20 °C and IR flow cell at 50 °C. The injection volume was set at 8 μL. The SGs identification was based on the RTs of SGs standards, being quantified by the standard calibration curves method.

### *2.5. Statistical Software*

All data analysis and statistical processing were performed using the STATSOFT STATISTICA 12.0 (2013) software (Tulsa, USA).

## *3. Results and Discussion*

The analytical method was developed according the analytical QbD approach, based on the procedure described in our previous study [33], adapted from recommendations defined in ICHQ8(R2) [246] guideline.

### *3.1. ATP, CMAs, and Method Scouting*

The ATP of this study was defined by separation, identification, and quantification of GLU, FRU, SUC, XYL, and MAN in SCH samples from a certified producer during three consecutive production years (2016, 2017, and 2018) through USA-LLE/HPLC-RI analytical method. FRU, GLU, and SUC were selected in this study because these are the most abundant SGs in SC-based food products. In addition, these SGs are also present in widely used adulterants, being added individually or as ingredient of corn syrups, beet syrup, invert syrups, or other low-cost syrups [311]. Similarly, MAN [312] and XYL [313] were also selected for their potential use as alternative sugary adulterants.

The definition of CMAs was based on chromatography performance of the analytical method, where were selected the TPA, PR, and ASY of each SG standard, as well the respective % RSD. The limits for CMAs values were established according the minimal requirements for a satisfactory chromatography performance, where was mandatory the identification of each sugar standard based on TPA and RT, PR values greater than 1.5, ASY values lower than 1.5, and RSD values not higher than 15% [130].

The method scouting was performed by several preliminary experiments. The extraction performance of analytical method was evaluated by comparison between LLE and USA-LLE, and other extraction-influencing parameters (data not shown). The results (TPA and RSD) obtained by USA-LLE were considerable superior than LLE. The use of ultrasound in the LLE possibly provides a better dispersion of the target SGs from samples to the extraction phase (ACT). However, no differences were observed between the different tested times (10, 20, and 30 min) of ultrasound. In addition, three different extraction solvents were evaluated, ACT, ACN, and MeOH, being that only the extraction performed with ACT provided satisfactory results. The poor results obtained by ACN and MeOH may be due to the fact that the mobile phase used in the chromatographic analysis contains high content (85%) of ACT. Also, different extraction solvent contents were studied (50, 60, and 70%) and no differences were observed. Similarly, the ratios 1:1, 1:2, and 1:3 (w/v) between sample and extraction solution ($H_2O$ and ACT) were evaluated. The ratio 1:3 was selected to avoid problems related with high viscosity of SCH samples. The scouting of chromatography performance was based on results from WATERS technology brief [314], where the analysis of FRU, GLU, and SUC in several fruit juices was performed by LC-RI with a X-Bridge BEH Amide XP column and a binary mobile phase (15% $H_2O^d$ with 0.05% TEA and 85% ACT) in isocratic gradient mode.

*3.2. QRA and CMPs*

The selection of CMPs was performed by QRA through an Ishikawa diagram constructed according the results obtained on method scouting step. Although several extraction-influencing parameters have been studied, no CMPs were selected for USA-LLE. On previous scouting step, none of studied parameters demonstrated that its range variability can affect the extraction efficiency of the method. The previously investigated parameters for USA-LLE were kept during further steps of method development. On the other hand, the chromatography performance can be affected by variability of several parameters from HPLC-RI analysis. The selected CMPs were the type of eluent B, content (%) of eluent B, column flow rate, and column temperature.

*3.3. KS*

The WATERS technology brief [314] provide an excellent source of valuable information for definition of influencing CMPs ranges and screening of KS. An FFD based on 43-level factors model was applied as design of experiments for KS screening, being investigated the eluent B (ACT, ACN, and MeOH), eluent

B content (75, 80, and 85%), column flow rate (300, 400, and 500 μL $min^{-1}$), and column temperature (60, 70, and 80 °C). Unexpectedly, the mobile phases with ACN and MeOH did not allow the separation of SGs under analysis. Moreover, ACN and MeOH caused a co-elution of all compounds, making it impossible to identify the five SGs under analysis. Although the most studies published of sugar analysis based on HPLC-RI use only aqueous eluents [273,280], organic eluents, such as ACN, already have been used successfully. For example, GLU, FRU, and SUC were separated and identified in molasses samples, utilizing an Utimate XB-NH2 column (5 μm, 4.6 × 250 mm) with a binary mobile phase composed by ACN and $H_2O$ (75:25%, v/v) [289]. Other study also used a binary mobile phase composed by ACN and $H_2O$ (40:60%, v v−1) in a Zorbax RX-SIL column (5 μm, 4.6 × 250 mm) for analysis of GLU, FRU, and SUC in honey samples [274]. Possibly, in our study, the combination of the short length (100 mm) and amide groups of column promotes a rapid elution of SGs, not allowing them to separate with these two organic eluents, even using a low column flow rate (300 μL $min^{-1}$). For this reason, the FFD for KS screening was really based on 33-level factors model. The CMAs (TPA, PR and ASY) results, CMPs and respective range values of KS FFD screening model are summarized in Table S62, Table S63 and Table S64, respectively.

*3.4. MODR*

The definition of MODR was based on HPLC analysis, wherein the CMA responses from the interactions of previous selected CMPs were evaluated through the 33-level factors model FFD defined previously in KS. The optimum CMAs responses from interactions between CMPs were exhaustively explored through PRA, RSM, and DA in order to define an MODR where the analytical method will achieve the purposed ATP. The MODR definition was achieved through the TPA, PR, and PA responses obtained from ACT content, column flow rate, and column temperature, and from its interactions. The PRA for TPA, PR, and PA are shown in Figure S21 (A), (B) and (C), respectively.

According to results, all CMPs demonstrated, individually, a significant influence on the TPA response, being that its influence decreased in the following order: column flow rate > ACT content > column temperature. However, only the interaction between ACT content and column flow rate presented a significant influence on the TPA response. Likewise, all CMPs showed an individual and significant influence on the PR response, wherein its influence decreased according this order: ACT content > column temperature > column flow rate. The PR response was also significantly influenced by interaction between the ACT content with column flow rate and column temperature. Regarding the results from PA response,

the ACT content and column temperature were the only CMPs with a significant effect. Thus, all CMPs confirmed its significant influence on CMAs responses, and consequently, in definition of MODR. The RSM plots of interaction between the range level of continuous CMPs (ACT content vs column flow rate, ACT content vs column temperature, and column flow rate vs column temperature), on TPA, PR, and PA responses are presented in Figure 45 (A), (B), (C), (D), (E), (F), (G), (H), (I), respectively.

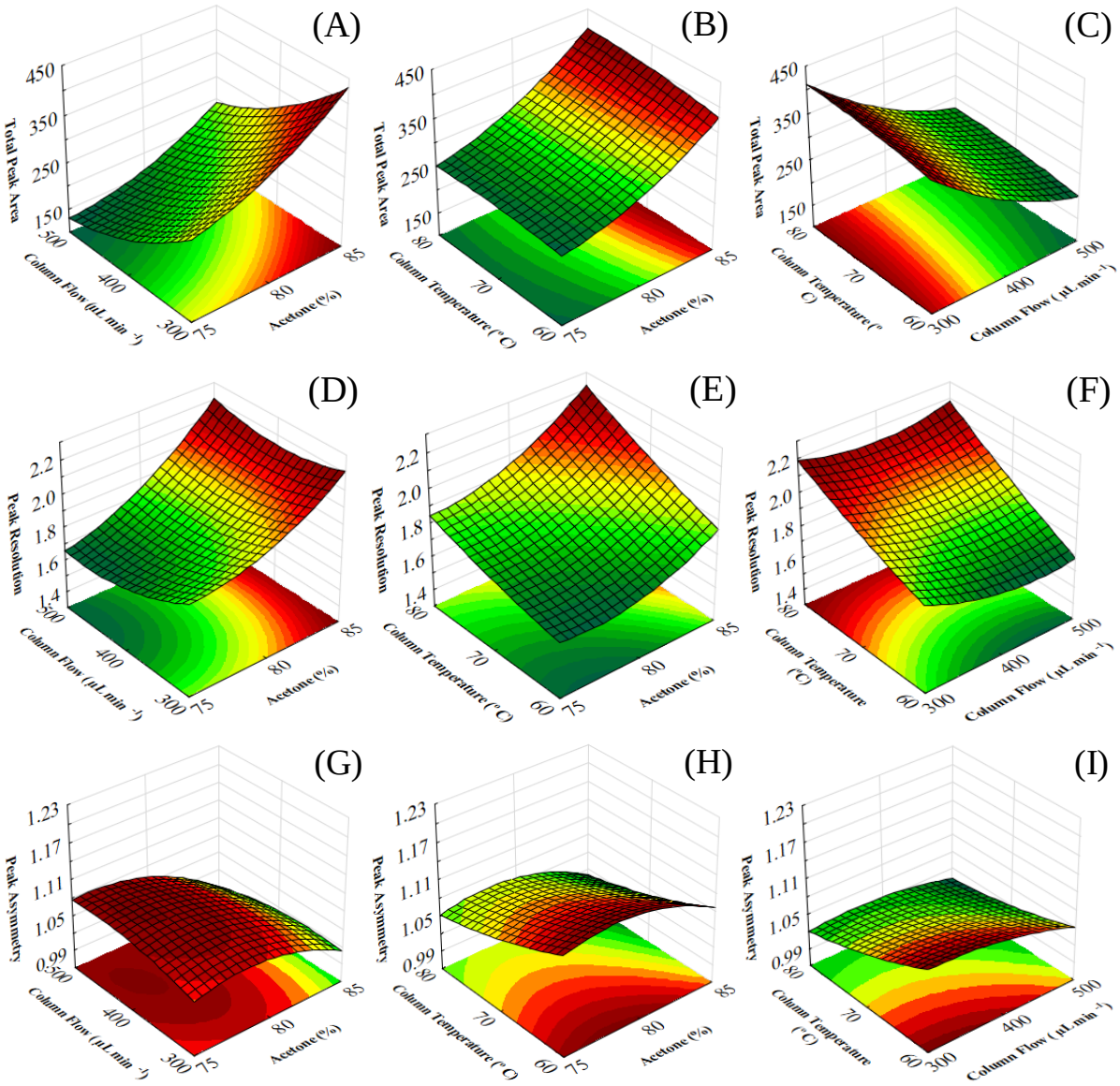


**Figure 45. The RSM plot of interactions between the continuous CMPs for definition of MODR regarding the TPA (A, B and C), PR (D, E and F) and ASY (G, H and I) results.**

Based on results, it was verified that the higher TPA values were obtained by the content of 85% ACT with a column flow rate of 300 µL $min^{-1}$ and a column temperature of 80 °C. The ACT content below 85% and column flow rate above 300 µL $min^{-1}$ caused a clearly decrease in TPA values. On the other hand, only smooth differences were observed between the studied ranges of column temperature, where 80 °C showed the high TPA values. The best values for PR and PA were also obtained with 85% ACT, 300 µL $min^{-1}$ and

80 °C, being that range values below 85% ACT and 80 °C demonstrated a large drop in PR values and an increase in PA values. The range values of column flow rate only showed slight differences on the PR and PA response.

The DA was performed by overlay of CMAs responses to establish the optimal range values of CMPs and obtain the highest DA index, and consequently, define the MODR. The DA values for TPA, PR, and PA were based on the optimum, medium and poor response results, being defined as: desirable (392, 2.2, and 1.0), acceptable (237, 1.8, and 1.1), and unacceptable (127, 1.4, and 1.2), respectively. The DA analysis plots for interactions between CMPs, namely the ACT content vs column flow rate, ACT content vs column temperature, and column flow rate vs column temperature, are presented in Figure 46 (A), (B) and (C), respectively.

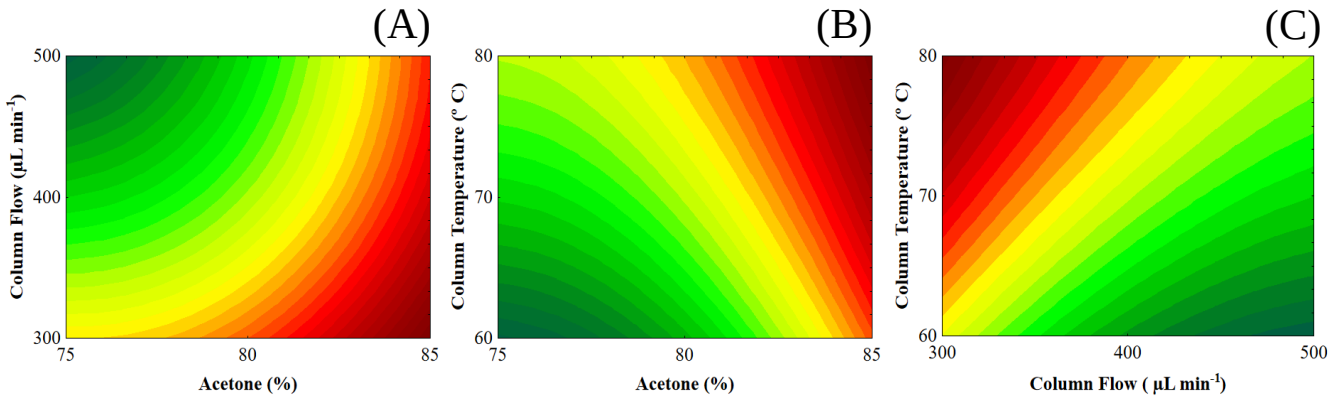


**Figure 46. The DA index plot of interactions between the continuous CMPs (A, B and C) for definition of MODR.**

As expected, the highest DA index was obtained in a region close to optimum conditions point, where the CMPs values were 85% of ACT, 300 µL $min^{-1}$ of column flow rate and 80 °C of column temperature, being that the region of interaction around the optimum point was defined as the MODR of analytical method. The data verification of MODR was based on the analysis of agreement between the predicted and observed values at optimum point, being described in Table S65. The results from data verification analysis demonstrated small differences between the observed and predicted values in CMA responses. However, the value of difference between the observed and predicted values was always close to 1%. The observed differences may be due to the fact that the predicted values were calculated by the response of CMAs based only in three levels of CMPs that cover a wide range. Consequently, slight variations on intermediate precision at the optimum point can promote a visible variability in the CMAs responses. For this reason, the MODR was evaluated by the analysis of the robustness at CMPs levels more closed to the optimal point, providing a rigorous and strict control of analytical method.

*3.5. Robustness and Method Control*

The control strategy of an analytical method performance during routine applications was based on evaluation of robustness, being normally achieve through the introduction of small and deliberate variations on the optimum conditions to verify if the analytical performance to remain unaffected. The evaluation of robustness was based on a new design of experiments performed at the optimum point into MODR. A fractional factorial design based on 33-level factors model was performed for robustness screening, where were evaluated the ACT content (84, 85, and 86%), column flow (290, 300, and 310 μL $min^{-1}$), and column temperature (79, 80, and 81 °C). The TPA, PR, and PA responses, CMPs, and respective range values for robustness screening model are summarized in Table S66, Table S67 and Table S68, respectively.

The DA was performed on results obtained from robustness screening model. The selection of DA values was based on RSD from TPA, PR, and PA responses at optimum point, being defined 0% as desirable, 0.5% as acceptable, and 1.0% as unacceptable. The DA plots for interactions between CMPs, namely the ACT content vs column flow, ACT content vs column temperature, and column flow vs column temperature, are presented in Figure 47 (A), (B) and (C), respectively.

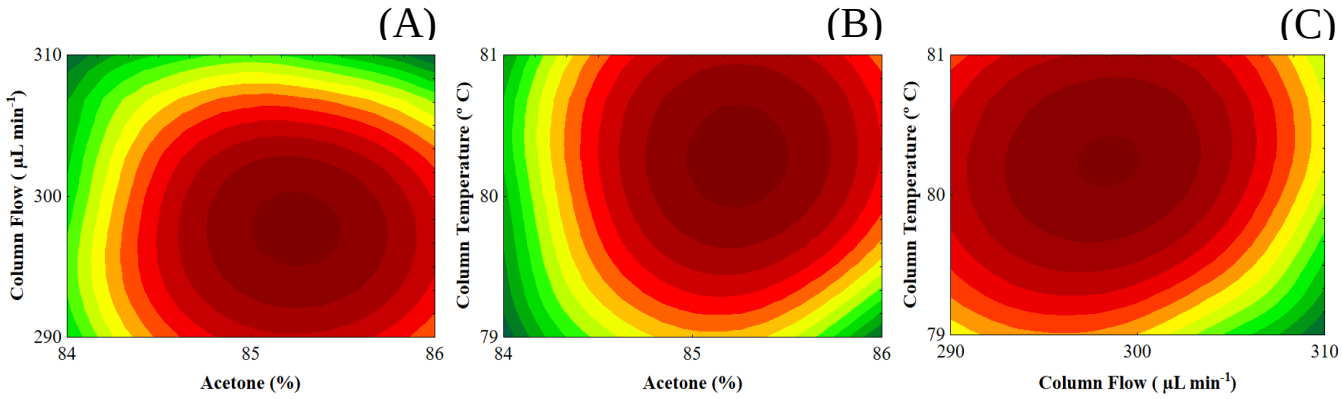


**Figure 47. The DA index plot of interactions between the continuous CMPs (A, B and C) for evaluation of robustness at optimum point into MODR according.**

The highest DA index was verified with an ACT content between 85 and 86%, a column flow between 290 and 300 μL $min^{-1}$, and a column temperature between 80 and 81 °C, being that all RSD values were below of 0.1%. The data verification of robustness screening results was completed by the agreement analysis between the predicted and observed values at optimal point. The results from data verification are summarized in Table S69. The difference between observed values and predicted values is very low, being that 100% of observed values for all CMAs were within the 95% confidence interval, demonstrating a high robustness level at MODR optimal point.

The method control was based on establishment of system suitability limits by generating large amount of data (100 cases) through the Monte Carlo bootstrapping simulation at CMP optimal point into MODR, followed by application of capability analysis for estimation of residual errors from CMAs responses. The capability analysis for TPA, PR and PA are presented in Figure 48 (A), (B) and (C), respectively.

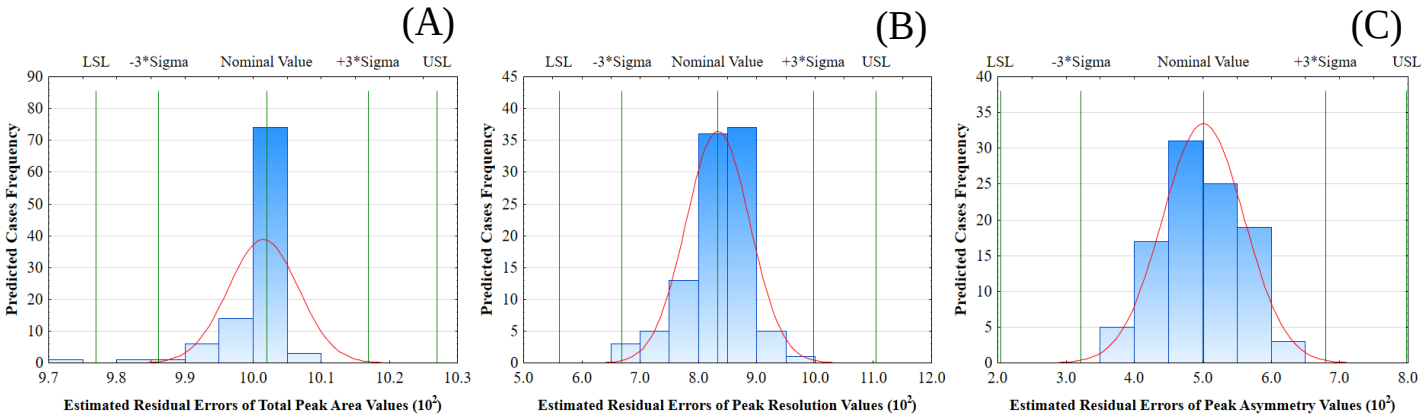


**Figure 48. The capability analysis plot regarding the TPA (A), PR (B) and ASY (C) residual error results.**

Most of cases (99%) from Monte Carlo bootstrapping simulation for TPA remained between the lower specification limit (0.098) and upper specification limit (0.103) established for residual error values (RSD < 0.1%). The Cpk for TPA was 2.01. For PR and PA response simulation, all cases (100%) were within the lower specification limit (0.056 and 0.020) and upper specification limit (0.083 and 0.080), where Cpk values were 1.70 and 1.60, respectively. The reference value of Cpk is 1.33, being the minimum value for a method to be considered robust (Tol et al. 2016). Thus, based on the obtained results from robustness screening and method control analysis at optimum point into MODR, our method demonstrated to have an exceptional robustness and prediction capacity.

### *3.6. Validation of the Analytical Method*

The analytical method was validated for the following parameters: selectivity, calibration function, linearity, accuracy, precision, matrix effect, LOD, and LOQ, being performed according to guidelines from IUPAC [130], and based on validation procedures established in our previous studies [33,159].

Selectivity evaluation was based on the analysis of chromatogram quality, namely the peak shape, resolution, RT, and the absence of interferences. The RTs are presented in Table 9. The chromatograms, (A) SCH sample spiked with SGs standards and (B) SCH sample, obtained at optimum conditions are presented in Figure 49.

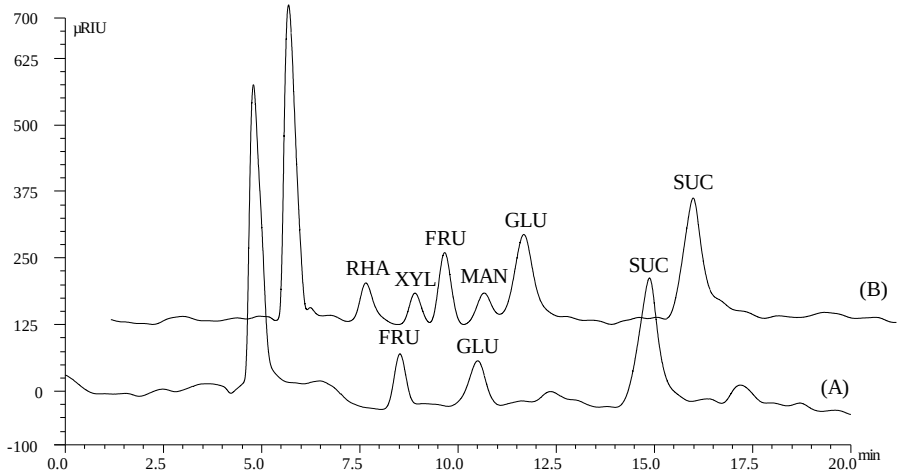


**Figure 49. The typical HPLC-RI chromatograms obtained for a SCH sample (A) and SCH sample spiked with SGs standards (B).**

The chromatograms showed that all SGs were clearly separated into a 20-min run time, and the peaks shape were a well-defined Gaussian. Moreover, our analytical method also demonstrated to have a high selectivity when applied to real SCH samples, where PR values of identified SGs were 3.0 (GLU), 4.2 (FRU), and 3.3 (SUC).

Calibration functions of GLU, FRU, SUC, XYL, and MAN were performed by construction of the standard calibration curves prepared with six concentrations levels, being plotted as TPA vs concentration level. For each calibration curve, the function model and correlation coefficient were determined. The linearity of calibration functions was verified by the suitability analysis of each function model through determination of Fisher variance (F test), where if the ratio $F_{theo}/F_{exp}$ value is higher than 1.0, the function model is suitable to describe the observed data without significant lack of fit. The results are summarized in Table 9. Two different function models, linear and polynomial, were proposed and tested to validate the suitability of calibration curve for each sugar under analysis. The correlation coefficients of calibration curves for all SGs presented values above 0.99 in linear and polynomial function models. However, the F test results demonstrated that the linear function model was not suitable ($F_{theo}/F_{exp} < 1$) for all SGs. Instead, the F test results confirmed that the polynomial function model was suitable to describe the TPA response vs concentration level for all SGs, where the values of ratio $F_{theo}/F_{exp}$ were always higher than 1. The evaluation of accuracy, precision, matrix effect, LOD, and LOQ was based on the described polynomial function models. The results are summarized in Table 10.

**Table 9. Calibration function and linearity results of SGs in SC-based syrups.**

| Sugars | RT (min)[a] | Concentration range (g $l^{-1}$) | Linear | | | | | Polynomial | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Regression equation | Correlation coefficient ($r^2$) | $F_{exp}$ Value[b1] | Diference[c1] $F_{theo}/F_{exp}$ | Function Suitability[d] | Regression equation | Correlation coefficient ($r^2$) | $F_{exp}$ Value[b2] | Diference[c2] $F_{theo}/F_{exp}$ | Function Suitability[d] |
| GLU | 8.48 | 157.30 - 3.09 | y = 0.0968x + 0.4109 | 0.9977 | 1.38 | 1.99 | Yes | y = -0.00004x2 + 0.1031x + 0.2725 | 0.9980 | 1.50 | 1.90 | Yes |
| FRU | 10.37 | 156.44 - 3.04 | y = 0.0859x + 0.3358 | 0.9990 | 1.13 | 2.42 | Yes | y = 0.00002x2 + 0.0895x + 0.2587 | 0.9992 | 1.43 | 2.00 | Yes |
| SUC | 14.32 | 178.06 - 7.65 | y = 0.1256x + 0.2178 | 0.9990 | 2.20 | 1.25 | Yes | y = -0.00004x2 + 0.133x + 0.0023 | 0.9993 | 1.67 | 1.71 | Yes |
| XYL | 7.51 | 160.13 - 4.36 | y = 0.0678x + 0.2748 | 0.9976 | 6.99 | 0.39 | No | y = -0.00007x2 + 0.0795x + 0.0117 | 0.9996 | 0.38 | 7.61 | Yes |
| MAN | 9.40 | 158.66 - 4.26 | y = 0.0761x + 0.1035 | 0.9996 | 0.74 | 3.69 | Yes | y = -0.00002x2 + 0.0796x + 0.0281 | 0.9998 | 2.26 | 1.26 | Yes |

[a] Retention time.

[b1] The Fisher value calculated experimentally with 16 degrees of freedom of experimental error and 6 degrees of freedom of lack of fit of function.

[b2] The Fisher value calculated experimentally with 16 degrees of freedom of experimental error and 5 degrees of freedom of lack of fit of function.

[c1] The Fisher value calculated experimentally is compared against the critical value of Fisher theoretical at the 95% with 16 degrees and 6 of freedom degrees. If the experimental data set describes a proposed function calibration of the form given then the condition $F_{theo.} > F_{exp}$ must be fulfilled.

[c2] The Fisher value calculated experimentally is compared against the critical value of Fisher theoretical at the 95% with 16 degrees and 5 of freedom degrees. If the experimental data set describes a proposed function calibration of the form given then the condition $F_{theo.} > F_{exp}$ must be fulfilled.

[d] The suitability of proposed function model to describe the observed data due to some significant lack of fit.

**Table 10. Accuracy, precision, matrix effect, LOD and LOQ results of SGs in SC-based syrups.**

| Sugars | Concentration range (g $l^{-1}$) | Accuracy | | Precison | | Matrix Effect | | LOD (g $kg^{-1}$ $_{SCH}$) | LOQ (g $kg^{-1}$ $_{SCH}$) |
|---|---|---|---|---|---|---|---|---|---|
| | | Recovery (%) | RSD (%) | Repeatability (% RSD) | Intermediate Precision (% RSD) | Variation Effect (%) | Significance ($p$ value < 0.05) | | |
| GLU | 27.24$^{HL}$ | 101.4 | 2.8 | 3.8 | 3.4 | 92.94 | 0.54 | 2.90 | 8.78 |
| | 11.28$^{ML}$ | 110.8 | 4.9 | 6.2 | 6.1 | | | | |
| | 4.63$^{LL}$ | 114.4 | 5.5 | 5.1 | 4.6 | | | | |
| FRU | 26.81 | 98.2 | 3.0 | 5.6 | 2.5 | 95.52 | 0.55 | 2.51 | 7.60 |
| | 11.10 | 108.4 | 4.5 | 6.1 | 6.1 | | | | |
| | 4.56 | 114.7 | 1.5 | 5.9 | 4.8 | | | | |
| SUC | 67.36 | 99.9 | 4.1 | 4.1 | 2.1 | 91.76 | 0.36 | 1.02 | 3.10 |
| | 27.89 | 112.6 | 2.7 | 5.4 | 3.7 | | | | |
| | 11.46 | 118.6 | 4.0 | 6.0 | 5.3 | | | | |
| XYL | 27.23 | 98.3 | 2.6 | 5.1 | 3.8 | 93.97 | 0.09 | 2.67 | 8.10 |
| | 11.01 | 115.5 | 1.2 | 6.4 | 3.7 | | | | |
| | 4.35 | 119.5 | 6.0 | 5.9 | 5.2 | | | | |
| MAN | 26.62 | 103.3 | 1.2 | 4.8 | 2.8 | 101.24 | 0.84 | 3.24 | 9.81 |
| | 10.76 | 108.2 | 3.4 | 4.8 | 2.7 | | | | |
| | 4.25 | 108.9 | 3.7 | 4.8 | 2.8 | | | | |

$^{LL}$ Low level concentration.

$^{ML}$ Medium level concentration.

$^{HL}$ High level concentration.

[a] The $p$ value calculated experimentally through ANOVA test between slopes obtained by calibration curves of sugars in SCH sample and solvent. If the obtained $p$ value was above that 0.05, no significant matrix effect was observed.

The accuracy was achieved by determination of recovery rate (%), being obtained by the ratio between the theoretical concentration value added to sample with experimental concentration values in a SCH sample spiked at low, medium, and high concentrations levels of each sugar. The analytical method proved to be strongly accurate at high-level concentrations. The recovery rates ranged between 98.2 (FRU) and 103.3% (MAN), wherein all recovery values at high-level concentrations remained within the recommended limits from literature guidelines (95-105%) [315]. However, the accuracy was slightly inferior at medium and low-level concentrations, where some recovery values were above the recommended limits. These values may be due to the fact that the IR detector presents some noise at the chromatograms baseline. The precision was determined by repeatability and intermediate precision values, and were obtained through the inter- and intraday performance tests, respectively. The intraday variation was analyzed by evaluating ten replicates on the same day and inter-day variation by four replicates for each day during 3 days. The precision results were expressed as % RSD. The precision of analytical method was very satisfactory, the repeatability values ranged between 3.8 (GLU) and 6.4% (XYL) and the intermediate precision values varied from 2.1 (SUC) to 6.1% (FRU), where all obtained values were below the maximum reference value (RSD < 10%) [315]. The matrix effect was determined by standard additions method, where the slopes from calibration curves of each sugar in $H_2O$:ACT solution and SCH sample were compared at same concentration levels. The appearance of significant differences between the slopes was statically evaluated by Student t test. The matrix effect results ranged between 91.76 (SUC) and 101.24% (MAN), wherein no significant differences were verified between slopes values from calibration curves, confirming that the matrix effect of analytical method was not significant. The LOD and LOQ were determinate based on standard deviations of interception and slope values from calibration curves performed in triplicate for each sugar, being calculated by following equations: $LOD = 3.3 \times \sigma/slope$ and $LOD = 10 \times \sigma/slope$. The LOD and LOQ values obtained through our analytical method were: 2.90 and 8.78 g $kg_{-1}$ for GLU, 2.51 and 7.60 g $kg^{-1}$ for FRU, 1.02 and 3.10 g $kg^{-1}$ for SUC, 2.67 and 8.10 g $kg^{-1}$ for XYL, and 3.24 and 9.81 g $kg^{-1}$ for MAN, respectively. Comparing the LOD and LOQ values obtained for our analytical method with those described in the study performed by Xu and colleagues [289], where a method also based on LC-RI was developed for sugar analysis in SC molasses samples, it was possible to confirm that the values obtained by our method are evidently lower to those described in the study by Xu and colleagues [289], which presented LOD and LOQ values of 5.41 and 27.09 g $kg^{-1}$ for GLU, 9.91 and 49.49 g $kg^{-1}$ for FRU, and 17.84 and 89.19 g $kg^{-1}$ for SUC, respectively.

*3.7. Method Application*

The applicability of USA-LLE/LC-RI analytical method was verified through the analysis of GLU, FRU, SUC, XYL, and MAN in SCH samples from a certified producer obtained during three consecutive production years (2016, 2017, and 2018). The results for the method applicability are summarized in Table S70.

Based on the obtained results, it was possible to confirm the applicability of the developed analytical method on SCH real samples. Moreover, the results also demonstrated its high repeatability when applied in real SCH samples, where the highest RSD value was 3.2%, being that all concentrations values were obviously above the LODs and LOQs from the validation procedure. Regarding the results from three SCH samples under analysis, only FRU, GLU, and SUC were identified and quantified in SCH samples under analysis, where the concentration values for FRU were 163.9 g $kg^{-1}$ (2016), 168.9 g $kg^{-1}$ (2017), and 173.4 g $kg^{-1}$ (2018); for GLU were 152.8 g $kg^{-1}$ (2016), 151.1 g $kg^{-1}$ (2017), and 164.0 g $kg^{-1}$ (2018); and for SUC were 303.5 g $kg^{-1}$ (2016), 307.0 g $kg^{-1}$ (2017), and 304.7 g $kg^{-1}$ (2018). Apparently, and according to concentrations values of FRU, GLU, and SUC from samples of the three production years, the typical SGs ratio of SCH product was 1:1:2 (GLU:FRU:SUC).

*4. Conclusions*

A precise and robust USA-LLE/LC-RI analytical method was successfully developed according to analytical QbD approach for GLU, FRU, SUC, XYL, and MAN analysis in real SCH samples. According to results obtained from method scouting, the more efficient procedure for SGs extraction from SCH samples was based on LLE assisted by ultrasounds during 10 min, with an extraction solution composed by $H_2O$:ACT (50:50%, v/v) in a ratio sample/solution of 1:3 (w/v). The MODR was based on chromatography performance, wherein its optimal conditions for HPLC-RI analysis was obtained with a BEH AMIDE column operating at a temperature of 80 °C, flow rate of 300 µL $min^{-1}$ and an eluent composed by $H_2O$:ACT (15:85%, v/v) in isocratic gradient mode. The method control procedure demonstrated through Monte Carlo simulation and capability analysis that the developed analytical method was highly robust at optimal point of MODR. The analytical method also proved through the validation procedures to be selective, accurate, precise, and without significant matrix effect, demonstrating lower LOD and LOQ values compared to other similar previous studies. The applicability of the method was confirmed with high repeatability by SGs analysis of real SCH samples provided by a certified producer during three consecutive

production years (2016, 2017, and 2018), where only GLU, FRU and SUC were identified and quantified in typical ratio of 1:1:2, respectively. In conclusion, it is possible to state that the application of USA-LLE/HPLC-RI analytical method provide a simple, effective, precise and robust strategy for the establishment of typicity of genuine SCH product, being a useful and promising tool to guarantee its authenticity in a global market.

## SECTION 4.2. SUGARS FINGERPRINTING OF THE SUGARCANE HONEY

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# Assessment of authenticity of sugarcane honey based on sugar profile and chemometric analysis

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*Abstract*

SCH is a black syrup produced in Madeira Island by traditional and peculiar manufacturing and storage processes, being recognized by its excellent quality and unique organoleptic proprieties. The aim of this study was to establish the SGs profile of SCH produced by a certified producer during seven years and compare it with syrups from non-certified regional producers and producers from other geographical origins (Spain, Egypt, Brazil and Australia). The SGs profile was performed through an USA-LLE/HPLC-RI analysis as a suitable and effective approach to define its typicality and authenticity. Chemometric analysis (ANOVA with post-hoc Tukey, PCA, PLS, LDA and HCA) allows a differentiation and discrimination between SCH samples and other SC-based syrups. The establishment of SGs profile proved to be an effective strategy for the definition of typicality of SCH, guaranteeing its traceability, authenticity and quality, and consequently, support its application to EU certification.

Keywords: Sugarcane Honey, syrups, sugars profile, typicality, traceability, authenticity

## 1. *Introduction*

SGs, also known as saccharides or simple CBHs, occurs naturally in plants formed via photosynthesis, being structurally composed only by molecules based on carbon, hydrogen, and oxygen. SGs are fundamental molecules in food quality, where have several key functions, such as energy source, sweetener, flavoring agent, texture properties, and are involved in food processing, namely in preservation against microorganisms, and mainly, in formation of taste and flavor compounds through BRs (e.g. enzymatic reactions, MLDR and caramelization) [316,317].

Recently, SGs were also used as food markers, being widely applied for traceability, authenticity and quality of high-sugar content products, such as honey [274], fruit juice [272] and syrup [318]. In addition, SGs have potential to solve an emerging and global problem in food domain, the adulteration of food products with a high added-value. In this context, the most desirable products for fraudulent actions are those exclusive to certain geo-graphical regions or obtained from traditional processes, with high economic impact. To overcome this problem, the EU assigned three types of certification label for regional or traditional food products: (i) PDO, (ii) PGI, and (iii) TSG [206–208]. The government of Madeira Island, Portugal, created a regional certification in order to protect its *suis generis* and traditional food product, the SCH. Also known as *"mel-de-cana"*, SCH is a crystalline black syrup with worldwide recognized unique and typical organoleptic properties that arise from the use of regional SC cultivars, and mainly, from its secular and traditional processing and storage conditions. However, its high economic value have led to the introduction on the market of low-quality SC-derived products from other geographical origins, mainly from Mediterranean (e.g. Spain and Egypt) and South America (e.g. Brazil) regions, but labelled as SCH, confusing the consumers about its quality, and consequently, affecting its notoriety [11,159].

Thus, the aim of this study was the establishment of SGs profile of SCH produced by a regional and certified producer during seven processing years (2007, 2013, 2014, 2015, 2016, 2017, and 2018) to define its typicality. Similarly, the SGs profiles of sugar-cane-based syrups from non-certified regional producers and from different geographic origins (Spain, Egypt, Brazil and Australia), were established. After, a chemometric analysis was performed to determine the predictive capacity of SGs and its potential as traceability markers of SCH. The USA-LLE/HPLC-RI analysis, previously developed, optimized and fully validated in our previous study [319], was used to establish the SGs profile of all investigated syrups. The chemometric analysis was based on procedures used in our previous studies [11,159], with some

modifications. The use of chromatographic techniques in combination with chemometric procedures for the establishment of SGs profile can be a useful approach and predictive strategy to monitor the traceability of SCH on the global market, and to support a further application to EU certification of geographical origin.

## *2. Materials and Methods*

### *2.1. Standards, Reagents, Materials and Software*

SGs standards, GLU, FRU, SUC, XYL, MAN and RHA were purchased from Sigma-Aldrich (St. Louis, USA). ACT, EtOH and TEA were purchased from Sigma-Aldrich (St. Louis, USA). All solvents and samples were filtered through 0.22 µm membrane filters from Millipore (Massachusetts, USA), before analysis. Ultrapure deionized water ($H_2O^d$) was purified with a Milli-Q ultra-pure water system from Millipore (Massachusetts, USA). The MAXI MIX Vortex Mixer was purchased from Thermo Scientific (Massachusetts, USA), BRANSON 2510 ultrasonic equipment was purchased from Bransonic (Connecti-cut, USA) and ROTOFIX 32A centrifuge equipment from Hettich (Kirchlengern, Germany). All data analysis and statistical processing were performed using the STATSOFT STA-TISTICA 12.0 (2013) software (Tulsa, USA).

### *2.2. Samples*

Samples from the traditional and certified producer FRS, Madeira Island, Portugal, were collected from lots subsequently placed on the market in 2007 (FRS07), 2013 (FRS13), 2014 (FRS14), 2015 (FRS15), 2016 (FRS16), 2017 (FRS17) and 2018 (FRS18). All other SC-based syrups samples were purchased on the regional market between 2014 and 2018: samples from the regional non-certified producers (ECAL14 and NCAL14) and regional homemade producer (GLA14) were obtained in 2014, samples from Brazil (MDBR14 and MCBR14) also in 2014, samples from Spain (ESP16), Egypt (EGPA16, EGPB16, EGPC16 and EGP17) and Australia (AUS17) in 2016 and 2017. All samples were stored under stable conditions (4 ºC, in the dark). Identification (ID), replicate number, ID replicate code, ID sample code, ID group code, processing year, processing type, geographic origin and regional certification, are described in Table S71.

### *2.3. SGs standards solutions preparation*

The preparation of SGs standard stock solutions (100 g $L^{-1}$) was done adding 500 mg of each standard in 5 mL $H_2O^d$:EtOH (50:50%, v/v), being stored at - 20 °C under stable conditions for three months. Working solutions of lower concentrations with all SGs standards were daily prepared by appropriate dilution with $H_2O^d$:ACT (50:50%, v/v).

*2.4. USA-LLE procedure*

The SGs extraction was performed adding 2.5 g SCH and 7.5 mL $H_2O^d$:ACT (50:50%, v/v) into a 50 mL PTFE centrifuge tube, followed by homogenization for 2 min and ultra-sonication during 10 min. After this, the solution was centrifuged at 4000 rpm for 15 min. A 2 mL aliquot from the upper part of the extraction solution (ACT phase) was transferred into an 8 mL glass flask. Before injection into the LC-RI system, all extracts were filtered through 0.22 µm membrane filters and transferred to LC vials.

*2.5. HPLC-IR analysis*

The SGs analysis was performed on a HPLC ULTIMATE 3000 series system acquired from Dionex (California, USA), equipped with a binary pump, an autosampler and a column compartment, coupled to a refractive index detector SHODEX R1-101 from Thermo Scientific (Massachusetts, USA). The instrument configuration and analysis were achieved with Chromeleon™ Chromatography Data System Software from Thermo Scientific (Massachusetts, USA). The chromatographic separation of SGs was carried on a X-Bridge BEH Amide XP (2.5 µm, 4.6 × 100 mm) column acquired from Waters Corporation (Massachusetts, USA). The binary mobile phase was composed by $H_2O^d$ with 0.05% TEA (eluent A) and ACT (eluent B), with an isocratic gradient (15% A and 85% B) at a constant flow rate at 300 µL $min^{-1}$. The temperatures were strictly controlled, and the column was kept at 80 ºC, sample manager at 20 ºC and IR flow cell at 50 ºC. The injection volume was set at 8 µL. The SGs identification was based on the RTs of SGs standards, being quantified by the standard calibration curves method, as described in Table S72.

*2.6. ºBrix value measurement procedure*

The ºBrix value was determined on an Automatic Digital Refractometer RX-5000 acquired from Atago (Tokyo, Japan), where sample without dilution were placed directly in the equipment plate.

*2.7. Chemometric analysis*

The chemometric analysis procedure was based on the developed procedures in our previous studies [11,159], being introduced some modifications based on the recommendations for analytical applications [160,182]. All samples were grouped in one of four groups formed according to the geographic origin, namely FRS07, FRS13, FRS14, FRS15, FRS16, FRS17 and FRS18 samples are classified into the regional certified producer group (CERT), ECAL14, NCAL14 and GLA14 samples into the regional non-certified producers group (NCERT), ESP16, EGP17, EGPA16, EGPB16 and EGPC16 samples into the Mediterranean region producers group (MED), and MDBR14, MCBR14 and AUS17 samples into the

southern hemisphere region producers group (STH). Four variables were used in the analysis, namely GLU, FRU, SUC and TOTAL. One-way ANOVA was achieved to determine the SGs with statistically significant differences ($p < 0.05$) based on its variance level between concentration values of all samples. Also, the Tukey post-hoc test was performed to determine the statistically significant differences ($p < 0.05$) between two pairs of samples. PCA and PLS analysis were applied on concentration values of SGs to obtain the preview of differentiation/correlation structure based on the variance of all samples, without classification and with classification according to the group, respectively. A V-fold with a V-value fixed in 7 was used for cross-validation. LDA was applied as supervised pattern recognition method to develop classification rules for the group assignment of samples (CERT, NCERT, MED and STH). A backward selection method (p value of 0.05 to enter/remove) was used to remove unpredictive variables from analysis, being obtained a classification structure based in CDFs. A V-fold with leave-one-out strategy was applied for CV. HCA was performed in order to determine the Euclidean linkage distances between all samples and complete an appropriate and visual measure of distance and linkage criterion based only in the predictive SGs.

## *3. Results and Discussion*

### *3.1. Establishment of SGs profile*

Through the application of USA-LLE/HPLC-RI analytical method was possible to quantify three SGs, GLU, FRU and SUG, and complete the establishment the SGs profile of all 18 syrups. The representative HPLC-RI chromatogram of SGs are showed in Figure S22. The ºBrix and mean concentrations values of SGs for each sample are described in Table 11.

**Table 11. ºBrix values, mean concentrations and one-way ANOVA results based on the concentration values of SGs in SC-based syrups.**

| Samples | Sample Code | ºBrix Value | FRU | | | GLU | | | SUC | | | TOTAL | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Conc. Mean (g $Kg^{-1}$) | RSD (%) | Tukey Test[a] (α < 0.05) | Conc. Mean (g $Kg^{-1}$) | RSD (%) | Tukey Test[a] (α < 0.05) | Conc. Mean (g $Kg^{-1}$) | RSD (%) | Tukey Test[a] (α < 0.05) | Conc. Sum (g $Kg^{-1}$) | Mean RSD (%) | Tukey Test[a] (α < 0.05) |
| FRS13 | A | 77.1 | 152.8 | 0.6 | F/J/K/L/O/Q/R | 132.7 | 0.8 | D/E/F/H/I/J/K/L/ M/N/O/Q/R | 296.3 | 1.4 | H/J/K/L/M/ O/Q/R | 581.8 | 0.9 | F/I/J/K/M/N/ O/Q/R |
| FRS14 | B | 77.1 | 155.5 | 0.5 | J/K/L/O/Q/R | 141.6 | 2.0 | F/J/K/L/M/N/ O/P/Q/R | 306.1 | 0.6 | H/J/K/L/M/ O/P/Q/R | 603.2 | 1.0 | J/M/N/O/P/Q/R |
| FRS15 | C | 77.2 | 158.5 | 0.8 | J/K/L/O/Q/R | 147.3 | 0.5 | G/J/L/M/N/ P/Q/R | 323.0 | 0.2 | J/K/L/M/N/ O/P/Q/R | 628.8 | 0.5 | J/M/P/R |
| FRS16 | D | 77.5 | 163.9 | 0.7 | H/J/K/L/O/Q/R | 152.8 | 0.7 | A/G/J/L/M/N/ P/Q/R | 303.5 | 0.6 | H/J/K/L/M/ O/P/Q/R | 620.2 | 0.7 | J/M/P/R |
| FRS17 | E | 77.0 | 168.9 | 3.2 | H/J/K/L/O/ P/Q/R | 151.1 | 1.4 | A/G/J/L/M/N/ P/Q/R | 307.0 | 1.2 | H/J/K/L/M/ O/P/Q/R | 627.0 | 1.9 | J/M/P/R |
| FRS18 | F | 79.0 | 173.4 | 0.5 | A/H/J/K/L/ O/P/Q/R | 164.0 | 0.2 | A/B/G/J/M/N/ P/Q/R | 304.7 | 0.7 | H/J/K/L/M/ O/P/Q/R | 642.1 | 0.5 | A/J/M/P/R |
| FRS07 | G | 78.3 | 167.1 | 2.0 | H/I/J/K/L/O/ P/Q/R | 130.4 | 1.0 | C/D/E/F/H/I/J/K/ L/M/N/O/Q/R | 313.3 | 1.2 | H/J/K/L/M/ O/P/Q/R | 610.8 | 1.4 | J/M/P/R |
| GLA14 | H | 75.7 | 144.1 | 0.3 | D/E/F/G/J/K/ L/M/N/Q/R | 151.6 | 3.2 | A/G/J/L/M/N/ P/Q/R | 353.8 | 2.8 | A/B/D/E/F/G/J/L/ M/N/P/Q/R | 649.5 | 2.1 | A/J/M/P/R |
| CAL14 | I | 77.8 | 160.3 | 2.8 | J/K/L/O/Q/R | 153.4 | 0.8 | A/G/J/L/M/N/ P/Q/R | 325.5 | 2.3 | J/K/L/M/N/O/ P/Q/R | 639.2 | 2.0 | J/M/P/R |
| NCAL14 | J | 76.9 | 61.7 | 4.2 | A/B/C/D/E/F/G/H/I/K/ L/M/N/O/P/Q/R | 59.0 | 3.5 | A/B/C/D/E/F/G/H/I/ K/L/M/N/O/P/Q/R | 414.0 | 2.0 | A/B/C/D/E/F/G/H/ I/K/L/N/P/Q | 534.7 | 3.2 | B/C/D/E/F/G/H/I/ K/L/M/N/O/Q/R |
| MDBR14 | K | 82.3 | 117.1 | 2.1 | A/B/C/D/E/F/G/H/I /J/L/M/N/P/Q/R | 160.8 | 0.6 | A/B/G/J/M/N/ P/Q/R | 365.1 | 3.2 | A/B/C/D/E/F/G/ I/J/L/N/P/Q | 643.0 | 2.0 | A/J/M/P/R |
| MCBR14 | L | 75.0 | 197.7 | 1.1 | A/B/C/D/E/F/G/H/I/ J/K/M/N/O/P/Q/R | 175.5 | 0.8 | A/B/C/D/E/G/H/I/ J/M/N/P/Q/R | 255.2 | 2.6 | A/B/C/D/E/F/G/H/ I/J/K/M/O/Q/R | 628.5 | 1.5 | J/M/P/R |
| EGPTA16 | M | 72.3 | 166.8 | 3.3 | H/J/K/L/O/P/Q/R | 210.0 | 3.0 | A/B/C/D/E/F/G/H/I/ J/K/L/O/P/Q/R | 398.5 | 0.5 | A/B/C/D/E/F/G/ H/I/L/N/P/Q | 775.3 | 2.3 | A/B/C/D/E/F/G/H/ I/J/K/L/N/O/P/Q/R |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| EGPTB16 | N | 76.0 | 170.4 | 1.6 | A/H/J/K/L/O/P/Q/R | 214.2 | 3.7 | A/B/C/D/E/F/G/H/I/ J/K/L/O/P/Q/R | 275.6 | 1.7 | C/H/I/J/K/M/ O/Q/R | 660.3 | 2.4 | A/B/J/M/P/R |
| EGPTC16 | O | 79.8 | 124.3 | 4.2 | A/B/C/D/E/F/G/H/ I/J/L/M/N/P/Q/R | 159.9 | 1.1 | A/B/G/J/M/N/P/Q/R | 376.7 | 1.7 | A/B/C/D/E/F/ G/I/L/N/O/P | 660.9 | 2.4 | A/B/J/M/P/R |
| EGPT17 | P | 74.3 | 148.1 | 3.9 | E/F/G/J/K/L/M/N/ O/Q/R | 123.8 | 0.1 | B/C/D/E/F/H/I/J/ K/L/M/N/O/Q/R | 260.6 | 4.0 | B/C/D/E/F/G/H/I/ J/K/M/O/Q/R | 532.5 | 2.6 | B/C/D/E/F/G/H/I/ K/L/M/N/O/Q |
| ESP16 | Q | 80.1 | 230.8 | 0.8 | A/B/C/D/E/F/G/H/I/ J/K/L/M/N/O/P/R | 238.7 | 0.3 | A/B/C/D/E/F/G/H/I/J/ K/L/M/N/O/P/R | 187.5 | 1.4 | A/B/C/D/E/F/G/H/I/J/ K/L/M/N/O/P/R | 657.0 | 0.8 | A/J/M/P/R |
| AUS18 | R | 77.4 | 42.4 | 2.3 | A/B/C/D/E/F/G/H/I/ J/K/L/M/N/O/P/Q | 33.0 | 4.7 | A/B/C/D/E/F/G/H/I/ J/K/L/M/N/O/P/Q | 400.7 | 3.4 | A/B/C/D/E/F/G/ H/I/L/N/P/Q | 476.1 | 3.5 | A/B/C/D/E/F/G/H/I /J/K/L/M/N/O/Q |

[a] Samples with concentration values statistically significant determined by one-way ANOVA with Post-hoc Tukey test ($p < 0.05$).

The SGs profile for each sample is presented in Figure 50.

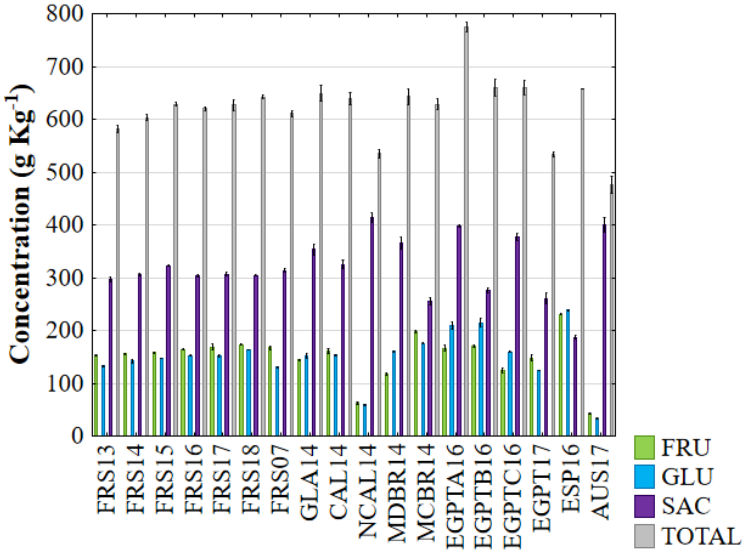


**Figure 50. The mean concentration values of SGs obtained by USA-LLE/HPLC-RI analytical method for the SC-based syrups.**

Different profiles were established through the quantification of GLU, FRU and SUC in all 18 samples of syrups under analysis. In fact, it is possible to see in Figure 50 that the samples from the certified producer (FRS07, FRS13, FRS14, FRS15, FRS16, FRS17 and FRS18) have very similar sugar profiles, where SUC had the higher concentration (296.3-323.0 g $Kg^{-1}$), followed by FRU (152.8-173.4 g $Kg^{-1}$) and GLU (130.4-164.0 g $Kg^{-1}$). Like-wise, SUC also had the higher concentration for most syrup samples, with the ESP16 sample being the exception. For ESP16 sample, FRU was the sugar in higher contribution. In addition, for NCAL14 and AUS17 samples, the concentration of SUC was greater than the sum of the concentrations of GLU and FRU. FRU was the second sugar in highest concentration for all samples from the certified producer, and also for samples CAL14, NCAL14, MCBR14, EGPT17, ESP16 and AUS18, while for GLA14, MDBR14, EGPTA16, EGPTB16 and EGPTC16 was GLU. The highest concentration of SUC was identified in the NCAL14 sample (414.0 g $Kg^{-1}$), and the lowest concentration was found in the ESP16 sample (187.5 g $Kg^{-1}$). For FRU and GLU, the higher concentrations were quantified in the ESP16 sample (230.8 g $Kg^{-1}$ and 238.7 g $Kg^{-1}$, respectively), while the lower concentrations were found in AUS18 (42.4 g $Kg^{-1}$ and 33.0 g $Kg^{-1}$, respectively). Finally, the high concentration of SGs (TOTAL: sum of SUC, GLU and FRU) was determined in EGPTA16 sample (775.3 g $Kg^{-1}$), and the lower concentration was identified in AUS18 sample (476.1 g $Kg^{-1}$).

*3.2. Chemometric analysis based on the SGs profile of SC-based syrups*

Chemometric analysis was performed in order to evaluate the predictive potential of establishment of SGs profile based on analysis of 18 SC-based syrups from different geographical origins and several types of processing as effective strategy to guarantee the traceability of SCH on the global market. There, four variables were used in the analysis, namely GLU, FRU, SUC and TOTAL.

*3.2.1. One-way ANOVA test*

One-way ANOVA was performed to determine the SGs with statistically significant differences between all samples. The ANOVA results, namely Probability (P) and Fischer (F) values, between all samples are described in Table 11. The post-hoc Tukey test was done to evaluate the similarity/dissimilarity between each pair of samples. The Tukey test results are summarized in Table 11. The ratio plot of statistically significant differences ($p_{tukey}$ values) is showed in Figure 51.

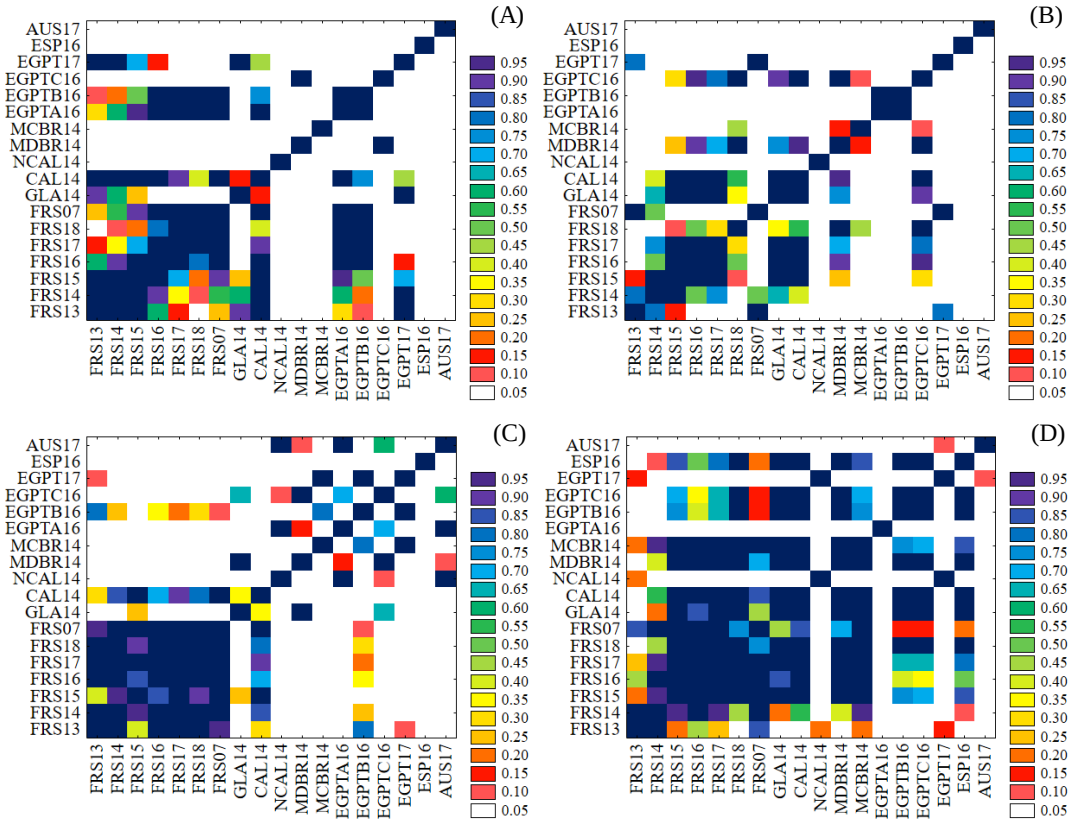


**Figure 51. The ratio plot of statistically significantly differences based on the concentration values of SGs in SC-based syrups by post-hoc Tukey test: (A) FRU; (B) GLU; (C) SUC; (D) TOTAL.**

All four variables presented statistically significant differences ($P < 0.05$) between all 18 samples, where GLU had the higher level of significant differences (F value = 268.4), followed by FRU (F value = 183.3), SUC (F value = 72.3) and TOTAL (F value = 40.4). Regarding the results from post-hoc Tukey test, the samples from certified producer presented the higher levels of similarity. For SUC no significant

differences were observed between SCH samples, where the low level of similarity was between FRS13 vs FRS15 ($p_{tukey}$ > 0.4). For FRU and TOTAL, only were verified significant differences between FRS13 vs FRS18. However, for GLU were observed some significant differences between samples from certified producer, namely FRS13 vs FRS16/FRS17/FRS18 and FRS14 vs FRS18. In fact, GLU presented the higher number of significant differences between all pairs of samples. On the other hand, TOTAL showed the lower number significant differences between all pairs, indicating that the total amount of the three major SGs is relatively close for most samples. Curiously, for SUC, exists a well-stablished pattern of similarity between the certified samples and also between non-certified samples, and a pattern of dissimilarity between certified samples and non-certified samples, suggesting the high potential of SUC as typicality marker of SCH.

### *3.2.2. PCA and PLS*

PCA and PLS were applied on SGs profile dataset to obtain the preview the differentiation/correlation structure based on the variance of samples, without classification (PCA) and with classification (PLS) according to the type of producer and geographical origin. The PCA and PLS information are summarized in Table S73. The loading results and VIP scores of PCA and PLS analysis for each SG are described in Table S74. The loading results of all samples (PCA) and four centroids (PLS) are described in Table S75. The PCA and PLS scores results of all samples are summarized in Table S76. The PCA loading scatter plot plots of all samples and SGs for PC1 and PC2 are showed in Figure 52 (A). The PLS loading scatter plot of all centroids and SGs for PLS1 and PLS2 are showed in Figure 52 (B).

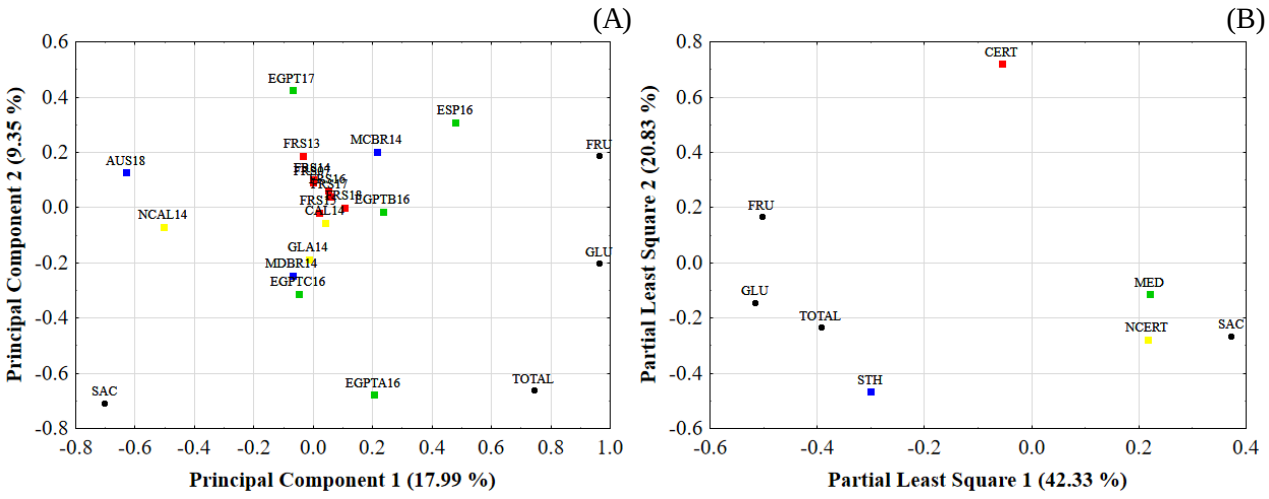


**Figure 52. The PCA (A) and PLS (B) loading scatter plot for based on SGs profiles of all SC-based syrups samples.**

The two main components of PCA analysis explained 27.35% of TVA) PCA loading scatter plot presented a very low variance among the samples from certified producer for PC1 and PC2, showing a high proximity of the SGs profile between the certified samples even when analyzed without group classification. Also, CAL14 sample from a regional and non-certified producer presented a substantial proximity to the certified samples for both PCs. On the contrary, a high variance was found between the samples from other geographical origin producers according the simultaneous projection of PC1 and PC2. However, in PC1, a reasonable proximity among samples from Mediterranean origin was observed.

A PLS analysis was performed based on the classification of samples according to the type of producer and geographical origin, namely centroid-CERT (C-CERT), centroid-NCERT (C-NCERT), centroid-MED (C-MED) and centroid-STH (C-STH). The two main components of PLS analysis (PLS1 and PLS2) were responsible for 63.15% of TVA. The PLS loading scatter plot showed that C-CERT centroid were undoubtedly separated from the other three centroids, confirming the high variance level for PLS1 and PLS2. Contrariwise, a low variance was obtained between C-NCERT and C-MED for PLS1 and PLS2. In PLS1 projection, C-STH also presented a low variance from C-NCERT and C-MED. PCA and PLS projections were influenced differently by SGs, where was possible to recognize the individual contribution of each SG. There, the concentrations of FRU, GLU and TOTAL mainly influenced the projection of C-STH, while SUC influenced the projection of C-NCERT and C-MED.

### *3.2.3. LDA*

LDA was applied to develop classification rules for the group assignment of samples (CERT, NCERT, MED and STH) based only on the most predictive SGs. The LDA information and CDF coefficients of the selected SGs are summarized in Table S74. The CDF coefficients and highest probability classification results of all samples are described in Table S77. The CDF coefficients scatter plot plots of the four groups centroids and selected SGs for CDF1 and CDF2 are presented in Figure 53.

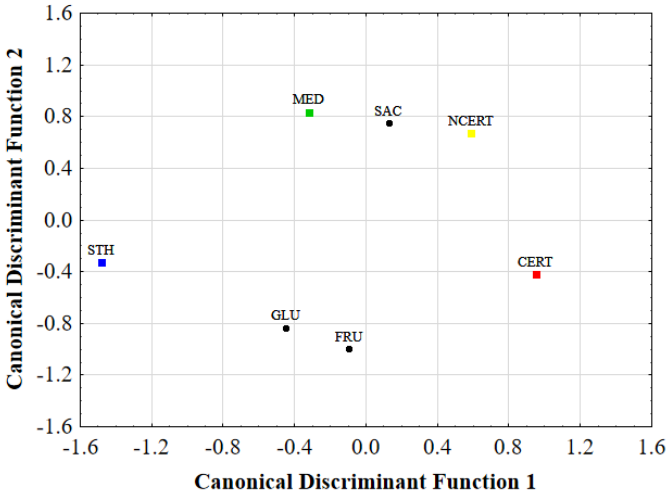


**Figure 53. The LDA loading scatter plot for based on SGs profiles of all SC-based syrups samples.**

Only TOTAL variable was removed from LDA analysis by the backward selection method ($p < 0.05$). All 18 samples were classified with a correct rate of 100 %. The projection based on the two main CDFs demonstrated a high level of discrimination between all four centroids. Once again, the higher level of discrimination was found between C-CERT and the other three centroids. In CDF 1, a very balanced level of discrimination was verified between all centroids, while in CDF 2, some proximity was observed between C-CERT and C-STH.

### *3.2.4. HCA*

HCA was performed in order to complete a suitable and visual measure of distance and linkage criterion between all 54 replicates based on the Euclidean linkage distances between the concentrations of FRU, GLU and SUC, being presented in Figure 54.

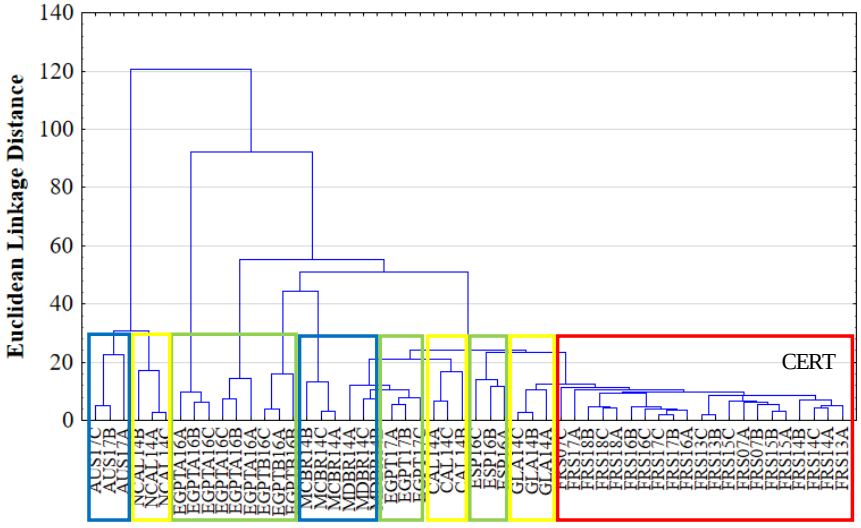


**Figure 54. The HCA dendrogram based on FDs profiles of all SC-based syrups samples.**

As expected, the Euclidean distances between the samples from certified producer were very low, proving the high similarity between these samples. Also, GLA14 sample from non-certified regional producers presented a low distance from the samples from certified producer. On the contrary, ENCAL14 and AUS17 presented the higher distance from the samples of certified producer, and also from the other non-certified samples.

## *4. Conclusions*

An USA-LLE/HPLC-RI analytical method was effectively applied for the establishment of SGs profiling based on the quantification of FRU, GLU and SUC in SC-based syrups from different types of certification and geographical origins. The SGs profile of SCH samples was characterized by its high concentration of SUC, being followed by FRU and GLU. Also, SUC was the main SG for other samples, with exception of ESP16. The obtained results from chemometric analysis showed a higher level of differentiation and discrimination between SCH samples from certified producer and other samples from non-certified and other geographical origins producers. Thus, we concluded that the establishment of SGs profile is an effective strategy for the definition of typicality of SCH, providing valuable markers for its traceability and authenticity on the market, and consequently, support its application to EU certification.

# CHAPTER 6. CONCLUSIONS AND FUTURE PERSPECTIVES

## SECTION 6.1. CONCLUSIONS

SCH is one of the Madeira Island products *per* excellence and it is now popular worldwide, being widely recognized by its *sui generis* and unique organoleptic properties that arise mainly from the use of regional SC cultivars and the circumstances of traditional processing and storage. However, its high economic value makes it a desirable target for counterfeiters, leading to the emergence of adulterated SCH with low-quality SC-derived syrups from others geographical regions, such as Brazil, Spain and Egypt. In order to protect the SCH product from possible frauds and adulterations and increase the consumer safety, becomes essential the development of powerful strategies for establishment of its typicality and authenticity.

Based on the work performed throughout this doctoral thesis it was possible, for the first time, to obtain reliable and robust information that allowed the establishment of genuineness of the SC cultivars from Madeira Island, and mainly, the typicality and authenticity of the SCH, providing a highly valuable platform to support its EU certification. This information was obtained based on three main analytical methods for fingerprinting the VOCs, FDs and SGs profiles, which each one was completely developed, optimized and validated. Thus, the main conclusions related to the results obtained in this doctoral thesis are:

- A HS-SPME/GC-MS method was developed for VOCs fingerprinting of SC-based syrups, providing a promising tool for differentiation and discrimination between SCH samples from certified and non-certified producers. The HS-SPME was optimized, which the high extraction efficiency was achieved with a DVB/CAR/PDMS fiber coating at 60 °C during 60 min. The method was validated following the IUPAC and AOAC guidelines. All calibration curves were expressed by polynomial functions to describe the concentration-response, being provided satisfactory values for the precision (repeatability 2.7-8.1% and intermediate precision 3.2-13.6%) and accuracy (recovery 86.4-107.6%), presenting low LOD (0.17-21.8 μg $Kg^{-1}$) and LOQ (0.51-66.0 μg $Kg^{-1}$).
- An analytical method based on the previously developed HS-SPME/GC-MS allowed the establishment of volatile profile from all six regional SC cultivars, being identified a total of 260 different VOCs. Afterwards, a chemometric analysis procedure based on ANOVA, PCA, PLS, LDA and HCA was applied, being demonstrated that it is possible to differentiate all regional SC cultivars only based on the 23 most predictive VOCs, principally between the CAN cultivar and others southern regional cultivars, VIO, ROX, AMA, VER and RAD.

- Similarly, the HS-SPME/GC-MS method was applied to monitor the volatile profile throughout all stages (S1, S2, S3, S4 and S5) of SCH processing during four years by a certified producer, where 187 different VOCs were identified. Chemometric analysis demonstrated that it was possible to establish a volatile profile for each stage based only in 35 most predictive VOCs, allowing to propose a preliminary model of VOCs formation pathways throughout the SCH processing.
- Once again, the HS-SPME/GC-MS method was successfully applied to SCH samples from certified producer, and compared with SC-based syrups from non-certified regional producers and other country producers (Brazil, Spain, Egypt and Australia). It was possible to identify 166 different VOCs, which 119 VOCs were common for all SC-based syrups. The 31 most predictive VOCs were selected based on the chemometric analysis, providing a high level of differentiation between samples from the certified producer and others regional non-certified producers, and principally, the producers from Mediterranean (Spain and Egypt) and south hemisphere (Brazil and Australia) regions.
- A MEPS/UHPLC-PDA analytical method combined with QbD approach for FDs profiling in SC-based syrups was successfully developed. The most efficient MEPS procedure was obtained with R-CX sorbent, ACN as elution solvent, 3x loading cycles and 500 µL sample volume, while the optimal conditions for UHPLC-PDA analysis was obtained with a CORTECS column, ACN as organic eluent, 50 °C temperature and 125 µL $min^{-1}$ flow rate. The method was validated following the IUPAC and AOAC guidelines. The concentration-response of method were described by polynomial functions, and the validation procedure proved that the method is selective, precise (repeatability 2.1-5.6% and intermediate precision 0.3-9.8%) and accurate (recoveries 91.9-112.1%), demonstrating no significant matrix effect and good LOD (10.1-243.4 µg $Kg^{-1}$) and LOQ (30.6-737.7 µg $Kg^{-1}$) values. The performance of the method was demonstrated by its application to real samples providing an effective analytical tool for typicality of genuine SCH.
- The MEPS/UHPLC-PDA method was successfully applied for FDs fingerprinting in SC-based syrups, being possible the quantification of FAL, FURL, 5 MF and 2FMK in SCH samples from certified producer and samples from others non-certified producers. This analytical method in combination with a chemometric analysis (ANOVA, PCA, PLS, LDA and HCA) proved that the

quantification of FDs is a valuable, suitable and effective tool for the traceability of SCH on the global market, promoting its authenticity and safety.

- An USA-LLE/LC-RI analytical method was successfully developed according to analytical QbD approach for SGs fingerprinting of SC based-syrups, being determined the concentration of GLU, FRU, SUC, XYL, and MAN. The most efficient procedure for SGs extraction was based on LLE assisted by ultrasounds during 10 min, with an extraction solution composed by $H_2O$:ACT (50:50%, v/v) in a ratio sample/solution of 1:3 (w/v). The best chromatography performance was obtained with a BEH AMIDE column, eluent composed by $H_2O$:ACT (15:85%, v/v), 80 °C temperature and 300 μL $min^{-1}$ flow rate in isocratic gradient mode. The polynomial function model was used to describe the concentration-response for all SGs. The validation procedure proved that the method is selective, accurate (recoveries 98.2-103.3%), precise (repeatability 3.8-6.4% and intermediate precision 2.1-6.1%), absence of significant matrix effect, demonstrating low LOD (1.0-3.2 g $Kg^{-1}$) and LOQ (3.1-9.8 g $Kg^{-1}$) values. The applicability of the method was confirmed in SCH samples from certified producer.
- The SGs fingerprinting was performed through an USA-LLE/HPLC-RI method, being quantified GLU, FRU and SUC in SCH samples from certified producer and compared with SC-based syrups from non-certified regional producers and other regions producers (Brazil, Spain, Egypt and Australia). Chemometric analysis (ANOVA, PCA, PLS, LDA and HCA) allows a differentiation and discrimination between SCH samples and other SC-based syrups, and consequently, the definition of typicality of SCH, guaranteeing its traceability, authenticity and quality on the market.

**SECTION 6.2. FUTURE PERSPECTIVES**

The main future perspective is to gather and compile all the significant technical advances and the valuable scientific information about the SCH product and respective traditional processing and storage, and also about the regional SC cultivars, into a data platform that supports the EU certification application. Likewise, the application for entry of regional SC cultivars into the National Catalog of Varieties is also envisaged, protecting a genetic heritage and biodiversity of the Madeira Island.

Although during this doctoral thesis have been obtained an important information about the SCH product, which are essential for its EU certification, currently still ongoing work to add to the results obtained, namely:

- Currently, a molecular method based on the establishment of molecular markers for the genetic characterization of six regional SC cultivars is being concluded. This work is being carried out in collaboration with the Department of Genetics and Biotechnology at the University of Trás-os-Montes and Alto Douro. For the first time, it is intended to unravelling the genetic diversity of SC cultivars from the Madeira Island using microsatellite markers associated with High Resolution Melting analysis technique. At the moment, only the statistical treatment of results and respective elaboration of the scientific article are ongoing, being expected to be completed during this year.
- Also, an analytical method based on MEPS/UHPLC-PDA was developed, optimized and validated according the QbD approach for phenolic acids fingerprinting, being achieve the identification and quantification of sixteen different phenolic acids. At this point, we only need to apply the method in SCH samples and other SC-based syrups. However, due to the inoperability of the UHPLC-PDA for a long period of time, it was not possible to finish this work within the deadline for the doctoral thesis, so it is expected to be completed in the near future.
- Similarly, an analytical method based on µSPE/UHPLC-PDA was developed and optimized according the QbD approach for organic acids fingerprinting, being fully separated and identified 12 different organic acids. For the same reason described previously was not possible to finish this work within the deadline for the doctoral thesis.
- Finally, an analytical method based on SPE clean-up procedure with 1H NMR was investigated and developed for AAs fingerprinting, being obtained promise results to achieve the establishment of AAs profile for SCH samples. However, due to the pandemic situation, it was not possible to continue the work, hoping to continue as soon as possible.

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# CURRICULUM VITAE

Pedro Silva has a Master Degree in Applied Biochemistry (2011) and a Degree in Biochemistry (2008), both from the University of Madeira, where during his professional career, he participated in 4 research projects, published 26 articles in specialized scientific journals, 1 book chapter and 32 posters at conferences, and also received 4 awards for his scientific work.

## Participation in Research Projects

- Project AD4MAC (2020/03/01 - 2021/03/31),
  Madeira Chemistry Research Centre, University of Madeira
- Project NewIndigo (2013/11/01 - 2016/02/28),
  Madeira Chemistry Research Centre, University of Madeira
- Projecto SambucusFRESH (2013/02/01 - 2014/10/31),
  Vila Real Chemistry Research Centre, University of Trás-os-Montes and Alto Douro
- Projecto BIOScreening (2011/12/01 - 2012/12/31),
  Madeira Chemistry Research Centre, University of Madeira

## Publications

*Book chapter*

1. Jorge Pereira, João Gonçalves, Catarina L. Silva, Berta Mendes, Pedro Silva, Vera Alves, José Figueira, José S. Câmara. "*Metabolomic applications of liquid chromatography: From food bioactive metabolites to disease biomarkers research*". In Metabolomic Applications of Liquid Chromatography. United States: Nova Science Publishers, 2012.

*Journal articles*

1. Pedro Silva, Jorge Freitas, Fernando M. Nunes, José S. Câmara, "*Chemical Differentiation of Sugarcane Cultivars Based on Volatile Profile and Chemometric Analysis*". Journal of Agricultural and Food Chemistry, 69 (11) (2021): 3548-3558.
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2. Jorge Freitas, Pedro Silva, Paulo Vaz-Pires, José S. Câmara. "*A Systematic AQbD Approach for Optimization of the Most Influential Experimental Parameters on Analysis of Fish Spoilage-Related Volatile Amines*". Foods, 9 (9), (2020): 1321.
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3. Pedro Silva, Catarina L. Silva, Rosa Perestrelo, Fernando M. Nunes, José S. Câmara. "*Application of Quality-by-Design Approach in the Analytical Method Development for Quantification of Sugars in Sugarcane Honey by Reversed-Phase Liquid Chromatography*". Food Analytical Methods, 13 (8) (2020): 1634-1649.
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6. Catarina L. Silva, Ana Olival, Rosa Perestrelo, Pedro Silva, Helena Tomás, José S. Câmara. "*Untargeted Urinary 1H NMR-Based Metabolomic Pattern as a Potential Platform in Breast Cancer Detection*". Metabolites, 9 (11) (2019): 269.
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8. Rosa Perestrelo, Catarina L. Silva, Pedro Silva, Sónia Medina, Regina Pereira, José S. Câmara. "*Untargeted fingerprinting of cider volatiles from different geographical regions by HS-SPME/GC-MS*". Microchemical Journal, 148 (2019): 643-651. http://dx.doi.org/10.1016/j.microc.2019.05.028
9. Sónia Medina, Jorge A. Pereira, Pedro Silva, Rosa Perestrelo, José S. Câmara. "*Food fingerprints – A valuable tool to monitor food authenticity and safety*". Food Chemistry, 278 (2019): 144-162. http://dx.doi.org/10.1016/j.foodchem.2018.11.046
10. Catarina L. Silva, Rosa Perestrelo, Pedro Silva, Helena Tomás, José S. Câmara. "*Implementing a central composite design for the optimization of solid phase microextraction to establish the urinary volatomic expression: a first approach for breast cancer*". Metabolomics, 4 (2019): 15. http://dx.doi.org/10.1007/s11306-019-1525-2
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15. Rosa Perestrelo, Catarina L. Silva, Pedro Silva, José S. Câmara. "*Unraveling Vitis vinifera L. grape maturity markers based on integration of terpenic pattern and chemometric methods*". Microchemical Journal, 142 (2018): 367-376. http://dx.doi.org/10.1016/j.microc.2018.07.017
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18. Rosa Perestrelo, Catarina L. Silva, Pedro Silva, José S. Câmara. "*Rapid spectrophotometric methods as a tool to assess the total phenolics and antioxidant potential over grape ripening: a case study of Madeira grapes*". Journal of Food Measurement and Characterization, 12 3 (2018): 1754-1762. http://dx.doi.org/10.1007/s11694-018-9790-8
19. Rosa Perestrelo, Catarina L. Silva, Pedro Silva, José S. Câmara. "*Establishment of the Volatile Signature of Wine-Based Aromatic Vinegars Subjected to Maceration*". Molecules, 23 2 (2018): 499. http://dx.doi.org/10.3390/molecules23020499
20. Pedro Silva, Catarina L. Silva, Rosa Perestrelo, Fernando M. Nunes, José S. Câmara. "*A useful strategy based on chromatographic data combined with quality-by-design approach for food analysis applications. The case study of furanic derivatives in sugarcane honey*". Journal of Chromatography A, 1520 (2017): 117-126.

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*Conference poster*

1. Pedro Silva, Catarina L. Silva, Rosa Perestrelo, Fernando M. Nunes, José S. Câmara. *Identification of phenolic acids of sugarcane honey as a powerful approach to establish its authenticity.* 32º The European Federation of Food Science and Technology International Conference (EFFoST2018), 6-8 November 2018, Nantes, France.
2. Pedro Silva, Jorge Freitas, Catarina L. Silva, Rosa Perestrelo, Fernando M. Nunes, José S. Câmara. *Influence of production process on the volatomic signature of sugarcane honey. From sugarcane to syrup.* 32º The European Federation of Food Science and Technology International Conference (EFFoST2018), 6-8 November 2018, Nantes, France.
3. Jorge Freitas, Pedro Silva, Paulo Vaz-Pires, José S. Câmara. *Volatile amines as a valuable approach for fish freshness evaluation.* 32º The European Federation of Food Science and Technology International Conference (EFFoST2018), 6-8 November 2018, Nantes, France.
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5. Rosa Perestrelo, Catarina L. Silva, Pedro Silva, José S. Câmara. *From volatome to odor: MS based volatomics as useful strategy to define Madeira wine aroma network(s) descriptors.* 5º Portuguese Mass Spectrometry Meeting (PTMS2017), 20-22 September 2017, Lisboa, Portugal.
6. Sandrine S. Ferreira, Pedro Silva, Amélia M. Silva, Fernando M. Nunes. *Identification and quantification of some carbohydrates on three different cultivars from Sambucus nigra L.*. 12º Carbohydrates National Group (GLUPOR12), 11-13 September 2017, Aveiro, Portugal.
7. Pedro Silva, Catarina L. Silva, Rosa Perestrelo, Fernando M. Nunes, José S. Câmara. *An useful strategy based on MEPS/UHPLC combined with Quality-by-Design approach for food analysis applications. The case study of furanic derivatives in sugarcane honey*. 45th International Symposium on High Performance Liquid Phase Separations and Related Techniques (HPLC2017), 18-22 June 2017, Prague, Czech Republic.

8. Pedro Silva, Jorge Freitas, Rosa Perestrelo, Catarina L. Silva, Fernando M. Nunes, José S. Câmara. *Volatomic pattern and multivariate analysis as useful approach to establish the authenticity and typicity of Sugarcane Honey*. 1st Food Chemistry Conference (CHEM2016), October 30-November 1, 2016, Amsterdam, The Netherlands.
9. Pedro Silva, Jorge Freitas, Rosa Perestrelo, Catarina L. Silva, Fernando M. Nunes, José S. Câmara. *Furanic profiling as an effective tool to establish authenticity and quality of sugarcane honey*. 1st Food Chemistry Conference (CHEM2016), October 30-November 1, 2016, Amsterdam, The Netherlands.
10. Pedro Silva, Jorge Freitas, Rosa M. Perestrelo, Catarina L. Silva, Fernando Nunes, José S. Câmara. *Establishment of sugarcane honey authenticity using highthrouput potential of chromatography*. 31st International Symposium on Chromatography (31ISC2016), 28 August-1 September 2016, Cork, Ireland.
11. Pedro Silva, Jorge Freitas, Rosa Perestrelo, Catarina L. Silva, José S. Câmara. *Semi-automatic MEPS as a powerful approach to isolate furanic derivatives from food matrices*. The honey as case study. 18th International Symposium on Advances in Extraction Technologies & 22nd International Symposium on Separation Sciences (ExTech-ISSS 2016), 3-6 July 2016, Torun, Poland.
12. Pedro Silva, Jorge Freitas, Rosa Perestrelo, Catarina L. Silva, José S. Câmara. *The highthrouput potential of chromatography on food authenticity establishment. The case study of sugarcane honey*. XVI Latin American Congress on Chromatography (XVICOLACRO) & 9th National Chromatography Meeting of the Portuguese Chemistry Society (9ENC), 5-9 January 2016, Lisbon, Portugal.
13. Pedro Silva, Jorge Freitas, Rosa Perestrelo, Catarina L. Silva, José S. Câmara. *Furanic profile of sugarcane honey as an effective tool to evaluate quality and prevent adulteration*. XVI Latin American Congress on Chromatography (XVICOLACRO) & 9th National Chromatography Meeting of the Portuguese Chemistry Society (9ENC), 5-9 January 2016, Lisbon, Portugal.
14. Pedro Silva, Miguel Ribeiro, Fernando M. Nunes. *Elderberry branches the potential and alternative source of phenolic compounds to food and pharmaceutical industries*. 12th Meeting of Food Chemistry of the Portuguese Chemistry Society (12EQA), 10-12 September 2014, Lisbon, Portugal.
15. Pedro Silva, Fernando M. Nunes. *Selection of finest cultivar and ripening stage of Sambucus nigra fruit through comparison of phenolic and enzymatic profiles*. 12th Meeting of Food Chemistry of the Portuguese Chemistry Society (12EQA), 10-12 September 2014, Lisbon, Portugal.
16. Raquel Guise, Luis Filipe-Ribeiro, Diana Nascimento, Olga Bessa, Pedro Silva, Fernando M. Nunes, Fernanda Cosme. *Influence of the structural features of carboxymethylcellulose on white wine tartaric stabilization*. 12th Meeting of Food Chemistry of the Portuguese Chemistry Society (12EQA), 10-12 September 2014, Lisbon, Portugal.
17. Pedro Silva, Fernando M. Nunes. *Development of HPLC-PDA-based methodology with new coreshell column Kinetex-C18 for assessment of phenolic profile of Sambucus nigra fruit*. 8th National Meeting of Chromatography of the Portuguese Society of Chemistry (8ENC), 2-4 December 2014, Covilhã, Portugal.
18. Pedro Silva, Fernando Aveiro, Catarina L. Silva, José Câmara. *Urinary volatomic profile of lung cancer patients as a powerful tool for finding potential biomarkers*. 8th National Meeting of Chromatography of the Portuguese Society of Chemistry (8ENC), 2-4 December 2014, Covilhã, Portugal.
19. Berta Mendes, Pedro Silva, Isabel Mendonça, Jorge Pereira, José Câmara. *Evaluation of the urinary profile of oxidative stress biomarkers and its correlation with cardiovascular disease*. 8th National Meeting of Chromatography of the Portuguese Society of Chemistry (8ENC), 2-4 December 2014, Covilhã, Portugal.
20. Catarina L. Silva, Pedro Silva, Fernando Aveiro, José S. Câmara. *Urinary metabolomic pattern as a powerful means to find potential lung cancer biomarkers*. XXII Porto Cancer Meeting & II Porto-Bordeaux Joint Meeting, 11-12 April 2014, Porto, Portugal.

21. Berta Mendes, Pedro Silva, Jorge Pereira, José S. Câmara. *Ultrafast and powerful strategy based on microextraction by packed sorbent and UHPLC-PDA determination for simultaneous determination of oxidative stress biomarkers*. 38th International Symposium on High Performance Liquid Phase Separations and Related Techniques (HPLC2012), 16-21 June 2012, California, USA.
22. Pedro Silva, Alexandre Nunes, Catarina L. Silva, Fernando Aveiro, José S. Câmara. *Comparison on volatile urinary metabolomic profile of lung cancer patients and normal individuals as a powerful tool for finding potential biomarkers*. 36th International Symposium on Capillary Chromatography (36ISCC), 27 May-1 June 2012, Riva del Garda, Italy.
23. Pedro Silva, Catarina L. Silva, Alexandre Nunes, Fernando Aveiro, José S. Câmara. *Non-invasive sampling process combined with HS-SPME / GC-qMS for detection lung cancer markers based on chromatographic profile of urinary organic metabolites*. 36th International Symposium on Capillary Chromatography (36ISCC), 27 May-1 June 2012, Riva del Garda, Italy.
24. Pedro Silva, Berta Mendes, Catarina L. Silva, Jorge Pereira, Fernando Aveiro, José S. Câmara. *A powerful and sensitive MEPS / UHPLC-PDA-based methodology for assessment of urinary biomarkers of oxidative stress in oncologic pathologies*. 36th International Symposium on Capillary Chromatography (36ISCC), 27 May-1 June 2012, Riva del Garda, Italy.
25. Berta Mendes, Pedro Silva, Jorge Pereira, Catarina L. Silva, José S. Câmara. *A reliable microextraction technique using a new eVol digitally controlled syringe combined with ultrahigh pressure liquid chromatography for quantification of urinary biomarkers of oxidative DNA damage*. 36th International Symposium on Capillary Chromatography (36ISCC), 27 May-1 June 2012, Riva del Garda, Italy.
26. Jorge Pereira, Berta Mendes, Pedro Silva, Catarina L. Silva, José S. Câmara. *Semi-automatic micro-extraction in packed syringe combined with ultrahigh pressure liquid chromatography as a fast and simplified methodology to assess oxidative damage through quantification of 8-iso-prostaglandin F2a biomarker in urine.* 36th International Symposium on Capillary Chromatography (36ISCC), 27 May-1 June 2012, Riva del Garda, Italy.
27. Alexandre Nunes, Pedro Silva, Fernando Aveiro, José S. Câmara. *Non-invasive sampling process combined with HS-SPME / GC-qMS for detection of lung cancer markers based on the chromatographic profile of urinary endogenous metabolites*. 7th National Meeting of Chromatography of the Portuguese Society of Chemistry (7ENC), 9-11 January 2012, Porto, Portugal.
28. Pedro Silva, Catarina L. Silva, Fernando Aveiro, José S. Câmara. *Solid-phase microextraction-based methodology in order to assess potential breast cancer biomarkers through volatile urinary metabolomic pattern*. 7th National Meeting of Chromatography of the Portuguese Society of Chemistry (7ENC), 9-11 January 2012, Porto, Portugal.
29. Pedro Silva, João Gonçalves, José S. Câmara. *Optimization of a solid-phase microextraction gas chromatography-mass spectrometry based methodology in order to assess breast cancer through urinary volatile metabolomic pattern*. EUROanalysis 2011, 11-15 September 2011, Belgrade, Serbia.
30. Pedro Silva, Catarina L. Silva, Rosa Perestrelo, José S. Câmara. *Development of solid-phase microextraction methodology followed by one-dimensional gas chromatography-mass spectrometry for Identification of Breast Cancer Biomarkers.* 34th International Symposium on Capillary Chromatography (34ISCC), 1-4 June 2010, Riva del Garda, Italia.
31. Pedro Silva, Nuno Nunes, José Aguiar, Alexandre Nunes, Rosa Perestrelo, José S. Câmara. *A faster and simpler sample preparation technique for screening the volatile composition of different coffee species.* 9º Encontro de Química dos Alimentos (9EQA), 29 April-2 May 2009, Angra do Heroísmo, Portugal.

**Prizes and awards received**

1. CASSS Travel Grant - 45th International Symposium on High Performance Liquid Phase Separations and Related Techniques. California Separation Science Society, 2017, California, USA.

2. Chromatography Tecnocroma Award for Best Communication in the HPLC Area. 8th National Meeting of Chromatography of the Portuguese Society of Chemistry, 2013, Covilhã, Portugal.
3. Shimadzu Award as Best Poster Presentation. 36th International Symposium on Capillary Chromatography (ISCC), 2012, Riva del Garda, Italy.
4. Recognition Prize for Scientific Research in Senology. Portuguese Society of Senology, 2012, Portugal.

**Others**

Guest Editor - Special Issue "*Sustainable Food Systems and Food Safety*", Sustainability (ISSN 2071-1050), MDPI, 2020.

# ANNEXES

# SUPPLEMENTARY FIGURES

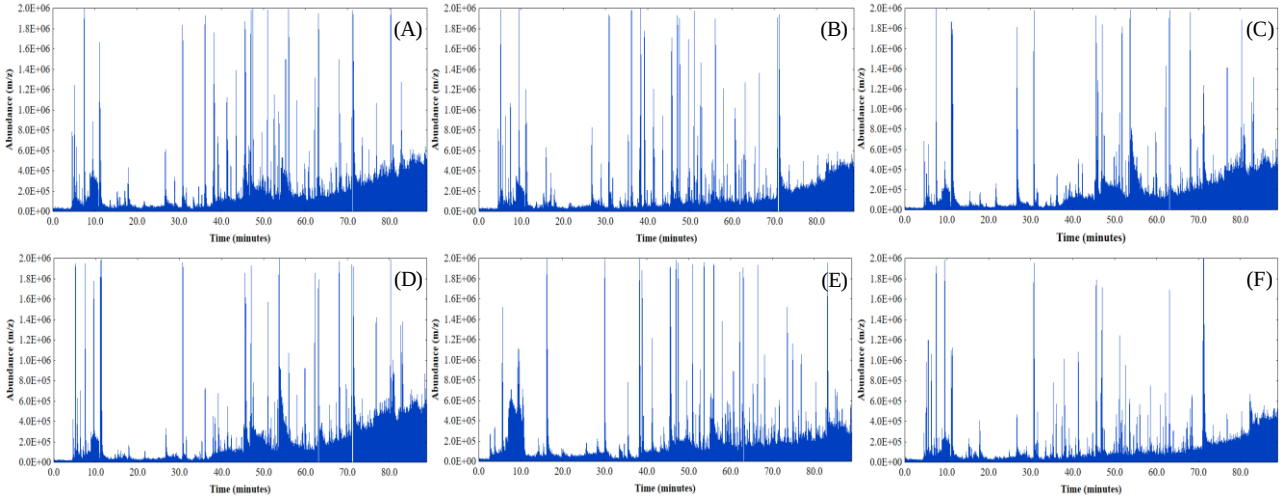


**Figure S1. The typical GC-MS chromatograms for amarela (A), radiada (B), roxa (C), verde (D), violeta (E) and canica (F) SC cultivars.**

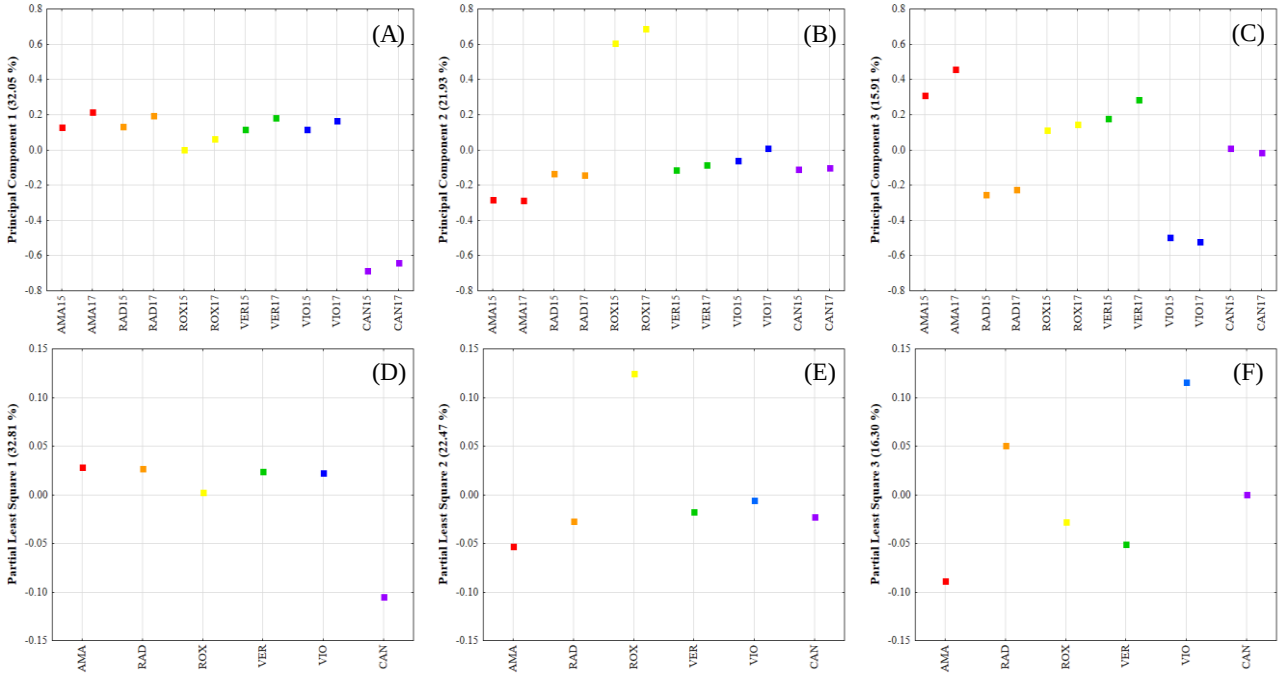


**Figure S2. The PCA loadings line plot of all cultivar samples based on the selected 259 VOCs for PC1 (A), PC2 (B) and PC3 (C), and the PLS loadings line plot of all cultivar samples for PLS1 (D), PLS2 (E) and PLS3 (F).**

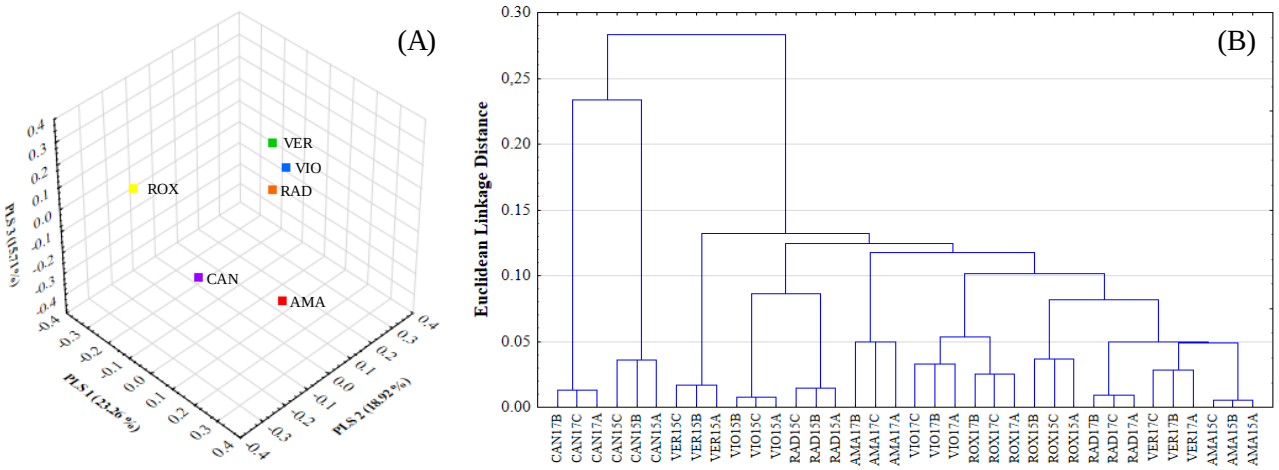


**Figure S3. The PLS 3D plot (A) and HCA dendrogram (B) for results from the matrix reduction procedure based on the VIP scores.**

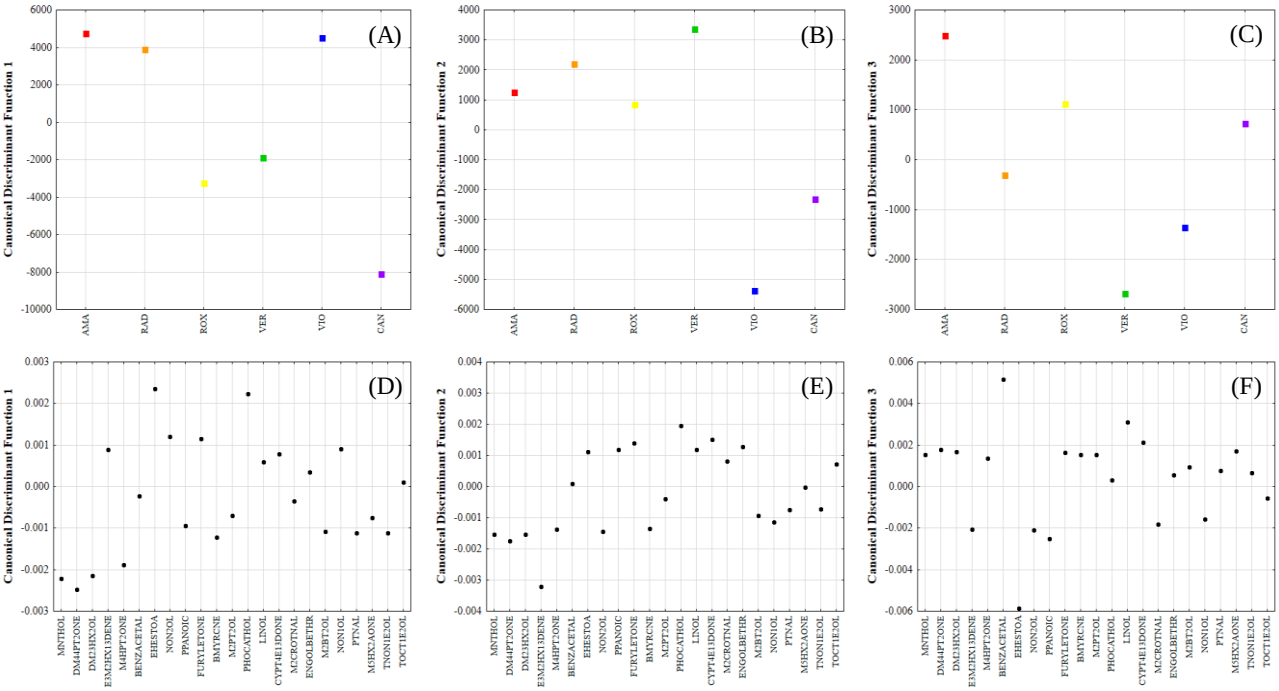


**Figure S4. The LDA line plots of all cultivars based on the 23 most predictive VOCs for to CDF1 (A), CDF2 (B) and CDF3 (C), and LDA line plots of the 23 most predictive VOCs for CDF1 (D), CDF2 (E) and CDF3 (F).**

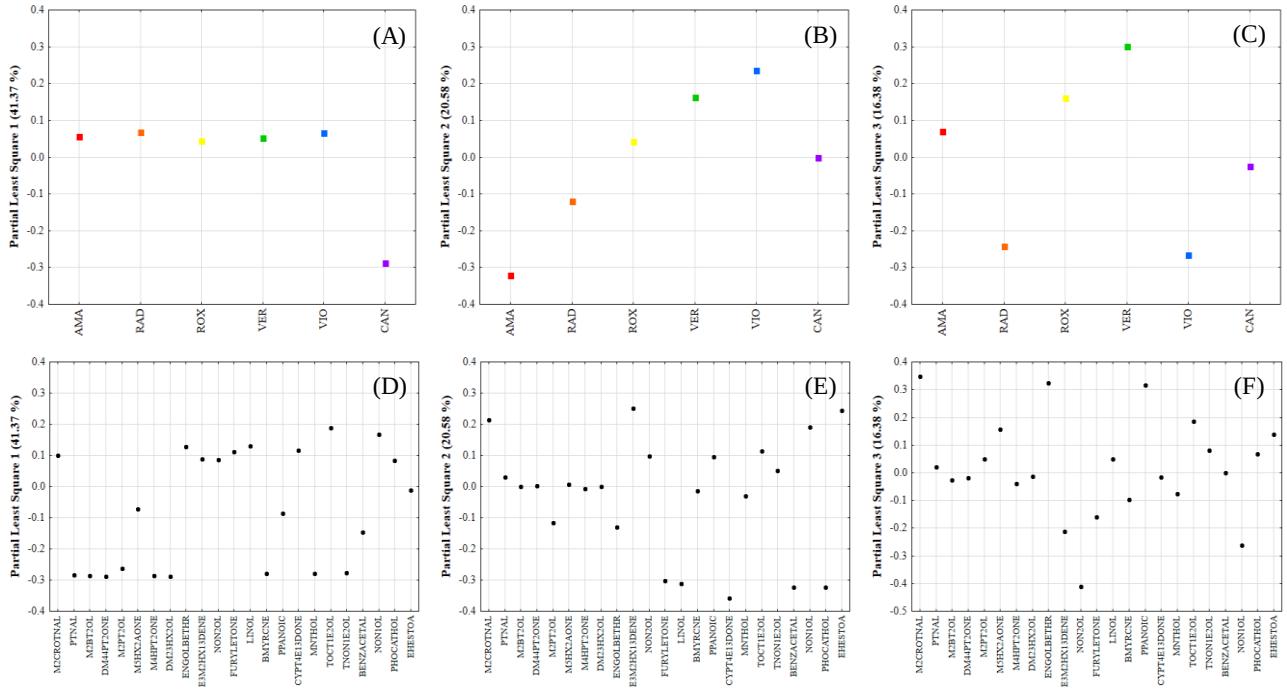


**Figure S5. The PLS loadings line plots of all cultivar samples based on the 23 most predictive VOCs for PLS1 (A), PLS2 (B) and PLS3 (C), and the PLS loadings line plots of the 23 most predictive VOCs for PLS1 (D), PLS2 (E) and PLS3 (F).**

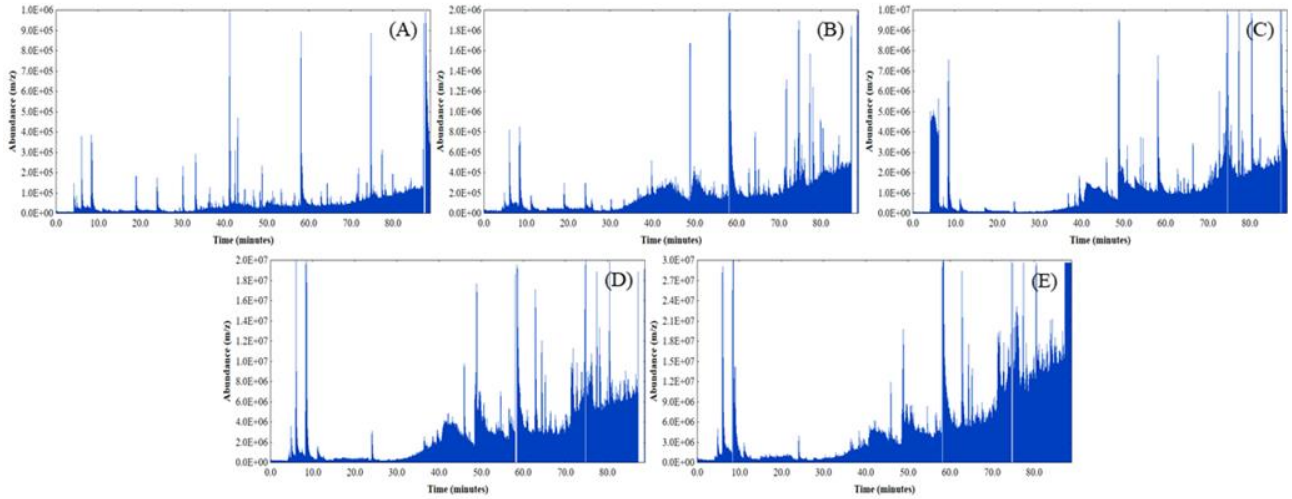


**Figure S6. The typical GC-MS chromatograms for stage 1 (A), stage 2 (B), stage 3 (C), stage 4 (D) and stage 5(E) of SCH processing.**

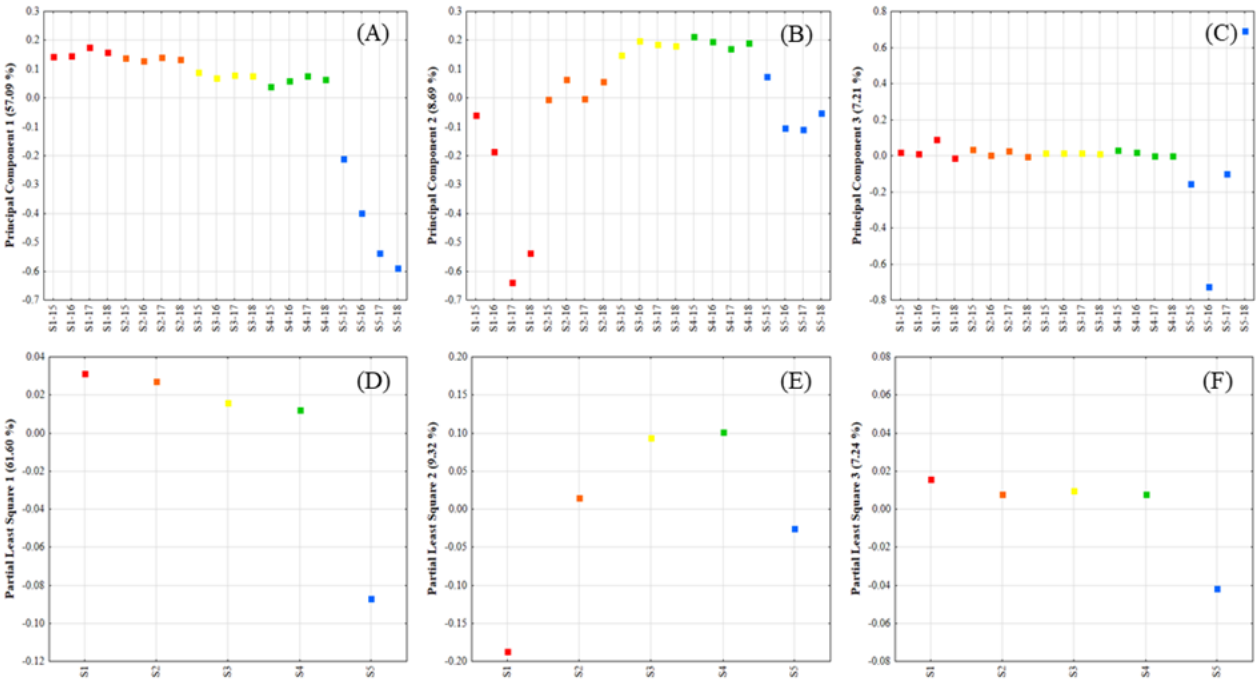


**Figure S7. The PCA loadings line plot of all stage samples based on the selected 187 VOCs for PC1 (A), PC2 (B) and PC3 (C), and the PLS loadings line plot of all cultivar samples for PLS1 (D), PLS2 (E) and PLS3 (F).**

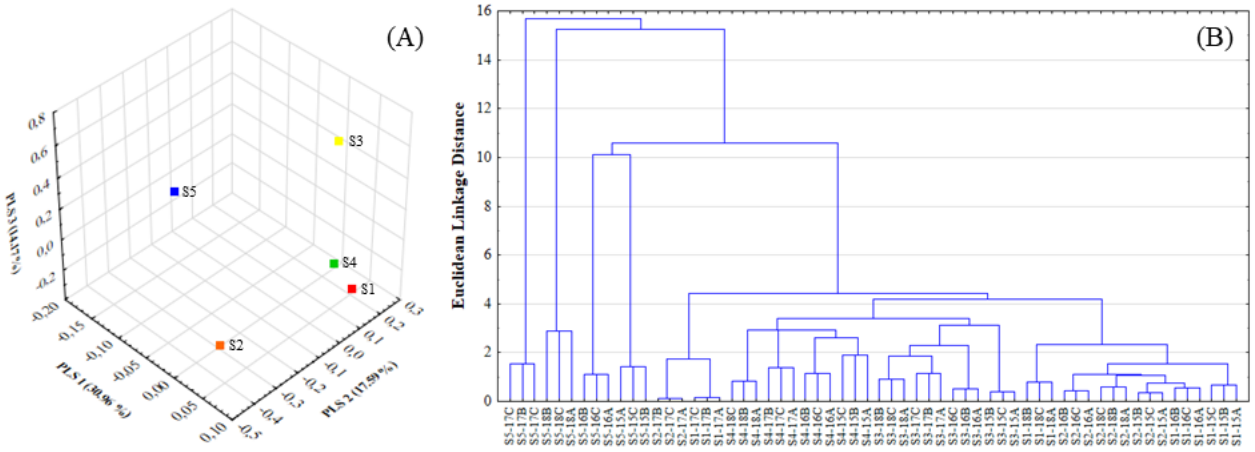


**Figure S8. The PLS 3D plot (A) and HCA dendrogram (B) for results from the matrix reduction procedure based on the VIP scores.**

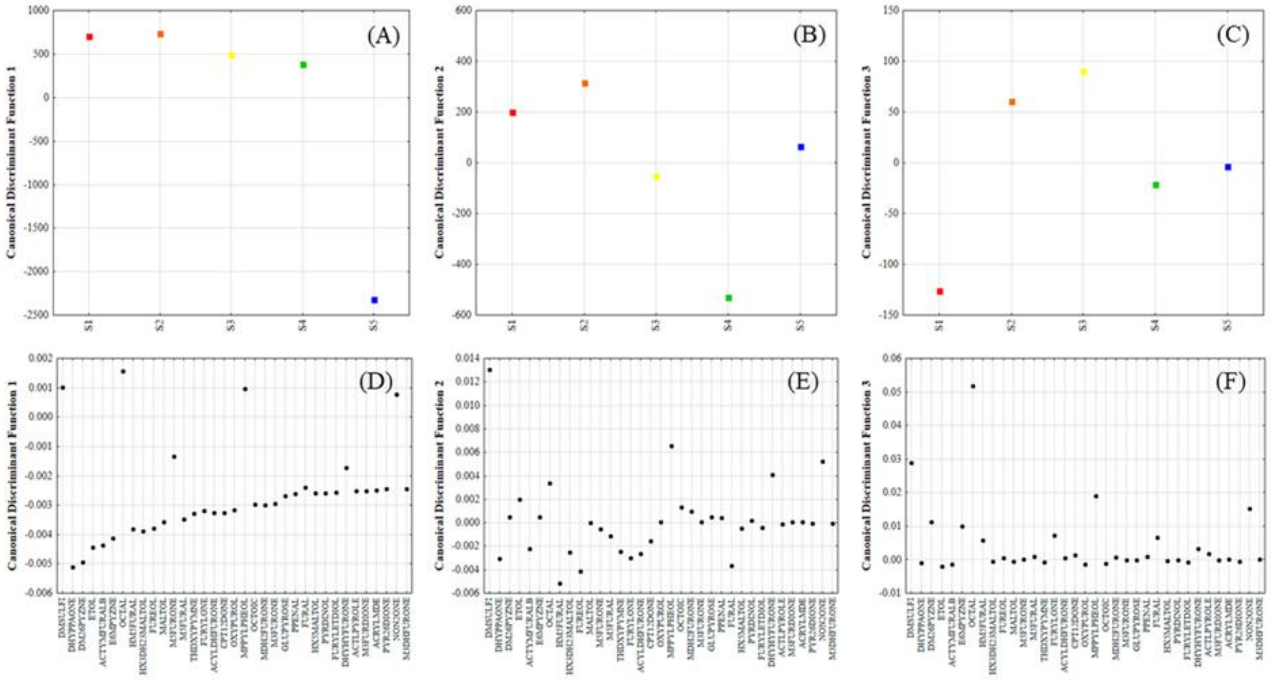


**Figure S9. The LDA line plots of all cultivars based on the 35 most predictive VOCs for to CDF1 (A), CDF2 (B) and CDF3 (C), and LDA line plots of the 35 most predictive VOCs for CDF1 (D), CDF2 (E) and CDF3 (F).**

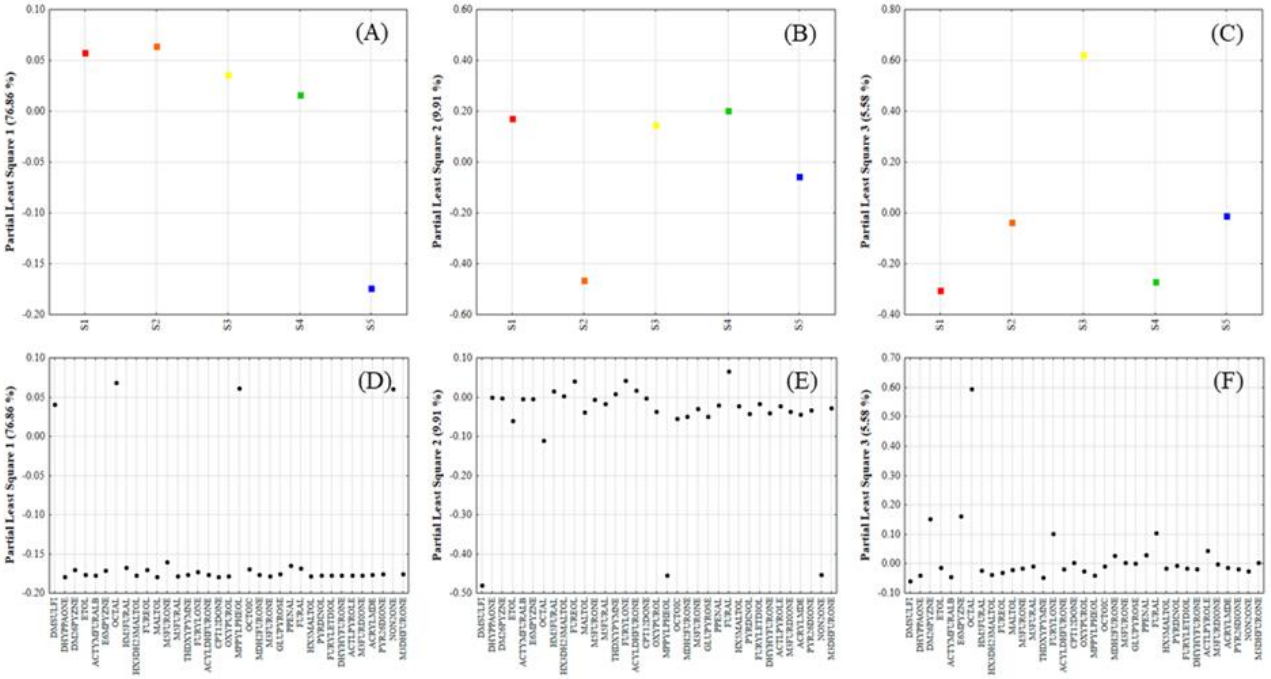


**Figure S10. The PLS loadings line plots of all cultivar samples based on the 35 most predictive VOCs for PLS1 (A), PLS2 (B) and PLS3 (C), and the PLS loadings line plots of the 35 most predictive VOCs for PLS1 (D), PLS2 (E) and PLS3 (F).**

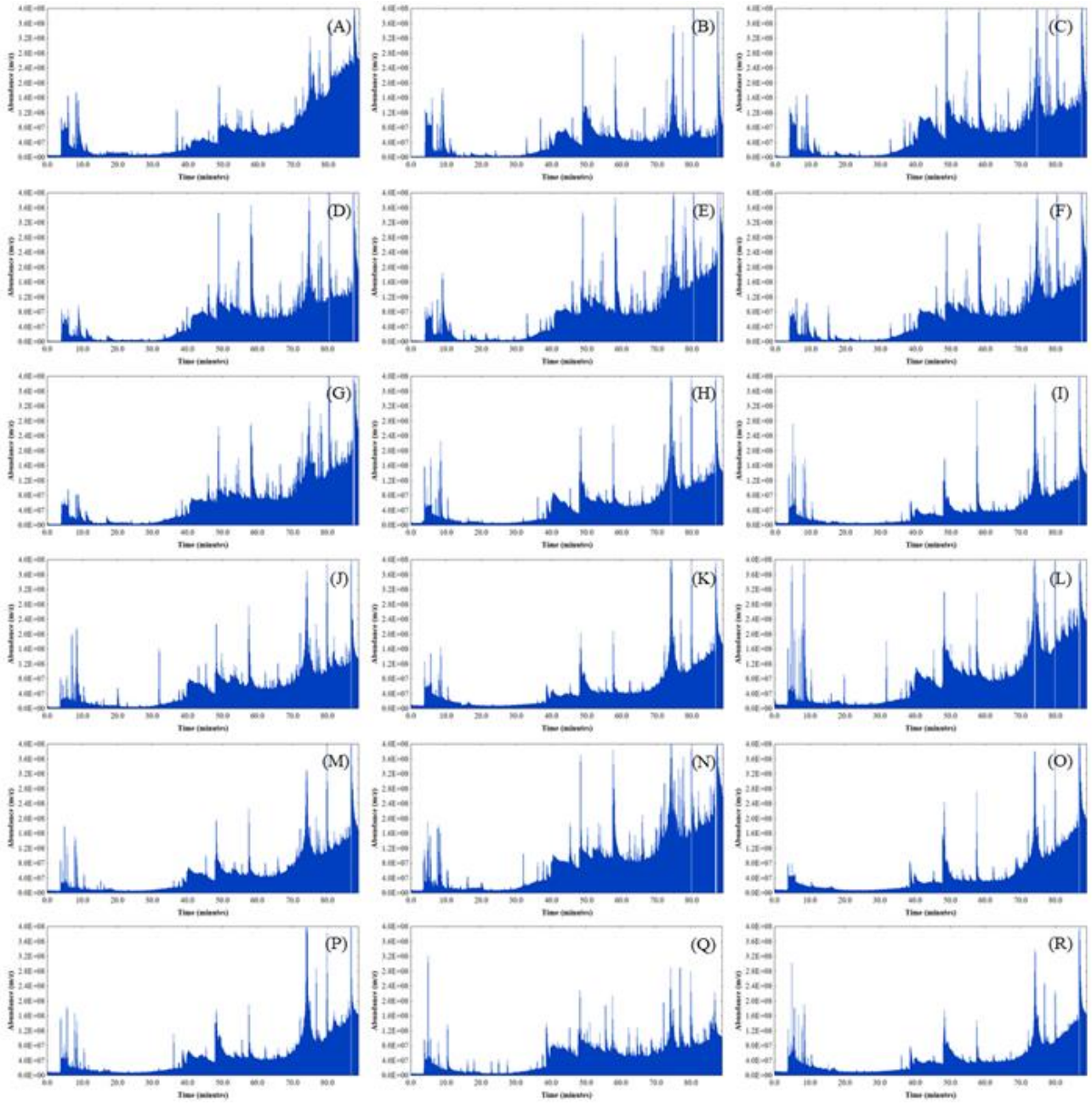


**Figure S11. The typical GC-MS chromatograms for FRS07 (A), FRS13 (B), FRS14 (C), FRS15 (D), FRS16 (E), FRS17 (F), FRS18 (G), ECAL14 (H), NCAL14 (I), GLA14 (J), ESP16 (K), EGP17 (L), EGPA16 (M), EGPB16 (N), EGPC16 (O), MDBR14 (P), MCBR14 (Q) and AUS17 (R) samples.**

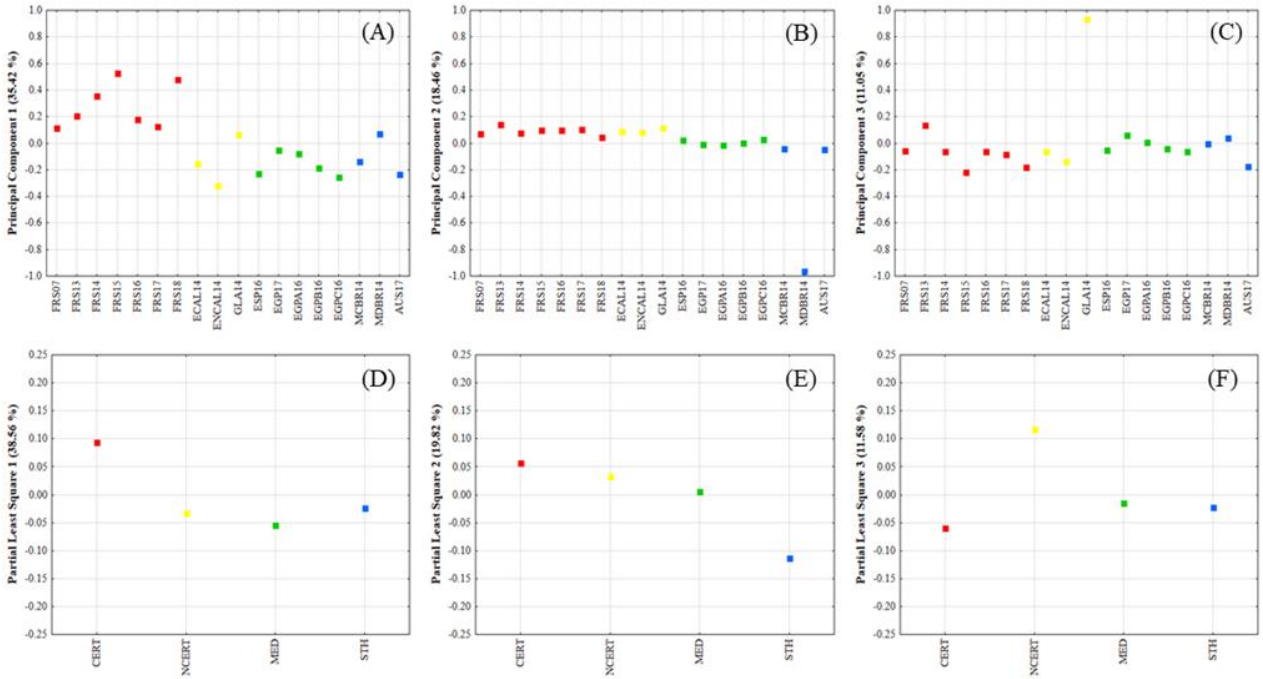


**Figure S12. The PCA loadings line plot of all stage samples based on the selected 144 VOCs for PC1 (A), PC2 (B) and PC3 (C), and the PLS loadings line plot of all cultivar samples for PLS1 (D), PLS2 (E) and PLS3 (F).**

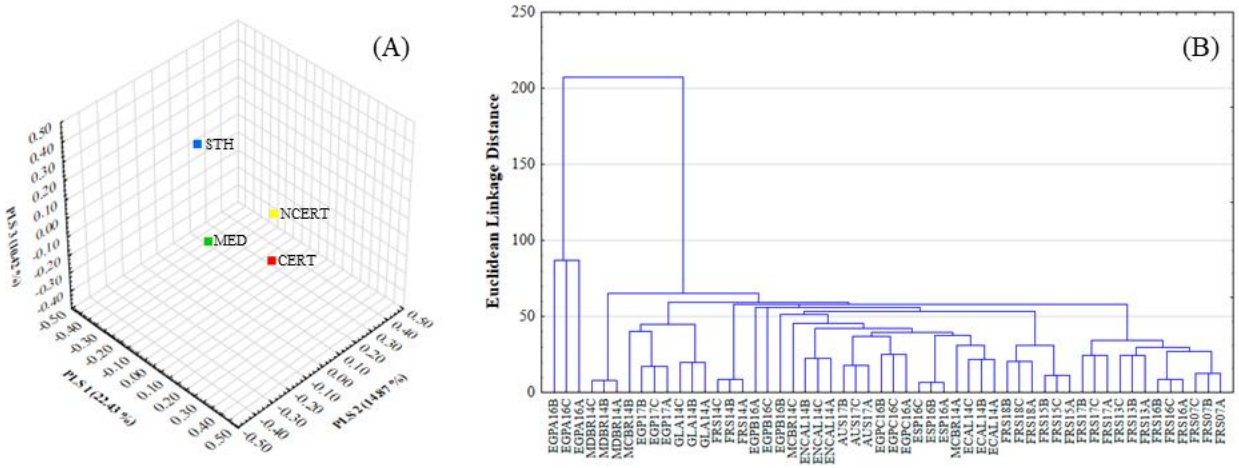


**Figure S13. The PLS 3D plot (A) and HCA dendrogram (B) for results from the matrix reduction procedure based on the VIP scores.**

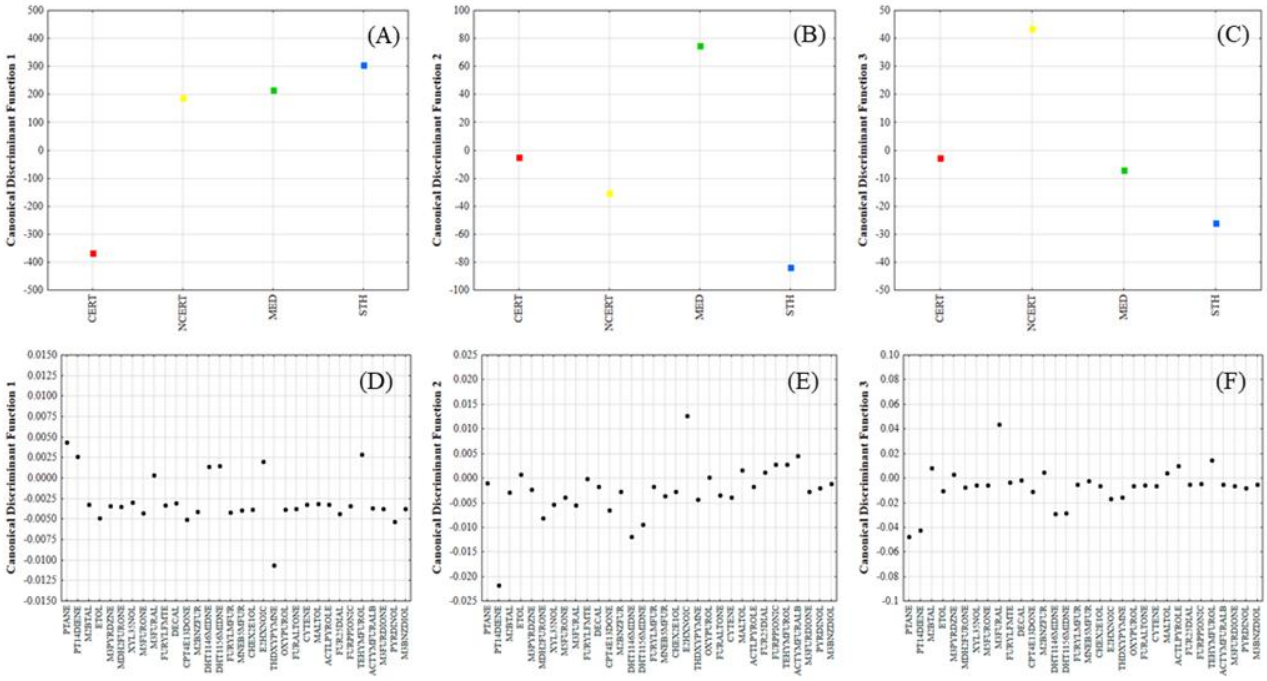


**Figure S14. The LDA line plots of all cultivars based on the 31 most predictive VOCs for to CDF1 (A), CDF2 (B) and CDF3 (C), and LDA line plots of the 35 most predictive VOCs for CDF1 (D), CDF2 (E) and CDF3 (F).**

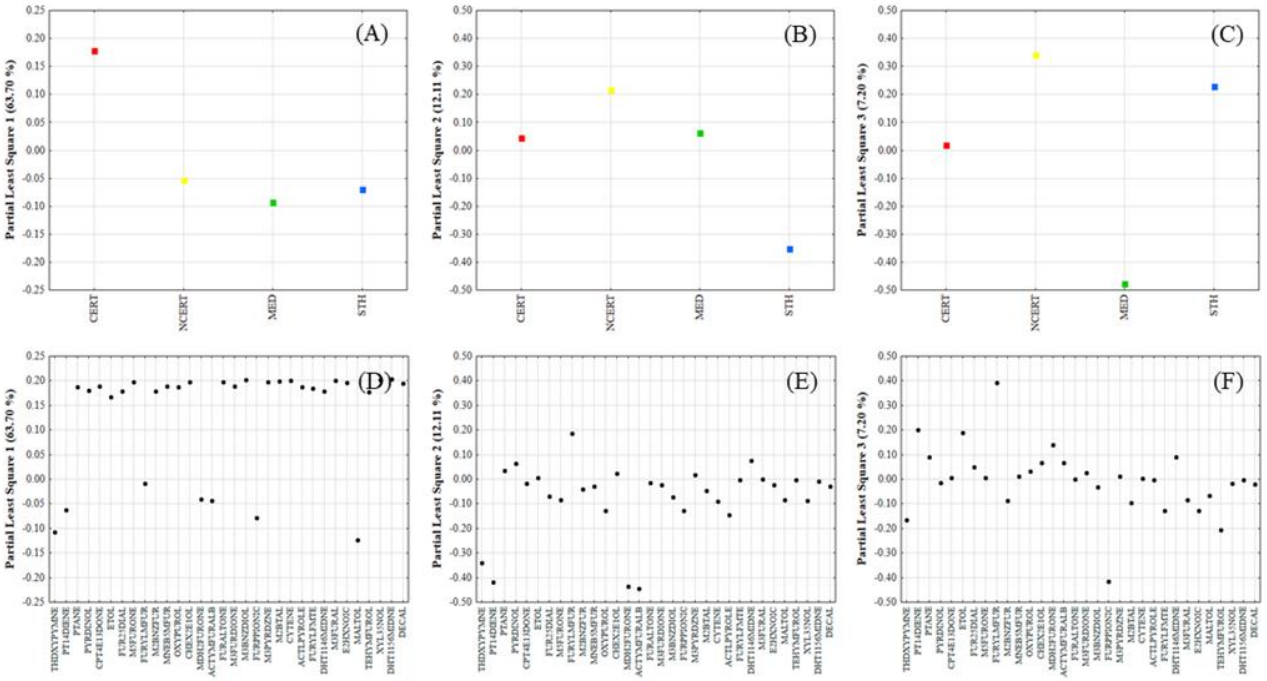


**Figure S15. The PLS loadings line plots of all cultivar samples based on the 31 most predictive VOCs for PLS1 (A), PLS2 (B) and PLS3 (C), and the PLS loadings line plots of the 31 most predictive VOCs for PLS1 (D), PLS2 (E) and PLS3 (F).**

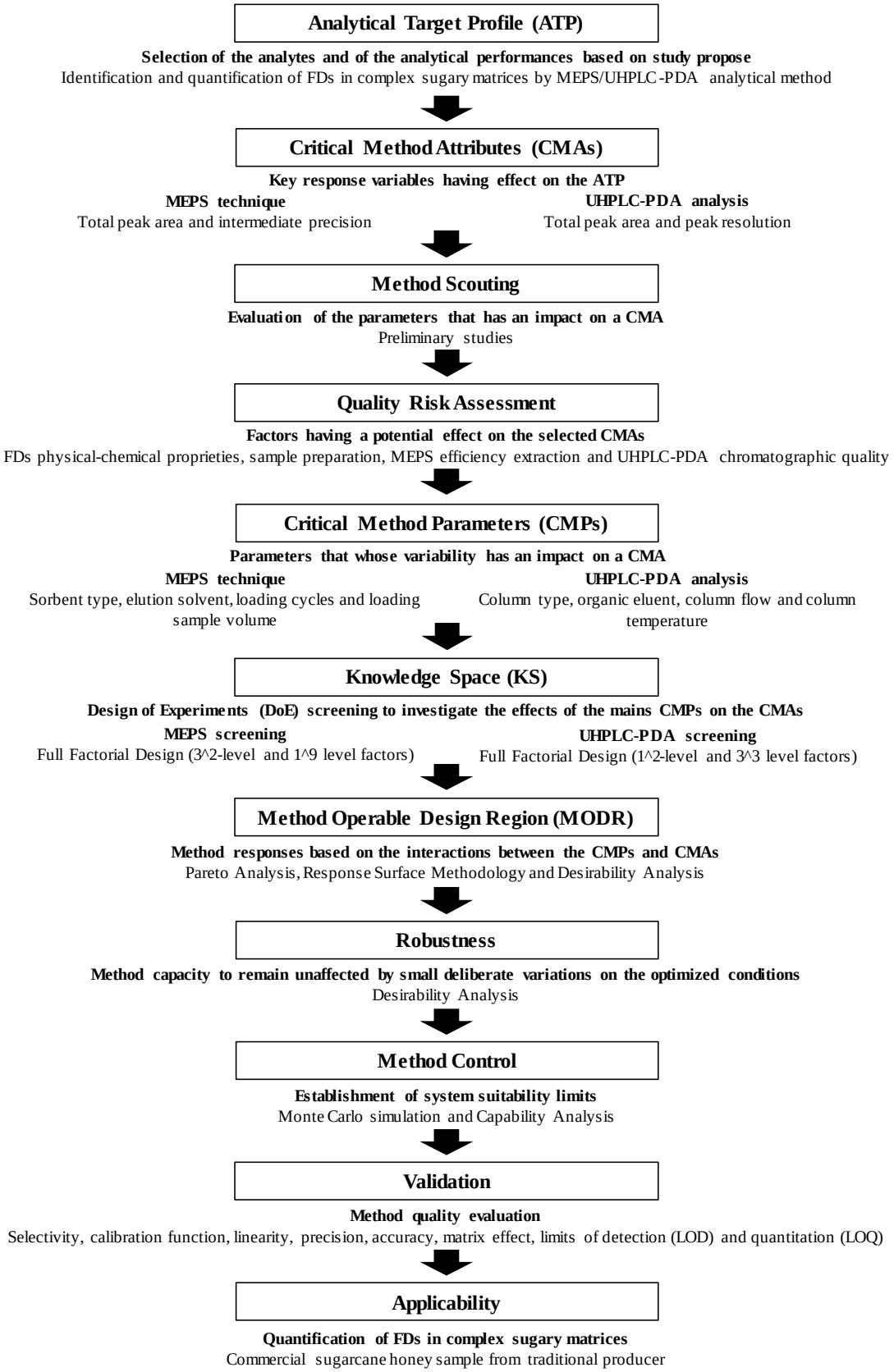


**Figure S16. Workflow chart for QbD approach-based analytical method development.**

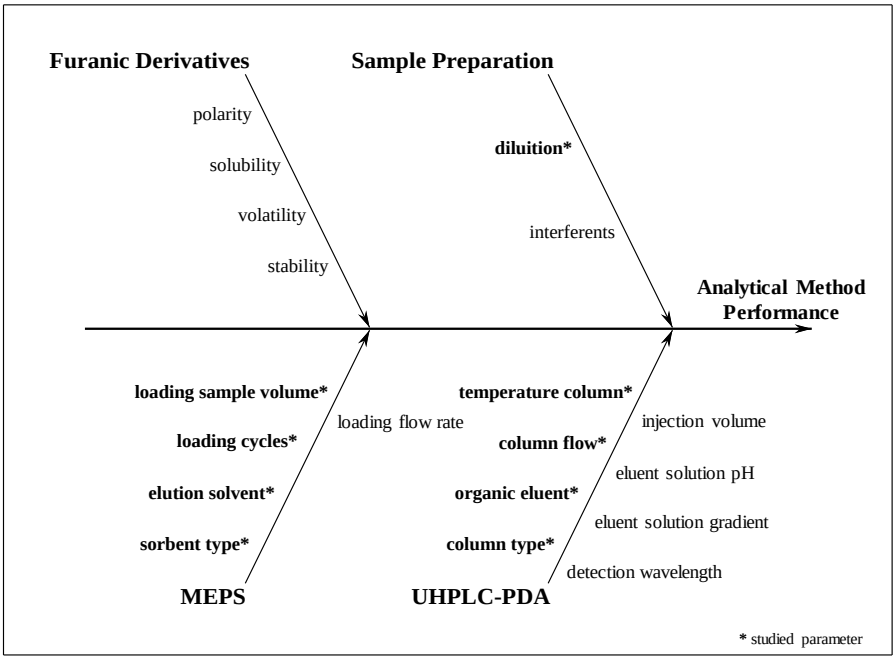


**Figure S17. Ishikawa diagram for the proposed MEPS-UHPLC-PDA analytical method for FDs profile in complex sugary matrices. The factors considered as CMPs are indicated as studied parameter. The other factors were fixed on the basis of preliminary experiments and scouting phase.**

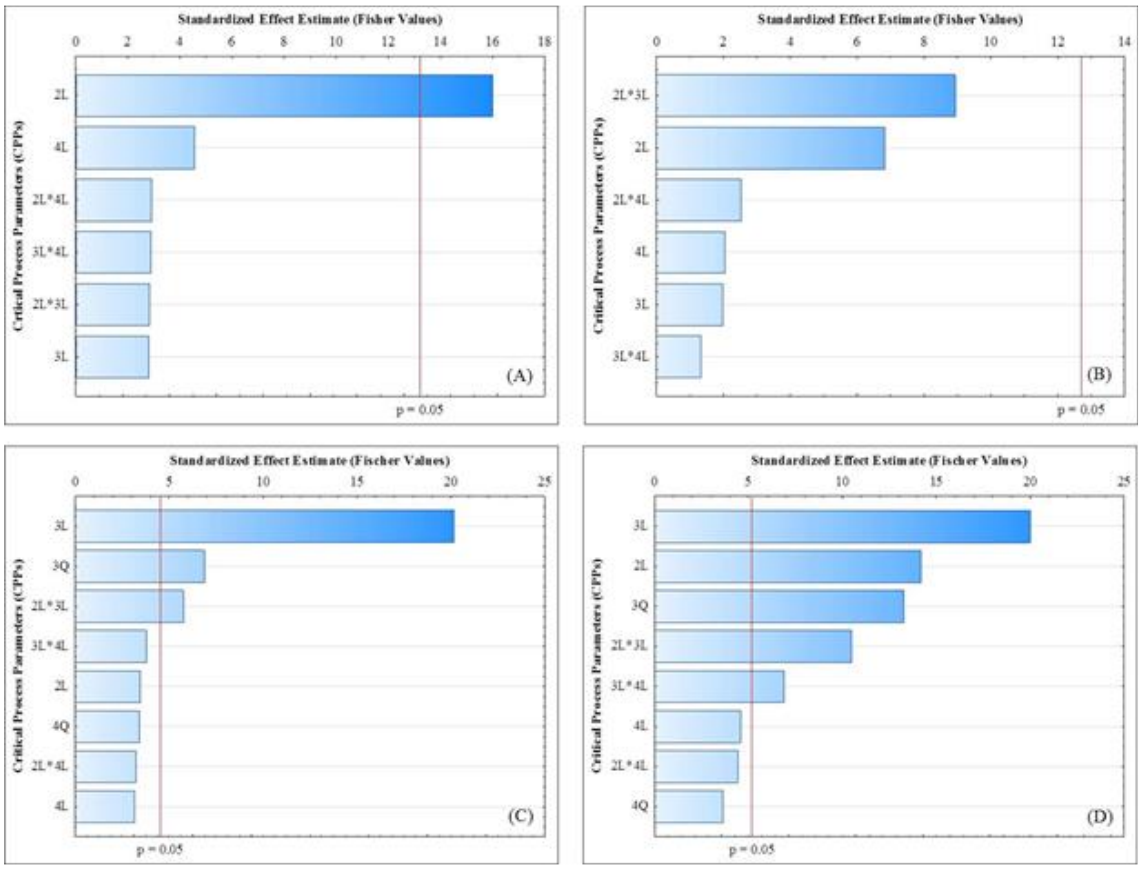


**Figure S18. Pareto chart plot of standardized effects of CMPs for definition of MEPS$_{R\text{-}CX}$-MODR regarding the TPA (A) and IP (B), and UHPLC$_{CORTECS}$-MODR regarding the TPA (C) and PR (D) results.**

**Abbreviations correspond to: (L) linear function model and (Q) quadratic function model. Numbers in SM Fig. 3 (A) and (B) correspond to: (2) elution solvent; (3) loading cycles; (4) loading volume. Numbers in SM Fig. 3 (C) and (D) correspond to: (1) column; (2) organic eluent; (3) column flow; and (4) column temperature.**

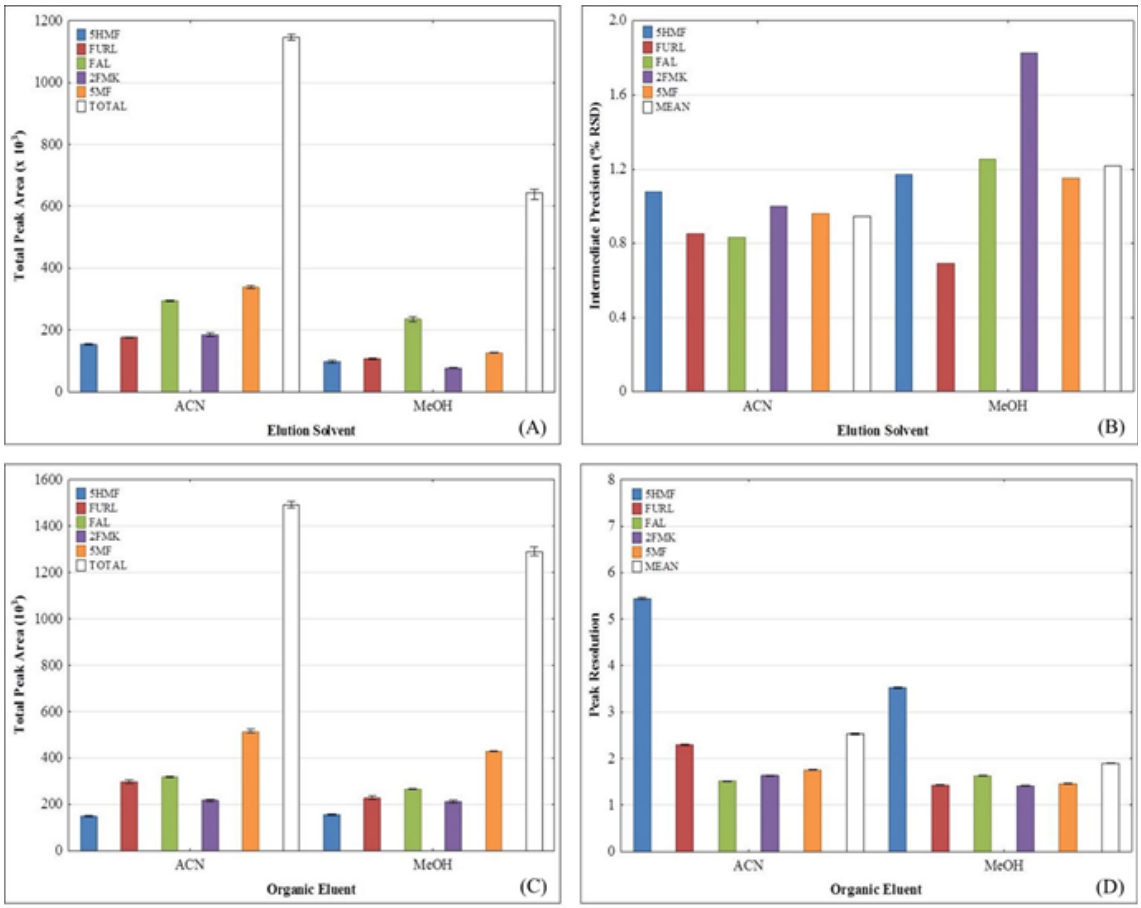


**Figure S19. Bar plot of evaluation of discontinuous CMPs for definition of MEPS$_{R\text{-}CX}$-MODR regarding the TPA (A) and IP (B) results for each elution solvent with optimal conditions, and UHPLC$_{CORTECS}$-MODR regarding the TPA (C) and PR (D) results for each organic eluent with optimal conditions.**

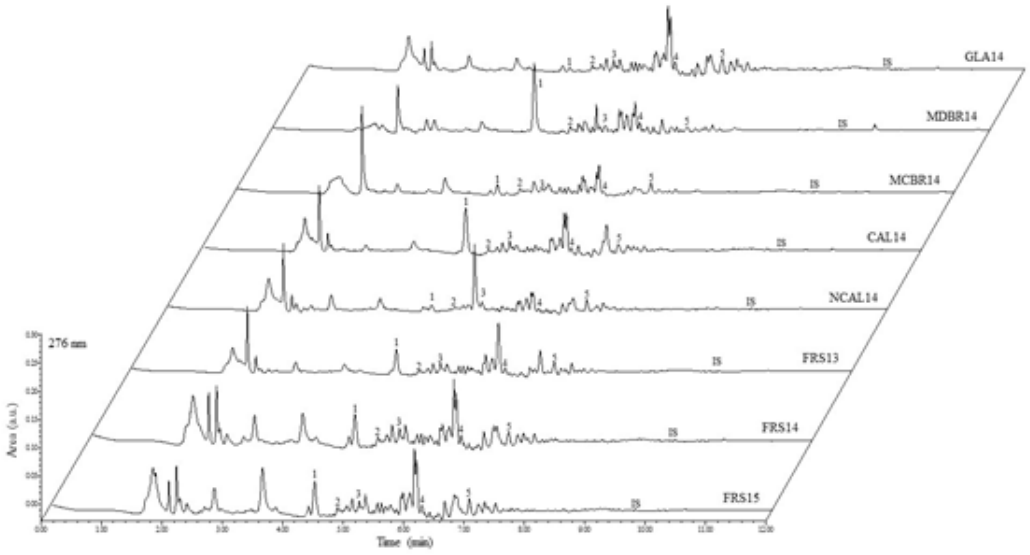


**Figure S20. Typical UHPLC-PDA chromatograms of FDs profile for all samples.**

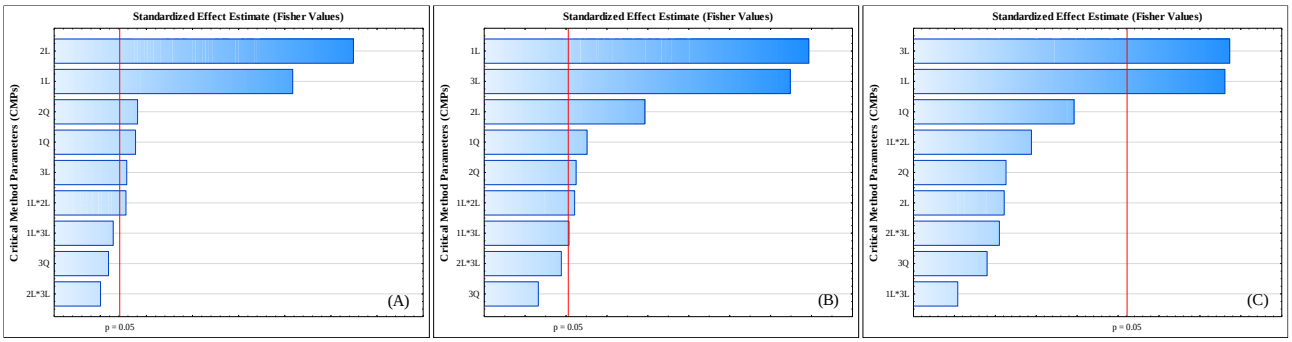


**Figure S21. Pareto chart plot of standardized effects of CMPs for definition of MODR regarding the TPA (A), PR (B), and ASY (C) results.**

**Abbreviations correspond to: (L) linear function model and (Q) quadratic function model. Numbers correspond to: (1) ACT content; (2) column flow; and (3) column temperature.**

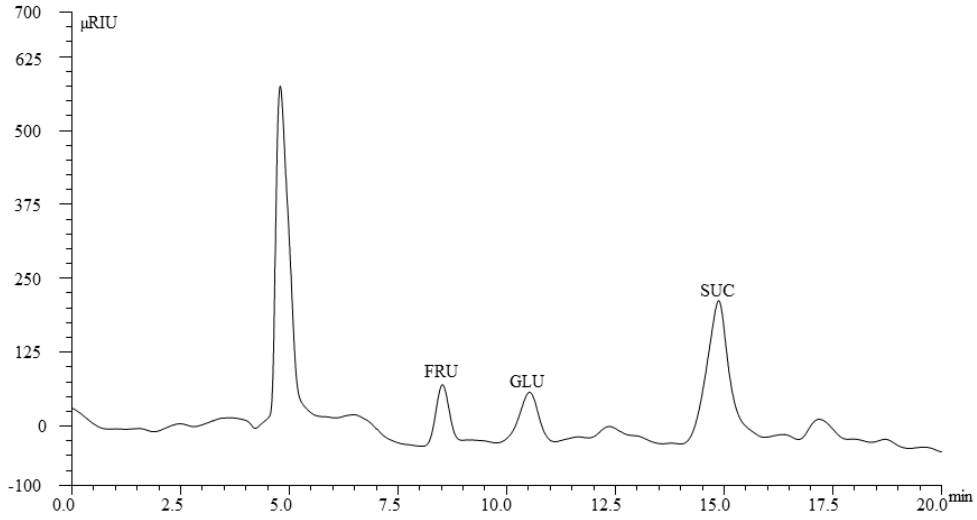


**Figure S22. The representative HPLC-RI chromatogram of SGs profile.**

# SUPPLEMENTARY TABLES

**Table S1. Main features of the sample extraction techniques (pros and cons) for food authenticity purpose.**

| | Sample volume | Solvents volume | Extraction time | Recoveries | Reuse | Cost-effective | Application range | Eco-friendly |
|---|---|---|---|---|---|---|---|---|
| *Liquid-liquid extractions* | | | | | | | | |
| LLE | ↑↑↑ | ↑↑↑ | ↑↑↑ | ↑ | ↑ | ↑↑↑ | ↑↑ | ↑ |
| LLME | ↑↑ | ↑↑ | ↑↑↑ | ↑↑ | ↑ | ↑↑ | ↑↑ | ↑↑ |
| DLLME | ↑ | ↑ | ↑ | ↑↑ | ↑ | ↑↑ | ↑↑ | ↑↑↑ |
| ILS | ↑ | ↑ | ↑ | ↑↑↑ | ↑ | ↑↑↑ | ↑↑ | ↑↑↑ |
| *Solid-phase extractions* | | | | | | | | |
| SPE | ↑↑ | ↑↑ | ↑↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ |
| µSPE, dSPE | ↑ | ↑ | ↑ | ↑↑↑ | ↑↑ | ↑ | ↑↑↑ | ↑↑↑ |
| SPME | ↑ | ↑ | ↑ | ↑↑↑ | ↑↑↑ | ↑↑ | ↑↑↑ | ↑↑↑ |
| MEPS | ↑ | ↑ | ↑ | ↑↑↑ | ↑↑↑ | ↑↑ | ↑↑↑ | ↑↑↑ |
| *Stir bar sorptive extractions* | | | | | | | | |
| SBSE | ↑↑ | ↑↑ | ↑ | ↑↑ | ↑↑↑ | ↑↑ | ↑↑↑ | ↑↑ |
| SCSE; RDSE | ↑ | ↑ | ↑ | ↑↑↑ | ↑↑ | ↑↑ | ↑↑ | ↑↑ |
| *QuEChERS* | ↑ | ↑ | ↑ | ↑↑ | ↑ | ↑↑ | ↑↑↑ | ↑↑↑ |
| µ-QuEChERS | ↑ | ↑ | ↑ | ↑↑↑ | ↑ | ↑↑↑ | ↑↑↑ | ↑↑↑ |
| *Microwave-assisted extractions* | | | | | | | | |
| MAE | ↑↑ | ↑↑ | ↑ | ↑↑↑ | ↑↑ | ↑ | ↑↑ | ↑↑↑ |

↑: low; ↑↑: medium; ↑↑↑: high

Abbreviations: µ-QuEChERS: micro-quick, easy, cheap, effective, rugged, and safe; µSPE: micro-solid phase extraction; DLLME: Dispersive liquid–liquid microextraction; dSPE: dispersive solid-phase extraction; ILS: ionic liquids; LLE: liquid-liquid extraction; LLME: liquid–liquid microextraction; MAE: microwave-assisted extraction; MEPS: microextraction by packed syringe; QuEChERS: quick, easy, cheap, effective, rugged, and safe; RDSE: rotating-disc sorbent extraction; SBSE: stir bar sorptive extraction; SCSE: stir cake sorptive extraction; SPE: solid-phase extraction; SPME: solid-phase microextraction.

**Table S2. Analytical techniques frequently used for monitoring food authentication issues (from 2016 to 2018).**

| Analytical Technique | Chemometric methods | Matrix | Food authentication issue | Reference |
|---|---|---|---|---|
| HPLC | Student´s t test | Honey | Geographical origin | (Lin, Loomes, Prijic, Schlothauer, & Stephens, 2017) |
| HPLC-LTQ-Orbitrap-MS | PCA | Tomato | Farming practices (organic *vs*. conventional) | (Martínez Bueno, Díaz-Galiano, Rajski, Cutillas, & Fernández-Alba, 2018) |
| HPTLC | -- | Cocoa | Geographical origin | (Pedan et al., 2017) |
| LC-MS | OPLS-DA | Shrub chaste and Agnus castus fruits | Varieties/cultivars | (Yahagi et al., 2016) |
| LC-MS/MS | ANOVA | Honey | Botanical origin | (Tette et al., 2017) |
| | -- | Apple juice | Adulteration | (Willems & Low, 2018) |
| LC-IT-TOF-MS | PCA, OPLS-DA, HCA | Semen *sojae praeparatum* | Geographical origin | (Guo, Zhang, et al., 2018) |
| LC-q-TOF-MS | PCA, PLS-DA | Coffee | Varieties/cultivars | (Souard et al., 2018) |
| LC-HRMS | ANOVA, PCA | Wheat | Farming practices (organic *vs*. conventional) | (Weesepoel et al., 2016) |
| | PCA, OPLS-DA | Garlic | Geographical origin | (Hrbek et al., 2018) |
| UHPLC-UV | ANOVA, PLS-DA, HCA | Mushroom | Geographical origin | (Li et al., 2016) |
| UHPLC-DAD | ANOVA, PCA, PLS, LDA, HCA | Sugarcane honey | Geographical origin | (Silva et al., 2018) |
| UHPLC-MS | PCA, OPLS-DA, ROC curve | Carrot | Farming practices (organic *vs*. conventional) | (Cubero-Leon et al., 2018) |
| UHPLC-q-TOF-MS | PCA, OPLS-DA | Date | Varieties/cultivars | (Farag, Handoussa, Fekry, & Wessjohann, 2016) |
| | PCA, OPLS-DA, ROC curve | Wheat | Geographical origin | (Righetti et al., 2018) |
| | PCA | Goldenberry | Farming practices (organic *vs*. conventional) | (Llano et al., 2018) |
| | ANOVA, OPLS-DA, VIP | Extra-virgin olive oil | | (Mohamed et al., 2018) |
| | ANOVA, Student´s t test, PCA, LDA, PLS-DA, SIMCA | Hazelnuts | | (Klockmann et al., 2016) |
| | PCA, OPLS-DA | Saffron | | (J. Rubert, Lacina, Zachariasova, & Hajslova, 2016) |
| | PCA, PLS-DA, DD-SIMCA | Coffee | | (Hoyos Ossa et al., 2018) |
| | PCA, OPLS-DA | Tiger nut | | (Rubert, Hurkova, Stranska, & Hajslova, 2018) |
| GCxGC | ANOVA, SWDA | Asiago PDO Cheese | Feed practices (pasture *vs*. silage) | (Segato et al., 2017) |
| GC-MS | HCA, PCA, OPLS-DA | Date | Varieties/cultivars | (Khalil et al., 2017) |

| | | | | |
|---|---|---|---|---|
| | PCA, HCA | Spices | | (Takaya et al., 2018) |
| | PCA, PLS-DA, HCA | Orange juice | Farming practices (organic *vs*. conventional) | (Cuevas et al., 2017) |
| | ANOVA | Cheese | Feed practices (pasture *vs*. silage) | (Caligiani, Nocetti, Lolli, Marseglia, & Palla, 2016) |
| | ANOVA | Honey | Botanical origin | (Pattamayutanon et al., 2017) |
| | PCA, LDA, RDA | Honey | Botanical/Geographical origin | (Patrignani et al., 2018) |
| | PCA, PLS-DA, RF | Rice | Geographical origin | (Lim, Mo, Lee, Long, Dong, et al., 2018) |
| | ANOVA, PCA, PLS-DA | Meat | Adulteration | (Trivedi et al., 2016) |
| | ANOVA, PCA | Coffee | | (Yang et al., 2016) |
| GC-IMS | PCA, LDA, *k*-NN | Honey | Botanical origin | (Gerhardt et al., 2018) |
| GC-FID | PCA, PCA-LDA, PLS, LS-SVM, RMSEP, RMSEC | Almond | Adulteration | (Esteki et al., 2017) |
| SIFT-MS | PCA, PLS-DA | Olive oil | Geographical origin | (Bajoub et al., 2018) |
| MALDI-TOF-MS | PCA, HCA | Wine | Varieties/cultivars | (Rešetar et al., 2016) |
| DART-QqQ-MS | -- | Wine | Adulteration | (Guo, Fang, et al., 2016) |
| PTR-TOF-MS | PCA | Wine | Geographic origin | (Campbell-Sills et al., 2016) |
| TLC-IA | PCA, PLS-DA, LDA, VIP; *k*-NN | Saffron | Adulteration | (Sereshti et al., 2018) |
| | PCA, OPLS-DA | Oregano | | (Black et al., 2016) |
| FTIR spectroscopy | LDA, SVM, OCPLS | Edible bird´s nest | Adulteration | (Guo, Wu, et al., 2018) |
| | PCA, PLS-DA, siPLS | Saffron | | (Petrakis & Polissiou, 2017) |
| | PLS-DA, GS-SVM | Mushroom | Geographical origin | (Sen et al., 2018) |
| FT-MIR spectroscopy | PCA, OCSIMCA | Paprika | Adulteration | (Horn et al., 2018) |
| FT-NIR spectroscopy | PCA, PLS-DA, SIMCA, *k*-NN | Açai | Adulteration | (Lobato et al., 2018) |
| FT-Raman spectroscopy | SLDA | Wines | Varieties/Geographical origin | (Magdas et al., 2018) |
| | PLS (iPLS-OPS), GA | Fruit nectars | Adulteration | (Miaw et al., 2018) |
| FTIR-ATR spectroscopy | HCA, MD-DA, CTA, DCA, MDS | Honey | Botanical origin | (Kasprzyk, Depciuch, Grabek-Lejko, & Parlinska-Wojtan, 2018) |
| MIR spectroscopy | PCA, PLS-DA, MB-PLS | Wines | Geographical origin | (Teixeira dos Santos et al., 2017) |
| | PCA, PLS-DA | Wine vinegars | Geographical origin | (Ríos-Reina et al., 2018) |
| NIR spectroscopy | PCA, LDA, SIMCA | Fish | Species | (Grassi et al., 2018) |
| | PCA, LDA, BPR | Maize | Varieties/cultivars | (Cui et al., 2018) |
| | PCA, SIMCA | Milk powder | Adulteration | (Karunathilaka et al., 2017) |
| Raman spectroscopy | PCA, MD-DA | Wine | Varieties/Geographical origin | (Mandrile et al., 2016) |
| | -- | Citrus fruits | Freshness | (Nekvapil et al., 2018) |
| UV spectroscopy | PCA, HCA, SIMCA | Honey | Botanical/Geographical origin | (Ansari et al., 2018) |
| | PCA | Apple | | (Eisenmann et al., 2016) |
| | ANOVA, PCA, OPLS | Cinnamon | Varieties/cultivars | (Farag et al., 2018) |
| NMR spectroscopy | PCA, LDA, LOOCV, RDRCV | Wine | | (Fan et al., 2018) |
| | PCA-LDA, PLS-DA, SIMCA, MCCV | Lentil | Geographical origin | (Longobardi et al., 2017) |

| | | | | |
|---|---|---|---|---|
| | ANOVA | Krill oil | Adulteration | (Akanbi & Barrow, 2018) |
| | -- | Butter | | (Fadzillah et al., 2017) |
| 2D-NMR spectroscopy | PCA, PLS | Vegetable oils | Botanical origin/Adulteration | (Gouilleux et al., 2018) |
| E-nose and E-tongue | PCA, PLS-DA, SVMDA | Honey | Botanical origin | (Gan et al., 2016) |
| E-nose, E-tongue and E-eye | ANOVA, LSD, PCA, *k*-NN | Vegetable oils | Botanical origin | (Buratti et al., 2018) |

Abbreviations: ANOVA: analysis of variance; ATR: attenuated total reflectance; BPR: biomimetic pattern recognition; CA: cluster analysis; CTA. classification tree analysis; DA: discriminant analysis; DART-QqQ-MS: direct analysis in real time- triple quadrupole mass spectrometry; DCA: detrended correspondence analysis; DD-SIMCA: data driven soft independent modelling of class analogy; FT-: Fourier transform GA: genetic algorithm; GC- FID: gas chromatography-flame ionization detector; GC-IMS: gas chromatography ion mobility spectrometer; GC-MS: gas chromatography mass spectrometry; GS-SVM: grid-search support vector machine; HCA; hierarchical cluster analysis; IA: imagen analysis; IMS: ion mobility spectrometry; iPLS: interval partial least squares; k-NN: k-nearest neighbours; LC-MS: liquid chromatography mass spectrometry; LDA: linear discriminant analysis; LOOCV: leave-one-out cross validation; LSD: least square difference; MB-PLS: multiblock partial least squares MD-DA: Mahalanobis distance-discriminant analysis; MDS: multidimensional scaling; MIR: mid- infrared; MS/MS: tandem mass spectrometry; NIR: near-infrared; NMR: nuclear magnetic resonance; OCPLS: one-class partial least squares, OCSIMCA: one-class soft independent modelling of class analogy; OPLS-DA: orthogonal projections to latent structures modelling discriminant analysis; OPS: ordered predictors selection; PCA: principal component analysis; PDA: photodiode array; PLS-DA: partial least squares-discriminant analysis; PTR: proton transfer reaction; RDRCV: repeated double random cross validation; RF: random forests; RMSEC: root mean square error of calibration; RMSEP: root mean square error of prediction; ROC: receiver operating characteristics; SIMCA: soft independent modelling of class analogy; SLDA: stepwise linear discriminant analysis; SVM: support vector machine; SVMDA: support vector machine discriminant analysis; TLC-IA: thin layer chromatography-image analysis; UHPLC: ultra-high performance liquid chromatography; UV: ultraviolet.

**Table S3. Identification of SCH samples by sample name, number code, production type, production year, geographical area and authenticity certification.**

| Sample name | Number code | Production type | Production year | Geographical area[a] | Authenticity certification |
|---|---|---|---|---|---|
| FRS13A1 | 1 | Industrial | 2013 | Funchal, Câmara de Lobos | Certified |
| FRS13A2 | 2 | | | | |
| FRS13B1 | 3 | Industrial | 2013 | Funchal, Câmara de Lobos | Certified |
| FRS13B2 | 4 | | | | |
| FRS14A1 | 5 | Industrial | 2014 | Funchal, Câmara de Lobos | Certified |
| FRS14A2 | 6 | | | | |
| FRS15A1 | 7 | Industrial | 2015 | Funchal, Câmara de Lobos | Certified |
| FRS15A2 | 8 | | | | |
| GLA141 | 9 | Home-made | 2014 | Santa Cruz, Machico | Non-Certified |
| GLA142 | 10 | | | | |
| FUN14A1 | 11 | Home-made | 2014 | Funchal, Câmara de Lobos | Non-Certified |
| FUN14A2 | 12 | | | | |
| CAL14A1 | 13 | Industrial | 2014 | Calheta, Ribeira Brava | Non-Certified |
| CAL14A2 | 14 | | | | |
| NCAL14A1 | 15 | Industrial | 2014 | Calheta, Ribeira Brava | Non-Certified |
| NCAL14A2 | 16 | | | | |

**Table S4. NIST database and common names, ID number, CAS number, abbreviations and molecular formula of identified VOCs in SCH samples.**

| ID Number[a] | CAS Number[b] | NIST Database Name | Common Name | Abbreviations | Molecular Formula |
|---|---|---|---|---|---|
| 1 | 75-07-0 | Acetaldehyde | Ethanal | ACTAL | C2H4O |
| 2 | 75-18-3 | Dimethyl Sulfide | Dimethylsulfide | DMS | C2H6S |
| 3 | 110-00-9 | Furan | Furan | FUR | C4H4O |
| 4 | 78-84-2 | 2-Methyl-Propanal | Isobutanal | MPPAL | C4H8O |
| 5 | 534-22-5 | 2-Methyl-Furan | α-Methylfuran | MFUR | C5H6O |
| 6 | 141-78-6 | Ethyl Acetate | Ethyl Acetate | EACT | C4H8O2 |
| 7 | 78-93-3 | 2-Butanone | 2-Butanone | BTONE | C4H8O |
| 8 | 96-17-3 | 2-Methyl-Butanal | α-Methylbutanal | M2BTAL | C5H10O |
| 9 | 590-86-3 | 3-Methyl-Butanal | β-Methylbutanal | M3BTAL | C5H10O |
| 10 | 64-17-5 | Ethyl alcohol | Ethanol | ETAOL | C2H6O |
| 11 | 625-86-5 | 2,5-Dimethyl-Furan | 2,5-Dimethylfuran | DMFUR | C6H8O |
| 12 | 105-37-3 | Ethyl Ester Propanoic Acid | Ethyl Propanoate | EESTPA | C5H10O2 |
| 13 | 97-62-1 | Ethyl Ester 2-Methyl-Propanoic Acid | 2-Ethyl Isobutanoate | EEST2MPA | C6H12O2 |
| 14 | 110-62-3 | Pentanal | Pentanal | PNTAL | C5H10O |
| 15 | 431-03-8 | 2,3-Butanedione | 2,3-Butanedione | BTDONE | C4H6O2 |
| 16 | 110-19-0 | 2-Methylpropyl Ester Acetic Acid | Isobutyl Acetate | MPESTAA | C6H12O2 |
| 17 | 1703-52-2 | 2-Ethyl-5-Methyl-Furan | 2-Ethyl-5-Methylfuran | E5MFUR | C7H10O |
| 18 | 105-54-4 | Ethyl Ester Butanoic Acid | Ethyl Butanoate | EESTBTA | C6H12O2 |
| 19 | 71-23-8 | 1-Propanol | n-Propanol | PPOL | C3H8O |
| 20 | 115-18-4 | 2-Methyl-3-Buten-2-ol | Dimethylvinylcarbinol | M3BT2OL | C5H10O |
| 21 | 5519-42-6 | 3,4,5-Trimethylpyrazole | 3,4,5-Trimethylpyrazole | TMPZLE | C6H10N2 |
| 22 | 600-14-6 | 2,3-Pentanedione | 2,3-Pentanedione | PTDONE | C5H8O2 |
| 23 | 872-50-4 | 1-Methyl-2-Pyrrolidinone | n-Methyl-α-Pyrrolidinone | M2PYRONE | C5H9NO |
| 24 | 624-92-0 | Dimethyl Disulfide | Dimethyldisulfide | DMDS | C2H6S2 |
| 25 | 66-25-1 | Hexanal | Hexanal | HEXAL | C6H12O |
| 26 | 78-83-1 | 2-Methyl-1-Propanol | Isobutanol | M1PPOL | C4H10O |
| 27 | 104-50-7 | 5-Butyldihydro-2(3H)-Furanone | γ-Octalactone | BH2FURONE | C8H14O2 |
| 28 | 694-54-2 | Tetrahydro-2H-Pyran-2-ol | δ-Valerolactol | THPYR2OL | C5H10O2 |

| | | | | | |
|---|---|---|---|---|---|
| 29 | 71-36-3 | 1-Butanol | n-Butanol | BUTOL | C4H10O |
| 30 | 1632-76-4 | 3-Methyl-Pyridazine | 3-Methylpyridazine | MPYRINE | C5H6N2 |
| 31 | 111-71-7 | Heptanal | Heptanal | HEPTAL | C7H14O |
| 32 | 5989-27-5 | D-Limonene | D-Limonene | LIMNE | C10H16 |
| 33 | 470-82-6 | Eucalyptol | 1,8-Cineole | EUCALPT | C10H18O |
| 34 | 1757-42-2 | 3-Methyl-Cyclopentanone | 3-Methylcyclopentanone | MCPTONE | C6H10O |
| 35 | 137-32-6 | 2-Methyl-1-Butanol | 2-Methyl-n-Butanol | M21BTOL | C5H12O |
| 36 | 123-51-3 | 3-Methyl-1-Butanol | Isopentanol | M31BTOL | C5H12O |
| 37 | 99-85-4 | 1-Methyl-4-(1-Methylethyl)-1,4-Cyclohexadiene | γ-Terpinene | M41MECHEX | C10H16 |
| 38 | 99-87-6 | 1-Methyl-4-(1-Methylethyl)-Benzene | p-Cymene | M41MEBENZ | C10H14 |
| 39 | 33933-78-7 | 5-Methyl-5-Nonanol | 5-Methyl-5-Nonanol | M5NOL | C10H22O |
| 40 | 3188-00-9 | Dihydro-2-Methyl-3(2H)-Furanone | Dihydro-2-Methyl-3-Furanone | D2MFURONE | C5H8O2 |
| 41 | 142-92-7 | Hexyl Ester Acetic Acid | n-Hexyl Acetate | HESTAA | C8H16O2 |
| 42 | 124-13-0 | Octanal | Octanal | OCTAL | C8H16O |
| 43 | 116-09-6 | 1-Hydroxy-2-Propanone | Hydroxyacetone | H2PPONE | C3H6O2 |
| 44 | 57266-86-1 | (Z)-2-Heptenal | (Z)-2-Heptenal | HPTAL | C7H12O |
| 45 | 585-25-1 | 2,3-Octanedione | 2,3-Octanedione | OCTDONE | C8H14O2 |
| 46 | 1558-17-4 | 4,6-Dimethyl-Pyrimidine | 4,6-Dimethylpyrimidine | DMPYDNE | C6H8N2 |
| 47 | 108-50-9 | 2,6-Dimethyl-Pyrazine | 2,6-Dimethylpyrazine | DMPYZNE | C6H8N2 |
| 48 | 18729-48-1 | 3-Methyl-Cyclopentanol | 3-Methylcyclopentanol | MCPTOL | C6H12O |
| 49 | 111-27-3 | 1-Hexanol | n-Hexanol | HEXOL | C6H14O |
| 50 | 1120-73-6 | 2-Methyl-2-Cyclopenten-1-one | 2-Methylcyclopent-2-enone | M2CPNTONE | C6H8O |
| 51 | 59303-05-8 | 5-Methyl-2-Furanmethanethiol | 5-Methyl-2-Furanmethanethiol | M2FURTHOL | C6H8OS |
| 52 | 13925-03-6 | 2-Ethyl-6-Methyl-Pyrazine | 2-Ethyl-6-methylpyrazine | E6MPYZNE | C7H10N2 |
| 53 | 124-19-6 | Nonanal | Nonanal | NONAL | C9H18O |
| 54 | 14667-55-1 | Trimethyl-Pyrazine | Trimethylpyrazine | TMPYZNE | C7H10N2 |
| 55 | 475-03-6 | 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | α-Ionene | T116TNP | C13H18 |
| 56 | 64-19-7 | Acetic Acid | Ethanoic Acid | ACETACD | C2H4O2 |
| 57 | 98-01-1 | Furfural | Furfural | FURAL | C5H4O2 |
| 58 | 21693-51-6 | 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | 1,5,8-Trimethyl-1,2,3,4-tetrahydronaphthalene | T158TNP | C13H18 |
| 59 | 112-31-2 | Decanal | Decanal | DECAL | C10H20O |
| 60 | 1192-62-7 | 1-(2-Furanyl)-Ethanone | 2-Acetylfuran | FURLETONE | C6H6O2 |
| 61 | 100-52-7 | Benzaldehyde | Phenylmethanal | BENZAL | C7H6O |

| | | | | | |
|---|---|---|---|---|---|
| 62 | 623-17-6 | Acetate 2-Furanmethanol | Furfuryl Acetate | ACTEFURMTOL | C7H8O3 |
| 63 | 111-87-5 | 1-Octanol | n-Octanol | OCTOL | C8H18O |
| 64 | 620-02-0 | 5-Methyl-2-Furancarboxaldehyde | 5-Methylfurfural | M2FURCBAL | C6H6O2 |
| 65 | 586-62-9 | 1-Methyl-4-(1-Methylethylidene)-Cyclohexene | α-Terpinolene | M41MEDCHEX | C10H16 |
| 66 | 756-02-5 | 2,3,3-Trimethyl-1,4-Pentadiene | 2,3,3-Trimethyl-1,4-Pentadiene | TM14PTNE | C8H14 |
| 67 | 3168-90-9 | 1-(2-Methyl-1-Cyclopenten-1-yl)-Ethanone | 1-(2-Methylcyclopenten-1-yl)ethanone | M1CPT1ONE | C8H12O |
| 68 | 4265-25-2 | 2-Methyl-Benzofuran | 2-Methylbenzofuran | MBENZFUR | C9H8O |
| 69 | 562-74-3 | 4-Methyl-1-(1-Methylethyl)-3-Cyclohexen-1-ol | 4-Terpineol | ME3CHX1OL | C10H18O |
| 70 | 24156-95-4 | 2,5,5-Trimethyl-1-Cyclopenten-1-one | 3,5,5-Trimethyl-2-Cyclopentenone | TM1CPTONE | C8H12O |
| 71 | 122-78-1 | Benzeneacetaldehyde | Phenylethanal | BENZACETAL | C8H8O |
| 72 | 872-05-9 | 1-Decene | n-Decene | DECNE | C10H20 |
| 73 | 98-00-0 | 2-Furanmethanol | Furfuryl Alcohol | FURMOL | C5H6O2 |
| 74 | 98-55-5 | .alpha.,.alpha.4-Trimethyl-3-Cyclohexene-1-Methanol | α-Terpineol | T3CHEX1MOL | C10H18O |
| 75 | 3857-25-8 | 5-Methyl-2-Furanmethanol | 5-Methyl-2-furfuryl Alcohol | M2FURMOL | C6H8O2 |
| 76 | 140-11-4 | Phenylmethyl Ester Acetic Acid | Benzyl Acetate | PMESTAA | C9H10O2 |
| 77 | 13679-43-1 | 2,2'-Methylenebis[5-Methyl-Furan | 2,2'-Methylenebis[5-Methyl-Furan | MBS5MFUR | C10H10O2 |
| 78 | 103-45-7 | 2-Phenylethyl Ester Acetic Acid | β-Phenethyl Acetate | PEESTAA | C10H12O2 |
| 79 | 150-76-5 | 4-Methoxy-Phenol | Mequinol | MXYPHOL | C7H8O2 |
| 80 | 100-51-6 | Benzyl Alcohol | α-Toluenol | BENZLOL | C7H8O |
| 81 | 60-12-8 | Phenylethyl Alcohol | β-Phenylethanol | PHEEOL | C8H10O |
| 82 | 1072-83-9 | 1-(1H-Pyrrol-2-yl)-Ethanone | 2-Acetylpyrrole | PYOL2YLONE | C6H7NO |
| 83 | 108-95-2 | Phenol | Phenol | PHEOL | C6H6O |
| 84 | 102-76-1 | Triacetin | Triacetin | TACTIN | C9H14O6 |
| 85 | 96-76-4 | 2,4-Bis(1,1-Dimethylethyl)-Phenol | 2,4-Di-Tert-Butylphenol | BDMEPHEOL | C14H22O |
| 86 | 119-61-9 | Benzophenone | Benzophenone | BENZPONE | C13H10O |
| 87 | 67-47-0 | 5-(Hydroxymethyl)-2-Furancarboxaldehyde | 5-Hydroxymethylfurfural | HM2FURAL | C6H6O3 |

[a] Identification number.
[b] Chemical Abstracts Service registry number.

**Table S5. Mean and RSD values of the identified VOCs in SCH samples from certified producer and non-certified producers.**

| Chemical Classes /Identified VOCs | Certified | | | | Non-Certified | | | |
|---|---|---|---|---|---|---|---|---|
| | FRS13A | FRS13B | FRS14A | FRS15A | GLA14A | FUN14A | CAL14A | NCAL14A |

| | Mean$^{x10}$ | RSD (%) | Mean$^{x10}$ | RSD (%) | Mean$^{x10}$ | RSD (%) | Mean$^{x10}$ | RSD (%) | Mean$^{x10}$ | RSD (%) | Mean$^{x10}$ | RSD (%) | Mean$^{x10}$ | RSD (%) | Mean$^{x10}$ | RSD (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Alcohols** | | | | | | | | | | | | | | | | |
| Ethanol | 2651.3 | 0.6 | 118.7 | 16.9 | 316.7 | 1.9 | 118.0 | 0.0 | 881.7 | 2.8 | 473.4 | 2.2 | 210.8 | 4.7 | 83.6 | 19.0 |
| 1-Propanol | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 1.0 | 8.7 | n.d. | | n.d. | |
| 2-Methyl-3-buten-2-ol | 0.6 | 3.2 | 1.0 | 15.8 | 0.4 | 10.5 | 0.2 | 2.4 | n.d. | | n.d. | | 1.0 | 3.2 | 1.6 | 17.8 |
| 2-Methyl-1-propanol | 29.5 | 1.4 | 37.4 | 2.7 | 7.8 | 7.4 | 4.7 | 1.4 | 13.7 | 18.0 | 30.5 | 4.1 | 10.0 | 14.0 | 2.3 | 6.1 |
| Tetrahydro-2H-pyran-2-ol | 1.7 | 10.4 | 1.8 | 2.0 | 0.6 | 5.7 | 1.0 | 8.3 | 0.2 | 5.1 | 0.5 | 13.9 | 1.0 | 14.5 | 1.1 | 11.9 |
| 1-Butanol | n.d. | | n.d. | | n.d. | | n.d. | | 0.4 | 4.9 | 0.7 | 15.1 | n.d. | | n.d. | |
| 2-Methyl-1-butanol | 47.7 | 0.2 | 30.0 | 12.7 | 15.2 | 17.4 | 16.6 | 10.2 | 24.5 | 16.2 | n.d. | | 21.8 | 19.4 | 10.4 | 8.6 |
| 3-Methyl-1-butanol | 40.6 | 0.8 | 18.0 | 11.9 | 11.0 | 3.0 | 13.9 | 11.6 | 31.0 | 16.2 | 48.0 | 14.0 | n.d. | | n.d. | |
| 5-Methyl-5-nonanol | 0.5 | 14.6 | n.d. | | n.d. | | n.d. | | 2.5 | 16.5 | 1.6 | 0.6 | n.d. | | n.d. | |
| 3-Methyl-cyclopentanol | n.d. | | n.d. | | n.d. | | n.d. | | 0.5 | 20.4 | 0.4 | 1.5 | n.d. | | n.d. | |
| 1-Hexanol | n.d. | | n.d. | | n.d. | | 1.2 | 4.9 | n.d. | | n.d. | | n.d. | | n.d. | |
| 1-Octanol | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 0.4 | 3.4 | n.d. | | n.d. | |
| Benzyl alcohol | 4.6 | 3.4 | 1.3 | 7.7 | 0.5 | 5.3 | 3.3 | 1.4 | 10.2 | 6.3 | 2.6 | 5.2 | n.d. | | n.d. | |
| Phenylethyl alcohol | 2.0 | 4.3 | n.d. | | n.d. | | n.d. | | 6.1 | 4.5 | 1.9 | 1.4 | n.d. | | n.d. | |
| TOTAL | 2778.5 | | 208.1 | | 352.2 | | 159.1 | | 970.7 | | 561.0 | | 244.6 | | 99.1 | |
| **Aldehydes** | | | | | | | | | | | | | | | | |
| Acetaldehyde | 15.7 | 4.6 | 10.2 | 13.6 | 8.2 | 8.4 | 5.9 | 6.1 | 6.6 | 5.5 | 12.5 | 3.7 | 6.9 | 14.2 | 5.0 | 17.0 |
| 2-Methyl-propanal | 6.9 | 3.2 | 22.2 | 16.7 | 12.3 | 16.7 | 2.3 | 1.8 | 0.2 | 15.7 | 1.0 | 16.8 | 29.0 | 19.9 | 14.7 | 11.4 |
| 2-Methyl-butanal | 20.8 | 1.2 | 48.1 | 16.3 | 29.8 | 19.5 | 14.4 | 4.3 | 0.7 | 7.6 | 1.7 | 16.7 | 68.5 | 6.3 | 52.0 | 17.9 |
| 3-Methyl-butanal | 12.6 | 1.8 | 27.4 | 18.9 | 13.6 | 15.4 | 11.7 | 2.0 | 1.3 | 3.5 | 3.0 | 6.8 | 26.6 | 2.6 | 18.1 | 6.3 |
| Pentanal | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 10.9 | 17.3 |
| Hexanal | 3.1 | 9.0 | 2.5 | 1.4 | 2.4 | 12.5 | 3.3 | 1.5 | n.d. | | n.d. | | 1.7 | 3.1 | 5.7 | 8.7 |
| Heptanal | n.d. | | 1.5 | 8.9 | 0.4 | 9.2 | 1.0 | 4.4 | n.d. | | 0.5 | 24.6 | 1.6 | 8.3 | 3.0 | 2.3 |
| Octanal | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 0.5 | 14.7 | n.d. | | n.d. | |
| (Z)-2-Heptenal | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 0.7 | 1.9 |
| Nonanal | 1.1 | 7.8 | 1.4 | 12.0 | 6.2 | 11.9 | 5.1 | 8.5 | 0.2 | 6.2 | 0.3 | 2.5 | 1.2 | 14.8 | 0.6 | 16.0 |
| Decanal | 3.2 | 1.9 | 2.2 | 6.2 | 8.9 | 7.0 | 2.4 | 9.5 | 0.4 | 14.7 | 0.5 | 5.6 | 1.3 | 15.5 | 1.4 | 18.7 |
| Benzaldehyde | 0.8 | 12.1 | 0.8 | 9.4 | 0.6 | 15.4 | 2.1 | 4.1 | 0.4 | 10.1 | 0.4 | 4.4 | 0.9 | 14.0 | 1.2 | 5.8 |
| Benzeneacetaldehyde | 4.4 | 1.1 | 11.7 | 16.9 | 4.7 | 5.4 | 9.6 | 7.2 | 1.2 | 4.4 | 4.0 | 3.1 | 8.9 | 16.3 | 8.1 | 7.3 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TOTAL | 68.7 | | 128.1 | | 87.1 | | 57.9 | | 11.1 | | 24.3 | | 146.6 | | 121.5 | |
| **Carboxylic Acids** | | | | | | | | | | | | | | | | |
| Acetic acid | 48.9 | 19.5 | 30.5 | 5.8 | 33.5 | 11.9 | 33.3 | 2.5 | 3.4 | 8.2 | 3.6 | 11.1 | 12.0 | 20.1 | 5.7 | 15.8 |
| TOTAL | 48.9 | | 30.5 | | 33.5 | | 33.3 | | 3.4 | | 3.6 | | 12.0 | | 5.7 | |
| **Esters** | | | | | | | | | | | | | | | | |
| Ethyl acetate | 29.3 | 2.9 | 20.0 | 17.0 | 46.1 | 4.2 | 25.7 | 6.4 | 180.3 | 3.0 | 183.5 | 5.1 | 52.5 | 10.9 | 8.8 | 16.1 |
| Ethyl propanoate | 4.1 | 3.8 | 0.2 | 5.5 | 0.3 | 16.5 | 0.4 | 8.8 | 2.7 | 13.8 | 5.6 | 8.7 | 0.5 | 4.3 | n.d. | |
| Ethyl 2-Methyl-Propanoate | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 0.6 | 5.7 | n.d. | | n.d. | |
| 2-Methylpropyl acetat | 2.7 | 4.8 | n.d. | | 0.3 | 11.5 | 0.4 | 9.5 | 2.1 | 9.5 | 3.2 | 2.6 | 0.8 | 8.2 | n.d. | |
| Ethyl butanoate | n.d. | | n.d. | | n.d. | | n.d. | | 0.6 | 6.9 | 1.2 | 2.9 | n.d. | | n.d. | |
| Hexyl acetat | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 0.4 | 14.2 | n.d. | | n.d. | |
| Phenylmethyl acetate | 3.9 | 0.9 | 0.8 | 17.6 | 0.5 | 12.0 | 8.7 | 2.7 | 25.9 | 3.8 | 7.3 | 1.3 | n.d. | | n.d. | |
| 2-Phenylethyl acetate | 30.9 | 1.4 | 9.5 | 0.8 | 8.1 | 6.4 | 60.6 | 0.4 | 158.4 | 19.8 | 123.1 | 3.6 | 3.0 | 15.8 | 2.0 | 3.1 |
| Triacetin | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 32.4 | 19.2 | n.d. | |
| TOTAL | 334.7 | | 30.5 | | 55.4 | | 95.8 | | 369.9 | | 324.7 | | 89.2 | | 10.8 | |
| **Furans** | | | | | | | | | | | | | | | | |
| Furan | 0.4 | 9.7 | 0.8 | 8.1 | 0.4 | 3.0 | 0.3 | 9.4 | 0.1 | 5.9 | 0.1 | 7.0 | 0.3 | 5.3 | 1.5 | 19.0 |
| 2-Methyl-furan | 0.7 | 17.0 | 1.8 | 6.8 | 1.3 | 3.4 | 1.2 | 7.6 | 0.2 | 15.3 | 0.3 | 4.7 | 0.6 | 10.9 | 3.1 | 8.5 |
| 2.5-Dimethyl-furan | 3.0 | 18.6 | 1.5 | 3.0 | 1.8 | 15.8 | 1.3 | 6.9 | 0.7 | 0.6 | 0.7 | 9.9 | 1.0 | 11.4 | 2.6 | 11.7 |
| 2-Ethyl-5-methyl-furan | 0.7 | 23.6 | 0.2 | 4.2 | 0.3 | 1.2 | 0.3 | 18.2 | 0.3 | 5.9 | 0.3 | 1.8 | n.d. | | n.d. | |
| 5-Butyldihydro-2(3H)-furanone | 3.7 | 12.2 | 3.9 | 0.4 | 2.6 | 1.2 | 1.4 | 0.6 | 0.3 | 19.3 | 1.1 | 0.3 | 2.8 | 13.1 | 1.6 | 8.9 |
| Dihydro-2-methyl-3(2H)-furanone | 38.9 | 2.9 | 103.4 | 13.6 | 32.3 | 15.4 | 24.4 | 2.0 | 0.6 | 19.6 | 3.2 | 10.6 | 99.9 | 14.9 | 37.1 | 3.8 |
| 5-Methyl-2-furanmethanethiol | 57.0 | 3.5 | 0.9 | 4.2 | 1.0 | 17.9 | 5.1 | 2.9 | 31.6 | 0.3 | 32.6 | 4.3 | 5.4 | 20.0 | 1.2 | 18.0 |
| Furfural | 9.2 | 7.9 | 6.6 | 9.5 | 7.7 | 2.9 | 1.2 | 6.7 | 0.3 | 19.0 | 0.4 | 3.5 | 22.6 | 19.6 | 2.5 | 15.4 |
| 1-(2-Furanyl)-ethanone | 16.0 | 7.0 | 11.8 | 7.6 | 12.3 | 12.9 | 8.9 | 18.5 | 3.6 | 8.7 | 5.5 | 7.9 | 102.1 | 19.0 | 17.8 | 12.3 |
| Acetate 2-furanmethanol | 0.6 | 7.4 | 0.4 | 11.6 | 0.5 | 6.9 | 0.9 | 8.5 | 0.4 | 4.0 | 1.6 | 7.1 | 0.4 | 15.6 | 0.5 | 18.5 |
| 5-Methyl-2-furancarboxaldehyde | 2.7 | 16.2 | 2.8 | 0.4 | 2.5 | 6.7 | 2.2 | 8.0 | 0.2 | 8.5 | n.d. | | 9.7 | 15.9 | 1.7 | 16.7 |
| 2-Methyl-benzofuran | 14.6 | 15.5 | 8.2 | 6.3 | 9.1 | 2.8 | 5.7 | 19.0 | 0.9 | 20.7 | 1.9 | 8.9 | 8.1 | 19.7 | 1.4 | 2.9 |
| 2-Furanmethanol | 9.0 | 3.0 | 11.3 | 10.6 | 7.1 | 5.5 | 12.3 | 4.6 | 2.4 | 0.8 | 4.2 | 5.3 | 8.3 | 13.8 | 36.5 | 17.7 |
| 5-Methyl-2-furanmethanol | 3.6 | 7.1 | 6.0 | 17.6 | 2.4 | 11.1 | 6.3 | 1.8 | n.d. | | 2.8 | 0.1 | 2.2 | 15.6 | 11.3 | 9.0 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,2'-Methylenebis[5-methyl-furan | 1.3 | 13.4 | 1.5 | 7.8 | 1.2 | 11.8 | 1.2 | 3.7 | 0.1 | 17.8 | 0.3 | 0.3 | n.d. | | n.d. | |
| 5-(Hydroxymethyl)-2-furfural | 1.7 | 6.3 | 0.6 | 15.2 | 1.6 | 6.5 | 1.7 | 13.3 | n.d. | | n.d. | | 34.1 | 19.6 | n.d. | |
| TOTAL | 162.9 | | 162.0 | | 84.0 | | 74.2 | | 41.7 | | 55.0 | | 297.6 | | 118.9 | |
| **Ketones** | | | | | | | | | | | | | | | | |
| 2-Butanone | n.d. | | 4.2 | 11.6 | 3.6 | 14.9 | 2.6 | 9.2 | n.d. | | n.d. | | 2.8 | 10.6 | 2.4 | 12.5 |
| 2,3-Butanedione | 3.2 | 0.8 | 5.7 | 3.5 | 2.3 | 1.5 | 8.9 | 6.0 | 1.6 | 1.1 | 2.3 | 3.8 | 2.4 | 11.7 | 6.9 | 1.5 |
| 2,3-Pentanedione | 1.2 | 4.6 | 2.5 | 10.6 | 1.1 | 2.4 | 1.2 | 4.4 | n.d. | | n.d. | | 1.7 | 0.2 | 1.8 | 1.6 |
| 3-Methyl-cyclopentanone | 0.6 | 6.0 | n.d. | | n.d. | | n.d. | | 0.3 | 1.8 | 0.9 | 5.3 | n.d. | | n.d. | |
| 1-Hydroxy-2-propanone | 14.5 | 15.2 | 10.0 | 15.6 | 14.4 | 14.4 | 4.8 | 0.1 | n.d. | | n.d. | | 20.7 | 10.2 | 10.3 | 18.0 |
| 2,3-Octanedione | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 1.0 | 0.0 |
| 2-Methyl-2-cyclopenten-1-one | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 0.9 | 11.5 | 0.7 | 7.1 |
| 1-(2-Methyl-1-cyclopenten-1-yl)-ethanone | 0.7 | 16.5 | 1.9 | 19.9 | 0.5 | 11.9 | 1.1 | 5.8 | n.d. | | n.d. | | n.d. | | n.d. | |
| 2,5,5-Trimethyl-1-cyclopenten-1-one | 0.9 | 3.2 | 1.5 | 17.1 | 1.3 | 15.8 | 1.4 | 9.2 | 0.3 | 15.0 | 0.6 | 1.0 | n.d. | | 2.4 | 7.3 |
| 1-(1H-Pyrrol-2-yl)-ethanone | 14.8 | 15.6 | 15.2 | 6.7 | 11.7 | 17.3 | 18.9 | 0.6 | 2.7 | 14.5 | 6.2 | 5.9 | 21.5 | 16.8 | 11.4 | 6.5 |
| Benzophenone | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 1.1 | 12.2 | n.d. | | n.d. | |
| TOTAL | 35.9 | | 41.1 | | 34.9 | | 38.9 | | 4.8 | | 11.0 | | 50.0 | | 36.9 | |
| **Nitrogen Compounds** | | | | | | | | | | | | | | | | |
| 3,4,5-Trimethylpyrazole | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 0.2 | 11.1 | n.d. | | n.d. | |
| 1-Methyl-2-pyrrolidinone | 1.0 | 16.2 | 0.9 | 0.6 | 0.4 | 10.1 | 0.5 | 14.5 | n.d. | | 0.3 | 4.5 | 0.7 | 2.1 | n.d. | |
| 3-Methyl-pyridazine | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 0.5 | 2.0 | 0.8 | 16.2 | 2.6 | 14.3 |
| 4,6-Dimethyl-pyrimidine | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 1.7 | 11.4 | 3.7 | 12.1 |
| 2,6-Dimethyl-pyrazine | 8.9 | 5.2 | 17.6 | 2.3 | 9.1 | 0.9 | 9.0 | 3.8 | 2.7 | 1.2 | 2.2 | 9.0 | 13.8 | 15.5 | 22.3 | 5.5 |
| 2-Ethyl-6-methyl-pyrazine | 1.2 | 3.6 | 1.7 | 3.5 | 1.3 | 17.0 | 1.2 | 5.2 | 0.4 | 13.6 | n.d. | | 1.7 | 10.5 | 3.4 | 2.1 |
| Trimethyl-pyrazine | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 0.6 | 7.7 |
| TOTAL | 11.2 | | 20.2 | | 10.7 | | 10.7 | | 3.1 | | 3.2 | | 18.7 | | 32.6 | |
| **Phenols** | | | | | | | | | | | | | | | | |
| 4-Methoxy-phenol | 0.8 | 12.8 | 0.9 | 10.5 | 0.8 | 18.3 | 0.7 | 18.1 | 0.3 | 1.6 | 0.5 | 0.2 | 2.3 | 13.2 | 1.5 | 0.4 |
| Phenol | 0.7 | 6.8 | 0.9 | 13.4 | 0.5 | 14.1 | 0.7 | 6.7 | 0.1 | 17.2 | 0.3 | 4.1 | 0.8 | 5.0 | 1.0 | 12.6 |
| 2,4-Bis(1,1-dimethylethyl)-phenol | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 0.4 | 0.4 | n.d. | | n.d. | |
| TOTAL | 1.5 | | 1.8 | | 1.3 | | 1.4 | | 0.4 | | 1.2 | | 3.1 | | 2.5 | |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sulfur Compounds** | | | | | | | | | | | | | | | | |
| Dimethyl sulfide | 2.45 | 13.1 | 5.1 | 6.5 | 3.7 | 9.0 | 0.6 | 12.3 | 0.3 | 10.9 | 0.3 | 11.1 | 1.7 | 1.0 | 39.0 | 10.2 |
| Dimethyl disulfide | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 2.3 | 19.0 | n.d. | |
| TOTAL | 2.45 | | 5.1 | | 3.7 | | 0.6 | | 0.3 | | 0.3 | | 4.0 | | 39.0 | |
| **Terpenoids** | | | | | | | | | | | | | | | | |
| D-Limonene | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 10.9 | 0.5 | n.d. | | n.d. | |
| Eucalyptol | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 0.7 | 1.3 | n.d. | | n.d. | |
| 1-Methyl-4-(1-Methylethyl)-1,4-Cyclohexadiene | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 0.7 | 7.3 | n.d. | | n.d. | |
| 1-Methyl-4-(1-Methylethyl)-Benzene | 9.7 | 6.4 | 4.7 | 4.8 | n.d. | | n.d. | | 1.3 | 9.8 | n.d. | | n.d. | | n.d. | |
| 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | 1.2 | 2.1 | 1.2 | 12.1 | 0.5 | 8.1 | 0.6 | 2.9 | 0.1 | 15.8 | 0.4 | 4.1 | 0.3 | 5.2 | 0.6 | 7.8 |
| 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | n.d. | | n.d. | | n.d. | | n.d. | | 0.2 | 9.7 | 0.3 | 2.8 | n.d. | | n.d. | |
| 1-Methyl-4-(1-Methylethylidene)-Cyclohexene | n.d. | | n.d. | | n.d. | | n.d. | | 0.4 | 17.6 | n.d. | | n.d. | | n.d. | |
| 2,3,3-Trimethyl-1,4-Pentadiene | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 1.1 | 5.2 | n.d. | | n.d. | |
| 4-Methyl-1-(1-Methylethyl)-3-Cyclohexen-1-ol | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 0.7 | 1.4 | n.d. | | n.d. | |
| α, α-4-Trimethyl-3-Cyclohexene-1-Methanol | n.d. | | n.d. | | n.d. | | n.d. | | n.d. | | 0.8 | 2.7 | n.d. | | n.d. | |
| TOTAL | 10.9 | | 5.9 | | 0.5 | | 0.6 | | 2.0 | | 15.6 | | 0.3 | | 0.6 | |

n.d. - not detected.

**Table S6. The fragment ion m/z values with the highest abundance within each fragmentation pattern, identification mode, highest abundance match according the NIST database, peak area range (minimum, maximum and mean values) and occurrence frequency percentage of identified VOCs in SCH samples from certified producer and non-certified producers**.

| RT (min)[a] | Identified VOCs | ID[b] | *m/z* | MP[c] (%) | Certified | | | | Non-Certified | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Min x 10 | Max x 10 | Mean x 10 | FO (%)[d] | Min x 10 | Max x 10 | Mean x 10 | FO (%)[d] |
| 4.64 | Acetaldehyde | MS | 29; 44; 43 | 88 | 5.9 | 15.7 | 10.0 | 100 | 5.0 | 12.5 | 7.8 | 100 |
| 4.96 | Dimethyl sulfide | MS | 47; 62; 45 | 95 | 0.6 | 5.1 | 3.0 | 100 | 0.3 | 39.0 | 10.3 | 100 |
| 5.49 | Furan | MS | 68; 39; 38 | 87 | 0.3 | 0.8 | 0.5 | 100 | n.d. | 1.5 | 0.5 | 100 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 5.68 | 2-Methyl-propanal | MS | 43; 41; 72 | 86 | 2.3 | 22.2 | 10.9 | 100 | 0.2 | 29.0 | 11.2 | 100 |
| 6.79 | 2-Methyl-furan | MS | 82; 53; 81 | 87 | 0.7 | 1.8 | 1.3 | 100 | 0.2 | 3.1 | 1.0 | 100 |
| 6.99 | Ethyl acetate | MS | 43; 61; 45 | 91 | 20.0 | 293.0 | 96.2 | 100 | 8.8 | 183.5 | 106.2 | 100 |
| 7.46 | 2-Butanone | St, MS | 43; 72; 29 | 80 | 2.6 | 4.2 | 3.5 | 75 | 2.4 | 2.8 | 2.6 | 50 |
| 7.82 | 2-Methyl-butanal | MS | 57; 29; 41 | 91 | 14.4 | 48.1 | 28.3 | 100 | 0.7 | 68.5 | 30.7 | 100 |
| 7.97 | 3-Methyl-butanal | MS | 44; 41; 43 | 87 | 11.7 | 27.4 | 16.3 | 100 | 1.3 | 26.6 | 12.3 | 100 |
| 8.58 | Ethyl Alcohol | St, MS | 31; 45; 46 | 90 | 118.0 | 2651.3 | 801.2 | 100 | 83.6 | 881.7 | 412.3 | 100 |
| 9.30 | 2,5-Dimethyl-furan | MS | 96; 95; 43 | 86 | 1.3 | 3.0 | 1.9 | 100 | 0.7 | 2.6 | 1.3 | 100 |
| 9.49 | Ethyl propanoate | MS | 29; 57; 27 | 83 | 0.2 | 4.1 | 1.3 | 100 | 0.5 | 5.6 | 2.9 | 75 |
| 9.75 | Ethyl 2-methyl-propanoate | MS | 43; 71; 41 | 80 | n.d. | n.d. | n.d. |  | 0.6 | 0.6 | 0.6 | 25 |
| 10.26 | Pentanal | MS | 44; 29; 41; | 90 | n.d. | n.d. | n.d. |  | 10.9 | 10.9 | 10.9 | 25 |
| 10.58 | 2,3-Butanedione | St, MS | 43; 86; 42 | 79 | 2.3 | 8.9 | 5.0 | 100 | 1.6 | 6.9 | 3.3 | 100 |
| 12.39 | 2-Methylpropyl acetate | MS | 43; 56; 73 | 82 | 0.3 | 2.7 | 1.2 | 75 | 0.8 | 3.2 | 2.0 | 75 |
| 13.58 | 2-Ethyl-5-methyl-furan | MS | 95; 110; 43 | 80 | 0.2 | 0.7 | 0.4 | 100 | 0.3 | 0.3 | 0.3 | 50 |
| 14.01 | Ethyl butanoate | MS | 71; 43; 29 | 96 | n.d. | n.d. | n.d. |  | 0.6 | 1.2 | 0.9 | 50 |
| 14.03 | 1-Propanol | MS | 31; 59; 42 | 80 | n.d. | n.d. | n.d. |  | 1.0 | 1.0 | 1.0 | 25 |
| 14.36 | 2-Methyl-3-buten-2-ol | MS | 71; 43; 59 | 73 | 0.2 | 1.0 | 0.5 | 100 | 1.0 | 1.6 | 1.3 | 50 |
| 15.31 | 3,4,5-Trimethylpyrazole | MS | 109; 110; 95 | 80 | n.d. | n.d. | n.d. |  | 0.2 | 0.2 | 0.2 | 25 |
| 16.14 | 2,3-Pentanedione | MS | 43; 29; 57 | 70 | 1.1 | 2.5 | 1.5 | 100 | 1.7 | 1.8 | 1.7 | 50 |
| 16.46 | 1-Methyl-2-pyrrolidinone | MS | 99; 44; 98 | 78 | 0.4 | 1.0 | 0.7 | 100 | 0.3 | 0.7 | 0.5 | 50 |
| 16.50 | Dimethyl disulfide | MS | 94; 79; 45 | 95 | n.d. | n.d. | n.d. |  | 2.3 | 2.3 | 2.3 | 25 |
| 17.05 | Hexanal | St, MS | 44; 56; 41 | 90 | 2.4 | 3.3 | 2.8 | 100 | 1.7 | 5.7 | 3.7 | 50 |
| 22.24 | 2-Methyl-1-propanol | St, MS | 43; 42; 41 | 81 | 4.7 | 37.4 | 19.9 | 100 | 2.3 | 30.5 | 14.1 | 100 |
| 22.66 | 5-Butyldihydro-2(3H)-furanone | MS | 85; 29; 56 | 82 | 1.4 | 3.9 | 2.9 | 100 | 0.3 | 2.8 | 1.5 | 100 |
| 25.21 | Tetrahydro-2H-pyran-2-ol | MS | 85; 41; 55 | 74 | 0.6 | 1.8 | 1.3 | 100 | 0.2 | 1.1 | 0.7 | 100 |
| 27.76 | 1-Butanol | MS | 56; 31; 41 | 78 | n.d. | n.d. | n.d. |  | 0.4 | 0.7 | 0.6 | 50 |
| 28.22 | 3-Methyl-pyridazine | MS | 94; 39; 40 | 72 | n.d. | n.d. | n.d. |  | 0.5 | 2.6 | 1.3 | 75 |
| 29.26 | Heptanal | MS | 44; 43; 41 | 82 | 0.4 | 1.5 | 1.0 | 75 | 0.5 | 3.0 | 1.7 | 75 |
| 29.43 | D-Limonene | MS | 68; 93; 67 | 95 | n.d. | n.d. | n.d. |  | 10.9 | 10.9 | 10.9 | 25 |
| 3n.d.7 | Eucalyptol | MS | 43; 81; 71 | 98 | n.d. | n.d. | n.d. |  | 0.7 | 0.7 | 0.7 | 25 |
| 31.07 | 3-Methyl-cyclopentanone | MS | 69; 55; 98 | 90 | 0.6 | 0.6 | 0.6 | 25 | 0.3 | 0.9 | 0.6 | 50 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 31.82 | 2-Methyl-1-butanol | St, MS | 57; 41; 56 | 90 | 15.2 | 47.7 | 27.4 | 100 | 10.4 | 48.0 | 26.2 | 100 |
| 32.96 | 3-Methyl-1-butanol | MS | 55; 42; 43 | 82 | 11.0 | 40.6 | 20.9 | 100 | 31.0 | 31.0 | 31.0 | 25 |
| 33.67 | 1-Methyl-4-(1-methylethyl)-1,4-cyclohexadiene | MS | 93; 91; 77 | 90 | n.d. | n.d. | n.d. | | 0.7 | 0.7 | 0.7 | 25 |
| 34.44 | 1-Methyl-4-(1-methylethyl)-benzene | MS | 119; 134; 91 | 95 | 4.7 | 9.7 | 7.2 | 50 | 1.3 | 1.3 | 1.3 | 25 |
| 34.51 | 5-Methyl-5-nonanol | MS | 101; 55; 45 | 74 | 0.5 | 0.5 | 0.5 | 25 | 1.6 | 2.5 | 2.0 | 50 |
| 35.97 | Dihydro-2-methyl-3(2H)-furanone | MS | 43; 72. 100 | 82 | 24.4 | 103.5 | 49.8 | 100 | 0.6 | 99.9 | 35.2 | 100 |
| 36.59 | Hexyl acetate | MS | 43; 56; 55 | 75 | n.d. | n.d. | n.d. | | 0.4 | 0.4 | 0.4 | 25 |
| 37.61 | Octanal | MS | 43; 44; 41 | 82 | n.d. | n.d. | n.d. | | 0.5 | 0.5 | 0.5 | 25 |
| 38.67 | 1-Hydroxy-2-propanone | MS | 43; 31; 74 | 80 | 4.8 | 14.5 | 10.9 | 100 | 10.3 | 20.7 | 15.5 | 50 |
| 39.28 | (Z)-2-Heptenal | MS | 41; 27; 55; | 87 | n.d. | n.d. | n.d. | | 0.7 | 0.7 | 0.7 | 25 |
| 39.40 | 2,3-Octanedione | MS | 43; 71; 99 | 75 | n.d. | n.d. | n.d. | | 1.0 | 1.0 | 1.0 | 25 |
| 39.65 | 4,6-Dimethyl-pyrimidine | MS | 108; 42; 39 | 72 | n.d. | n.d. | n.d. | | 1.7 | 3.7 | 2.7 | 50 |
| 40.17 | 2,6-Dimethyl-pyrazine | MS | 108; 42; 40 | 90 | 8.9 | 17.6 | 11.2 | 100 | 2.2 | 22.3 | 10.2 | 100 |
| 41.42 | 3-Methyl-cyclopentanol | MS | 57; 71; 41 | 77 | n.d. | n.d. | n.d. | | 0.4 | 0.5 | 0.5 | 50 |
| 41.93 | 1-Hexanol | MS | 56; 43; 55 | 80 | 1.2 | 1.2 | 1.2 | 25 | n.d. | n.d. | n.d. | |
| 42.42 | 2-Methyl-2-cyclopenten-1-one | MS | 67; 96; 53 | 87 | n.d. | n.d. | n.d. | | 0.7 | 0.9 | 0.8 | 50 |
| 42.48 | 5-Methyl-2-furanmethanethiol | MS | 95; 43; 96 | 84 | 0.9 | 57.0 | 16.0 | 100 | 1.2 | 32.6 | 17.7 | 100 |
| 43.58 | 2-Ethyl-6-methyl-pyrazine | MS | 121; 122; 39 | 86 | 1.2 | 1.7 | 1.3 | 100 | 0.4 | 3.4 | 1.8 | 75 |
| 43.29 | Nonanal | MS | 57; 41; 43 | 96 | 1.1 | 6.2 | 3.4 | 100 | 0.2 | 1.2 | 0.6 | 100 |
| 44.55 | Trimethyl-Pyrazine | MS | 42; 122; 81 | 78 | n.d. | n.d. | n.d. | | 0.6 | 0.6 | 0.6 | 25 |
| 46.65 | 1,2,3,4-Tetrahydro-1,1,6-trimethyl-naphthalene | MS | 159; 174; 146 | 93 | 0.5 | 1.2 | 0.9 | 100 | 0.1 | 0.6 | 0.4 | 100 |
| 47.74 | Acetic acid | MS | 43; 45; 60 | 90 | 30.5 | 48.9 | 36.5 | 100 | 3.4 | 12.0 | 6.2 | 100 |
| 48.17 | Furfural | St, MS | 96; 95; 39 | 92 | 1.2 | 9.2 | 6.2 | 100 | 0.3 | 22.6 | 6.5 | 100 |
| 48.33 | 1,2,3,4-Tetrahydro-1,5,8-trimethyl-naphthalene | MS | 159; 174; 129 | 88 | n.d. | n.d. | n.d. | | 0.2 | 0.3 | 0.2 | 50 |
| 49.81 | Decanal | St, MS | 43; 41; 57 | 96 | 2.2 | 8.9 | 4.2 | 100 | 0.4 | 1.4 | 0.9 | 100 |
| 5n.d.5 | 1-(2-Furanyl)-ethanone | St, MS | 95; 110; 39 | 90 | 8.9 | 16.0 | 12.2 | 100 | 3.6 | 102.1 | 32.2 | 100 |
| 50.83 | Benzaldehyde | St, MS | 106; 105; 77 | 96 | 0.6 | 2.1 | 1.1 | 100 | 0.4 | 1.2 | 0.7 | 100 |
| 51.55 | 2-Furanmethanol acetate | MS | 81; 98; 43 | 84 | 0.4 | 0.9 | 0.6 | 100 | 0.4 | 1.6 | 0.7 | 100 |
| 52.40 | 1-Octanol | MS | 56; 55; 41 | 78 | n.d. | n.d. | n.d. | | 0.4 | 0.4 | 0.4 | 25 |
| 53.22 | 5-Methyl-2-furancarboxaldehyde | MS | 110; 109; 53 | 92 | 2.2 | 2.8 | 2.5 | 100 | 0.2 | 9.7 | 3.9 | 75 |
| 53.25 | 1-Methyl-4-(1-methylethylidene)-cyclohexene | MS | 93; 121; 136 | 89 | n.d. | n.d. | n.d. | | 0.4 | 0.4 | 0.4 | 25 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 53.37 | 2,3,3-Trimethyl-1,4-pentadiene | MS | 95; 41; 67 | 73 | n.d. | n.d. | n.d. | | 1.1 | 1.1 | 1.1 | 25 |
| 53.53 | 1-(2-Methyl-1-cyclopenten-1-yl)-ethanone | MS | 109; 43; 81 | 75 | 0.5 | 1.9 | 1.1 | 100 | n.d. | n.d. | n.d. | |
| 54.08 | 2-Methyl-benzofuran | MS | 131; 132; 103 | 95 | 5.7 | 14.6 | 9.4 | 100 | 0.9 | 8.1 | 3.1 | 100 |
| 54.38 | 4-Methyl-1-(1-methylethyl)-3-cyclohexen-1-ol | MS | 71; 43; 93 | 78 | n.d. | n.d. | n.d. | | 0.7 | 0.7 | 0.7 | 25 |
| 54.54 | 2,5,5-Trimethyl-1-cyclopenten-1-one | MS | 109; 124; 81 | 74 | 0.9 | 1.5 | 1.3 | 100 | 0.3 | 2.4 | 1.1 | 75 |
| 56.52 | Benzeneacetaldehyde | MS | 91; 92; 120 | 82 | 4.4 | 11.7 | 7.6 | 100 | 1.2 | 8.9 | 5.5 | 100 |
| 56.81 | 1-Decene | MS | 55; 41; 56 | 78 | 0.5 | 2.1 | 1.3 | 50 | n.d. | n.d. | n.d. | |
| 57.34 | 2-Furanmethanol | St, MS | 98; 41; 81 | 97 | 7.1 | 12.3 | 9.9 | 100 | 2.4 | 36.5 | 12.9 | 100 |
| 58.76 | α,α-4-trimethyl-3-cyclohexene-1-methanol | MS | 59; 93; 121 | 96 | n.d. | n.d. | n.d. | | 0.8 | 0.8 | 0.8 | 25 |
| 6n.d.3 | 5-Methyl-2-furanmethanol | MS | 95; 112; 43 | 96 | 2.4 | 6.3 | 4.6 | 100 | 2.2 | 11.3 | 5.4 | 75 |
| 60.32 | Phenylmethyl acetate | MS | 108; 91; 90 | 96 | 0.5 | 8.7 | 3.5 | 100 | 7.3 | 25.9 | 16.6 | 50 |
| 61.29 | 2.2'-Methylenebis[5-methyl-furan | MS | 176; 43; 161 | 93 | 1.2 | 1.5 | 1.3 | 100 | 0.1 | 0.3 | 0.2 | 50 |
| 63.89 | 2-Phenylethyl acetate | MS | 104; 43; 91 | 83 | 8.1 | 60.6 | 27.3 | 100 | 2.0 | 158.4 | 71.6 | 100 |
| 65.96 | 4-Methoxy-phenol | MS | 109; 124; 81 | 82 | 0.7 | 0.9 | 0.8 | 100 | 0.3 | 2.3 | 1.1 | 100 |
| 66.26 | Benzyl alcohol | MS | 79; 108; 77 | 97 | 0.5 | 4.6 | 2.4 | 100 | 2.6 | 10.2 | 6.4 | 50 |
| 68.58 | Phenylethyl alcohol | MS | 91; 92; 122 | 80 | 2.0 | 2.0 | 2.0 | 25 | 1.9 | 6.1 | 4.0 | 50 |
| 69.79 | 1-(1H-Pyrrol-2-yl)-ethanone | MS | 94; 109; 66 | 95 | 11.7 | 18.9 | 15.2 | 100 | 2.7 | 21.5 | 10.4 | 100 |
| 71.09 | Phenol | MS | 94; 66; 65 | 88 | 0.5 | 0.9 | 0.7 | 100 | 0.1 | 1.0 | 0.6 | 100 |
| 73.27 | Triacetin | MS | 43; 103; 145 | 90 | n.d. | n.d. | n.d. | | 32.4 | 32.4 | 32.4 | 25 |
| 80.64 | 2,4-Bis(1,1-dimethylethyl)-phenol | MS | 191; 57; 206 | 75 | n.d. | n.d. | n.d. | | 0.4 | 0.4 | 0.4 | 25 |
| 85.84 | Benzophenone | MS | 105; 77; 182 | 80 | n.d. | n.d. | n.d. | | 1.1 | 1.1 | 1.1 | 25 |
| 86.33 | 5-(Hydroxymethyl)-2-furancarboxaldehyde | St,MS | 97; 126; 41 | 95 | 0.6 | 1.7 | 1.4 | 100 | 34.1 | 34.1 | 34.1 | 25 |

[a] retention time (RT) in ion chromatograms obtained by GC-MS.
[b] metabolite identification (ID) using standard compound (St) or mass spectra of the NIST database (MS).
[c] match percentage (MP) of compound obtained by the NIST database.
[d] occurrence frequency percentage (FO) of compound in each sample group.
[x 10] relative peak area values are multiplied by 10.
n.d. - not detected.

**Table S7. Potential markers of authenticity and typicity identified in volatomic profile of SCH samples from certified producer and non-certified producers.**

| **RT (min)[a]** | **Identified VOCs** | **Mean Values [x 10]** | | | ***One-way Significance*** | |
|---|---|---|---|---|---|---|
| | | **Certified** | **Non-Certified** | **%Change[b]** | **Z** | ***p (α< 0.05)*** |
| 14.01 | Ethyl ester butanoic acid | n.d. | 0.9 | | 5.7 | 0.032 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 16.46 | 1-Methyl-2-pyrrolidinone | 0.7 | 0.5 | -30.8 | 9.9 | 0.007 |
| 22.66 | 5-Butyldihydro-2(3H)-furanone | 2.9 | 1.5 | -48.6 | 7.4 | 0.016 |
| 25.21 | Tetrahydro-2H-pyran-2-ol | 1.3 | 0.7 | -44.1 | 5.7 | 0.031 |
| 27.76 | 1-Butanol | n.d. | 0.6 | | 6.4 | 0.024 |
| 28.22 | 3-Methyl-pyridazine | n.d. | 1.3 | | 6.9 | 0.020 |
| 34.44 | 1-Methyl-4-(1-methylethyl)-benzene | 7.2 | 1.3 | -81.9 | 4.6 | 0.049 |
| 39.65 | 4.6-Dimethyl-pyrimidine | n.d. | 2.7 | | 5.5 | 0.035 |
| 41.42 | 3-Methyl-cyclopentanol | n.d. | 0.5 | | 6.6 | 0.022 |
| 42.42 | 2-Methyl-2-cyclopenten-1-one | n.d. | 0.8 | | 6.8 | 0.021 |
| 43.29 | Nonanal | 3.4 | 0.6 | -83.2 | 11.0 | 0.005 |
| 46.65 | 1,2,3,4-Tetrahydro-1,1,6-trimethyl-naphthalene | 0.9 | 0.4 | -58.4 | 13.4 | 0.003 |
| 47.74 | Acetic acid | 36.5 | 6.2 | -83.1 | 81.8 | 0.000 |
| 48.33 | 1,2,3,4-Tetrahydro-1,5,8-trimethyl-naphthalene | n.d. | 0.2 | | 5.6 | 0.033 |
| 49.81 | Decanal | 4.2 | 0.9 | -78.5 | 9.5 | 0.008 |
| 53.53 | 1-(2-Methyl-1-cyclopenten-1-yl)-ethanone | 1.1 | n.d. | | 24.9 | 0.000 |
| 54.08 | 2-Methyl-benzofuran | 9.4 | 3.1 | -67.3 | 13.8 | 0.002 |
| 61.29 | 2,2'-Methylenebis[5-methyl-furan] | 1.3 | 0.2 | -82.0 | 241.5 | 0.000 |

[a] retention time (RT) in ion chromatograms obtained by GC-MS.
[b] percentage change of certified production from others types production, calculated from the arithmetic mean values of each group, positive and negative percentages indicate higher levels of volatile compound in samples from certified producer and others producers, respectively.
[x 10] relative peak area values are multiplied by 10.
n.d. - not detected.

**Table S8. ID replicate number, ID replicate code, ID sample code, ID variety code, variety empirical name, harvest year and geographical area of SC samples.**

| ID Replicate Number | ID Replicate Code | ID Sample Code | ID Variety Code | Variety Empirical Name | Harvest Year | Geographical Area |
|---|---|---|---|---|---|---|
| 1 | AMA15A | | | | | |
| 2 | AMA15B | AMA15 | | | 2015 | |
| 3 | AMA15C | | | | | |
| 4 | AMA17A | | AMA | *"Amarela"* | | Ribeira Brava, Madeira Island (Portugal) |
| 5 | AMA17B | AMA17 | | | 2017 | |
| 6 | AMA17C | | | | | |
| 7 | RAD15A | RAD15 | RAD | *"Radiada"* | 2015 | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 8 | RAD15B | | | | | |
| 9 | RAD15C | | | | | Ribeira Brava, Madeira Island (Portugal) |
| 10 | RAD17A | | | | | |
| 11 | RAD17B | RAD17 | | | 2017 | |
| 12 | RAD17C | | | | | |
| 13 | ROX15A | | | | | |
| 14 | ROX15B | ROX15 | | | 2015 | |
| 15 | ROX15C | | ROX | *"Roxa"* | | Ribeira Brava, Madeira Island (Portugal) |
| 16 | ROX17A | | | | | |
| 17 | ROX17B | ROX17 | | | 2017 | |
| 18 | ROX17C | | | | | |
| 19 | VER15A | | | | | |
| 20 | VER15B | VER15 | | | 2015 | |
| 21 | VER15C | | VER | *"Verde"* | | Ribeira Brava, Madeira Island (Portugal) |
| 22 | VER17A | | | | | |
| 23 | VER17B | VER17 | | | 2017 | |
| 24 | VER17C | | | | | |
| 25 | VIO15A | | | | | |
| 26 | VIO15B | VIO15 | | | 2015 | |
| 27 | VIO15C | | VIO | *"Violeta"* | | Ribeira Brava, Madeira Island (Portugal) |
| 28 | VIO17A | | | | | |
| 29 | VIO17B | VIO17 | | | 2017 | |
| 30 | VIO17C | | | | | |
| 31 | CAN15A | | | | | |
| 32 | CAN15B | CAN15 | | | 2015 | |
| 33 | CAN15C | | CAN | *"Canica"* | | Machico, Madeira Island (Portugal) |
| 34 | CAN17A | | | | | |
| 35 | CAN17B | CAN17 | | | 2017 | |
| 36 | CAN17C | | | | | |

**Table S9. ID number, retention time, main ions (m/z), target ion, match percent, identification type, IUPAC name, NIST database, abbreviation, CAS number, molecular formula and main chemical class of identified VOCs in SC samples.**

| ID Number | RT (min)[1] | m/z | TI[2] | MP[3] (%) | ID Type[4] | IUPAC Name | NIST Database Name | Abbreviation | CAS Number | Molecular Formula | Main Chemical Class |
|---|---|---|---|---|---|---|---|---|---|---|---|

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.634 | 43; 42; 41 | 43 | 87 | RS; MS | pentane | Pentane | PTANE | 109-66-0 | C5H12 | Hydrocarbon |
| 2 | 4.751 | 42; 55; 70 | 42 | 84 | MS | pent-1-ene | 1-Pentene | PT1ENE | 109-67-1 | C5H10 | Hydrocarbon |
| 3 | 4.786 | 43; 42; 41 | 43 | 90 | MS | 2-methylpentane | 2-Methyl-Pentane | M2PTANE | 107-83-5 | C6H14 | Hydrocarbon |
| 4 | 4.938 | 57; 41; 56 | 57 | 83 | RS; MS | hexane | Hexane | HXANE | 110-54-3 | C6H14 | Hydrocarbon |
| 5 | 5.046 | 59; 45; 74 | 59 | 90 | RS; MS | ethoxyethane | Ethyl Ether | EETHR | 60-29-7 | C4H10O | Ether |
| 6 | 5.007 | 69; 41; 84 | 69 | 82 | MS | (Z)-4-methylpent-2-ene | cis-4-Methyl-2-Pentene | CM4PT2ENE | 691-38-3 | C6H12 | Hydrocarbon |
| 7 | 5.179 | 67; 68; 53 | 67 | 87 | MS | (3Z)-penta-1,3-diene | cis-Piperylene | CPIPERLNE | 1574-41-0 | C5H8 | Hydrocarbon |
| 8 | 5.196 | 56; 41; 55 | 56 | 91 | MS | 2-methylpent-1-ene | 2-Methyl-1-Pentene | M2PT1ENE | 763-29-1 | C6H12 | Hydrocarbon |
| 9 | 5.306 | 41;69; 84 | 41 | 80 | MS | (Z)-3-methylpent-2-ene | cis-3-Methyl-2-Pentene | CM3PT2ENE | 922-62-3 | C6H12 | Hydrocarbon |
| 10 | 5.352 | 43; 71; 57 | 71 | 79 | MS | 3-methylhexane | 3-Methyl-Hexane | M3HXANE | 589-34-4 | C7H16 | Hydrocarbon |
| 11 | 5.392 | 67; 68; 53 | 67 | 91 | MS | penta-1,4-diene | 1,4-Pentadiene | PT14DIENE | 591-93-5 | C5H8 | Hydrocarbon |
| 12 | 5.467 | 47; 48; 45 | 47 | 84 | RS; MS | methanethiol | Methanethiol | METHIOL | 74-93-1 | CH4S | Sulfur |
| 13 | 5.526 | 67; 68; 53 | 67 | 78 | MS | (3E)-penta-1,3-diene | trans-Piperylene | TPIPERLNE | 2004-70-8 | C5H8 | Hydrocarbon |
| 14 | 5.566 | 43; 57; 71 | 57 | 90 | RS; MS | heptane | Heptane | HPTANE | 142-82-5 | C7H16 | Hydrocarbon |
| 15 | 5.641 | 59; 87; 57 | 59 | 78 | MS | 2-ethoxy-2-methylpropane | tert-Butyl Ethyl Ether | BEETHR | 637-92-3 | C6H14O | Ether |
| 16 | 5.672 | 44; 43; 42 | 42 | 80 | RS; MS | acetaldehyde | Ethanal | ETAL | 75-07-0 | C2H4O | Aldehyde |
| 17 | 6.200 | 47; 62; 45 | 47 | 90 | MS | methylsulfanylmethane | Dimethyl Sulfide | DMSULFI | 75-18-3 | C2H6S | Sulfur |
| 18 | 6.343 | 43; 71; 70 | 71 | 91 | MS | 4-methylheptane | 4-Methyl-Heptane | M4HPTANE | 589-53-7 | C8H18 | Hydrocarbon |
| 19 | 7.002 | 43; 41; 57 | 57 | 90 | RS; MS | octane | Octane | OCTANE | 111-65-9 | C8H18 | Hydrocarbon |
| 20 | 7.020 | 58; 57; 59 | 58 | 87 | RS; MS | propanal | Propanal | PPAL | 123-38-6 | C3H6O | Aldehyde |
| 21 | 7.044 | 68; 39; 40 | 68 | 91 | RS; MS | furan | Furan | FUR | 110-00-9 | C4H4O | Furan |
| 22 | 7.202 | 43; 85; 57 | 43 | 91 | MS | 2,4-dimethylheptane | 2,4-Dimethyl-Heptane | DM24HPTANE | 2213-23-2 | C9H20 | Hydrocarbon |
| 23 | 7.400 | 43; 41; 72 | 72 | 90 | MS | 2-methylpropanal | 2-Methyl-Propanal | MPPAL | 78-84-2 | C4H8O | Aldehyde |
| 24 | 7.480 | 43; 58; 39 | 58 | 77 | MS | propan-2-one | 2-Propanone | PP2ONE | 67-64-1 | C3H6O | Ketone |
| 25 | 7.865 | 43; 74; 59 | 74 | 85 | MS | methyl acetate | Methyl Ester Acetic Acid | MESTAA | 79-20-9 | C3H6O2 | Ester |
| 26 | 8.054 | 56; 41; 55 | 56 | 87 | MS | 2-methylhept-2-ene | 2-Methyl-2-Heptene | M2HPTENE | 627-97-4 | C8H16 | Hydrocarbon |
| 27 | 8.215 | 41; 70; 39 | 70 | 82 | MS | (E)-but-2-enal | Crotonal | CROTNAL | 4170-30-3 | C4H6O | Aldehyde |
| 28 | 8.431 | 43; 84; 85 | 84 | 83 | MS | 2,3-dimethylheptane | 2,3-Dimethyl-Heptane | DM23HPTANE | 3074-71-3 | C9H20 | Hydrocarbon |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 29 | 8.536 | 43; 85; 41 | 85 | 90 | MS | 4-methyloctane | 4-Methyl-Octane | M4OCTANE | 2216-34-4 | C9H20 | Hydrocarbon |
| 30 | 9.455 | 82; 53; 81 | 82 | 98 | MS | 2-methylfuran | 2-Methyl-Furan | M2FUR | 534-22-5 | C5H6O | Furan |
| 31 | 9.481 | 43; 70; 55 | 70 | 94 | MS | 2,4-dimethylhept-1-ene | 2,4-Dimethyl-1-Heptene | DM24HPT1ENE | 19549-87-2 | C9H18 | Hydrocarbon |
| 32 | 9.816 | 43; 61; 70 | 61 | 86 | RS; MS | ethyl acetate | Ethyl Ester Acetic Acid | EESTAA | 141-78-6 | C4H8O2 | Ester |
| 33 | 10.146 | 43; 57; 85 | 57 | 90 | RS; MS | nonane | Nonane | NNANE | 111-84-2 | C9H20 | Hydrocarbon |
| 34 | 10.441 | 43; 72; 57 | 72 | 80 | RS; MS | butan-2-one | 2-Butanone | BT2ONE | 78-93-3 | C4H8O | Ketone |
| 35 | 11.089 | 57; 41; 58 | 57 | 90 | MS | 2-methylbutanal | 2-Methyl-Butanal | M2BTAL | 96-17-3 | C5H10O | Aldehyde |
| 36 | 11.353 | 44; 41, 43 | 44 | 96 | MS | 3-methylbutanal | 3-Methyl-Butanal | M3BTAL | 590-86-3 | C5H10O | Aldehyde |
| 37 | 12.143 | 31; 45; 46 | 31 | 91 | RS; MS | ethanol | Ethyl Alcohol | ETOL | 64-17-5 | C2H6O | Alcohol |
| 38 | 12.684 | 78; 77; 52 | 78 | 88 | RS; MS | Benzene | Benzene | BNZ | 71-43-2 | C6H6 | Benzene |
| 39 | 13.280 | 57; 43; 41 | 57 | 85 | MS | 3-ethylheptane | 3-Ethyl-Heptane | E3HPTANE | 15869-80-4 | C9H20 | Hydrocarbon |
| 40 | 13.526 | 81; 53; 96 | 81 | 84 | MS | 2-ethylfuran | 2-Ethyl-Furan | E2FUR | 3208-16-0 | C6H8O | Furan |
| 41 | 13.837 | 57; 75; 102 | 57 | 83 | MS | ethyl propanoate | Ethyl Ester Propanoic Acid | EESTPA | 105-37-3 | C5H10O2 | Ester |
| 42 | 14.389 | 43; 71; 41 | 71 | 91 | MS | ethyl 2-methylpropanoate | 2-Methyl Ethyl Ester Propanoic Acid | M2EESTPA | 97-62-1 | C6H12O2 | Ester |
| 43 | 14.495 | 55; 84; 39 | 55 | 80 | MS | 2-methylbut-2-enal | 2-Methyl-Crotonal | M2CROTNAL | 1115-11-3 | C5H8O | Aldehyde |
| 44 | 15.112 | 43; 61; 73 | 61 | 82 | MS | propyl acetate | Propyl Ester Acetic Acid | PESTAA | 109-60-4 | C5H10O2 | Ester |
| 45 | 15.226 | 57; 86; 42 | 57 | 83 | MS | pentan-3-one | 3-Pentanone | PT3ONE | 96-22-0 | C5H10O | Ketone |
| 46 | 15.407 | 44; 41; 58 | 58 | 80 | RS; MS | pentanal | Pentanal | PTNAL | 110-62-3 | C5H10O | Aldehyde |
| 47 | 15.545 | 43; 86; 41 | 86 | 80 | MS | butane-2,3-dione | 2,3-Butanedione | BT23DONE | 431-03-8 | C4H6O2 | Ketone |
| 48 | 16.362 | 41; 71; 57 | 71 | 78 | MS | 2,3,4-trimethylhexane | 2,3,4-Trimethyl-Hexane | TM234HXANE | 921-47-1 | C9H20 | Hydrocarbon |
| 49 | 16.699 | 57; 43; 41 | 57 | 83 | RS; MS | decane | Decane | DCANE | 124-18-5 | C10H22 | Hydrocarbon |
| 50 | 16.739 | 43; 57; 71 | 57 | 84 | MS | 2,6-dimethylnonane | 2,6-Dimethyl-Nonane | DM26NNANE | 17302-28-2 | C11H24 | Hydrocarbon |
| 51 | 17.327 | 57; 43; 85 | 57 | 84 | MS | 2,5-dimethylnonane | 2,5-Dimethyl-Nonane | DM25NNANE | 17302-27-1 | C11H24 | Hydrocarbon |
| 52 | 17.778 | 43; 58; 57 | 58 | 83 | MS | 4-methylpentan-2-one | 4-Methyl-2-Pentanone | M4PT2ONE | 108-10-1 | C6H12O | Ketone |
| 53 | 18.238 | 59; 55; 73 | 59 | 86 | MS | 2-methylbutan-2-ol | 2-Methy-2-Butanol | M2BT2OL | 75-85-4 | C5H12O | Alcohol |
| 54 | 18.558 | 43; 56; 73 | 61 | 82 | MS | 2-methylpropyl acetate | 2-Methyl-Propyl Ester Acetic Acid | M2PESTAA | 110-19-0 | C6H12O2 | Ester |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 55 | 18.705 | 93; 92; 77 | 93 | 90 | MS | 2,7,7-trimethyl-3-oxatricyclo[4.1.1.02,4]octane | α-Pinene | APNENE | 80-56-8 | C10H16 | Terpene |
| 56 | 19.031 | 43; 57; 58 | 57 | 80 | MS | 4,4-dimethylpentan-2-one | 4,4-Dimethyl-2-Pentanone | DM44PT2ONE | 590-50-1 | C7H14O | Ketone |
| 57 | 19.280 | 55; 84; 57 | 55 | 89 | MS | pent-1-en-3-one | 1-Penten-3-one | PT1E3ONE | 1629-58-9 | C5H8O | Ketone |
| 58 | 20.416 | 57; 71; 43 | 71 | 79 | MS | 5-butylnonane | 5-Butyl-Nonane | B5NONANE | 17312-63-9 | C13H28 | Hydrocarbon |
| 59 | 20.960 | 57; 43; 71 | 57 | 83 | MS | 3,6-dimethyldecane | 3,6-Dimethyl-Decane | DM36DCANE | 17312-53-7 | C12H26 | Hydrocarbon |
| 60 | 21.599 | 71; 43; 59 | 71 | 83 | MS | 2-methylbut-3-en-2-ol | 2-Methyl-3-Buten-2-ol | M3BT2OL | 115-18-4 | C5H10O | Alcohol |
| 61 | 22.378 | 57; 43; 41 | 57 | 75 | MS | 5-methyldecane | 5-Methyl-Decane | M5DCANE | 13151-35-4 | C11H24 | Hydrocarbon |
| 62 | 22.856 | 43; 71; 51 | 71 | 80 | MS | 4-methyldecane | 4-Methyl-Decane | M4DCANE | 2847-72-5 | C11H24 | Hydrocarbon |
| 63 | 24.547 | 43; 57; 100 | 57 | 90 | MS | pentane-2,3-dione | 2,3-Pentanedione | PTDONE | 600-14-6 | C5H8O2 | Ketone |
| 64 | 25.650 | 88; 43; 57 | 88 | 90 | MS | methyl 3,3-dimethylbutanoate | 3,3-Dimethyl-Methyl Ester Butanoic Acid | DM33MESTBA | 30540-29-5 | C7H14O2 | Ester |
| 65 | 26.145 | 43; 58; 100 | 58 | 90 | MS | hexan-2-one | 2-Hexanone | HX2ONE | 591-78-6 | C6H12O | Ketone |
| 66 | 26.194 | 43; 71; 57 | 71 | 81 | MS | 4-methylundecane | 4-Methyl-Undecane | M4UNCANE | 2980-69-0 | C12H26 | Hydrocarbon |
| 67 | 26.562 | 44; 56; 43 | 56 | 94 | RS; MS | hexanal | Hexanal | HXAL | 66-25-1 | C6H12O | Aldehyde |
| 68 | 28.766 | 43; 42; 41 | 42 | 87 | RS; MS | 2-methylpropan-1-ol | 2-Methyl-1-Propanol | M2PP1OL | 78-83-1 | C4H10O | Alcohol |
| 69 | 29.460 | 59; 45; 87 | 59 | 80 | MS | 2-methylpentan-2-ol | 2-Methyl-2-Pentanol | M2PT2OL | 590-36-3 | C6H14O | Alcohol |
| 70 | 30.332 | 91; 106; 51 | 91 | 91 | MS | ethylbenzene | Ethyl-Benzene | ETBNZ | 100-41-4 | C8H10 | Benzene |
| 71 | 30.481 | 43; 70; 55 | 70 | 77 | MS | 3-methylbutyl acetate | 3-Methyl Butyl Ester Acetic Acid | M3BESTAA | 123-92-2 | C7H14O2 | Ester |
| 72 | 30.970 | 91; 106; 105 | 91 | 97 | MS | 1,2-dimethylbenzene | o-Xylene | OXYLNE | 95-47-6 | C8H10 | Benzene |
| 73 | 31.184 | 45; 55; 73 | 45 | 82 | MS | pentan-2-ol | 2-Pentanol | PT2OL | 6032-29-7 | C5H12O | Alcohol |
| 74 | 31.578 | 91; 106; 105 | 91 | 97 | MS | 1,4-dimethylbenzene | p-Xylene | PXYLNE | 106-42-3 | C8H10 | Benzene |
| 75 | 32.219 | 43; 58; 57 | 58 | 82 | MS | 5-methylhexan-2-one | 5-Methyl-2-Hexanone | M5HX2AONE | 110-12-3 | C7H14O | Ketone |
| 76 | 31.552 | 87; 43; 102 | 87 | 83 | MS | methyl 2-ethylpentanoate | 2-Ethyl Methyl Ester Pentanoic Ester | E2MESTPTA | 816-16-0 | C8H16O2 | Ester |
| 77 | 33.137 | 56; 31; 41 | 56 | 84 | RS; MS | butan-1-ol | 1-Butanol | BT1OL | 71-36-3 | C4H10O | Alcohol |
| 78 | 33.392 | 93; 91; 77 | 93 | 91 | MS | (5S)-2-methyl-5-propan-2-ylcyclohexa-1,3-diene | α-Phellandrene | APHELDNE | 99-83-2 | C10H16 | Terpene |
| 79 | 34.134 | 59; 73; 31 | 59 | 91 | MS | 2-methylpentan-3-ol | 2-Methyl-3-Pentanol | M2PT3OL | 565-67-3 | C6H14O | Alcohol |
| 80 | 34.482 | 57; 41: 43 | 57 | 84 | MS | pent-1-en-3-ol | 1-Penten-3-ol | PT1E3OL | 616-25-1 | C5H10O | Alcohol |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| 81 | 34.773 | 121; 93; 136 | 121 | 98 | MS | 1-methyl-4-propan-2-ylcyclohexa-1,3-diene | α-Terpinene | ATERPNNE | 99-86-5 | C10H16 | Terpene |
| 82 | 35.372 | 55; 56; 73 | 55 | 80 | MS | butyl prop-2-enoate | Butyl Ester 2-Propenoic Acid | BTESTPPEA | 141-32-2 | C7H12O2 | Ester |
| 83 | 35.689 | 91; 106; 105 | 91 | 93 | MS | 1,3-dimethylbenzene | m-Xylene | MXYLNE | 108-38-3 | C8H10 | Benzene |
| 84 | 35.845 | 43; 58; 71 | 58 | 92 | MS | heptan-2-one | 2-Heptanone | HPT2ONE | 110-43-0 | C7H14O | Ketone |
| 85 | 36.061 | 44; 70; 43 | 70 | 90 | RS; MS | heptanal | Heptanal | HPTAL | 111-71-7 | C7H14O | Aldehyde |
| 86 | 36.508 | 68; 93; 67 | 68 | 94 | RS; MS | (4R)-1-methyl-4-prop-1-en-2-ylcyclohexene | D-Limonene | DLIMNENE | 5989-27-5 | C10H16 | Terpene |
| 87 | 37.160 | 59; 55; 73 | 59 | 79 | MS | hexan-3-ol | 3-Hexanol | HX3OL | 623-37-0 | C6H14O | Alcohol |
| 88 | 37.200 | 93; 77; 91 | 93 | 94 | MS | 3-methylidene-6-propan-2-ylcyclohexene | β-Phellandrene | BPHELDNE | 555-10-2 | C10H16 | Terpene |
| 89 | 37.292 | 43; 81; 93 | 81 | 88 | MS | 1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane | Eucalyptol | EUCPTOL | 470-82-6 | C10H18O | Terpenoid |
| 90 | 37.530 | 95; 138; 67 | 95 | 84 | MS | 1-methyl-3-propan-2-ylcyclohexane | m-Menthane | MMTHANE | 16580-24-8 | C10H20 | Terpenoid |
| 91 | 37.772 | 43; 58; 85 | 58 | 89 | MS | 4-methylheptan-2-one | 4-Methyl-2-Heptanone | M4HPT2ONE | 6137-06-0 | C8H16O | Ketone |
| 92 | 37.856 | 45; 41; 56 | 45 | 78 | MS | 3-methylpentan-2-ol | 3-Methyl-2-Pentanol | M2PT2OL | 565-60-6 | C6H14O | Alcohol |
| 93 | 38.574 | 57; 41; 56 | 57 | 83 | RS; MS | 2-methylbutan-1-ol | 2-Methyl-1-Butanol | M2BT1OL | 137-32-6 | C5H12O | Alcohol |
| 94 | 38.644 | 55; 42; 70 | 55 | 90 | MS | 3-methylbutan-1-ol | 3-Methyl-1-Butanol | M3BT1OL | 123-51-3 | C5H12O | Alcohol |
| 95 | 38.715 | 105; 120; 77 | 105 | 90 | MS | 1-ethyl-2-methylbenzene | o-Ethyltoluene | OETOLENE | 611-14-3 | C9H12 | Benzene |
| 96 | 38.948 | 105; 120; 91 | 120 | 85 | MS | 1-ethyl-3-methylbenzene | m-Ethyltoluene | METOLENE | 620-14-4 | C9H12 | Benzene |
| 97 | 39.430 | 45; 41; 69 | 45 | 90 | MS | hexan-2-ol | 2-Hexanol | HX2OL | 626-93-7 | C6H14O | Alcohol |
| 98 | 39.509 | 59; 31; 45 | 59 | 90 | MS | 2-ethoxyethanol | Ethylene Glycol Ethyl Ether | ENGOLEETHR | 110-80-5 | C4H10O2 | Ether |
| 99 | 40.058 | 43; 58; 71 | 58 | 64 | MS | 6-methylheptan-2-one | 6-Methyl-2-Heptanone | M6HPT2ONE | 928-68-7 | C8H16O | Ketone |
| 100 | 40.291 | 105; 120; 77 | 105 | 92 | MS | 1,2,4-trimethylbenzene | Pseudocumene | PSEUDCUMNE | 95-63-6 | C9H12 | Benzene |
| 101 | 40.443 | 43; 58; 85 | 58 | 90 | MS | 4,6-dimethylheptan-2-one | 4,6-Dimethyl-2-Heptanone | DM46HPT2ONE | 19549-80-5 | C9H18O | Ketone |
| 102 | 40.831 | 59; 55; 70 | 59 | 84 | MS | 2,3-dimethylhexan-2-ol | 2,3-Dimethyl-2-Hexanol | DM23HX2OL | 19550-03-9 | C8H18O | Alcohol |
| 103 | 40.925 | 43; 57; 72 | 57 | 84 | MS | octan-3-one | 3-Octanone | OCT3ONE | 106-68-3 | C8H16O | Ketone |
| 104 | 41.201 | 104; 103; 78 | 104 | 95 | MS | ethenylbenzene | Styrene | STYNE | 100-42-5 | C8H8 | Benzene |
| 105 | 41.225 | 43; 57; 71 | 71 | 84 | MS | 5-methylheptan-2-one | 5-Methyl-2-Heptanone | M5HPTAONE | 18217-12-4 | C8H16O | Ketone |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| 106 | 41.401 | 42; 55; 70 | 55 | 88 | RS; MS | pentan-1-ol | 1-Pentanol | PT1OL | 71-41-0 | C5H12O | Alcohol |
| 107 | 41.548 | 105; 120; 91 | 120 | 83 | MS | 1-ethyl-4-methylbenzene | p-Ethyltoluene | PETOLENE | 622-96-8 | C9H12 | Benzene |
| 108 | 42.183 | 119; 134; 91 | 119 | 95 | MS | 1-methyl-4-propan-2-ylbenzene | p-Cymene | PCYMNE | 99-87-6 | C10H14 | Terpenoid |
| 109 | 42.429 | 105; 120; 77 | 105 | 95 | MS | 1,3,5-trimethylbenzene | Mesitylene | MESTLNE | 108-67-8 | C9H12 | Benzene |
| 110 | 42.623 | 87; 45; 43 | 87 | 82 | MS | 4-methylheptan-4-ol | 4-Methyl-4-Heptanol | M4HPT4OL | 598-01-6 | C8H18O | Alcohol |
| 111 | 43.151 | 55; 73; 43 | 55 | 80 | MS | heptan-4-ol | 4-Heptanol | HPT4OL | 589-55-9 | C7H16O | Alcohol |
| 112 | 43.220 | 43; 58; 71 | 58 | 94 | RS; MS | octan-2-one | 2-Octanone | OCT2ONE | 111-13-7 | C8H16O | Ketone |
| 113 | 43.513 | 43; 56; 84 | 84 | 80 | RS; MS | octanal | Octanal | OCTAL | 124-13-0 | C8H16O | Aldehyde |
| 114 | 44.239 | 45; 43; 88 | 88 | 83 | MS | 3-hydroxybutan-2-one | 3-Hydroxy-2-Butanone | HXY3BT2ONE | 513-86-0 | C4H8O2 | Ketone |
| 115 | 44.294 | 55; 70; 43 | 55 | 79 | MS | oct-1-en-3-one | 1-Octen-3-one | OCT3E1ONE | 4312-99-6 | C8H14O | Ketone |
| 116 | 44.946 | 57; 41; 39 | 57 | 78 | MS | (E)-pent-2-en-1-ol | trans-2-Pentenol | TPT1E2OL | 1576-96-1 | C5H10O | Alcohol |
| 117 | 45.122 | 82; 56; 41 | 82 | 76 | MS | 2,2,6-trimethylcyclohexan-1-one | 2,2,6-Trimethyl-Cyclohexanone | TM226CHXONE | 2408-37-9 | C9H16O | Ketone |
| 118 | 45.290 | 45; 55; 83 | 55 | 79 | MS | heptan-2-ol | 2-Heptanol | HPT2OL | 543-49-7 | C7H16O | Alcohol |
| 119 | 45.426 | 57; 41; 39 | 57 | 86 | MS | (Z)-pent-2-en-1-ol | cis-2-Pentenol | CPT1E2OL | 1576-95-0 | C5H10O | Alcohol |
| 120 | 45.615 | 43; 31; 74 | 74 | 80 | MS | 1-hydroxypropan-2-one | 1-Hydroxy-2-Propanone | HXY1PP2ONE | 116-09-6 | C3H6O2 | Ketone |
| 121 | 46.014 | 83; 55; 112 | 83 | 83 | MS | 5-methylhex-4-en-3-one | 5-Methyl-4-Hexen-3-one | M5HX3E4ONE | 13905-10-7 | C7H12O | Ketone |
| 122 | 46.336 | 105; 120; 77 | 105 | 80 | MS | 1,2,3-trimethylbenzene | Hemimellitene | HEMIMLTNE | 526-73-8 | C9H12 | Benzene |
| 123 | 46.355 | 43; 41; 69 | 69 | 92 | MS | 6-methylhept-5-en-2-one | 6-Methyl-5-Hepten-2-one | M6HPT2E5ONE | 110-93-0 | C8H14O | Ketone |
| 124 | 46.666 | 55; 42; 70 | 55 | 83 | MS | pent-2-ene | 2-Pentene | PT2ENE | 109-68-2 | C5H10 | Hydrocarbon |
| 125 | 47.293 | 56; 43; 55 | 56 | 84 | RS; MS | hexan-1-ol | 1-Hexanol | HX1OL | 111-27-3 | C6H14O | Alcohol |
| 126 | 47.639 | 82; 39; 54 | 82 | 78 | MS | cyclopent-2-en-1-one | 2-Cyclopenten-1-one | CY2PT1EONE | 930-30-3 | C5H6O | Ketone |
| 127 | 48.262 | 67; 96; 53 | 67 | 84 | MS | 2-methylcyclopent-2-en-1-one | 2-Methyl-2-Cyclopenten-1-one | M2CY2PT1EONE | 1120-73-6 | C6H8O | Ketone |
| 128 | 48.293 | 117; 118; 91 | 117 | 80 | MS | [(E)-prop-1-enyl]benzene | β-Methy-Styrene | BMSTYNE | 637-50-3 | C9H10 | Benzene |
| 129 | 48.694 | 69; 55; 73 | 69 | 80 | MS | octan-4-ol | 4-Octanol | OCT4OL | 589-62-8 | C8H18O | Alcohol |
| 130 | 49.013 | 41; 67; 82 | 67 | 80 | MS | (Z)-hex-3-en-1-ol | cis-3-Hexen-1-ol | CHX1E3OL | 928-96-1 | C6H12O | Alcohol |
| 131 | 49.099 | 58; 43; 71 | 58 | 95 | MS | nonan-2-one | 2-Nonanone | NON2ONE | 821-55-6 | C9H18O | Ketone |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| 132 | 49.328 | 57; 41; 43 | 57 | 93 | RS; MS | nonanal | Nonanal | NONAL | 124-19-6 | C9H18O | Aldehyde |
| 133 | 49.978 | 57; 45; 41 | 59 | 78 | MS | 2-butoxyethanol | Ethylene Glycol Butyl Ether | ENGOLBETHR | 111-76-2 | C6H14O2 | Ether |
| 134 | 50.046 | 83; 55; 41 | 83 | 83 | MS | 1-ethyl-1-methylcyclopentane | 1-Ethyl-1-Methyl-Cyclopentane | E1M1CYPTANE | 3726-47-4 | C8H16 | Hydrocarbon |
| 135 | 50.253 | 55; 43; 111 | 55 | 93 | MS | oct-3-en-2-one | 3-Octen-2-one | OCT2E3ONE | 1669-44-9 | C8H14O | Ketone |
| 136 | 50.612 | 45; 55; 41 | 45 | 86 | MS | octan-2-ol | 2-Octanol | OCT2OL | 123-96-6 | C8H18O | Alcohol |
| 137 | 50.812 | 67; 95; 124 | 67 | 82 | MS | (3E)-3-ethyl-2-methylhexa-1,3-diene | 3-Ethyl-2-Methyl-1,3-Hexadiene | E3M2HX13DENE | 61142-36-7 | C9H16 | Terpene |
| 138 | 51.178 | 175; 57; 41 | 175 | 93 | MS | 1,3-ditert-butylbenzene | 1,3-Bis(1,1-Dimethylethyl)-Benzene | BI13DME11BNZ | 1014-60-4 | C14H22 | Benzene |
| 139 | 51.323 | 41; 55; 70 | 41 | 83 | MS | (E)-oct-2-enal | trans-2-Octenal | TOCT2EAL | 2548-87-0 | C8H14O | Aldehyde |
| 140 | 51.677 | 117; 132; 115 | 117 | 80 | MS | 1-ethenyl-3-ethylbenzene | m-Ethyl-Styrene | MESTYNE | 7525-62-4 | C10H12 | Benzene |
| 141 | 51.733 | 43; 58; 71 | 58 | 82 | MS | 5-methylheptan-2-one | 5-Methyl-2-Heptanone | M5HPT2ONE | 18217-12-4 | C8H16O | Ketone |
| 142 | 51.915 | 58; 43; 71 | 58 | 83 | MS | decan-2-one | 2-Decanone | DEC2ONE | 693-54-9 | C10H20O | Ketone |
| 143 | 52.160 | 57; 43; 72; | 57 | 86 | MS | oct-1-en-3-ol | 1-Octen-3-ol | OCT3E1OL | 3391-86-4 | C8H16O | Alcohol |
| 144 | 52.338 | 81; 110; 53 | 81 | 86 | MS | (2E,4E)-hepta-2,4-dienal | trans,trans-2,4-Heptadienal | TTHPT22DEAL | 4313-03-5 | C7H10O | Aldehyde |
| 145 | 52.406 | 70; 56; 55 | 70 | 83 | MS | heptan-1-ol | 1-Heptanol | HPT1OL | 111-70-6 | C7H16O | Alcohol |
| 146 | 52.697 | 81; 67; 68 | 81 | 83 | MS | (3Z,5Z)-octa-3,5-diene | cis,cis-3,5-Octadiene | CCOCT35DENE | 7348-80-3 | C8H14 | Hydrocarbon |
| 147 | 52.959 | 43; 102; 59 | 102 | 75 | MS | methyl 2-oxopropanoate | 2-Oxo-Methyl Ester Propanoic Acid | OM2ESTPPA | 600-22-6 | C4H6O3 | Ester |
| 148 | 53.063 | 59; 43; 55 | 59 | 77 | MS | 2,6-dimethyloct-7-en-2-ol | Dihydromyrcenol | DHMYRCNOL | 18479-58-8 | C10H20O | Terpenoid |
| 149 | 53.170 | 112; 69; 41 | 112 | 97 | MS | (2R)-5-methyl-2-propan-2-ylcyclohexan-1-one | trans-Menthone | TMTHONE | 10458-14-7 | C10H18O | Terpenoid |
| 150 | 53.292 | 96; 95; 39 | 96 | 97 | RS; MS | 2-furanaldehyde | Furfural | FURAL | 98-01-1 | C5H4O2 | Furan |
| 151 | 54.868 | 43; 45; 60 | 60 | 91 | RS; MS | Acetic Acid | Ethanoic Acid | ETNOIC | 64-19-7 | C2H4O2 | Carboxylic Acid |
| 152 | 54.122 | 57; 41; 55 | 57 | 57 | MS | 2-ethylhexan-1-ol | 2-Ethyl-1-Hexanol | E2HX1OL | 104-76-7 | C8H18O | Alcohol |
| 153 | 54.884 | 57; 43; 55 | 57 | 86 | RS; MS | decanal | Decanal | DECAL | 112-31-2 | C10H2O | Aldehyde |
| 154 | 54.886 | 81; 53; 126 | 81 | 93 | MS | furan-2-ylmethyl formate | Furfuryl Formate | FURYLFMTE | 13493-97-5 | C6H6O3 | Furan |
| 155 | 55.267 | 57; 41; 55 | 57 | 91 | MS | (E)-hept-2-en-1-ol | trans-2-Hepten-1-ol | THPT1E2OL | 33467-76-4 | C7H14O | Alcohol |
| 156 | 55.575 | 45; 69; 55 | 69 | 83 | MS | nonan-2-ol | 2-Nonanol | NON2OL | 628-99-9 | C9H20O | Alcohol |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| 157 | 55.443 | 95; 110; 39 | 95 | 90 | RS; MS | 1-(furan-2-yl)ethanone | 1-(2-Furanyl)-Ethanone | FURYLETONE | 1192-62-7 | C6H6O2 | Furan |
| 158 | 56.022 | 95; 43; 81 | 95 | 84 | MS | (3E,5E)-octa-3,5-dien-2-one | 3,5-Octadien-2-one | OCT35DE2ONE | 38284-27-4 | C8H12O | Ketone |
| 159 | 56.414 | 106; 105; 77 | 106 | 94 | RS; MS | Benzaldehyde | Benzaldehyde | BENZAL | 100-52-7 | C7H6O | Benzene |
| 160 | 56.771 | 81; 98; 52 | 81 | 95 | MS | furan-2-ylmethyl acetate | Furfuryl Acetate | FURYLACTE | 623-17-6 | C7H8O3 | Furan |
| 161 | 56.947 | 71; 43; 41 | 71 | 90 | RS; MS | 3,7-dimethylocta-1,6-dien-3-ol | Linalool | LINOL | 78-70-6 | C10H18O | Terpene |
| 162 | 57.081 | 41; 93; 69 | 93 | 80 | MS | 7-methyl-3-methylideneocta-1,6-diene | β-Myrcene | BMYRCNE | 123-35-3 | C10H16 | Terpene |
| 163 | 57.530 | 56; 55; 70 | 56 | 91 | RS; MS | octan-1-ol | 1-Octanol | OCT1OL | 111-87-5 | C8H18O | Alcohol |
| 164 | 58.065 | 43; 93; 139 | 93 | 95 | MS | (1R,4S)-1-methyl-4-propan-2-ylcyclohex-2-en-1-ol | trans-p-2-Menthen-1-ol | TMNTH1E2OL | 29803-81-4 | C10H18O | Terpenoid |
| 165 | 58.338 | 74; 45; 73 | 74 | 82 | MS | propanoic acid | Propanoic Acid | PPANOIC | 79-09-4 | C3H6O2 | Carboxylic Acid |
| 166 | 58.627 | 45; 43; 57; 75 | 57 | 90 | MS | butane-2,3-diol | 2,3-Butanediol | BT23DIOL | 513-85-9 | C4H10O2 | Alcohol |
| 167 | 58.650 | 63; 78; 45 | 63 | 82 | MS | methylsulfinylmethane | Dimethyl Sulfoxide | DMSULFO | 67-68-5 | C2H6OS | Sulfur |
| 168 | 58.917 | 95; 138; 67 | 95 | 84 | MS | 1-methyl-3-propan-2-ylidenecyclohexane | m-Menth-3-ene | MMTH3ENE | 13828-34-7 | C10H18 | Terpene |
| 169 | 59.032 | 81; 55; 97 | 81 | 90 | MS | [(1S,2S)-2-ethylcyclopentyl]methanol | Trans-(2-Ethylcyclopentyl)-Methanol | T2ECYPTMTOL | 36258-08-9 | C8H16O | Alcohol |
| 170 | 59.265 | 95; 43; 93 | 95 | 93 | MS | (1,7,7-trimethyl-2-bicyclo[2.2.1]heptanyl) acetate | Bornyl Acetate | BORNYLACTE | 76-49-3 | C12H20O2 | Ester |
| 171 | 59.565 | 96; 42; 68 | 96 | 86 | MS | cyclopent-4-ene-1,3-dione | 4-Cyclopentene-1,3-dione | CYPT4E13DONE | 930-60-9 | C5H4O2 | Ketone |
| 172 | 59.658 | 71; 81; 95 | 71 | 94 | RS; MS | 5-methyl-2-propan-2-ylcyclohexan-1-ol | Menthol | MNTHOL | 89-78-1 | C10H20O | Terpenoid |
| 173 | 59.677 | 58; 43; 71 | 58 | 95 | MS | undecan-2-one | 2-Undecanone | UNDEC2ONE | 112-12-9 | C11H22O | Ketone |
| 174 | 59.851 | 134; 78; 105 | 134 | 83 | MS | 2-(furan-2-yl)furan | 2-(2-Furanyl)-Furan | FURYLFUR | 5905-00-0 | C8H6O2 | Furan |
| 175 | 60.210 | 57; 41; 54 | 57 | 89 | MS | (E)-oct-2-en-1-ol | trans-2-Octen-1-ol | TOCT1E2OL | 18409-17-1 | C8H16O | Alcohol |
| 176 | 60.351 | 57; 41; 43 | 57 | 82 | MS | (E)-non-2-en-1-ol | trans-2-Nonen-1-ol | TNON1E2OL | 31502-14-4 | C9H18O | Alcohol |
| 177 | 60.719 | 45; 59; 72 | 59 | 90 | MS | 2-(2-ethoxyethoxy)ethanol | Diethylene Glycol Ethyl Ether | DENGOLEETHR | 111-90-0 | C6H14O3 | Ether |
| 178 | 60.791 | 109; 124; 81 | 109 | 82 | MS | 3,5,5-trimethylcyclopent-2-en-1-one | 3,5,5-Trimethyl-2-Cyclopenten-1-one | TM355CYPT1E2ONE | 24156-95-4 | C8H12O | Ketone |
| 179 | 61.117 | 43; 93; 139 | 93 | 89 | MS | 4-tert-butylcyclohex-2-en-1-ol | cis-p-2-Menthen-1-ol | CMNTH1E2OL | 29803-82-5 | C10H18O | Terpenoid |

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| 180 | 61.133 | 137; 123; 152 | 137 | 91 | MS | 2,6,6-trimethylcyclohexene-1-carbaldehyde | β-Cyclocitral | BCYCITAL | 432-25-7 | C10H16O | Terpenoid |
| 181 | 62.190 | 91; 92; 120 | 91 | 90 | MS | 2-phenylacetaldehyde | Benzeneacetaldehyde | BENZACETAL | 122-78-1 | C8H8O | Benzene |
| 182 | 62.284 | 56; 55; 43 | 56 | 90 | MS | nonan-1-ol | 1-Nonanol | NON1OL | 143-08-8 | C9H20O | Alcohol |
| 183 | 62.615 | 98; 41; 81 | 98 | 83 | RS; MS | furan-2-ylmethanol | Furfuryl Alcohol | FUR2OL | 98-00-0 | C5H6O2 | Furan |
| 184 | 62.815 | 97; 79; 95 | 97 | 90 | MS | (5-ethylcyclopenten-1-yl)methanol | Phoracanthol | PHOCATHOL | 36431-59-1 | C8H14O | Alcohol |
| 185 | 63.440 | 55; 68; 81 | 55 | 83 | MS | (Z)-non-3-en-1-ol | cis-3-Nonen-1-ol | ZNONE3OL | 10340-23-5 | C9H18O | Alcohol |
| 186 | 63.478 | 84; 43; 139 | 84 | 95 | MS | (1R,6S)-3-methyl-6-propan-2-ylcyclohex-2-en-1-ol | cis-Piperitol | CPIPETOL | 16721-38-3 | C10H18O | Terpenoid |
| 187 | 63.636 | 134; 119; 91 | 134 | 94 | MS | 1-ethenyl-4-methoxybenzene | p-Methoxy-Styrene | PMTXYESTYNE | 637-69-4 | C9H10O | Benzene |
| 188 | 63.727 | 55; 83; 41 | 55 | 78 | MS | (2E)-3-ethylpenta-2,4-dien-1-ol | (2Z)-3-Ethyl-2,4-Pentadien-1-ol | E3PT1DE24OL | 000-00-0 | C7H12O | Alcohol |
| 189 | 63.995 | 57; 55; 71 | 57 | 94 | MS | 4-butoxybutan-1-ol | Butylene Glycol Monobutyl Ether | BNGOLBETHR | 4161-24-4 | C8H18O2 | Ether |
| 190 | 64.200 | 59; 93; 121 | 59 | 85 | MS | 2-[(1R)-4-methylcyclohex-3-en-1-yl]propan-2-ol | α-Terpineol | ATERPINOL | 98-55-5 | C10H18O | Terpenoid |
| 191 | 64.222 | 55; 56; 112 | 55 | 89 | MS | cyclooctane-1,5-dione | 1,5-Cyclooctanedione | CYOCTD15ONE | 1489-74-3 | C8H12O2 | Ketone |
| 192 | 64.323 | 121; 93; 136 | 121 | 90 | MS | 1-methyl-4-propan-2-ylcyclohexa-1,4-diene | γ-Terpinene | GTERPINE | 99-85-4 | C10H16 | Terpene |
| 193 | 64.718 | 57; 43; 41 | 57 | 78 | MS | (E)-dec-2-en-1-ol | trans-2-Decenol | TDECE2OL | 18409-18-2 | C10H20O | Alcohol |
| 194 | 64.731 | 72; 55; 45 | 72 | 84 | MS | prop-2-enoic acid | 2-Propenoic Acid | PPE2NOIC | 79-10-7 | C3H4O2 | Carboxylic Acid |
| 195 | 64.863 | 45; 41; 43 | 45 | 90 | MS | undecan-2-ol | 2-Undecanol | UNDEC2OL | 1653-30-1 | C11H24O | Alcohol |
| 196 | 65.068 | 134; 133; 119 | 134 | 91 | MS | 3-ethylbenzaldehyde | 3-Ethyl-Benzaldehyde | E3BNZAL | 34246-54-3 | C9H10O | Benzene |
| 197 | 65.330 | 122; 121; 93 | 122 | 83 | MS | 3-hydroxybenzaldehyde | 3-Hydroxy-Benzaldehyde | HXY3BENZAL | 100-83-4 | C7H6O2 | Phenol |
| 198 | 65.475 | 55; 56; 41 | 55 | 76 | MS | (E)-non-2-ene | trans-2-Nonene | TNONENE | 6434-78-2 | C9H18 | Hydrocarbon |
| 199 | 65.578 | 41; 98; 69 | 98 | 83 | MS | (E)-2-methylpent-2-enal | 2-Methyl-2-Pentenal | M2PNTE2AL | 623-36-9 | C6H10O | Aldehyde |
| 200 | 65.918 | 67; 55; 81 | 67 | 76 | MS | (Z)-dec-5-en-1-ol | cis-5-Decenol | CDEC5E1OL | 51652-47-2 | C10H20O | Alcohol |
| 201 | 66.228 | 84; 43; 139 | 84 | 97 | MS | (1R,6R)-3-methyl-6-propan-2-ylcyclohex-2-en-1-ol | trans-Piperitol | TPIPETOL | 16721-39-4 | C10H18O | Terpenoid |
| 202 | 66.391 | 134; 133; 105 | 134 | 78 | MS | 4-ethylbenzaldehyde | 4-Ethyl-Benzaldehyde | E4BNZAL | 4748-78-1 | C9H10O | Benzene |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 203 | 66.510 | 128; 129; 127 | 128 | 80 | MS | naphthalene | Naphthalene | NPHNE | 91-20-3 | C10H8 | Naphthalene |
| 204 | 66.624 | 55; 43; 70 | 70 | 91 | RS; MS | decan-1-ol | 1-Decanol | DEC1OL | 112-30-1 | C10H22O | Alcohol |
| 205 | 66.664 | 55; 70; 56 | 55 | 96 | MS | cyclodecane | Cyclodecane | CDECANE | 293-96-9 | C10H20 | Hydrocarbon |
| 206 | 67.230 | 81; 47; 67 | 81 | 87 | MS | (2E,4E)-deca-2,4-dienal | trans,trans-2,4-Decadienal | TTDEC24DENAL | 25152-84-5 | C10H16O | Aldehyde |
| 207 | 67.532 | 98; 55; 42 | 98 | 82 | MS | cyclopentane-1,2-dione | 1,2-Cyclopentanedione | CPT12DONE | 3008-40-0 | C5H6O2 | Ketone |
| 208 | 67.847 | 67; 41; 54 | 67 | 89 | MS | cyclodecene | Cyclodecene | CDECENE | 3618-12-0 | C10H18 | Hydrocarbon |
| 209 | 68.067 | 68; 41; 81 | 68 | 91 | MS | (Z)-dec-4-en-1-ol | cis-4-Decenol | CDEC4E1OL | 57074-37-0 | C10H20O | Alcohol |
| 210 | 68.915 | 57; 91; 148 | 57 | 88 | MS | 1-phenylbutan-2-one | 1-Phenyl-2-Butanone | PHYLBT2ONE | 1007-32-5 | C10H12O | Benzene |
| 211 | 69.029 | 107; 79; 77 | 107 | 91 | MS | (2-methylphenyl)methanol | α-Methyl-Benzenemethanol | MBNZMTOL | 98-85-1 | C8H10O | Benzene |
| 212 | 69.080 | 81; 41; 67 | 81 | 83 | MS | (2E,4Z)-deca-2,4-dienal | trans,cis-2,4-Decadienal | TCDEC24DENAL | 25152-83-4 | C10H16O | Aldehyde |
| 213 | 69.212 | 70; 39; 41 | 70 | 82 | MS | cyclohex-2-en-1-ol | 2-Cyclohexenol | CHEX2E1OL | 822-67-3 | C6H10O | Alcohol |
| 214 | 69.476 | 73; 88; 41 | 73 | 80 | MS | 2-ethylhexanoic acid | 2-Ethyl Hexanoic Acid | E2HEXOIC | 149-57-5 | C8H16O2 | Carboxylic Acid |
| 215 | 69.769 | 112; 69; 41 | 112 | 80 | MS | 3-methylcyclopentane-1,2-dione | 3-Methyl-1,2-Cyclopentanedione | M3CPT12DONE | 765-70-8 | C6H8O2 | Ketone |
| 216 | 70.128 | 131; 132; 103 | 131 | 83 | MS | (E)-3-phenylprop-2-enal | trans-Cinnamaldehyde | TCINAMAL | 14371-10-9 | C9H8O | Benzene |
| 217 | 70.617 | 60; 73; 43 | 60 | 76 | RS; MS | heptanoic acid | Heptanoic Acid | HEPTOIC | 111-14-8 | C7H14O2 | Carboxylic Acid |
| 218 | 71.026 | 109; 124, 81 | 109 | 92 | MS | 4-methoxyphenol | Mequinol | MEQNOL | 150-76-5 | C7H8O2 | Phenol |
| 219 | 71.092 | 128; 57; 85 | 128 | 78 | MS | 1,3-diazinane-2,4,5-trione | 2,4,5-Trihydroxypyrimidine | THDXYPYMNE | 67-52-7 | C4H4N2O3 | Nitrogen |
| 220 | 71.409 | 131; 132; 103 | 131 | 76 | MS | (Z)-3-phenylprop-2-enal | cis-Cinnamaldehyde | CCINAMAL | 57194-69-1 | C9H8O | Benzene |
| 221 | 71.559 | 79; 108; 77 | 79 | 92 | MS | phenylmethanol | Benzenemethanol | BENZMTOL | 100-51-6 | C7H8O | Benzene |
| 222 | 71.682 | 147; 148; 119 | 147 | 94 | MS | 2,4,6-trimethylbenzaldehyde | Mesitaldehyde | MESIAL | 487-68-3 | C10H12O | Benzene |
| 223 | 72.376 | 57; 70; 127 | 57 | 87 | MS | 2-ethylhexyl octanoate | 2-Ethylhexyl Ester Octanoic Acid | EHESTOA | 63321-70-0 | C16H32O2 | Ester |
| 224 | 72.907 | 91; 92; 122 | 91 | 78 | MS | 2-phenylethanol | Benzeneethanol | BENZETOL | 60-12-8 | C8H10O | Benzene |
| 225 | 72.929 | 42; 44, 31 | 42 | 78 | MS | butane-1,4-diol | 1,4-Butanediol | BT14DIOL | 110-63-4 | C4H10O2 | Alcohol |
| 226 | 73.968 | 177; 43; 91 | 177 | 97 | MS | (E)-4-(2,6,6-trimethylcyclohexen-1-yl)but-3-en-2-one | β-Ionone | BIONNE | 14901-07-6 | C13H20O | Terpenoid |
| 227 | 74.232 | 124; 95; 107 | 124 | 50 | MS | 2-methylbenzene-1,4-diol | 2-Methyl-1,4-Benzenediol | M2BNZ14DIOL | 95-71-6 | C7H8O2 | Benzene |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 228 | 74.246 | 88; 73; 101 | 88 | 81 | MS | 2-ethylheptanoic acid | 2-Ethyl Heptanoic Acid | EHPTOIC | 149-57-5 | C8H16O2 | Carboxylic Acid |
| 229 | 74.422 | 55; 43; 69 | 55 | 94 | MS | dodecan-1-ol | 1-Dodecanol | DODEC1OL | 112-53-8 | C12H26O | Alcohol |
| 230 | 74.631 | 131; 103;146 | 131 | 76 | MS | (E)-4-phenylbut-3-en-2-one | Benzalacetone | BNZONE | 122-57-6 | C10H10O | Benzene |
| 231 | 74.950 | 126; 71; 43 | 126 | 93 | MS | 3-hydroxy-2-methylpyran-4-one | Maltol | MALTOL | 118-71-8 | C6H6O3 | Pyran |
| 232 | 75.126 | 94; 109; 66 | 94 | 75 | MS | 1-(1H-pyrrol-2-yl)ethanone | 2-Acetylpyrrole | ACTLPYROLE | 1072-83-9 | C6H7NO | Nitrogen |
| 233 | 75.164 | 41; 55; 83 | 41 | 96 | MS | (2E,4E)-deca-2,4-dien-1-ol | 2,4-Decadien-1-ol | DEC24DIE1OL | 14507-02-9 | C10H18O | Alcohol |
| 234 | 75.978 | 98; 97; 53 | 98 | 82 | MS | (1S,5R)-6,8-dioxabicyclo[3.2.1]oct-2-en-4-one | Levoglucosenone | LEVGLCONE | 37112-31-5 | C6H6O3 | Ketone |
| 235 | 76.247 | 94; 66; 65 | 94 | 95 | RS; MS | phenol | Phenol | PHEOL | 108-95-2 | C6H6O | Phenol |
| 236 | 76.679 | 95; 126; 67 | 95 | 75 | MS | 1-(furan-2-yl)-2-hydroxyethanone | 1-(2-Furanyl)-2-Hydroxy-Ethanone | FURYLHXYEONE | 17678-19-2 | C6H6O3 | Furan |
| 237 | 77.333 | 57; 43; 71 | 71 | 75 | MS | 4,6-dimethyldodecane | 4,6-Dimethyl-Dodecane | DM45DODCANE | 17312-63-9 | C13H28 | Hydrocarbon |
| 238 | 77.352 | 88; 101; 43 | 88 | 89 | MS | ethyl decanoate | Ethyl Ester Decanoic Acid | EESDECA | 110-38-3 | C12H24O2 | Ester |
| 239 | 78.059 | 43; 103; 42 | 103 | 85 | MS | 1-methylpiperidin-4-one | 1-Methyl-4-Piperidinone | M1PIP4DIONE | 1445-73-4 | C6H11NO | Nitrogen |
| 240 | 78.233 | 57; 85; 41 | 57 | 83 | MS | 2,2-dimethylheptan-3-one | 2,2-Dimethyl-3-Heptanone | DM22HPT3ONE | 19078-97-8 | C9H18O | Ketone |
| 241 | 78.184 | 60; 73; 43 | 60 | 80 | RS; MS | octanoic acid | Octanoic Acid | OCTOIC | 124-07-2 | C8H16O2 | Carboxylic Acid |
| 242 | 79.187 | 31; 43; 42 | 31 | 83 | MS | 1,3-dihydroxypropan-2-one | 1,3-Dihydroxy-2-Propanone | DHYPPAONE | 96-26-4 | C3H6O3 | Ketone |
| 243 | 80.862 | 94; 138; 77 | 94 | 82 | MS | 2-phenoxyethanol | 2-Phenoxy-Ethanol | PHENXYOL | 122-99-6 | C8H10O2 | Benzene |
| 244 | 80.906 | 134; 133; 105 | 134 | 78 | MS | benzene-1,3-dicarbaldehyde | Isophthalaldehyde | ISOPHTAL | 626-19-7 | C8H6O2 | Benzene |
| 245 | 81.320 | 55; 83; 69 | 55 | 83 | MS | cyclotetradecane | Cyclotetradecane | CTTDECANE | 295-17-0 | C14H28 | Hydrocarbon |
| 246 | 81.611 | 60; 73; 57 | 60 | 87 | RS; MS | nonanoic acid | Nonanoic Acid | NONOIC | 112-05-0 | C9H18O2 | Carboxylic Acid |
| 247 | 81.853 | 107; 122; 77 | 107 | 78 | MS | 2-ethylphenol | 2-Ethyl-Phenol | E2PHEOL | 90-00-6 | C8H10O | Phenol |
| 248 | 82.628 | 135; 150; 77 | 135 | 88 | MS | 4-ethenyl-2-methoxyphenol | 2-Methoxy-4-Vinyl-Phenol | MXY2VYL4PHEOL | 7786-61-0 | C9H10O2 | Phenol |
| 249 | 82.875 | 82; 81; 54 | 82 | 80 | MS | 4-Methyl-1H-imidazole | 4-Methylimidazole | M4IMDZOLE | 822-36-6 | C4H6N2 | Nitrogen |
| 250 | 84.049 | 133; 105; 148 | 133 | 80 | MS | 1-tert-butyl-3-methylbenzene | m-tert-Butyl-Toluene | MTBTLNE | 1075-38-3 | C11H16 | Benzene |
| 251 | 84.676 | 154; 139; 111 | 154 | 82 | MS | 2,6-dimethoxyphenol | Syringol | SYNGOL | 91-10-1 | C8H10O3 | Phenol |
| 252 | 84.890 | 60; 73; 41 | 60 | 96 | RS; MS | decanoic acid | Decanoic Acid | DECOIC | 334-48-5 | C10H20O2 | Carboxylic Acid |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 253 | 85.090 | 43; 42; 144 | 144 | 87 | MS | 3,5-dihydroxy-6-methyl-2,3-dihydropyran-4-one | 3-Hydroxy-2,3-Dihydro-Maltol | HX3DH23MALTOL | 28564-83-2 | C6H8O4 | Pyran |
| 254 | 86.052 | 142; 43; 68 | 142 | 84 | MS | 3,5-dihydroxy-2-methylpyran-4-one | 5-Hydroxy-Maltol | HX5MALTOL | 1073-96-7 | C6H6O4 | Pyran |
| 255 | 86.550 | 45; 89; 58 | 89 | 82 | MS | 2-[2-(2-hydroxyethoxy)ethoxy]ethanol | Triethylene Glycol | TETYNEGLOL | 112-27-6 | C6H14O4 | Ether |
| 256 | 88.144 | 105; 122; 77 | 105 | 81 | RS; MS | benzoic acid | Benzoic Acid | BNZOIC | 65-85-0 | C7H6O2 | Benzene |
| 257 | 89.084 | 91; 120; 121 | 91 | 95 | MS | 2-methylbenzaldehyde | 2-Methyl-Benzaldehyde | M2BNZAL | 529-20-4 | C8H8O | Benzene |
| 258 | 89.701 | 60; 73; 43 | 60 | 85 | MS | undecanoic acid | Undecanoic Acid | UNDECOIC | 112-37-8 | C11H22O2 | Carboxylic Acid |
| 259 | 90.106 | 95; 39; 68 | 95 | 81 | MS | 1H-pyridin-4-one | 4-Pyridinol | PYRDINOL | 626-64-2 | C5H5NO | Nitrogen |
| 260 | 90.399 | 109; 80; 53 | 109 | 76 | MS | 4-aminophenol | 4-Amino-Phenol | AMIPHEOL | 123-30-8 | C6H7NO | Phenol |

[1]RT - Retention Time in minutes.
[2]TI - Target Ion.
[3]MP - Match Percent.
[4]ID - Identification Type method used: RS (Reference Standard) and MS (NIST14 Mass Spectral Library).

**Table S10A. Mean and relative standard deviation values of identified VOCs in sugarcane samples from "Amarela", "Radiada" and "Roxa" cultivars.**

| Volatile Organic Compound | Relative Peak Areas (x $10^3$) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | AMA | | | | RAD | | | | ROX | | | |
| | 2015 | | 2017 | | 2015 | | 2017 | | 2015 | | 2017 | |
| | Mean | RSD[1] (%) | Mean | RSD[1] (%) | Mean | RSD[1] (%) | Mean | RSD[1] (%) | Mean | RSD[1] (%) | Mean | RSD[1] (%) |
| Pentane | 2.4 | 4.2 | 1.8 | 4.3 | 4.4 | 5.6 | 4.2 | 3.6 | 8.2 | 1.0 | 5.5 | 7.3 |
| 1-Pentene | 1.5 | 7.0 | 1.5 | 2.0 | 1.8 | 9.6 | 1.7 | 7.7 | 2.8 | 1.7 | 2.7 | 4.9 |
| 2-Methyl-Pentane | 0.9 | 1.8 | 1.5 | 3.1 | 1.2 | 7.6 | 2.0 | 5.5 | 4.4 | 3.1 | 7.3 | 8.8 |
| Hexane | 2.1 | 13.0 | 1.5 | 11.0 | 1.2 | 5.0 | 1.3 | 9.1 | 4.0 | 1.3 | 3.7 | 8.5 |
| Ethyl Ether | 5.9 | 9.7 | 0.3 | 7.0 | 3.6 | 4.6 | 0.7 | 3.4 | 0.8 | 3.3 | 1.3 | 9.6 |
| cis-4-Methyl-2-Pentene | 0.4 | 2.4 | 0.6 | 10.4 | 0.2 | 6.1 | 1.2 | 11.1 | 0.9 | 1.6 | 4.2 | 13.1 |
| cis-Piperylene | 3.0 | 17.5 | 2.0 | 5.5 | 5.1 | 8.3 | 6.4 | 1.2 | 10.4 | 2.2 | 20.0 | 9.3 |
| 2-Methyl-1-Pentene | 16.6 | 5.2 | 1.0 | 3.9 | 44.4 | 10.2 | 0.5 | 5.5 | 16.7 | 3.2 | 2.3 | 1.3 |
| cis-3-Methyl-2-Pentene | 1.0 | 0.9 | 1.1 | 5.8 | 7.6 | 5.3 | 4.2 | 2.6 | 1.0 | 3.7 | 1.3 | 7.8 |
| 3-Methyl-Hexane | 0.4 | 6.4 | 0.2 | 12.7 | 0.7 | 5.4 | 0.5 | 2.7 | 0.9 | 1.2 | 0.9 | 9.2 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,4-Pentadiene | 11.2 | 9.2 | 3.2 | 4.2 | 12.8 | 3.9 | 4.5 | 4.9 | 27.6 | 1.8 | 6.7 | 10.6 |
| Methanethiol | 3.2 | 0.5 | 3.1 | 0.7 | 4.0 | 1.2 | 4.8 | 2.7 | 7.9 | 1.8 | 6.2 | 3.3 |
| trans-Piperylene | 4.0 | 4.3 | 2.3 | 6.8 | 2.6 | 7.5 | 1.5 | 12.8 | 5.6 | 1.9 | 3.0 | 0.3 |
| Heptane | 9.8 | 8.0 | 8.7 | 2.9 | 6.9 | 2.9 | 5.4 | 8.5 | 15.3 | 3.4 | 10.5 | 3.3 |
| tert-Butyl Ethyl Ether | 57.7 | 6.7 | 0.1 | 0.2 | 70.2 | 0.2 | 0.4 | 4.2 | 47.4 | 1.1 | 0.4 | 6.6 |
| Ethanal | 53.9 | 0.0 | 73.5 | 5.9 | 38.7 | 3.1 | 21.9 | 5.0 | 44.9 | 2.8 | 32.1 | 4.6 |
| Dimethyl Sulfide | 785.5 | 2.0 | 807.3 | 3.6 | 583.5 | 2.7 | 417.8 | 4.7 | 323.7 | 1.7 | 294.5 | 7.1 |
| 4-Methyl-Heptane | 20.2 | 10.4 | 7.8 | 3.5 | 12.9 | 3.3 | 4.0 | 0.6 | 17.1 | 3.2 | 6.6 | 3.5 |
| Octane | 5.2 | 8.3 | 4.4 | 9.5 | 7.0 | 3.8 | 6.9 | 4.5 | 9.8 | 6.1 | 8.2 | 4.7 |
| Propanal | 10.6 | 2.2 | 9.1 | 2.2 | 8.1 | 7.6 | 3.6 | 8.4 | 11.3 | 3.2 | 5.8 | 2.0 |
| Furan | 9.0 | 5.7 | 11.0 | 5.3 | 9.8 | 3.8 | 6.7 | 1.1 | 10.4 | 4.4 | 7.5 | 1.9 |
| 2,4-Dimethyl-Heptane | 11.8 | 3.0 | 22.7 | 8.1 | 16.4 | 1.5 | 19.6 | 1.1 | 25.2 | 3.4 | 29.5 | 2.1 |
| 2-Methyl-Propanal | 24.6 | 1.1 | 20.5 | 0.8 | 39.0 | 1.9 | 40.8 | 4.9 | 74.5 | 1.6 | 54.0 | 8.2 |
| 2-Propanone | 321.3 | 0.1 | 269.1 | 10.0 | 477.8 | 4.0 | 420.1 | 3.5 | 93.0 | 3.6 | 78.3 | 3.2 |
| Methyl Ester Acetic Acid | 2.2 | 2.3 | 3.9 | 7.6 | 0.9 | 7.9 | 1.5 | 10.8 | 2.2 | 3.7 | 30.2 | 8.1 |
| 2-Methyl-2-Heptene | 0.6 | 3.9 | 0.4 | 5.5 | 2.0 | 1.3 | 1.2 | 3.2 | 3.2 | 2.2 | 2.0 | 5.8 |
| Crotonal | 0.3 | 3.0 | 0.2 | 9.8 | 3.0 | 12.1 | 2.5 | 3.4 | 4.2 | 0.9 | 4.7 | 6.6 |
| 2,3-Dimethyl-Heptane | 1.1 | 0.2 | 2.9 | 6.7 | 1.5 | 1.3 | 2.3 | 11.0 | 2.3 | 2.8 | 5.5 | 8.5 |
| 4-Methyl-Octane | 8.8 | 1.4 | 10.7 | 10.2 | 7.9 | 3.5 | 8.5 | 9.0 | 21.8 | 1.2 | 18.8 | 7.7 |
| 2-Methyl-Furan | 1.9 | 12.0 | 1.7 | 7.2 | 3.6 | 6.2 | 2.8 | 2.2 | 1.2 | 1.6 | 1.2 | 15.9 |
| 2,4-Dimethyl-1-Heptene | 5.6 | 9.7 | 7.6 | 3.4 | 8.5 | 2.4 | 6.8 | 5.3 | 29.0 | 5.1 | 20.0 | 14.1 |
| Ethyl Ester Acetic Acid | 23.4 | 7.9 | 49.7 | 6.1 | 15.9 | 3.6 | 21.8 | 8.8 | 447.1 | 2.7 | 552.6 | 9.3 |
| Nonane | 1.6 | 4.5 | 1.4 | 8.3 | 2.5 | 4.6 | 4.3 | 6.5 | 5.4 | 2.3 | 4.9 | 5.8 |
| 2-Butanone | 12.8 | 9.3 | 9.4 | 6.2 | 5.3 | 6.6 | 3.9 | 2.6 | 18.7 | 1.5 | 12.2 | 8.0 |
| 2-Methyl-Butanal | 88.5 | 2.7 | 111.0 | 5.5 | 70.4 | 1.0 | 61.4 | 3.2 | 64.1 | 4.8 | 51.8 | 11.7 |
| 3-Methyl-Butanal | 77.6 | 2.1 | 116.3 | 13.5 | 51.2 | 3.3 | 57.8 | 3.4 | 57.6 | 4.8 | 44.9 | 11.2 |
| Ethyl Alcohol | 434.8 | 1.6 | 535.5 | 5.0 | 860.0 | 2.7 | 988.2 | 0.1 | 780.1 | 3.6 | 825.5 | 12.4 |
| Benzene | 1.4 | 0.4 | 2.3 | 1.1 | 10.3 | 0.6 | 8.2 | 0.8 | 18.7 | 7.2 | 10.6 | 1.2 |
| 3-Ethyl-Heptane | 2.9 | 1.1 | 2.6 | 12.6 | 1.6 | 5.4 | 1.5 | 3.2 | 3.2 | 0.5 | 3.3 | 13.5 |
| 2-Ethyl-Furan | 14.3 | 0.7 | 11.2 | 12.2 | 32.0 | 1.4 | 20.9 | 7.6 | 22.1 | 1.4 | 28.0 | 5.7 |
| Ethyl Ester Propanoic Acid | 0.3 | 1.4 | 0.5 | 7.8 | 7.7 | 2.2 | 8.8 | 2.5 | 58.2 | 1.6 | 94.4 | 6.4 |
| 2-Methyl Ethyl Ester Propanoic Acid | 0.3 | 0.9 | 0.4 | 5.1 | 0.2 | 0.7 | 0.2 | 1.0 | 20.8 | 3.1 | 30.5 | 1.9 |
| 2-Methyl-Crotonal | 2.3 | 1.5 | 1.4 | 9.4 | 0.8 | 1.4 | 0.8 | 0.2 | 5.7 | 2.1 | 5.8 | 0.9 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Propyl Ester Acetic Acid | 0.7 | 2.7 | 0.8 | 10.3 | 0.9 | 2.2 | 0.8 | 3.4 | 10.3 | 2.2 | 16.4 | 4.8 |
| 3-Pentanone | 80.4 | 13.0 | 60.4 | 6.6 | 100.2 | 6.8 | 93.9 | 2.0 | 93.2 | 2.9 | 97.5 | 11.9 |
| Pentanal | 0.5 | 3.6 | 0.4 | 2.1 | 0.3 | 13.3 | 0.2 | 1.3 | 3.9 | 3.9 | 2.3 | 9.1 |
| 2,3-Butanedione | 23.3 | 6.6 | 23.6 | 7.7 | 39.3 | 1.5 | 43.2 | 2.9 | 39.6 | 0.2 | 38.3 | 11.3 |
| 2,3,4-Trimethyl-Hexane | 0.3 | 3.3 | 0.4 | 2.4 | 0.7 | 3.4 | 0.5 | 1.4 | 1.6 | 5.9 | 0.9 | 8.8 |
| Decane | 0.5 | 2.0 | 0.4 | 1.8 | 0.2 | 2.9 | 0.2 | 5.0 | 3.8 | 2.8 | 3.0 | 0.3 |
| 2,6-Dimethyl-Nonane | 2.2 | 2.6 | 1.6 | 0.7 | 1.2 | 9.1 | 1.0 | 7.2 | 2.7 | 1.3 | 2.7 | 9.5 |
| 2,5-Dimethyl-Nonane | 0.4 | 2.8 | 0.6 | 8.6 | 1.0 | 3.3 | 1.4 | 7.0 | 6.2 | 3.0 | 7.4 | 8.3 |
| 4-Methyl-2-Pentanone | 1.1 | 4.7 | 1.0 | 2.3 | 0.2 | 3.7 | 0.2 | 0.9 | 0.4 | 3.9 | 0.3 | 3.4 |
| 2-Methy-2-Butanol | 0.4 | 6.2 | 0.4 | 5.0 | 0.2 | 2.3 | 0.2 | 1.5 | 0.5 | 5.2 | 0.4 | 3.5 |
| 2-Methyl-Propyl Ester Acetic Acid | 1.5 | 1.9 | 2.0 | 5.0 | 1.8 | 6.8 | 1.7 | 2.9 | 9.8 | 3.1 | 19.0 | 1.1 |
| α-Pinene | 0.1 | 2.5 | 0.1 | 3.6 | 0.2 | 6.8 | 0.2 | 5.7 | 1.4 | 2.7 | 2.0 | 11.5 |
| 4,4-Dimethyl-2-Pentanone | 0.1 | 4.1 | 0.1 | 11.5 | 0.2 | 11.1 | 0.1 | 1.4 | 0.3 | 1.5 | 0.3 | 3.6 |
| 1-Penten-3-one | 0.3 | 3.2 | 0.4 | 6.8 | 0.2 | 4.9 | 0.3 | 4.7 | 4.3 | 2.7 | 4.7 | 11.1 |
| 5-Butyl-Nonane | 3.0 | 3.2 | 4.0 | 5.7 | 1.8 | 2.1 | 2.1 | 1.0 | 7.9 | 3.1 | 9.2 | 4.2 |
| 3,6-Dimethyl-Decane | 0.2 | 2.0 | 0.3 | 5.4 | 0.7 | 1.4 | 0.8 | 5.9 | 0.4 | 2.4 | 0.6 | 4.6 |
| 2-Methyl-3-Buten-2-ol | 0.8 | 6.1 | 0.4 | 4.7 | 2.5 | 5.3 | 1.8 | 7.9 | 18.7 | 5.1 | 11.2 | 13.6 |
| 5-Methyl-Decane | 1.1 | 5.3 | 1.7 | 8.5 | 0.9 | 5.5 | 1.0 | 7.1 | 1.1 | 3.7 | 1.3 | 7.1 |
| 4-Methyl-Decane | 1.1 | 2.2 | 2.4 | 1.6 | 0.6 | 7.9 | 0.9 | 2.8 | 1.8 | 2.9 | 2.4 | 15.2 |
| 2,3-Pentanedione | 12.6 | 6.0 | 20.3 | 7.3 | 1.3 | 9.5 | 1.0 | 1.7 | 2.4 | 7.1 | 3.8 | 6.7 |
| 3,3-Dimethyl-Methyl Ester Butanoic Acid | 0.8 | 2.5 | 1.0 | 5.5 | 1.5 | 1.7 | 3.1 | 8.5 | 13.0 | 3.4 | 25.1 | 9.6 |
| 2-Hexanone | 0.6 | 3.0 | 0.6 | 9.9 | 0.8 | 0.3 | 0.6 | 2.2 | 2.4 | 4.3 | 1.3 | 6.8 |
| 4-Methyl-Undecane | 0.6 | 0.2 | 0.7 | 3.7 | 0.5 | 0.8 | 0.6 | 0.2 | 5.4 | 0.8 | 4.3 | 4.4 |
| Hexanal | 8.6 | 2.1 | 7.0 | 4.9 | 13.3 | 2.9 | 9.2 | 7.8 | 46.9 | 2.2 | 43.5 | 7.1 |
| 2-Methyl-1-Propanol | 36.3 | 0.4 | 42.6 | 10.4 | 23.6 | 6.4 | 25.2 | 5.0 | 20.8 | 3.0 | 20.1 | 8.6 |
| 2-Methyl-2-Pentanol | 0.4 | 6.8 | 0.3 | 4.4 | 0.2 | 2.0 | 0.2 | 3.5 | 0.3 | 2.5 | 0.3 | 2.6 |
| Ethyl-Benzene | 28.1 | 0.1 | 34.8 | 4.9 | 37.5 | 5.7 | 43.6 | 4.6 | 75.0 | 3.2 | 99.1 | 6.5 |
| 3-Methyl Butyl Ester Acetic Acid | 9.8 | 12.1 | 7.9 | 1.6 | 24.7 | 7.2 | 20.4 | 10.5 | 24.8 | 3.7 | 20.4 | 10.8 |
| o-Xylene | 20.2 | 5.2 | 11.9 | 0.3 | 9.9 | 11.4 | 8.8 | 2.0 | 32.2 | 2.6 | 22.3 | 6.6 |
| 2-Pentanol | 0.5 | 1.7 | 0.3 | 3.4 | 5.5 | 6.4 | 3.4 | 2.0 | 92.1 | 2.4 | 68.1 | 6.3 |
| p-Xylene | 8.4 | 6.3 | 6.6 | 0.1 | 25.6 | 12.7 | 11.2 | 5.4 | 47.5 | 3.9 | 44.3 | 6.7 |
| 5-Methyl-2-Hexanone | 0.7 | 7.1 | 0.6 | 1.7 | 0.4 | 0.8 | 0.2 | 6.7 | 3.5 | 2.0 | 2.9 | 4.5 |
| 2-Ethyl Methyl Ester Pentanoic Acid | 0.6 | 0.3 | 0.4 | 6.4 | 15.6 | 5.0 | 28.2 | 3.1 | 294.3 | 3.1 | 466.8 | 1.1 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-Butanol | 0.7 | 2.5 | 0.6 | 2.4 | 2.2 | 11.2 | 1.4 | 10.0 | 13.0 | 5.1 | 18.0 | 5.1 |
| α-Phellandrene | 0.2 | 3.2 | 0.1 | 5.4 | 0.8 | 2.6 | 0.8 | 1.4 | 0.4 | 3.2 | 0.4 | 5.8 |
| 2-Methyl-3-Pentanol | 4.0 | 0.1 | 6.2 | 3.4 | 2.5 | 2.0 | 3.6 | 2.6 | 27.2 | 3.3 | 30.7 | 9.4 |
| 1-Penten-3-ol | 73.2 | 0.6 | 59.0 | 2.7 | 152.0 | 8.9 | 108.0 | 7.7 | 222.6 | 4.9 | 153.5 | 7.8 |
| α-Terpinene | 0.5 | 0.6 | 0.4 | 3.1 | 0.1 | 5.5 | 0.1 | 4.9 | 0.2 | 2.5 | 0.1 | 7.7 |
| Butyl Ester 2-Propenoic Acid | 4.4 | 0.8 | 6.2 | 6.0 | 4.6 | 6.8 | 1.6 | 10.7 | 10.4 | 3.6 | 19.1 | 4.6 |
| m-Xylene | 1.8 | 2.6 | 1.6 | 7.6 | 15.0 | 9.6 | 15.1 | 4.8 | 40.5 | 2.5 | 31.7 | 4.1 |
| 2-Heptanone | 182.1 | 3.2 | 127.0 | 1.7 | 761.6 | 2.2 | 764.5 | 4.3 | 111.7 | 4.7 | 83.1 | 5.5 |
| Heptanal | 0.5 | 3.5 | 0.4 | 6.7 | 11.1 | 0.6 | 9.3 | 1.7 | 8.2 | 5.6 | 5.0 | 5.2 |
| D-Limonene | 0.1 | 10.9 | 0.2 | 1.5 | 0.2 | 3.7 | 0.2 | 2.6 | 3.1 | 3.7 | 2.7 | 2.8 |
| 3-Hexanol | 0.3 | 4.2 | 0.2 | 10.0 | 1.7 | 0.8 | 2.1 | 4.6 | 0.6 | 2.4 | 0.4 | 7.8 |
| β-Phellandrene | 0.3 | 2.0 | 0.2 | 2.3 | 1.4 | 1.0 | 1.6 | 1.3 | 0.3 | 1.6 | 0.4 | 4.8 |
| Eucalyptol | 0.2 | 8.2 | 0.2 | 9.4 | 0.1 | 13.5 | 0.2 | 2.7 | 0.2 | 2.4 | 0.1 | 2.2 |
| m-Menthane | 0.1 | 1.1 | 0.1 | 4.2 | 0.2 | 2.0 | 0.2 | 6.0 | 1.6 | 3.1 | 2.6 | 7.5 |
| 4-Methyl-2-Heptanone | 0.3 | 4.1 | 0.3 | 3.0 | 28.4 | 10.7 | 23.6 | 4.1 | 3.9 | 3.9 | 2.2 | 8.1 |
| 3-Methyl-2-Pentanol | 11.3 | 1.0 | 18.4 | 12.6 | 82.1 | 3.3 | 96.5 | 3.5 | 84.7 | 3.0 | 85.7 | 4.3 |
| 2-Methyl-1-Butanol | 160.3 | 5.3 | 231.7 | 8.2 | 193.9 | 3.7 | 189.6 | 5.5 | 136.7 | 4.0 | 231.3 | 13.8 |
| 3-Methyl-1-Butanol | 443.5 | 0.9 | 621.3 | 7.6 | 245.4 | 1.5 | 434.4 | 0.6 | 462.0 | 3.1 | 543.4 | 3.9 |
| o-Ethyltoluene | 1.9 | 3.1 | 1.5 | 13.3 | 5.9 | 0.3 | 3.8 | 1.2 | 8.5 | 0.6 | 8.1 | 4.7 |
| m-Ethyltoluene | 2.1 | 5.0 | 1.0 | 3.0 | 3.6 | 3.9 | 3.9 | 2.0 | 13.5 | 3.7 | 14.8 | 7.3 |
| 2-Hexanol | 59.0 | 2.3 | 78.3 | 6.0 | 49.7 | 3.3 | 63.4 | 10.5 | 3.1 | 1.5 | 1.5 | 13.7 |
| Ethylene Glycol Ethyl Ether | 0.1 | 9.3 | 0.2 | 9.9 | 1.8 | 2.3 | 1.2 | 0.9 | 2.6 | 3.1 | 2.8 | 2.8 |
| 6-Methyl-2-Heptanone | 2.7 | 8.6 | 1.6 | 1.5 | 2.3 | 0.7 | 1.5 | 0.7 | 3.6 | 2.6 | 2.2 | 0.3 |
| Pseudocumene | 2.2 | 2.3 | 3.3 | 1.8 | 5.8 | 3.1 | 4.0 | 5.9 | 7.7 | 3.8 | 7.6 | 5.9 |
| 4,6-Dimethyl-2-Heptanone | 0.7 | 2.8 | 0.9 | 1.0 | 1.0 | 1.9 | 0.7 | 2.4 | 1.6 | 5.1 | 1.1 | 7.3 |
| 2,3-Dimethyl-2-Hexanol | 0.4 | 5.1 | 0.3 | 6.5 | 0.3 | 2.8 | 0.2 | 6.2 | 2.2 | 5.2 | 1.1 | 5.7 |
| 3-Octanone | 6.6 | 3.3 | 5.3 | 2.6 | 22.3 | 4.9 | 16.0 | 3.2 | 23.3 | 2.9 | 18.9 | 8.5 |
| Styrene | 26.5 | 1.3 | 44.1 | 2.8 | 33.5 | 5.8 | 33.6 | 5.8 | 83.5 | 2.8 | 120.2 | 9.9 |
| 5-Methyl-2-Heptanone | 6.4 | 5.3 | 4.3 | 2.2 | 17.7 | 3.9 | 10.0 | 3.4 | 8.8 | 2.7 | 8.7 | 11.0 |
| 1-Pentanol | 31.3 | 4.2 | 48.0 | 8.5 | 27.9 | 1.8 | 32.6 | 5.2 | 4.8 | 2.8 | 4.2 | 5.8 |
| p-Ethyltoluene | 0.2 | 6.5 | 0.4 | 3.8 | 2.3 | 1.9 | 3.1 | 4.0 | 6.8 | 2.2 | 8.3 | 10.4 |
| p-Cymene | 2.1 | 1.4 | 1.4 | 0.2 | 2.2 | 0.4 | 2.5 | 3.3 | 3.7 | 5.4 | 3.8 | 0.0 |
| Mesitylene | 8.4 | 0.8 | 12.6 | 4.7 | 1.2 | 2.7 | 1.3 | 0.1 | 0.4 | 1.7 | 0.5 | 7.8 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 4-Methyl-4-Heptanol | 1.8 | 0.2 | 1.1 | 4.9 | 0.6 | 10.2 | 0.5 | 2.6 | 0.2 | 3.3 | 0.1 | 8.8 |
| 4-Heptanol | 0.5 | 3.4 | 0.4 | 7.5 | 2.9 | 5.4 | 2.4 | 0.1 | 3.5 | 3.2 | 3.0 | 6.9 |
| 2-Octanone | 36.6 | 7.8 | 23.3 | 6.2 | 115.6 | 1.7 | 99.0 | 0.2 | 20.6 | 2.6 | 13.0 | 9.5 |
| Octanal | 0.2 | 2.2 | 0.2 | 4.3 | 0.1 | 11.3 | 0.2 | 5.8 | 4.4 | 5.4 | 4.1 | 1.7 |
| 3-Hydroxy-2-Butanone | 0.3 | 7.2 | 0.2 | 12.5 | 0.3 | 1.3 | 0.5 | 2.2 | 0.1 | 1.8 | 0.1 | 12.2 |
| 1-Octen-3-one | 15.6 | 3.0 | 22.1 | 6.8 | 7.4 | 2.6 | 6.4 | 3.0 | 3.2 | 3.8 | 2.9 | 10.1 |
| trans-2-Pentenol | 12.8 | 5.2 | 10.8 | 3.5 | 22.6 | 4.0 | 23.7 | 1.4 | 23.4 | 3.4 | 24.4 | 7.6 |
| 2,2,6-Trimethyl-Cyclohexanone | 2.5 | 4.9 | 2.2 | 6.6 | 3.2 | 7.0 | 3.0 | 2.8 | 4.8 | 2.9 | 5.4 | 4.3 |
| 2-Heptanol | 531.4 | 5.3 | 575.8 | 2.4 | 530.4 | 8.7 | 567.5 | 11.3 | 270.3 | 3.6 | 276.8 | 4.7 |
| cis-2-Pentenol | 214.3 | 3.5 | 301.2 | 10.2 | 138.5 | 13.4 | 191.0 | 5.6 | 147.6 | 2.8 | 148.4 | 5.0 |
| 1-Hydroxy-2-Propanone | 20.3 | 0.3 | 23.6 | 4.6 | 9.3 | 3.5 | 11.0 | 7.9 | 5.4 | 2.3 | 6.9 | 3.2 |
| 5-Methyl-4-Hexen-3-one | 1.5 | 9.6 | 1.2 | 0.2 | 3.2 | 8.9 | 2.2 | 8.2 | 2.0 | 2.7 | 1.5 | 12.8 |
| Hemimellitene | 4.9 | 8.6 | 4.1 | 4.2 | 3.5 | 7.2 | 2.3 | 3.7 | 9.2 | 3.3 | 7.7 | 9.6 |
| 6-Methyl-5-Hepten-2-one | 14.7 | 4.2 | 20.0 | 8.2 | 9.4 | 3.5 | 13.2 | 0.8 | 17.2 | 0.3 | 25.0 | 2.7 |
| 2-Pentene | 287.3 | 5.2 | 325.7 | 11.6 | 456.2 | 0.7 | 422.4 | 5.1 | 143.1 | 3.6 | 96.5 | 3.8 |
| 1-Hexanol | 542.7 | 2.8 | 677.6 | 6.4 | 392.5 | 6.7 | 413.2 | 2.8 | 701.8 | 2.2 | 658.5 | 4.3 |
| 2-Cyclopenten-1-one | 1.2 | 7.4 | 1.0 | 12.3 | 11.4 | 10.5 | 9.7 | 0.8 | 14.8 | 6.5 | 8.1 | 5.0 |
| 2-Methyl-2-Cyclopenten-1-one | 0.2 | 0.6 | 0.3 | 8.1 | 3.7 | 4.5 | 3.1 | 5.5 | 3.2 | 5.1 | 2.9 | 1.6 |
| β-Methy-Styrene | 0.3 | 6.0 | 0.2 | 5.3 | 1.7 | 3.1 | 2.0 | 2.5 | 4.1 | 1.3 | 3.4 | 10.6 |
| 4-Octanol | 3.7 | 5.7 | 3.5 | 5.1 | 4.0 | 1.1 | 3.5 | 5.3 | 2.3 | 5.8 | 1.7 | 3.0 |
| cis-3-Hexen-1-ol | 15.0 | 10.4 | 11.2 | 12.1 | 6.8 | 0.7 | 8.7 | 2.6 | 10.7 | 3.4 | 9.7 | 12.6 |
| 2-Nonanone | 57.2 | 4.3 | 48.5 | 4.1 | 370.9 | 4.0 | 330.3 | 10.2 | 60.4 | 1.5 | 60.9 | 14.0 |
| Nonanal | 82.7 | 2.3 | 88.3 | 5.7 | 78.2 | 1.2 | 87.7 | 0.3 | 24.7 | 6.2 | 13.5 | 11.7 |
| Ethylene Glycol Butyl Ether | 27.8 | 3.1 | 27.2 | 5.7 | 2.9 | 1.0 | 2.5 | 4.1 | 10.3 | 3.2 | 15.2 | 13.6 |
| 1-Ethyl-1-Methyl-Cyclopentane | 2.2 | 2.8 | 1.6 | 3.0 | 3.0 | 4.1 | 3.9 | 2.2 | 17.6 | 4.8 | 12.3 | 10.2 |
| 3-Octen-2-one | 2.8 | 8.8 | 2.9 | 12.3 | 85.0 | 3.3 | 164.4 | 4.5 | 7.4 | 4.7 | 6.9 | 4.8 |
| 2-Octanol | 78.0 | 0.2 | 99.2 | 10.9 | 158.9 | 10.5 | 166.3 | 4.8 | 10.4 | 0.9 | 10.7 | 1.9 |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | 0.3 | 4.3 | 0.3 | 8.4 | 0.3 | 6.8 | 0.3 | 2.6 | 0.9 | 1.0 | 1.0 | 10.7 |
| 1,3-Bis(1,1-Dimethylethyl)-Benzene | 0.4 | 1.3 | 0.3 | 6.0 | 0.2 | 2.0 | 0.2 | 0.6 | 0.2 | 6.2 | 0.2 | 14.2 |
| trans-2-Octenal | 0.9 | 2.0 | 0.8 | 4.4 | 8.5 | 3.3 | 9.9 | 0.3 | 22.2 | 5.4 | 17.9 | 4.8 |
| m-Ethyl-Styrene | 9.7 | 5.4 | 10.7 | 6.2 | 8.5 | 2.8 | 9.9 | 4.7 | 2.1 | 1.9 | 1.1 | 6.1 |
| 5-Methyl-2-Heptanone | 0.7 | 3.9 | 0.6 | 7.1 | 0.6 | 7.4 | 0.5 | 3.6 | 0.9 | 3.4 | 0.8 | 6.8 |
| 2-Decanone | 2.4 | 4.0 | 1.8 | 6.7 | 2.7 | 3.8 | 2.0 | 12.8 | 1.7 | 3.7 | 1.2 | 13.3 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-Octen-3-ol | 135.1 | 10.2 | 116.5 | 8.5 | 135.5 | 0.0 | 105.3 | 6.8 | 145.0 | 6.1 | 122.2 | 5.4 |
| trans,trans-2,4-Heptadienal | 1.9 | 4.1 | 2.2 | 4.4 | 4.3 | 2.5 | 4.6 | 5.5 | 2.6 | 4.4 | 2.9 | 9.6 |
| 1-Heptanol | 52.4 | 0.9 | 53.5 | 10.1 | 55.3 | 0.8 | 49.9 | 0.2 | 52.6 | 3.0 | 59.4 | 11.7 |
| cis,cis-3,5-Octadiene | 2.3 | 13.4 | 1.7 | 8.6 | 2.2 | 4.1 | 2.1 | 1.4 | 1.0 | 6.3 | 1.4 | 7.9 |
| 2-Oxo-Methyl Ester Propanoic Acid | 142.4 | 8.5 | 171.8 | 9.2 | 91.1 | 0.3 | 116.6 | 4.6 | 15.1 | 1.9 | 15.9 | 8.9 |
| Dihydromyrcenol | 15.3 | 2.4 | 20.0 | 12.9 | 11.8 | 6.8 | 13.1 | 5.5 | 9.4 | 3.7 | 11.8 | 5.0 |
| trans-Menthone | 0.1 | 9.8 | 0.1 | 3.6 | 0.9 | 8.3 | 1.1 | 10.5 | 0.4 | 4.7 | 0.4 | 4.8 |
| Furfural | 62.1 | 4.4 | 79.3 | 3.4 | 64.9 | 7.1 | 88.0 | 2.2 | 75.8 | 3.2 | 54.7 | 3.3 |
| Ethanoic Acid | 1884.8 | 1.3 | 2262.6 | 13.3 | 1967.9 | 8.6 | 2388.6 | 1.7 | 1360.3 | 3.2 | 1538.3 | 4.4 |
| 2-Ethyl-1-Hexanol | 31.9 | 4.3 | 34.2 | 12.1 | 13.8 | 6.6 | 13.2 | 2.8 | 31.9 | 5.0 | 29.7 | 4.1 |
| Decanal | 25.2 | 3.8 | 33.3 | 1.8 | 43.5 | 9.1 | 52.0 | 1.5 | 63.0 | 4.9 | 65.2 | 4.8 |
| Furfuryl Formate | 49.0 | 4.5 | 55.5 | 5.4 | 46.3 | 3.5 | 56.3 | 2.6 | 32.0 | 1.8 | 32.1 | 2.0 |
| trans-2-Hepten-1-ol | 22.3 | 7.4 | 22.1 | 11.9 | 20.9 | 12.0 | 19.5 | 11.7 | 43.3 | 4.0 | 42.5 | 10.1 |
| 2-Nonanol | 20.7 | 5.5 | 24.4 | 3.5 | 378.8 | 1.5 | 344.5 | 4.7 | 4.1 | 2.6 | 3.8 | 1.7 |
| 1-(2-Furanyl)-Ethanone | 306.4 | 2.2 | 365.3 | 9.5 | 492.2 | 1.4 | 456.3 | 5.2 | 60.9 | 2.1 | 69.3 | 6.7 |
| 3,5-Octadien-2-one | 10.9 | 5.0 | 12.5 | 7.1 | 6.8 | 3.1 | 7.2 | 5.9 | 25.6 | 5.2 | 21.7 | 2.3 |
| Benzaldehyde | 29.1 | 2.2 | 31.9 | 10.8 | 27.7 | 1.4 | 23.3 | 8.5 | 42.9 | 3.2 | 33.4 | 0.4 |
| Furfuryl Acetate | 0.4 | 3.4 | 0.4 | 6.6 | 0.4 | 2.2 | 0.4 | 6.5 | 0.9 | 4.4 | 0.8 | 7.9 |
| Linalool | 6.6 | 3.3 | 7.4 | 8.0 | 5.1 | 8.3 | 4.9 | 2.3 | 6.2 | 5.4 | 6.1 | 4.1 |
| β-Myrcene | 0.8 | 6.0 | 1.0 | 3.2 | 1.2 | 13.3 | 1.0 | 9.4 | 1.5 | 3.6 | 1.1 | 3.9 |
| 1-Octanol | 83.0 | 3.1 | 93.3 | 8.3 | 73.8 | 5.3 | 65.8 | 1.5 | 124.7 | 2.9 | 123.7 | 11.4 |
| trans-p-2-Menthen-1-ol | 0.1 | 5.4 | 0.1 | 2.2 | 0.7 | 2.9 | 0.9 | 7.2 | 0.6 | 3.4 | 0.6 | 7.3 |
| Propanoic Acid | 4.2 | 5.5 | 4.6 | 7.7 | 1.0 | 0.1 | 0.9 | 2.4 | 1.5 | 4.4 | 1.5 | 6.7 |
| 2,3-Butanediol | 231.1 | 0.3 | 338.0 | 7.0 | 431.1 | 3.7 | 451.8 | 1.8 | 57.7 | 3.0 | 57.3 | 10.0 |
| Dimethyl Sulfoxide | 62.1 | 4.9 | 68.7 | 7.3 | 32.0 | 5.4 | 35.2 | 2.8 | 19.5 | 3.5 | 25.3 | 4.3 |
| m-Menth-3-ene | 49.7 | 2.0 | 58.2 | 6.5 | 44.1 | 1.0 | 55.2 | 4.0 | 6.5 | 4.3 | 7.8 | 6.4 |
| Trans-(2-Ethylcyclopentyl)-Methanol | 20.6 | 3.1 | 28.6 | 4.7 | 33.6 | 1.7 | 35.7 | 4.4 | 33.6 | 3.0 | 39.8 | 13.9 |
| Bornyl Acetate | 9.1 | 1.2 | 10.6 | 6.1 | 4.8 | 0.7 | 5.4 | 1.8 | 9.4 | 3.6 | 10.2 | 14.2 |
| 4-Cyclopentene-1,3-dione | 271.0 | 1.4 | 308.9 | 6.3 | 268.6 | 3.0 | 269.8 | 1.0 | 142.0 | 2.2 | 97.1 | 2.7 |
| Menthol | 2.8 | 5.5 | 3.6 | 1.8 | 10.5 | 3.3 | 10.2 | 11.3 | 0.5 | 5.3 | 0.3 | 10.8 |
| 2-Undecanone | 9.4 | 2.4 | 11.1 | 10.4 | 24.6 | 4.4 | 32.2 | 10.7 | 7.0 | 1.7 | 7.3 | 4.1 |
| 2-(2-Furanyl)-Furan | 2.4 | 4.0 | 3.5 | 6.3 | 3.0 | 1.9 | 3.6 | 1.7 | 3.8 | 3.9 | 4.0 | 10.2 |
| trans-2-Octen-1-ol | 38.0 | 9.9 | 45.9 | 10.4 | 53.6 | 1.6 | 47.6 | 8.4 | 101.3 | 3.6 | 99.3 | 2.0 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|
| trans-2-Nonen-1-ol | 24.0 | 8.8 | 22.4 | 6.2 | 14.5 | 3.3 | 14.9 | 4.3 | 34.4 | 2.4 | 30.5 | 5.2 |
| Diethylene Glycol Ethyl Ether | 63.6 | 3.7 | 70.0 | 12.0 | 53.0 | 1.3 | 45.0 | 3.5 | 71.2 | 4.0 | 65.3 | 2.2 |
| 3,5,5-Trimethyl-2-Cyclopenten-1-one | 12.6 | 10.7 | 17.5 | 9.3 | 13.9 | 6.5 | 10.9 | 1.7 | 20.5 | 3.2 | 12.3 | 9.7 |
| cis-p-2-Menthen-1-ol | 1.9 | 3.5 | 1.5 | 3.5 | 3.8 | 2.3 | 3.3 | 3.1 | 2.4 | 4.8 | 2.8 | 9.9 |
| β-Cyclocitral | 3.2 | 5.8 | 3.1 | 5.9 | 4.7 | 2.8 | 4.4 | 0.9 | 10.5 | 4.2 | 10.0 | 5.8 |
| Benzeneacetaldehyde | 91.3 | 5.6 | 94.5 | 6.5 | 35.0 | 0.7 | 38.2 | 3.0 | 18.8 | 3.9 | 18.2 | 7.1 |
| 1-Nonanol | 25.0 | 4.2 | 31.2 | 12.8 | 36.8 | 1.0 | 43.0 | 1.5 | 30.4 | 4.4 | 32.7 | 4.3 |
| Furfuryl Alcohol | 60.2 | 2.2 | 58.2 | 3.8 | 78.2 | 11.4 | 89.0 | 0.3 | 72.5 | 1.0 | 81.3 | 3.9 |
| Phoracanthol | 66.3 | 0.7 | 76.6 | 6.8 | 12.4 | 3.3 | 17.0 | 3.2 | 10.4 | 2.8 | 10.2 | 12.0 |
| cis-3-Nonen-1-ol | 18.0 | 2.4 | 21.1 | 9.9 | 8.2 | 5.5 | 9.6 | 3.7 | 10.2 | 1.4 | 11.8 | 6.1 |
| cis-Piperitol | 3.7 | 1.2 | 3.0 | 7.5 | 1.7 | 7.9 | 2.3 | 7.5 | 0.6 | 2.8 | 0.6 | 7.6 |
| p-Methoxy-Styrene | 5.3 | 0.3 | 6.7 | 10.5 | 1.6 | 2.7 | 1.6 | 3.6 | 23.4 | 1.8 | 27.8 | 8.6 |
| (2Z)-3-Ethyl-2,4-Pentadien-1-ol | 9.3 | 2.9 | 10.5 | 9.9 | 7.0 | 0.5 | 6.8 | 2.7 | 6.6 | 0.8 | 6.7 | 2.6 |
| Butylene Glycol Monobutyl Ether | 13.7 | 4.8 | 17.5 | 7.3 | 12.0 | 6.1 | 16.7 | 5.8 | 8.8 | 1.3 | 9.4 | 7.7 |
| α-Terpineol | 2.4 | 3.5 | 2.0 | 4.7 | 2.3 | 1.8 | 2.2 | 1.2 | 1.0 | 0.2 | 1.1 | 14.0 |
| 1,5-Cyclooctanedione | 2.1 | 3.3 | 2.0 | 1.6 | 4.2 | 0.5 | 0.5 | 2.3 | 2.0 | 5.2 | 2.1 | 4.2 |
| γ-Terpinene | 1.8 | 1.9 | 2.0 | 4.9 | 3.2 | 0.2 | 4.0 | 12.4 | 6.3 | 2.4 | 6.6 | 12.9 |
| trans-2-Decenol | 6.2 | 1.3 | 7.2 | 8.1 | 7.0 | 6.7 | 7.4 | 2.6 | 12.4 | 5.3 | 10.1 | 6.7 |
| 2-Propenoic Acid | 8.8 | 1.3 | 12.9 | 11.3 | 1.0 | 5.3 | 1.0 | 2.8 | 0.5 | 4.9 | 0.5 | 4.7 |
| 2-Undecanol | 4.4 | 8.3 | 4.6 | 6.4 | 83.2 | 4.6 | 76.2 | 0.1 | 3.5 | 4.6 | 2.3 | 8.7 |
| 3-Ethyl-Benzaldehyde | 6.1 | 8.8 | 5.3 | 4.4 | 4.9 | 3.8 | 4.3 | 3.6 | 6.3 | 4.3 | 6.0 | 5.2 |
| 3-Hydroxy-Benzaldehyde | 13.0 | 0.1 | 19.5 | 13.2 | 1.9 | 8.2 | 1.7 | 4.6 | 4.5 | 3.3 | 4.8 | 8.8 |
| trans-2-Nonene | 3.4 | 1.6 | 3.4 | 6.9 | 4.7 | 6.1 | 4.8 | 12.3 | 0.5 | 3.2 | 0.4 | 6.3 |
| 2-Methyl-2-Pentenal | 14.5 | 3.2 | 17.0 | 5.6 | 7.3 | 7.7 | 7.4 | 1.5 | 6.8 | 4.2 | 6.6 | 2.2 |
| cis-5-Decenol | 5.2 | 2.5 | 5.3 | 5.0 | 105.3 | 8.8 | 110.7 | 10.1 | 2.7 | 6.0 | 1.7 | 13.3 |
| trans-Piperitol | 2.3 | 12.0 | 2.3 | 7.8 | 4.6 | 6.1 | 5.5 | 2.8 | 0.9 | 4.3 | 0.9 | 11.8 |
| 4-Ethyl-Benzaldehyde | 3.4 | 2.3 | 3.7 | 8.7 | 3.0 | 10.5 | 2.9 | 1.3 | 5.5 | 5.0 | 5.2 | 6.0 |
| Naphthalene | 16.4 | 0.4 | 17.0 | 12.4 | 7.5 | 0.7 | 8.3 | 0.9 | 19.1 | 3.5 | 20.4 | 8.2 |
| 1-Decanol | 31.0 | 1.4 | 36.2 | 10.4 | 17.0 | 2.0 | 19.3 | 5.7 | 19.7 | 6.1 | 16.9 | 7.8 |
| Cyclodecane | 108.9 | 10.0 | 134.2 | 12.0 | 89.5 | 5.4 | 87.3 | 2.3 | 67.0 | 2.6 | 65.2 | 4.0 |
| trans,trans-2,4-Decadienal | 12.0 | 2.2 | 18.5 | 6.5 | 19.4 | 0.5 | 23.4 | 8.4 | 49.8 | 1.2 | 54.6 | 4.7 |
| 1,2-Cyclopentanedione | 545.7 | 2.7 | 603.5 | 9.8 | 425.5 | 2.0 | 454.4 | 0.6 | 186.6 | 2.4 | 201.0 | 3.4 |
| Cyclodecene | 2.2 | 0.5 | 2.3 | 13.5 | 2.0 | 2.5 | 2.1 | 6.1 | 1.9 | 4.3 | 1.5 | 9.7 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| cis-4-Decenol | 1.8 | 2.6 | 1.7 | 12.2 | 3.0 | 0.1 | 3.1 | 7.5 | 0.6 | 3.8 | 0.6 | 5.2 |
| 1-Phenyl-2-Butanone | 7.4 | 1.1 | 8.5 | 5.9 | 7.5 | 2.7 | 7.2 | 5.6 | 15.2 | 5.6 | 15.3 | 3.1 |
| Phenethyl Alcohol | 12.6 | 6.6 | 15.0 | 9.0 | 2.2 | 1.3 | 2.3 | 8.4 | 5.7 | 1.4 | 5.3 | 2.9 |
| trans,cis-2,4-Decadienal | 8.2 | 2.9 | 9.6 | 5.3 | 12.9 | 2.5 | 15.2 | 4.8 | 42.7 | 5.1 | 44.1 | 8.5 |
| 2-Cyclohexenol | 76.5 | 3.8 | 82.0 | 5.0 | 37.0 | 0.2 | 47.4 | 1.1 | 4.6 | 3.5 | 4.5 | 10.9 |
| 2-Ethyl Hexanoic Acid | 20.5 | 1.3 | 28.1 | 4.0 | 4.1 | 1.4 | 4.4 | 4.6 | 49.9 | 2.7 | 55.2 | 1.9 |
| 3-Methyl-1,2-Cyclopentanedione | 27.0 | 2.7 | 34.6 | 3.8 | 46.7 | 1.8 | 52.8 | 2.2 | 8.6 | 0.0 | 9.2 | 7.7 |
| trans-Cinnamaldehyde | 9.2 | 0.8 | 11.6 | 4.1 | 5.8 | 0.6 | 5.7 | 3.5 | 7.8 | 2.0 | 8.6 | 3.7 |
| Heptanoic Acid | 82.6 | 4.7 | 77.6 | 6.2 | 37.0 | 1.6 | 30.4 | 2.0 | 86.7 | 0.4 | 80.7 | 10.7 |
| Mequinol | 28.6 | 6.8 | 27.4 | 0.1 | 19.9 | 1.2 | 24.6 | 3.1 | 81.3 | 3.5 | 84.2 | 0.3 |
| 2,4,5-Trihydroxypyrimidine | 67.0 | 5.1 | 71.0 | 1.7 | 11.1 | 11.4 | 16.0 | 6.5 | 10.4 | 3.3 | 10.9 | 7.6 |
| cis-Cinnamaldehyde | 8.8 | 7.4 | 9.3 | 5.2 | 8.6 | 7.0 | 8.9 | 1.2 | 7.6 | 4.0 | 8.0 | 6.4 |
| Benzenemethanol | 46.5 | 0.7 | 50.2 | 10.1 | 22.5 | 8.9 | 26.9 | 5.3 | 106.3 | 3.4 | 141.1 | 6.8 |
| Mesitaldehyde | 5.0 | 1.4 | 6.0 | 6.3 | 2.1 | 0.7 | 2.9 | 2.7 | 6.0 | 4.3 | 6.5 | 8.7 |
| 2-Ethylhexyl Ester Octanoic Acid | 1.1 | 8.7 | 1.4 | 10.3 | 3.0 | 4.6 | 2.9 | 2.4 | 0.8 | 5.4 | 0.8 | 6.8 |
| Benzeneethanol | 95.5 | 6.7 | 117.1 | 8.4 | 28.9 | 0.0 | 32.9 | 6.4 | 47.9 | 3.8 | 47.8 | 11.8 |
| 1,4-Butanediol | 83.2 | 1.1 | 93.9 | 3.9 | 65.0 | 0.2 | 72.7 | 6.6 | 62.7 | 5.1 | 60.3 | 1.5 |
| β-Ionone | 13.3 | 6.6 | 15.2 | 10.0 | 11.8 | 3.4 | 11.6 | 3.0 | 44.1 | 5.7 | 36.8 | 3.6 |
| 2-Methyl-1,4-Benzenediol | 21.1 | 4.2 | 26.7 | 6.8 | 12.9 | 0.7 | 19.0 | 1.0 | 4.0 | 0.8 | 3.4 | 6.1 |
| 2-Ethyl Heptanoic Acid | 1.0 | 4.5 | 1.1 | 11.5 | 5.5 | 4.8 | 5.2 | 0.9 | 1.6 | 0.3 | 1.6 | 5.0 |
| 1-Dodecanol | 12.8 | 8.9 | 10.5 | 10.2 | 5.4 | 7.6 | 6.5 | 7.2 | 15.2 | 1.9 | 10.7 | 2.5 |
| Benzalacetone | 18.3 | 0.7 | 18.7 | 1.8 | 9.3 | 3.4 | 8.6 | 0.9 | 10.2 | 4.5 | 10.8 | 13.1 |
| Maltol | 97.5 | 5.2 | 151.4 | 4.2 | 128.6 | 1.1 | 173.1 | 3.5 | 65.5 | 3.9 | 66.3 | 5.4 |
| 2-Acetylpyrrole | 18.5 | 1.7 | 18.6 | 4.6 | 20.9 | 4.0 | 19.9 | 1.1 | 0.6 | 4.8 | 0.6 | 3.5 |
| 2,4-Decadien-1-ol | 8.2 | 2.0 | 10.9 | 10.8 | 7.8 | 0.6 | 8.1 | 1.6 | 7.7 | 3.4 | 8.4 | 3.6 |
| Levoglucosenone | 9.0 | 2.2 | 10.5 | 11.1 | 16.4 | 4.3 | 12.8 | 2.5 | 9.0 | 3.5 | 8.3 | 5.5 |
| Phenol | 36.8 | 12.1 | 46.0 | 11.0 | 39.2 | 7.3 | 46.6 | 1.1 | 63.1 | 6.3 | 51.9 | 6.0 |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | 48.4 | 4.9 | 45.7 | 10.7 | 28.6 | 0.4 | 22.7 | 1.1 | 5.2 | 3.6 | 4.5 | 8.1 |
| 4,6-Dimethyl-Dodecane | 20.2 | 6.2 | 25.7 | 13.3 | 30.9 | 1.4 | 31.4 | 3.5 | 3.5 | 2.6 | 3.6 | 9.7 |
| Ethyl Ester Decanoic Acid | 5.8 | 0.6 | 6.1 | 12.3 | 5.2 | 2.5 | 5.8 | 3.1 | 5.1 | 3.7 | 5.3 | 4.3 |
| 1-Methyl-4-Piperidinone | 1.6 | 12.8 | 1.4 | 12.1 | 0.5 | 2.8 | 0.6 | 2.8 | 0.4 | 3.4 | 0.4 | 8.4 |
| 2,2-Dimethyl-3-Heptanone | 2.7 | 1.6 | 2.9 | 12.2 | 102.8 | 2.5 | 112.3 | 0.2 | 4.1 | 1.9 | 3.9 | 5.5 |
| Octanoic Acid | 30.2 | 1.4 | 39.4 | 9.5 | 1.3 | 4.6 | 1.5 | 11.2 | 18.6 | 5.1 | 17.6 | 12.3 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,3-Dihydroxy-2-Propanone | 82.2 | 5.1 | 92.9 | 10.2 | 43.3 | 0.2 | 38.9 | 6.5 | 2.0 | 3.9 | 1.3 | 12.3 |
| 2-Phenoxy-Ethanol | 6.9 | 1.1 | 7.8 | 5.9 | 6.2 | 4.3 | 5.5 | 3.6 | 17.8 | 1.6 | 15.3 | 11.2 |
| Isophthalaldehyde | 5.0 | 6.8 | 4.4 | 8.6 | 4.8 | 4.0 | 4.3 | 1.5 | 5.4 | 3.2 | 4.8 | 5.3 |
| Cyclotetradecane | 8.6 | 0.5 | 9.4 | 9.5 | 2.2 | 1.8 | 2.8 | 4.7 | 4.9 | 1.8 | 4.9 | 4.9 |
| Nonanoic Acid | 15.5 | 8.2 | 19.6 | 10.6 | 1.7 | 1.7 | 1.4 | 3.8 | 47.2 | 4.3 | 42.5 | 5.8 |
| 2-Ethyl-Phenol | 15.5 | 7.1 | 19.9 | 7.1 | 12.2 | 1.9 | 15.3 | 4.3 | 26.5 | 1.9 | 26.6 | 6.8 |
| 2-Methoxy-4-Vinyl-Phenol | 61.9 | 1.6 | 64.8 | 4.0 | 53.3 | 0.2 | 55.3 | 8.0 | 32.3 | 0.2 | 29.1 | 8.7 |
| 4-Methylimidazole | 1.2 | 9.1 | 1.0 | 4.5 | 18.9 | 5.7 | 22.8 | 6.1 | 24.2 | 1.1 | 29.0 | 12.6 |
| m-tert-Butyl-Toluene | 15.6 | 4.1 | 17.7 | 6.7 | 16.9 | 2.0 | 17.3 | 6.5 | 18.8 | 4.5 | 17.7 | 6.5 |
| Syringol | 22.4 | 10.2 | 20.4 | 7.8 | 17.8 | 0.8 | 19.4 | 0.7 | 13.7 | 1.2 | 13.1 | 6.3 |
| Decanoic Acid | 33.7 | 1.2 | 31.6 | 11.5 | 6.1 | 7.5 | 5.2 | 1.0 | 32.8 | 4.9 | 29.8 | 9.3 |
| 3-Hydroxy-2,3-Dihydro-Maltol | 58.3 | 1.2 | 64.1 | 3.3 | 18.5 | 3.5 | 19.0 | 1.2 | 42.3 | 3.6 | 37.6 | 11.8 |
| 5-Hydroxy-Maltol | 36.2 | 5.2 | 37.3 | 5.6 | 71.6 | 1.5 | 68.6 | 2.4 | 41.6 | 5.6 | 30.5 | 9.8 |
| Triethylene Glycol | 1.2 | 4.6 | 1.0 | 13.4 | 1.3 | 7.2 | 1.0 | 8.4 | 5.5 | 2.9 | 5.8 | 4.9 |
| Benzoic Acid | 13.5 | 7.9 | 19.8 | 3.1 | 6.0 | 0.9 | 6.7 | 1.0 | 5.4 | 4.9 | 5.5 | 5.4 |
| 2-Methyl-Benzaldehyde | 193.4 | 1.3 | 209.8 | 6.9 | 132.7 | 6.1 | 184.7 | 4.2 | 255.2 | 5.1 | 230.2 | 6.2 |
| Undecanoic Acid | 32.5 | 5.8 | 31.7 | 10.7 | 4.7 | 0.0 | 5.6 | 3.3 | 30.9 | 1.0 | 29.9 | 5.9 |
| 4-Pyridinol | 92.0 | 0.4 | 117.0 | 13.7 | 5.4 | 1.8 | 4.7 | 5.9 | 46.0 | 1.0 | 39.9 | 7.3 |
| 4-Amino-Phenol | 49.8 | 1.2 | 51.9 | 6.9 | 6.0 | 5.7 | 5.9 | 1.1 | 2.0 | 3.3 | 1.7 | 11.9 |

[1]RSD - Relative Standard Deviation values.

**Table S10B. Mean and relative standard deviation values of identified VOCs in sugarcane samples from "Verde", "Violeta" and "Canica" cultivars.**

| Volatile Organic Compound | VER | | | | VIO | | | | CAN | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2015 | | 2017 | | 2015 | | 2017 | | 2015 | | 2017 | |
| | Mean | RSD[1] (%) | Mean | RSD[1] (%) | Mean | RSD[1] (%) | Mean | RSD[1] (%) | Mean | RSD[1] (%) | Mean | RSD[1] (%) |
| Pentane | 2.6 | 4.2 | 2.1 | 8.9 | 3.0 | 1.1 | 3.6 | 5.3 | 2.2 | 0.2 | 2.1 | 7.3 |
| 1-Pentene | 1.1 | 7.3 | 1.5 | 0.8 | 0.8 | 1.5 | 1.0 | 5.9 | 2.0 | 0.8 | 3.4 | 3.3 |
| 2-Methyl-Pentane | 2.8 | 3.3 | 3.7 | 5.5 | 1.0 | 3.6 | 1.2 | 5.3 | 0.1 | 0.5 | 0.2 | 9.8 |
| Hexane | 2.2 | 3.7 | 2.2 | 11.2 | 1.6 | 7.7 | 1.6 | 8.1 | 20.4 | 3.6 | 10.6 | 1.2 |
| Ethyl Ether | 0.3 | 2.9 | 0.2 | 6.4 | 1.4 | 4.0 | 1.0 | 4.0 | 5.3 | 7.3 | 2.5 | 11.0 |
| cis-4-Methyl-2-Pentene | 0.1 | 0.6 | 2.5 | 2.9 | 0.2 | 6.9 | 0.5 | 8.2 | 0.2 | 5.2 | 0.5 | 0.9 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| cis-Piperylene | 11.0 | 1.2 | 8.2 | 4.4 | 1.4 | 5.3 | 2.4 | 12.9 | 3.8 | 3.1 | 3.0 | 4.0 |
| 2-Methyl-1-Pentene | 90.5 | 5.7 | 1.4 | 7.2 | 35.4 | 11.9 | 1.0 | 3.9 | 83.1 | 2.4 | 45.3 | 0.9 |
| cis-3-Methyl-2-Pentene | 3.1 | 1.8 | 2.1 | 2.4 | 1.3 | 7.8 | 1.4 | 10.1 | 1.4 | 8.2 | 1.9 | 3.1 |
| 3-Methyl-Hexane | 0.9 | 6.2 | 0.6 | 0.4 | 1.0 | 8.8 | 1.3 | 6.9 | 2.4 | 1.0 | 3.1 | 3.5 |
| 1,4-Pentadiene | 7.2 | 5.6 | 5.8 | 0.6 | 2.0 | 5.2 | 1.8 | 6.8 | 5.4 | 13.0 | 2.4 | 2.4 |
| Methanethiol | 3.3 | 1.4 | 4.3 | 5.2 | 1.9 | 3.3 | 2.3 | 5.7 | 3.3 | 6.4 | 3.7 | 3.8 |
| trans-Piperylene | 1.7 | 7.7 | 1.5 | 9.4 | 0.7 | 0.9 | 0.9 | 7.6 | 2.3 | 2.2 | 1.5 | 5.3 |
| Heptane | 2.3 | 0.1 | 1.4 | 1.8 | 8.7 | 0.0 | 5.3 | 0.1 | 11.3 | 0.5 | 13.9 | 5.2 |
| tert-Butyl Ethyl Ether | 160.7 | 3.7 | 1.2 | 0.4 | 75.9 | 7.5 | 1.0 | 4.1 | 257.5 | 3.0 | 306.6 | 8.2 |
| Ethanal | 70.8 | 2.2 | 65.7 | 0.8 | 11.4 | 12.5 | 17.4 | 4.0 | 56.9 | 3.3 | 67.4 | 1.4 |
| Dimethyl Sulfide | 489.1 | 2.3 | 590.5 | 9.9 | 495.3 | 0.1 | 606.4 | 13.3 | 233.2 | 5.6 | 298.5 | 5.2 |
| 4-Methyl-Heptane | 105.0 | 2.4 | 1.8 | 1.5 | 33.1 | 5.8 | 1.0 | 5.5 | 117.0 | 10.0 | 181.9 | 2.0 |
| Octane | 3.4 | 7.0 | 2.1 | 9.0 | 1.3 | 8.2 | 1.5 | 8.8 | 8.0 | 9.0 | 10.4 | 6.7 |
| Propanal | 8.2 | 5.5 | 5.8 | 2.8 | 4.9 | 9.4 | 3.4 | 4.9 | 24.9 | 13.3 | 18.0 | 5.8 |
| Furan | 7.8 | 7.9 | 7.6 | 1.6 | 4.7 | 10.4 | 5.3 | 2.4 | 5.9 | 9.2 | 4.7 | 2.8 |
| 2,4-Dimethyl-Heptane | 17.9 | 2.0 | 20.6 | 6.8 | 13.6 | 2.0 | 21.4 | 5.9 | 11.6 | 3.5 | 12.3 | 8.5 |
| 2-Methyl-Propanal | 83.5 | 3.7 | 90.6 | 1.3 | 22.0 | 0.2 | 21.4 | 2.2 | 26.3 | 0.9 | 28.9 | 1.6 |
| 2-Propanone | 466.4 | 0.1 | 464.8 | 6.9 | 169.6 | 4.9 | 76.0 | 12.8 | 749.5 | 4.9 | 652.7 | 4.0 |
| Methyl Ester Acetic Acid | 5.0 | 4.4 | 7.1 | 5.1 | 0.8 | 3.5 | 1.6 | 3.0 | 0.3 | 1.0 | 0.4 | 3.4 |
| 2-Methyl-2-Heptene | 0.8 | 1.5 | 0.4 | 1.7 | 0.9 | 3.5 | 0.9 | 1.4 | 24.9 | 5.1 | 35.0 | 1.1 |
| Crotonal | 5.1 | 5.2 | 4.4 | 4.8 | 3.3 | 1.8 | 7.6 | 4.0 | 1.8 | 0.2 | 1.8 | 3.6 |
| 2,3-Dimethyl-Heptane | 2.1 | 4.6 | 2.9 | 11.5 | 0.7 | 5.1 | 0.9 | 3.2 | 0.6 | 4.7 | 0.3 | 4.8 |
| 4-Methyl-Octane | 8.9 | 3.5 | 10.4 | 1.3 | 8.5 | 0.6 | 11.1 | 4.3 | 5.7 | 6.7 | 6.7 | 5.7 |
| 2-Methyl-Furan | 1.7 | 8.1 | 1.1 | 7.8 | 1.9 | 3.3 | 1.4 | 12.7 | 1.2 | 11.4 | 1.6 | 11.9 |
| 2,4-Dimethyl-1-Heptene | 12.2 | 0.1 | 10.2 | 6.6 | 27.1 | 6.3 | 10.8 | 1.8 | 344.3 | 8.6 | 428.1 | 1.0 |
| Ethyl Ester Acetic Acid | 65.0 | 5.9 | 71.9 | 6.7 | 9.6 | 4.9 | 16.9 | 9.1 | 46.1 | 7.1 | 64.6 | 1.3 |
| Nonane | 1.6 | 4.3 | 2.6 | 5.5 | 2.6 | 1.4 | 3.7 | 11.6 | 4.6 | 3.4 | 6.4 | 2.4 |
| 2-Butanone | 20.5 | 5.2 | 16.5 | 5.8 | 6.5 | 2.7 | 6.3 | 2.5 | 32.5 | 1.3 | 31.4 | 6.4 |
| 2-Methyl-Butanal | 99.3 | 4.5 | 79.8 | 0.2 | 14.7 | 11.1 | 14.5 | 10.8 | 72.3 | 5.2 | 66.2 | 2.7 |
| 3-Methyl-Butanal | 88.3 | 7.2 | 85.6 | 2.6 | 25.2 | 8.7 | 13.5 | 1.9 | 91.9 | 3.0 | 65.6 | 0.2 |
| Ethyl Alcohol | 556.5 | 4.1 | 661.9 | 3.3 | 907.8 | 2.2 | 1048.8 | 7.8 | 187.7 | 5.9 | 192.0 | 0.5 |
| Benzene | 13.2 | 4.8 | 9.9 | 0.2 | 5.5 | 7.0 | 8.8 | 2.2 | 5.5 | 6.9 | 5.2 | 1.0 |
| 3-Ethyl-Heptane | 0.8 | 3.7 | 0.6 | 0.4 | 1.0 | 3.5 | 1.8 | 14.7 | 8.3 | 3.5 | 6.0 | 2.7 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Ethyl-Furan | 16.5 | 3.7 | 38.3 | 2.3 | 18.6 | 6.3 | 20.1 | 13.2 | 21.1 | 8.2 | 16.2 | 3.8 |
| Ethyl Ester Propanoic Acid | 1.3 | 4.7 | 1.9 | 7.6 | 0.2 | 5.9 | 0.2 | 3.3 | 0.8 | 6.1 | 1.0 | 12.3 |
| 2-Methyl Ethyl Ester Propanoic Acid | 0.2 | 3.9 | 0.2 | 4.5 | 0.2 | 1.8 | 0.1 | 11.0 | 0.2 | 5.6 | 0.3 | 2.1 |
| 2-Methyl-Crotonal | 7.0 | 5.0 | 6.2 | 2.6 | 3.0 | 4.3 | 2.6 | 7.1 | 1.3 | 3.5 | 1.0 | 3.4 |
| Propyl Ester Acetic Acid | 0.7 | 3.1 | 0.8 | 5.1 | 0.1 | 2.9 | 0.0 | 1.2 | 0.3 | 7.3 | 0.4 | 4.2 |
| 3-Pentanone | 121.4 | 5.0 | 110.6 | 12.2 | 58.4 | 8.1 | 65.6 | 1.1 | 163.9 | 9.3 | 139.6 | 3.8 |
| Pentanal | 1.3 | 1.5 | 1.1 | 12.9 | 1.0 | 1.5 | 0.9 | 4.7 | 14.2 | 9.0 | 11.9 | 4.4 |
| 2,3-Butanedione | 39.5 | 4.2 | 39.0 | 2.0 | 26.9 | 0.5 | 30.7 | 9.9 | 13.2 | 2.0 | 17.0 | 5.8 |
| 2,3,4-Trimethyl-Hexane | 0.1 | 7.4 | 0.2 | 8.3 | 0.5 | 9.0 | 0.5 | 7.9 | 11.3 | 13.2 | 13.8 | 1.8 |
| Decane | 2.2 | 0.3 | 2.0 | 3.1 | 4.8 | 9.7 | 4.9 | 1.2 | 23.5 | 9.5 | 14.2 | 13.1 |
| 2,6-Dimethyl-Nonane | 0.7 | 6.3 | 0.6 | 0.4 | 1.4 | 0.9 | 0.9 | 5.1 | 14.6 | 11.5 | 22.1 | 2.4 |
| 2,5-Dimethyl-Nonane | 0.9 | 3.9 | 1.3 | 9.7 | 1.4 | 13.1 | 1.8 | 1.0 | 0.3 | 1.1 | 0.3 | 6.5 |
| 4-Methyl-2-Pentanone | 1.2 | 0.9 | 0.9 | 3.5 | 0.6 | 3.3 | 0.4 | 0.4 | 29.6 | 2.8 | 21.0 | 5.2 |
| 2-Methy-2-Butanol | 0.1 | 1.0 | 0.2 | 1.3 | 0.5 | 4.3 | 0.3 | 8.7 | 3.5 | 10.7 | 4.2 | 0.7 |
| 2-Methyl-Propyl Ester Acetic Acid | 2.8 | 2.2 | 5.6 | 2.6 | 0.5 | 4.3 | 0.6 | 1.2 | 0.8 | 9.3 | 1.1 | 0.6 |
| α-Pinene | 0.4 | 2.8 | 0.2 | 1.0 | 0.5 | 1.4 | 0.7 | 4.8 | 1.6 | 0.4 | 1.0 | 5.5 |
| 4,4-Dimethyl-2-Pentanone | 0.2 | 0.7 | 0.2 | 2.9 | 0.1 | 11.3 | 0.1 | 3.1 | 4.5 | 7.1 | 4.4 | 3.8 |
| 1-Penten-3-one | 1.9 | 9.1 | 2.1 | 7.8 | 0.9 | 3.9 | 1.3 | 1.4 | 9.5 | 10.1 | 7.7 | 0.7 |
| 5-Butyl-Nonane | 0.5 | 1.7 | 0.6 | 3.2 | 1.3 | 6.8 | 2.4 | 2.0 | 0.6 | 6.8 | 0.8 | 9.5 |
| 3,6-Dimethyl-Decane | 0.2 | 0.1 | 0.1 | 6.2 | 0.2 | 13.9 | 0.3 | 5.5 | 0.1 | 4.7 | 0.1 | 12.0 |
| 2-Methyl-3-Buten-2-ol | 0.7 | 0.7 | 0.6 | 1.6 | 1.4 | 2.1 | 2.0 | 8.0 | 0.8 | 3.7 | 0.7 | 8.4 |
| 5-Methyl-Decane | 0.8 | 1.1 | 1.1 | 5.7 | 0.9 | 3.3 | 1.4 | 1.3 | 0.3 | 3.6 | 0.4 | 1.2 |
| 4-Methyl-Decane | 0.3 | 2.0 | 0.3 | 10.6 | 0.8 | 7.4 | 0.9 | 8.5 | 1.1 | 7.5 | 0.9 | 3.6 |
| 2,3-Pentanedione | 8.4 | 4.0 | 10.2 | 3.4 | 0.8 | 2.8 | 0.6 | 6.9 | 3.3 | 5.0 | 1.9 | 13.3 |
| 3,3-Dimethyl-Methyl Ester Butanoic Acid | 0.3 | 9.6 | 0.3 | 0.1 | 0.9 | 12.0 | 0.8 | 4.0 | 0.4 | 0.4 | 0.4 | 3.2 |
| 2-Hexanone | 0.8 | 3.3 | 0.5 | 5.4 | 1.2 | 1.3 | 0.9 | 1.6 | 0.9 | 3.1 | 0.8 | 4.4 |
| 4-Methyl-Undecane | 1.8 | 2.8 | 1.1 | 12.2 | 1.6 | 0.8 | 2.8 | 5.7 | 0.6 | 5.1 | 0.7 | 6.6 |
| Hexanal | 37.2 | 0.6 | 21.7 | 2.3 | 0.7 | 2.7 | 0.2 | 4.7 | 75.2 | 0.7 | 59.3 | 10.3 |
| 2-Methyl-1-Propanol | 16.1 | 3.5 | 22.3 | 9.6 | 51.8 | 0.9 | 50.4 | 5.8 | 7.8 | 6.2 | 10.4 | 14.1 |
| 2-Methyl-2-Pentanol | 0.2 | 4.3 | 0.2 | 14.2 | 0.2 | 4.0 | 0.2 | 2.8 | 0.7 | 2.5 | 0.7 | 7.9 |
| Ethyl-Benzene | 25.5 | 4.8 | 29.6 | 3.5 | 3.5 | 1.3 | 44.0 | 2.6 | 17.9 | 8.6 | 17.5 | 3.6 |
| 3-Methyl Butyl Ester Acetic Acid | 12.1 | 14.2 | 12.3 | 2.3 | 3.6 | 1.6 | 1.1 | 7.0 | 11.5 | 0.6 | 8.6 | 9.2 |
| o-Xylene | 17.5 | 1.4 | 11.0 | 12.4 | 14.5 | 7.9 | 9.9 | 7.5 | 53.8 | 1.8 | 69.6 | 2.4 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Pentanol | 7.9 | 2.1 | 8.2 | 2.4 | 7.7 | 1.7 | 6.3 | 3.9 | 2.1 | 4.6 | 3.3 | 11.4 |
| p-Xylene | 36.6 | 1.1 | 38.4 | 8.7 | 28.3 | 0.7 | 30.6 | 3.0 | 39.9 | 1.5 | 29.2 | 5.5 |
| 5-Methyl-2-Hexanone | 0.3 | 4.9 | 0.4 | 5.1 | 0.5 | 3.3 | 0.3 | 6.5 | 1.3 | 0.2 | 1.7 | 10.9 |
| 2-Ethyl Methyl Ester Pentanoic Acid | 12.0 | 0.5 | 8.5 | 2.6 | 4.4 | 4.0 | 5.8 | 9.1 | 28.3 | 7.7 | 21.2 | 4.7 |
| 1-Butanol | 0.4 | 1.6 | 0.5 | 7.5 | 11.5 | 2.9 | 18.5 | 8.7 | 0.5 | 4.4 | 0.3 | 3.6 |
| α-Phellandrene | 5.8 | 4.1 | 7.8 | 1.6 | 1.6 | 2.6 | 2.5 | 3.2 | 174.9 | 1.3 | 87.5 | 5.2 |
| 2-Methyl-3-Pentanol | 9.2 | 2.0 | 12.8 | 7.4 | 4.0 | 8.4 | 3.6 | 3.6 | 3.3 | 10.1 | 2.8 | 9.6 |
| 1-Penten-3-ol | 38.5 | 2.9 | 45.3 | 8.8 | 95.2 | 5.7 | 112.8 | 3.4 | 180.5 | 12.7 | 112.5 | 1.5 |
| α-Terpinene | 5.0 | 3.8 | 7.8 | 0.4 | 0.4 | 2.2 | 0.6 | 2.9 | 40.5 | 6.3 | 29.6 | 7.4 |
| Butyl Ester 2-Propenoic Acid | 3.6 | 2.9 | 5.1 | 1.4 | 4.5 | 1.7 | 6.5 | 10.3 | 16.6 | 5.0 | 9.1 | 8.2 |
| m-Xylene | 1.5 | 2.7 | 1.9 | 11.9 | 12.0 | 0.6 | 16.5 | 0.1 | 30.9 | 1.7 | 23.0 | 5.5 |
| 2-Heptanone | 225.8 | 13.6 | 145.9 | 4.3 | 504.1 | 3.0 | 620.8 | 0.8 | 312.3 | 14.2 | 345.7 | 3.2 |
| Heptanal | 0.8 | 6.8 | 0.8 | 3.2 | 1.7 | 3.3 | 1.3 | 10.8 | 4.9 | 12.8 | 4.1 | 2.0 |
| D-Limonene | 0.2 | 2.5 | 0.1 | 1.5 | 1.3 | 10.4 | 1.6 | 8.9 | 1.8 | 10.3 | 1.3 | 3.9 |
| 3-Hexanol | 3.2 | 2.6 | 3.5 | 8.4 | 1.7 | 2.2 | 1.9 | 7.1 | 0.8 | 3.5 | 0.5 | 3.5 |
| β-Phellandrene | 2.0 | 3.4 | 4.3 | 4.0 | 9.2 | 0.3 | 10.0 | 10.5 | 392.9 | 6.1 | 316.7 | 5.1 |
| Eucalyptol | 0.3 | 5.1 | 0.4 | 1.6 | 0.1 | 3.4 | 0.1 | 1.2 | 0.8 | 1.2 | 0.5 | 4.0 |
| m-Menthane | 0.3 | 6.6 | 0.4 | 4.0 | 0.5 | 4.9 | 0.7 | 5.4 | 2.1 | 8.1 | 2.6 | 2.6 |
| 4-Methyl-2-Heptanone | 2.4 | 8.8 | 2.1 | 1.6 | 1.9 | 2.9 | 1.6 | 6.4 | 409.5 | 10.5 | 436.8 | 0.2 |
| 3-Methyl-2-Pentanol | 5.1 | 3.3 | 7.1 | 2.8 | 89.7 | 0.3 | 92.9 | 8.8 | 1.8 | 4.4 | 3.7 | 5.4 |
| 2-Methyl-1-Butanol | 83.9 | 4.8 | 119.9 | 6.7 | 139.2 | 9.5 | 182.6 | 1.8 | 18.0 | 8.5 | 25.5 | 3.6 |
| 3-Methyl-1-Butanol | 278.0 | 5.4 | 418.2 | 6.7 | 314.8 | 1.3 | 564.4 | 5.7 | 32.0 | 10.2 | 35.4 | 5.1 |
| o-Ethyltoluene | 6.5 | 3.6 | 5.4 | 2.7 | 2.1 | 2.5 | 3.8 | 6.1 | 6.5 | 7.0 | 6.2 | 4.4 |
| m-Ethyltoluene | 7.0 | 3.8 | 9.5 | 4.0 | 6.1 | 0.7 | 7.1 | 2.8 | 2.7 | 9.5 | 2.0 | 5.4 |
| 2-Hexanol | 3.1 | 1.2 | 1.8 | 12.8 | 5.5 | 1.0 | 8.6 | 3.8 | 1.9 | 5.3 | 1.8 | 2.2 |
| Ethylene Glycol Ethyl Ether | 9.2 | 1.9 | 18.9 | 6.0 | 2.4 | 11.3 | 1.8 | 1.7 | 1.4 | 3.0 | 2.3 | 13.3 |
| 6-Methyl-2-Heptanone | 2.0 | 1.4 | 1.7 | 5.2 | 2.0 | 5.3 | 1.4 | 1.7 | 8.1 | 15.2 | 7.5 | 1.8 |
| Pseudocumene | 4.4 | 2.5 | 5.3 | 0.1 | 2.2 | 1.4 | 3.8 | 7.3 | 4.9 | 5.8 | 5.1 | 11.3 |
| 4,6-Dimethyl-2-Heptanone | 0.9 | 5.1 | 0.8 | 4.7 | 0.4 | 0.1 | 0.3 | 2.8 | 43.8 | 10.9 | 59.8 | 2.2 |
| 2,3-Dimethyl-2-Hexanol | 0.2 | 10.3 | 0.3 | 3.7 | 0.2 | 11.0 | 0.4 | 8.4 | 20.1 | 7.2 | 19.1 | 4.2 |
| 3-Octanone | 1.0 | 2.7 | 0.8 | 2.2 | 17.1 | 0.8 | 21.5 | 0.7 | 0.4 | 9.7 | 0.3 | 3.9 |
| Styrene | 48.5 | 2.3 | 64.2 | 1.0 | 49.0 | 1.8 | 58.1 | 13.0 | 24.0 | 4.3 | 30.6 | 0.1 |
| 5-Methyl-2-Heptanone | 10.1 | 5.4 | 9.6 | 5.3 | 7.4 | 0.2 | 8.0 | 7.3 | 18.5 | 8.8 | 26.4 | 0.5 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-Pentanol | 28.7 | 4.9 | 47.3 | 1.8 | 6.7 | 5.8 | 8.8 | 2.0 | 4.8 | 1.8 | 5.9 | 2.6 |
| p-Ethyltoluene | 4.5 | 1.7 | 5.3 | 2.7 | 3.2 | 6.4 | 4.5 | 1.7 | 2.6 | 5.1 | 1.9 | 3.6 |
| p-Cymene | 11.8 | 3.8 | 17.1 | 6.0 | 3.4 | 6.8 | 3.7 | 1.8 | 46.6 | 11.9 | 32.3 | 4.4 |
| Mesitylene | 8.6 | 4.3 | 11.7 | 0.8 | 14.2 | 1.1 | 15.2 | 0.1 | 9.8 | 13.4 | 8.3 | 4.4 |
| 4-Methyl-4-Heptanol | 0.4 | 9.8 | 0.4 | 3.5 | 0.4 | 7.4 | 0.2 | 1.4 | 1.0 | 6.8 | 0.7 | 0.3 |
| 4-Heptanol | 3.9 | 0.3 | 3.5 | 4.1 | 1.9 | 8.9 | 1.4 | 4.1 | 17.6 | 12.2 | 10.5 | 0.2 |
| 2-Octanone | 40.1 | 9.1 | 29.0 | 4.2 | 73.0 | 8.1 | 82.0 | 2.4 | 75.3 | 13.1 | 88.0 | 9.2 |
| Octanal | 1.5 | 7.3 | 2.2 | 8.1 | 1.6 | 5.0 | 1.8 | 5.6 | 4.3 | 10.3 | 4.0 | 6.2 |
| 3-Hydroxy-2-Butanone | 0.2 | 9.0 | 0.2 | 7.5 | 0.3 | 9.1 | 0.2 | 5.9 | 0.1 | 3.0 | 0.1 | 2.0 |
| 1-Octen-3-one | 3.4 | 0.2 | 4.1 | 6.8 | 0.2 | 14.3 | 0.2 | 12.0 | 23.5 | 0.7 | 15.0 | 0.8 |
| trans-2-Pentenol | 15.7 | 0.3 | 23.6 | 10.3 | 14.7 | 2.6 | 22.5 | 1.1 | 14.9 | 7.6 | 17.2 | 2.7 |
| 2,2,6-Trimethyl-Cyclohexanone | 1.9 | 0.8 | 2.2 | 5.1 | 2.7 | 6.5 | 3.2 | 10.4 | 3.9 | 5.2 | 3.7 | 1.0 |
| 2-Heptanol | 653.4 | 1.9 | 601.6 | 6.7 | 629.7 | 5.4 | 755.5 | 0.7 | 435.8 | 9.0 | 411.3 | 9.4 |
| cis-2-Pentenol | 209.5 | 0.1 | 293.4 | 7.5 | 95.3 | 2.2 | 132.1 | 11.4 | 147.1 | 5.5 | 128.5 | 5.2 |
| 1-Hydroxy-2-Propanone | 90.8 | 3.9 | 120.8 | 5.1 | 6.1 | 0.8 | 4.4 | 2.6 | 4.0 | 9.7 | 4.6 | 5.3 |
| 5-Methyl-4-Hexen-3-one | 2.2 | 0.2 | 2.6 | 5.2 | 3.1 | 3.9 | 3.4 | 1.5 | 2.0 | 8.9 | 1.7 | 3.4 |
| Hemimellitene | 5.7 | 3.2 | 5.4 | 1.7 | 3.7 | 7.7 | 4.6 | 2.4 | 3.8 | 17.4 | 2.7 | 5.2 |
| 6-Methyl-5-Hepten-2-one | 10.2 | 1.7 | 15.6 | 8.9 | 9.4 | 2.4 | 13.4 | 8.1 | 43.7 | 5.2 | 41.4 | 2.7 |
| 2-Pentene | 452.5 | 1.0 | 338.5 | 13.1 | 495.7 | 2.2 | 476.8 | 0.2 | 346.6 | 11.1 | 430.6 | 1.1 |
| 1-Hexanol | 650.6 | 2.7 | 742.2 | 0.6 | 360.8 | 0.4 | 462.9 | 2.2 | 115.5 | 11.4 | 191.5 | 0.6 |
| 2-Cyclopenten-1-one | 14.6 | 9.1 | 15.4 | 8.4 | 1.5 | 5.5 | 2.0 | 4.5 | 9.1 | 10.6 | 13.9 | 9.0 |
| 2-Methyl-2-Cyclopenten-1-one | 3.7 | 6.8 | 3.4 | 7.8 | 6.1 | 4.4 | 0.6 | 7.7 | 4.2 | 6.3 | 5.0 | 4.1 |
| β-Methy-Styrene | 3.3 | 1.8 | 3.4 | 1.3 | 2.3 | 1.5 | 2.8 | 12.9 | 0.8 | 6.5 | 0.7 | 0.1 |
| 4-Octanol | 3.9 | 2.4 | 3.4 | 9.7 | 3.4 | 6.3 | 4.3 | 0.9 | 6.3 | 5.0 | 5.2 | 0.1 |
| cis-3-Hexen-1-ol | 5.4 | 3.6 | 7.2 | 0.3 | 4.3 | 0.3 | 5.2 | 0.7 | 1.6 | 5.5 | 1.6 | 5.4 |
| 2-Nonanone | 12.7 | 2.0 | 20.0 | 7.9 | 146.7 | 2.2 | 261.6 | 5.7 | 1.4 | 5.5 | 1.2 | 0.9 |
| Nonanal | 38.8 | 3.7 | 48.1 | 7.4 | 36.8 | 1.2 | 48.7 | 5.2 | 4.2 | 1.6 | 3.2 | 14.1 |
| Ethylene Glycol Butyl Ether | 22.7 | 3.8 | 23.5 | 2.1 | 5.5 | 7.5 | 5.4 | 4.3 | 1.7 | 5.8 | 1.3 | 11.0 |
| 1-Ethyl-1-Methyl-Cyclopentane | 7.3 | 5.4 | 6.6 | 7.3 | 4.7 | 0.6 | 4.0 | 14.9 | 64.5 | 9.5 | 52.0 | 5.0 |
| 3-Octen-2-one | 8.0 | 4.2 | 8.7 | 4.1 | 2.4 | 12.1 | 3.0 | 3.5 | 36.5 | 5.5 | 30.2 | 5.2 |
| 2-Octanol | 112.0 | 1.4 | 82.7 | 0.6 | 251.1 | 3.7 | 298.1 | 3.4 | 52.4 | 14.0 | 55.2 | 5.8 |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | 0.3 | 2.7 | 0.3 | 10.6 | 2.4 | 0.9 | 2.5 | 5.4 | 0.2 | 2.2 | 0.3 | 14.3 |
| 1,3-Bis(1,1-Dimethylethyl)-Benzene | 0.2 | 11.3 | 0.2 | 4.5 | 0.5 | 1.1 | 0.4 | 10.5 | 29.5 | 13.2 | 37.1 | 7.2 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|
| trans-2-Octenal | 2.4 | 2.0 | 1.5 | 3.3 | 9.7 | 0.4 | 9.8 | 1.0 | 35.9 | 9.8 | 27.8 | 6.6 |
| m-Ethyl-Styrene | 0.5 | 1.6 | 0.4 | 5.5 | 2.6 | 5.2 | 3.6 | 9.6 | 13.5 | 9.5 | 21.8 | 9.5 |
| 5-Methyl-2-Heptanone | 0.8 | 4.4 | 0.7 | 1.1 | 0.5 | 1.7 | 0.5 | 12.9 | 19.2 | 13.3 | 13.6 | 3.2 |
| 2-Decanone | 1.7 | 1.5 | 1.6 | 6.9 | 6.5 | 0.9 | 7.9 | 6.5 | 11.9 | 14.1 | 18.6 | 12.2 |
| 1-Octen-3-ol | 198.9 | 3.3 | 168.5 | 12.9 | 156.8 | 1.5 | 115.8 | 5.7 | 328.2 | 11.5 | 264.8 | 4.9 |
| trans,trans-2,4-Heptadienal | 4.8 | 1.8 | 5.5 | 6.1 | 3.6 | 6.0 | 3.1 | 2.1 | 1.7 | 10.4 | 1.3 | 1.6 |
| 1-Heptanol | 79.3 | 7.9 | 87.7 | 2.2 | 85.0 | 6.6 | 85.1 | 4.7 | 13.1 | 2.3 | 16.5 | 10.4 |
| cis,cis-3,5-Octadiene | 1.0 | 10.4 | 0.9 | 1.6 | 1.8 | 0.3 | 2.6 | 5.1 | 0.7 | 4.9 | 0.9 | 5.3 |
| 2-Oxo-Methyl Ester Propanoic Acid | 153.9 | 2.9 | 203.9 | 4.7 | 108.5 | 6.8 | 99.1 | 0.7 | 55.8 | 4.0 | 48.8 | 0.8 |
| Dihydromyrcenol | 15.3 | 7.0 | 19.1 | 2.8 | 12.6 | 2.0 | 11.3 | 6.9 | 12.1 | 6.2 | 9.9 | 1.2 |
| trans-Menthone | 18.0 | 4.2 | 25.6 | 14.1 | 1.8 | 1.9 | 2.2 | 1.5 | 82.3 | 11.3 | 67.6 | 4.4 |
| Furfural | 78.6 | 3.5 | 76.0 | 8.7 | 82.4 | 4.8 | 84.4 | 2.3 | 31.9 | 7.3 | 36.5 | 0.6 |
| Ethanoic Acid | 1925.2 | 1.5 | 2142.7 | 0.1 | 523.1 | 2.2 | 534.2 | 0.8 | 19.4 | 1.7 | 11.9 | 8.8 |
| 2-Ethyl-1-Hexanol | 20.7 | 2.5 | 28.4 | 1.5 | 13.7 | 12.9 | 17.2 | 10.3 | 44.1 | 12.8 | 49.0 | 2.9 |
| Decanal | 59.8 | 6.2 | 64.6 | 4.5 | 26.0 | 3.4 | 20.7 | 0.3 | 45.9 | 4.9 | 38.4 | 1.5 |
| Furfuryl Formate | 60.9 | 1.8 | 67.0 | 0.6 | 10.0 | 3.7 | 14.7 | 9.7 | 9.5 | 4.1 | 8.7 | 2.9 |
| trans-2-Hepten-1-ol | 49.0 | 5.3 | 48.8 | 5.5 | 24.5 | 2.5 | 26.4 | 3.9 | 10.6 | 6.2 | 15.9 | 7.8 |
| 2-Nonanol | 21.4 | 1.4 | 22.0 | 1.8 | 351.5 | 1.6 | 413.3 | 2.1 | 47.1 | 2.5 | 52.1 | 9.7 |
| 1-(2-Furanyl)-Ethanone | 63.0 | 9.3 | 70.5 | 2.9 | 46.7 | 7.0 | 47.8 | 1.3 | 33.6 | 3.6 | 32.3 | 6.3 |
| 3,5-Octadien-2-one | 19.0 | 0.7 | 23.9 | 10.9 | 8.9 | 2.3 | 11.0 | 2.9 | 36.4 | 4.7 | 29.4 | 5.8 |
| Benzaldehyde | 22.8 | 1.0 | 26.2 | 3.2 | 25.1 | 11.1 | 23.6 | 1.1 | 33.4 | 2.6 | 41.9 | 0.8 |
| Furfuryl Acetate | 0.5 | 1.7 | 0.5 | 5.0 | 0.2 | 4.9 | 0.2 | 8.4 | 0.3 | 4.6 | 2.5 | 2.9 |
| Linalool | 1.5 | 8.6 | 1.3 | 0.9 | 1.2 | 8.7 | 1.2 | 12.5 | 0.9 | 12.7 | 1.1 | 4.2 |
| β-Myrcene | 0.2 | 1.7 | 0.2 | 1.4 | 1.3 | 4.4 | 1.2 | 11.1 | 5.2 | 3.8 | 4.7 | 0.7 |
| 1-Octanol | 95.4 | 3.8 | 103.2 | 12.7 | 89.0 | 3.2 | 106.5 | 6.5 | 34.3 | 4.5 | 32.9 | 3.8 |
| trans-p-2-Menthen-1-ol | 52.9 | 4.2 | 73.4 | 2.6 | 2.2 | 0.4 | 2.9 | 4.7 | 111.0 | 11.1 | 91.4 | 5.0 |
| Propanoic Acid | 18.5 | 2.0 | 18.6 | 8.2 | 0.5 | 3.0 | 0.5 | 11.8 | 11.2 | 5.0 | 8.8 | 5.5 |
| 2,3-Butanediol | 67.1 | 4.0 | 75.5 | 1.7 | 133.3 | 2.7 | 267.7 | 11.5 | 57.3 | 6.8 | 51.8 | 1.6 |
| Dimethyl Sulfoxide | 99.9 | 0.1 | 103.7 | 3.3 | 50.3 | 2.2 | 69.5 | 5.4 | 5.6 | 1.9 | 5.3 | 10.7 |
| m-Menth-3-ene | 31.5 | 0.4 | 45.9 | 5.5 | 13.8 | 7.1 | 12.8 | 8.5 | 6.2 | 4.0 | 7.0 | 1.7 |
| Trans-(2-Ethylcyclopentyl)-Methanol | 39.2 | 2.8 | 40.8 | 6.3 | 32.0 | 0.7 | 38.1 | 9.6 | 10.7 | 5.2 | 14.2 | 1.0 |
| Bornyl Acetate | 8.0 | 3.9 | 9.4 | 3.2 | 9.4 | 1.9 | 11.0 | 4.7 | 0.9 | 7.5 | 1.0 | 7.1 |
| 4-Cyclopentene-1,3-dione | 79.7 | 3.3 | 99.1 | 2.8 | 19.1 | 9.1 | 14.0 | 8.0 | 39.9 | 1.5 | 48.2 | 7.0 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Menthol | 3.1 | 3.7 | 3.1 | 10.5 | 2.6 | 0.9 | 2.6 | 1.0 | 45.2 | 1.0 | 42.3 | 5.4 |
| 2-Undecanone | 2.4 | 4.9 | 3.3 | 0.9 | 1.0 | 3.8 | 1.8 | 11.8 | 2.4 | 7.8 | 1.7 | 3.7 |
| 2-(2-Furanyl)-Furan | 1.5 | 2.4 | 2.3 | 11.0 | 1.1 | 4.7 | 0.9 | 10.7 | 0.5 | 4.2 | 0.6 | 3.6 |
| trans-2-Octen-1-ol | 63.2 | 0.1 | 72.5 | 0.1 | 50.7 | 0.1 | 53.4 | 5.1 | 15.0 | 5.1 | 15.1 | 12.8 |
| trans-2-Nonen-1-ol | 26.8 | 6.4 | 28.8 | 4.7 | 22.4 | 6.9 | 25.7 | 6.5 | 68.9 | 5.4 | 63.3 | 8.3 |
| Diethylene Glycol Ethyl Ether | 56.8 | 2.5 | 60.8 | 3.4 | 50.0 | 9.5 | 43.5 | 2.3 | 53.9 | 14.4 | 60.4 | 1.9 |
| 3,5,5-Trimethyl-2-Cyclopenten-1-one | 18.3 | 5.4 | 16.8 | 2.3 | 17.1 | 5.7 | 11.6 | 0.7 | 12.9 | 12.6 | 15.7 | 6.2 |
| cis-p-2-Menthen-1-ol | 2.7 | 0.8 | 33.7 | 6.6 | 3.4 | 0.3 | 3.9 | 3.9 | 5.0 | 6.4 | 4.2 | 0.5 |
| β-Cyclocitral | 9.6 | 6.7 | 8.8 | 3.0 | 6.6 | 3.7 | 5.9 | 4.5 | 19.7 | 10.5 | 15.4 | 3.1 |
| Benzeneacetaldehyde | 14.6 | 4.9 | 17.8 | 0.7 | 13.6 | 3.2 | 12.7 | 9.2 | 80.9 | 1.5 | 77.3 | 2.1 |
| 1-Nonanol | 28.2 | 5.6 | 31.1 | 5.1 | 75.8 | 2.5 | 84.7 | 0.0 | 9.1 | 4.1 | 9.6 | 2.9 |
| Furfuryl Alcohol | 42.7 | 6.5 | 51.2 | 5.4 | 13.2 | 2.0 | 12.1 | 14.8 | 52.0 | 5.2 | 55.0 | 0.9 |
| Phoracanthol | 12.5 | 12.3 | 13.5 | 3.1 | 9.7 | 2.6 | 10.5 | 9.8 | 5.6 | 5.7 | 6.3 | 3.4 |
| cis-3-Nonen-1-ol | 16.6 | 6.1 | 21.2 | 7.0 | 14.6 | 14.1 | 14.1 | 11.2 | 15.3 | 7.6 | 12.7 | 10.4 |
| cis-Piperitol | 27.4 | 4.4 | 29.3 | 7.3 | 2.3 | 2.1 | 2.8 | 1.9 | 46.0 | 4.3 | 39.7 | 5.4 |
| p-Methoxy-Styrene | 4.2 | 5.3 | 5.2 | 7.7 | 0.3 | 3.2 | 0.4 | 1.9 | 2.8 | 3.0 | 3.5 | 0.9 |
| (2Z)-3-Ethyl-2,4-Pentadien-1-ol | 7.7 | 6.8 | 7.2 | 15.3 | 4.3 | 2.1 | 4.5 | 6.9 | 1.3 | 1.9 | 1.7 | 13.8 |
| Butylene Glycol Monobutyl Ether | 10.8 | 0.5 | 15.3 | 10.9 | 8.4 | 1.7 | 8.8 | 3.5 | 1.4 | 0.3 | 1.2 | 3.6 |
| α-Terpineol | 0.5 | 6.5 | 0.5 | 6.2 | 0.2 | 16.4 | 0.2 | 10.0 | 5.6 | 3.0 | 4.5 | 2.7 |
| 1,5-Cyclooctanedione | 2.4 | 13.6 | 2.9 | 2.6 | 2.5 | 11.9 | 2.9 | 0.9 | 4.8 | 5.9 | 4.2 | 1.9 |
| γ-Terpinene | 3.1 | 4.1 | 3.6 | 6.1 | 4.6 | 4.2 | 5.5 | 3.3 | 1.8 | 7.7 | 1.6 | 0.8 |
| trans-2-Decenol | 11.3 | 1.8 | 11.6 | 5.7 | 6.6 | 0.8 | 6.7 | 1.7 | 3.2 | 0.7 | 3.6 | 0.7 |
| 2-Propenoic Acid | 0.2 | 8.1 | 0.2 | 2.7 | 0.5 | 2.0 | 0.5 | 1.6 | 0.9 | 1.5 | 1.3 | 4.6 |
| 2-Undecanol | 0.9 | 2.7 | 1.1 | 4.0 | 21.9 | 0.7 | 27.2 | 0.9 | 2.5 | 7.5 | 1.9 | 12.3 |
| 3-Ethyl-Benzaldehyde | 5.0 | 2.9 | 5.5 | 2.6 | 3.2 | 1.0 | 3.9 | 12.7 | 6.2 | 4.6 | 6.9 | 5.9 |
| 3-Hydroxy-Benzaldehyde | 11.9 | 1.7 | 13.5 | 9.7 | 0.9 | 0.2 | 1.0 | 4.6 | 1.5 | 2.8 | 1.7 | 4.3 |
| trans-2-Nonene | 1.5 | 2.8 | 1.5 | 8.8 | 1.6 | 0.7 | 1.1 | 8.2 | 1.8 | 3.5 | 1.8 | 8.9 |
| 2-Methyl-2-Pentenal | 9.0 | 3.1 | 11.6 | 15.1 | 3.7 | 2.2 | 4.0 | 2.4 | 9.5 | 12.1 | 10.0 | 11.3 |
| cis-5-Decenol | 4.5 | 1.1 | 4.3 | 6.0 | 88.0 | 3.3 | 88.9 | 6.3 | 18.3 | 9.1 | 14.0 | 1.9 |
| trans-Piperitol | 20.2 | 3.3 | 24.9 | 7.3 | 2.0 | 6.5 | 2.2 | 7.0 | 35.6 | 1.4 | 31.8 | 5.4 |
| 4-Ethyl-Benzaldehyde | 3.4 | 0.6 | 3.4 | 1.9 | 3.4 | 0.2 | 3.3 | 4.2 | 4.4 | 12.5 | 5.0 | 1.3 |
| Naphthalene | 13.2 | 3.2 | 16.0 | 13.1 | 10.7 | 3.6 | 9.0 | 10.5 | 1.3 | 9.6 | 1.4 | 9.1 |
| 1-Decanol | 14.0 | 1.0 | 17.0 | 7.3 | 19.0 | 9.1 | 22.6 | 0.7 | 19.2 | 5.8 | 19.3 | 6.0 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cyclodecane | 67.6 | 3.7 | 71.7 | 3.4 | 34.7 | 3.1 | 33.4 | 3.4 | 41.8 | 6.0 | 42.3 | 3.4 |
| trans,trans-2,4-Decadienal | 16.0 | 7.5 | 18.5 | 12.7 | 19.0 | 13.0 | 22.4 | 4.7 | 4.1 | 6.0 | 4.4 | 0.6 |
| 1,2-Cyclopentanedione | 567.8 | 2.4 | 626.0 | 2.9 | 238.4 | 3.8 | 213.0 | 1.6 | 264.4 | 1.9 | 216.1 | 1.5 |
| Cyclodecene | 3.3 | 2.0 | 3.3 | 8.2 | 1.9 | 1.5 | 1.8 | 13.4 | 0.5 | 3.1 | 0.6 | 2.4 |
| cis-4-Decenol | 0.7 | 2.9 | 0.8 | 1.4 | 1.2 | 3.1 | 1.5 | 4.0 | 2.8 | 4.5 | 2.9 | 9.0 |
| 1-Phenyl-2-Butanone | 6.0 | 1.8 | 7.5 | 10.8 | 13.5 | 2.2 | 12.6 | 0.9 | 8.8 | 5.6 | 8.4 | 6.1 |
| Phenethyl Alcohol | 20.4 | 1.0 | 22.2 | 11.7 | 4.2 | 1.8 | 4.3 | 0.2 | 9.6 | 1.4 | 8.0 | 5.5 |
| trans,cis-2,4-Decadienal | 12.4 | 4.8 | 13.5 | 13.5 | 11.5 | 6.2 | 16.6 | 5.0 | 3.2 | 2.3 | 3.1 | 5.1 |
| 2-Cyclohexenol | 66.3 | 3.6 | 77.1 | 1.0 | 10.9 | 3.0 | 12.4 | 1.5 | 8.2 | 1.7 | 8.6 | 5.0 |
| 2-Ethyl Hexanoic Acid | 16.6 | 9.7 | 20.6 | 8.0 | 1.1 | 7.7 | 1.0 | 1.3 | 17.4 | 1.4 | 14.1 | 4.4 |
| 3-Methyl-1,2-Cyclopentanedione | 64.5 | 1.9 | 70.1 | 5.2 | 2.2 | 7.2 | 2.8 | 0.6 | 7.0 | 4.8 | 7.3 | 3.2 |
| trans-Cinnamaldehyde | 9.4 | 2.8 | 9.1 | 4.0 | 4.8 | 1.4 | 4.9 | 4.4 | 8.3 | 5.0 | 7.7 | 3.3 |
| Heptanoic Acid | 48.2 | 0.3 | 57.1 | 8.2 | 1.8 | 7.7 | 1.3 | 0.9 | 103.3 | 7.5 | 106.1 | 9.7 |
| Mequinol | 90.6 | 9.8 | 129.2 | 2.3 | 45.4 | 0.8 | 48.1 | 6.8 | 7.5 | 2.8 | 8.0 | 6.4 |
| 2,4,5-Trihydroxypyrimidine | 8.2 | 8.8 | 8.9 | 1.9 | 16.3 | 7.6 | 11.9 | 6.7 | 15.6 | 8.1 | 18.1 | 11.6 |
| cis-Cinnamaldehyde | 8.2 | 1.1 | 8.8 | 2.3 | 4.3 | 6.8 | 4.7 | 7.0 | 8.6 | 5.6 | 8.5 | 7.9 |
| Benzenemethanol | 82.4 | 2.7 | 84.9 | 8.8 | 40.0 | 1.2 | 43.5 | 11.9 | 18.5 | 11.3 | 11.2 | 3.7 |
| Mesitaldehyde | 6.0 | 1.2 | 6.0 | 0.9 | 3.2 | 9.9 | 3.6 | 9.4 | 6.4 | 7.0 | 6.0 | 5.6 |
| 2-Ethylhexyl Ester Octanoic Acid | 9.2 | 3.7 | 9.8 | 2.9 | 4.3 | 3.0 | 4.7 | 7.9 | 4.4 | 0.7 | 3.9 | 0.7 |
| Benzeneethanol | 61.1 | 0.9 | 65.9 | 10.8 | 29.4 | 4.0 | 32.8 | 6.2 | 42.4 | 11.0 | 44.7 | 6.1 |
| 1,4-Butanediol | 69.1 | 8.2 | 67.2 | 7.1 | 37.1 | 3.6 | 40.7 | 6.0 | 48.7 | 3.1 | 54.5 | 9.2 |
| β-Ionone | 28.8 | 8.6 | 22.1 | 11.9 | 19.1 | 14.0 | 18.5 | 3.6 | 56.0 | 13.9 | 49.4 | 1.2 |
| 2-Methyl-1,4-Benzenediol | 20.3 | 3.6 | 25.9 | 8.6 | 7.1 | 2.4 | 0.8 | 7.2 | 1.6 | 13.1 | 2.0 | 0.4 |
| 2-Ethyl Heptanoic Acid | 2.4 | 2.6 | 2.9 | 7.1 | 10.5 | 5.7 | 15.3 | 12.8 | 1.8 | 14.0 | 1.9 | 13.5 |
| 1-Dodecanol | 3.7 | 6.5 | 3.3 | 10.4 | 6.0 | 4.2 | 5.5 | 2.2 | 13.1 | 3.2 | 12.0 | 5.4 |
| Benzalacetone | 8.8 | 1.7 | 10.0 | 2.9 | 5.3 | 7.5 | 5.1 | 2.2 | 10.7 | 5.1 | 11.9 | 1.6 |
| Maltol | 186.6 | 2.8 | 239.2 | 3.1 | 2.7 | 1.4 | 22.7 | 3.1 | 77.1 | 2.2 | 72.3 | 7.9 |
| 2-Acetylpyrrole | 13.1 | 7.7 | 12.5 | 8.6 | 1.1 | 10.6 | 1.0 | 9.5 | 2.6 | 6.7 | 2.3 | 13.4 |
| 2,4-Decadien-1-ol | 8.9 | 0.4 | 9.7 | 6.9 | 8.8 | 4.7 | 9.8 | 2.4 | 4.6 | 1.8 | 4.0 | 0.7 |
| Levoglucosenone | 17.0 | 0.5 | 15.1 | 10.4 | 1.0 | 8.3 | 1.4 | 6.5 | 4.3 | 1.9 | 4.0 | 6.6 |
| Phenol | 26.9 | 7.6 | 22.3 | 9.3 | 38.4 | 6.4 | 41.7 | 7.0 | 37.9 | 6.7 | 39.4 | 0.0 |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | 9.6 | 4.4 | 10.0 | 2.1 | 24.5 | 1.7 | 26.2 | 3.8 | 6.0 | 1.1 | 7.0 | 1.4 |
| 4,6-Dimethyl-Dodecane | 28.3 | 0.6 | 27.8 | 12.7 | 1.4 | 2.6 | 1.9 | 6.2 | 10.9 | 8.5 | 11.8 | 7.1 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ethyl Ester Decanoic Acid | 6.1 | 5.7 | 7.0 | 6.4 | 9.2 | 3.1 | 10.0 | 0.8 | 1.4 | 1.1 | 1.8 | 12.2 |
| 1-Methyl-4-Piperidinone | 1.9 | 5.1 | 1.5 | 13.6 | 0.7 | 1.3 | 0.7 | 1.6 | 4.7 | 3.0 | 4.3 | 3.2 |
| 2,2-Dimethyl-3-Heptanone | 102.9 | 4.4 | 183.6 | 8.3 | 1.4 | 4.6 | 1.0 | 5.2 | 38.5 | 6.1 | 37.4 | 3.1 |
| Octanoic Acid | 12.2 | 12.2 | 17.7 | 2.6 | 1.6 | 14.5 | 1.5 | 6.7 | 19.5 | 11.3 | 16.6 | 5.7 |
| 1,3-Dihydroxy-2-Propanone | 135.8 | 6.6 | 180.8 | 2.4 | 1.2 | 3.0 | 1.2 | 11.7 | 1.2 | 0.5 | 1.5 | 5.1 |
| 2-Phenoxy-Ethanol | 17.7 | 1.1 | 16.9 | 3.9 | 13.1 | 11.8 | 13.9 | 5.3 | 55.8 | 0.5 | 49.5 | 0.9 |
| Isophthalaldehyde | 3.9 | 10.1 | 4.0 | 1.2 | 3.6 | 1.3 | 3.2 | 5.2 | 6.1 | 3.9 | 6.5 | 0.7 |
| Cyclotetradecane | 7.2 | 1.3 | 7.8 | 2.4 | 2.1 | 9.2 | 3.0 | 3.8 | 3.1 | 2.7 | 3.0 | 8.4 |
| Nonanoic Acid | 14.9 | 11.2 | 14.1 | 3.2 | 1.2 | 2.8 | 1.2 | 1.5 | 57.2 | 1.9 | 50.9 | 1.0 |
| 2-Ethyl-Phenol | 32.1 | 12.4 | 36.2 | 0.7 | 22.8 | 0.3 | 26.7 | 13.1 | 11.4 | 4.6 | 13.5 | 4.5 |
| 2-Methoxy-4-Vinyl-Phenol | 77.4 | 6.1 | 83.4 | 2.5 | 64.5 | 0.5 | 69.4 | 4.2 | 4.6 | 0.6 | 4.2 | 2.4 |
| 4-Methylimidazole | 15.3 | 13.6 | 20.4 | 4.7 | 10.8 | 8.2 | 8.8 | 2.7 | 103.4 | 4.4 | 99.9 | 10.6 |
| m-tert-Butyl-Toluene | 11.9 | 1.8 | 14.6 | 2.3 | 11.2 | 2.1 | 9.7 | 2.3 | 16.1 | 1.1 | 16.5 | 2.9 |
| Syringol | 23.3 | 5.4 | 21.3 | 7.0 | 12.3 | 12.1 | 11.9 | 1.5 | 14.1 | 3.9 | 14.0 | 1.9 |
| Decanoic Acid | 29.4 | 6.6 | 31.0 | 4.8 | 1.9 | 0.7 | 1.5 | 1.8 | 32.9 | 8.2 | 35.3 | 12.5 |
| 3-Hydroxy-2,3-Dihydro-Maltol | 19.1 | 0.4 | 24.5 | 6.2 | 1.2 | 10.0 | 1.4 | 0.4 | 4.7 | 5.2 | 5.2 | 12.2 |
| 5-Hydroxy-Maltol | 38.0 | 4.3 | 30.6 | 1.9 | 1.4 | 10.7 | 1.6 | 14.2 | 47.5 | 4.4 | 44.4 | 1.4 |
| Triethylene Glycol | 12.1 | 4.7 | 14.8 | 0.4 | 2.1 | 2.2 | 1.7 | 9.6 | 5.1 | 2.3 | 4.4 | 4.6 |
| Benzoic Acid | 14.3 | 0.6 | 13.6 | 11.2 | 21.2 | 3.3 | 19.6 | 2.3 | 3.3 | 1.8 | 3.1 | 8.5 |
| 2-Methyl-Benzaldehyde | 487.1 | 3.4 | 580.0 | 5.3 | 531.0 | 2.9 | 616.0 | 1.2 | 20.6 | 5.5 | 17.6 | 13.0 |
| Undecanoic Acid | 24.4 | 9.9 | 29.6 | 0.8 | 2.0 | 3.3 | 1.5 | 1.3 | 68.7 | 7.9 | 71.6 | 5.2 |
| 4-Pyridinol | 88.1 | 5.1 | 93.9 | 5.3 | 17.6 | 4.2 | 18.1 | 5.6 | 66.2 | 7.6 | 72.3 | 5.1 |
| 4-Amino-Phenol | 37.6 | 5.0 | 40.3 | 4.2 | 14.0 | 6.4 | 18.0 | 2.2 | 4.7 | 5.8 | 4.0 | 6.6 |

[1]RSD - Relative Standard Deviation values.

**Table S11. Mean, minimum and maximum peak area values of identified VOCs in SC samples.**

| Volatile Organic Compound | Relative Peak Areas (x $10^3$) | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | AMA | | | RAD | | | ROX | | | VER | | | VIO | | | CAN | | |
| | Min | Max | Mean | Min | Max | Mean | Min | Max | Mean | Min | Max | Mean | Min | Max | Mean | Min | Max | Mean |
| Pentane | 1.7 | 2.5 | 2.1 | 4.1 | 4.7 | 4.3 | 5.1 | 8.3 | 6.9 | 1.9 | 2.7 | 2.4 | 3.0 | 3.7 | 3.3 | 1.9 | 2.3 | 2.2 |
| 1-Pentene | 1.4 | 1.6 | 1.5 | 1.5 | 2.0 | 1.7 | 2.6 | 2.9 | 2.8 | 1.0 | 1.5 | 1.3 | 0.8 | 1.0 | 0.9 | 2.0 | 3.5 | 2.7 |
| 2-Methyl-Pentane | 0.9 | 1.6 | 1.2 | 1.1 | 2.1 | 1.6 | 4.3 | 7.9 | 5.8 | 2.7 | 3.9 | 3.3 | 1.0 | 1.2 | 1.1 | 0.1 | 0.2 | 0.1 |
| Hexane | 1.3 | 2.4 | 1.8 | 1.1 | 1.4 | 1.2 | 3.4 | 4.0 | 3.8 | 1.9 | 2.4 | 2.2 | 1.5 | 1.8 | 1.6 | 10.5 | 21.1 | 15.5 |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ethyl Ether | 0.3 | 6.4 | 3.1 | 0.7 | 3.8 | 2.2 | 0.8 | 1.5 | 1.1 | 0.2 | 0.4 | 0.3 | 1.0 | 1.4 | 1.2 | 2.2 | 5.7 | 3.9 |
| cis-4-Methyl-2-Pentene | 0.4 | 0.7 | 0.5 | 0.2 | 1.4 | 0.7 | 0.9 | 4.8 | 2.6 | 0.1 | 2.6 | 1.3 | 0.2 | 0.6 | 0.4 | 0.2 | 0.5 | 0.3 |
| cis-Piperylene | 1.9 | 3.5 | 2.5 | 4.7 | 6.5 | 5.8 | 10.2 | 21.9 | 15.2 | 7.9 | 11.1 | 9.6 | 1.3 | 2.7 | 1.9 | 2.9 | 3.9 | 3.4 |
| 2-Methyl-1-Pentene | 0.9 | 17.5 | 8.8 | 0.5 | 48.9 | 22.5 | 2.2 | 17.3 | 9.5 | 1.3 | 95.7 | 46.0 | 0.9 | 39.6 | 18.2 | 44.9 | 85.0 | 64.2 |
| cis-3-Methyl-2-Pentene | 1.0 | 1.2 | 1.1 | 4.1 | 8.0 | 5.9 | 0.9 | 1.4 | 1.1 | 2.0 | 3.2 | 2.6 | 1.2 | 1.5 | 1.3 | 1.3 | 2.0 | 1.7 |
| 3-Methyl-Hexane | 0.2 | 0.4 | 0.3 | 0.5 | 0.8 | 0.6 | 0.8 | 0.9 | 0.9 | 0.6 | 0.9 | 0.7 | 0.9 | 1.4 | 1.2 | 2.3 | 3.2 | 2.7 |
| 1,4-Pentadiene | 3.1 | 12.3 | 7.2 | 4.2 | 13.3 | 8.6 | 6.0 | 28.1 | 17.1 | 5.8 | 7.7 | 6.5 | 1.7 | 2.1 | 1.9 | 2.3 | 6.1 | 3.9 |
| Methanethiol | 3.1 | 3.2 | 3.2 | 4.0 | 4.9 | 4.4 | 5.9 | 8.1 | 7.0 | 3.3 | 4.5 | 3.8 | 1.9 | 2.5 | 2.1 | 3.0 | 3.9 | 3.5 |
| trans-Piperylene | 2.2 | 4.1 | 3.1 | 1.3 | 2.8 | 2.0 | 3.0 | 5.7 | 4.3 | 1.3 | 1.8 | 1.6 | 0.6 | 0.9 | 0.8 | 1.4 | 2.4 | 1.9 |
| Heptane | 8.5 | 10.6 | 9.3 | 4.9 | 7.1 | 6.1 | 10.2 | 15.9 | 12.9 | 1.3 | 2.3 | 1.8 | 5.3 | 8.7 | 7.0 | 11.2 | 14.7 | 12.6 |
| tert-Butyl Ethyl Ether | 0.1 | 61.6 | 28.9 | 0.4 | 70.4 | 35.3 | 0.4 | 47.9 | 23.9 | 1.2 | 166.6 | 81.0 | 1.0 | 81.6 | 38.5 | 249.7 | 331.7 | 282.0 |
| Ethanal | 53.9 | 77.8 | 63.7 | 20.8 | 39.9 | 30.3 | 30.6 | 46.1 | 38.5 | 65.1 | 72.3 | 68.2 | 10.0 | 18.1 | 14.4 | 55.1 | 68.4 | 62.2 |
| Dimethyl Sulfide | 770.0 | 836.6 | 796.4 | 398.0 | 599.1 | 500.6 | 273.5 | 329.2 | 309.1 | 478.1 | 648.6 | 539.8 | 494.6 | 687.1 | 550.9 | 220.1 | 314.0 | 265.8 |
| 4-Methyl-Heptane | 7.5 | 22.3 | 14.0 | 4.0 | 13.3 | 8.5 | 6.4 | 17.7 | 11.9 | 1.8 | 107.6 | 53.4 | 1.0 | 35.1 | 17.1 | 105.4 | 185.5 | 149.5 |
| Octane | 4.0 | 5.6 | 4.8 | 6.6 | 7.3 | 7.0 | 7.9 | 10.4 | 9.0 | 1.9 | 3.7 | 2.7 | 1.2 | 1.7 | 1.4 | 7.3 | 11.1 | 9.2 |
| Propanal | 8.9 | 10.8 | 9.8 | 3.3 | 8.7 | 5.9 | 5.6 | 11.6 | 8.5 | 5.7 | 8.6 | 7.0 | 3.3 | 5.3 | 4.1 | 16.9 | 28.2 | 21.4 |
| Furan | 8.5 | 11.6 | 10.0 | 6.6 | 10.2 | 8.3 | 7.3 | 10.8 | 8.9 | 7.1 | 8.4 | 7.7 | 4.2 | 5.5 | 5.0 | 4.6 | 6.4 | 5.3 |
| 2,4-Dimethyl-Heptane | 11.5 | 24.5 | 17.3 | 16.2 | 19.8 | 18.0 | 24.4 | 30.1 | 27.4 | 17.6 | 22.0 | 19.3 | 13.4 | 22.6 | 17.5 | 11.2 | 13.3 | 11.9 |
| 2-Methyl-Propanal | 20.4 | 24.9 | 22.6 | 38.3 | 42.8 | 39.9 | 49.6 | 75.7 | 64.3 | 80.4 | 91.8 | 87.0 | 20.9 | 22.1 | 21.7 | 26.1 | 29.4 | 27.6 |
| 2-Propanone | 242.3 | 321.5 | 295.2 | 405.3 | 496.9 | 449.0 | 75.9 | 96.3 | 85.7 | 432.6 | 496.9 | 465.6 | 66.3 | 177.8 | 122.8 | 626.3 | 786.0 | 701.1 |
| Methyl Ester Acetic Acid | 2.2 | 4.2 | 3.1 | 0.8 | 1.6 | 1.2 | 2.1 | 32.7 | 16.2 | 4.8 | 7.5 | 6.0 | 0.8 | 1.7 | 1.2 | 0.3 | 0.5 | 0.4 |
| 2-Methyl-2-Heptene | 0.4 | 0.6 | 0.5 | 1.1 | 2.0 | 1.6 | 1.9 | 3.3 | 2.6 | 0.3 | 0.8 | 0.6 | 0.9 | 0.9 | 0.9 | 23.6 | 35.4 | 29.9 |
| Crotonal | 0.1 | 0.3 | 0.2 | 2.5 | 3.4 | 2.8 | 4.2 | 5.0 | 4.5 | 4.2 | 5.4 | 4.8 | 3.3 | 7.9 | 5.5 | 1.7 | 1.9 | 1.8 |
| 2,3-Dimethyl-Heptane | 1.1 | 3.1 | 2.0 | 1.5 | 2.5 | 1.9 | 2.2 | 6.0 | 3.9 | 2.0 | 3.2 | 2.5 | 0.7 | 0.9 | 0.8 | 0.3 | 0.7 | 0.5 |
| 4-Methyl-Octane | 8.6 | 11.8 | 9.7 | 7.6 | 9.3 | 8.2 | 17.4 | 22.1 | 20.3 | 8.6 | 10.6 | 9.7 | 8.4 | 11.6 | 9.8 | 5.3 | 7.0 | 6.2 |
| 2-Methyl-Furan | 1.6 | 2.2 | 1.8 | 2.7 | 3.9 | 3.2 | 1.0 | 1.4 | 1.2 | 1.0 | 1.9 | 1.4 | 1.2 | 2.0 | 1.7 | 1.1 | 1.8 | 1.4 |
| 2,4-Dimethyl-1-Heptene | 5.1 | 7.9 | 6.6 | 6.5 | 8.7 | 7.7 | 17.2 | 30.5 | 24.5 | 9.5 | 12.3 | 11.2 | 10.6 | 28.8 | 18.9 | 314.7 | 432.6 | 386.2 |
| Ethyl Ester Acetic Acid | 21.5 | 52.8 | 36.5 | 15.3 | 23.7 | 18.9 | 435.1 | 603.7 | 499.8 | 61.2 | 76.7 | 68.4 | 9.1 | 18.4 | 13.2 | 42.8 | 65.4 | 55.3 |
| Nonane | 1.3 | 1.7 | 1.5 | 2.4 | 4.6 | 3.4 | 4.7 | 5.6 | 5.2 | 1.5 | 2.7 | 2.1 | 2.6 | 4.1 | 3.1 | 4.4 | 6.6 | 5.5 |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Butanone | 8.8 | 14.0 | 11.1 | 3.8 | 5.7 | 4.6 | 11.2 | 19.0 | 15.4 | 15.5 | 21.6 | 18.5 | 6.2 | 6.7 | 6.4 | 29.4 | 33.4 | 31.9 |
| 2-Methyl-Butanal | 86.2 | 117.1 | 99.8 | 59.4 | 71.1 | 65.9 | 45.7 | 67.2 | 57.9 | 79.6 | 103.8 | 89.5 | 12.9 | 16.4 | 14.6 | 64.5 | 76.1 | 69.3 |
| 3-Methyl-Butanal | 76.0 | 131.9 | 96.9 | 49.5 | 59.7 | 54.5 | 39.9 | 60.4 | 51.3 | 82.0 | 94.7 | 86.9 | 13.2 | 27.4 | 19.4 | 65.5 | 94.7 | 78.7 |
| Ethyl Alcohol | 427.8 | 562.6 | 485.2 | 837.1 | 989.4 | 924.1 | 723.0 | 928.0 | 802.8 | 533.8 | 683.8 | 609.2 | 887.9 | 1130.3 | 978.3 | 176.6 | 198.9 | 189.9 |
| Benzene | 1.4 | 2.4 | 1.9 | 8.1 | 10.3 | 9.2 | 10.5 | 20.0 | 14.6 | 9.8 | 13.8 | 11.5 | 5.1 | 9.0 | 7.1 | 5.1 | 5.9 | 5.4 |
| 3-Ethyl-Heptane | 2.3 | 3.0 | 2.8 | 1.5 | 1.7 | 1.6 | 2.8 | 3.7 | 3.2 | 0.6 | 0.8 | 0.7 | 0.9 | 2.0 | 1.4 | 5.9 | 8.6 | 7.2 |
| 2-Ethyl-Furan | 9.8 | 14.4 | 12.7 | 19.3 | 32.4 | 26.4 | 21.8 | 29.6 | 25.0 | 15.9 | 39.1 | 27.4 | 17.4 | 22.8 | 19.4 | 15.6 | 22.8 | 18.6 |
| Ethyl Ester Propanoic Acid | 0.3 | 0.6 | 0.4 | 7.5 | 9.1 | 8.3 | 57.3 | 100.4 | 76.3 | 1.3 | 2.1 | 1.6 | 0.2 | 0.2 | 0.2 | 0.7 | 1.2 | 0.9 |
| 2-Methyl Ethyl Ester Propanoic Acid | 0.3 | 0.4 | 0.3 | 0.2 | 0.2 | 0.2 | 20.1 | 31.0 | 25.6 | 0.2 | 0.2 | 0.2 | 0.1 | 0.2 | 0.1 | 0.2 | 0.3 | 0.2 |
| 2-Methyl-Crotonal | 1.3 | 2.3 | 1.8 | 0.8 | 0.8 | 0.8 | 5.6 | 5.8 | 5.7 | 6.1 | 7.4 | 6.6 | 2.4 | 3.1 | 2.8 | 1.0 | 1.3 | 1.2 |
| Propyl Ester Acetic Acid | 0.7 | 0.9 | 0.8 | 0.8 | 1.0 | 0.9 | 10.0 | 17.2 | 13.3 | 0.7 | 0.9 | 0.8 | 0.0 | 0.1 | 0.1 | 0.3 | 0.4 | 0.3 |
| 3-Pentanone | 56.4 | 90.9 | 70.4 | 92.0 | 107.0 | 97.0 | 85.9 | 109.1 | 95.4 | 97.2 | 127.4 | 116.0 | 53.7 | 66.4 | 62.0 | 134.3 | 179.0 | 151.7 |
| Pentanal | 0.4 | 0.5 | 0.4 | 0.2 | 0.3 | 0.2 | 2.1 | 4.0 | 3.1 | 1.0 | 1.4 | 1.2 | 0.9 | 1.1 | 1.0 | 11.4 | 15.5 | 13.1 |
| 2,3-Butanedione | 21.8 | 25.4 | 23.5 | 38.7 | 44.4 | 41.2 | 34.0 | 42.7 | 39.0 | 37.8 | 41.1 | 39.2 | 26.8 | 33.7 | 28.8 | 13.0 | 18.0 | 15.1 |
| 2,3,4-Trimethyl-Hexane | 0.3 | 0.4 | 0.4 | 0.5 | 0.7 | 0.6 | 0.8 | 1.7 | 1.2 | 0.1 | 0.2 | 0.1 | 0.5 | 0.6 | 0.5 | 9.8 | 14.1 | 12.5 |
| Decane | 0.4 | 0.5 | 0.4 | 0.2 | 0.2 | 0.2 | 3.0 | 3.9 | 3.4 | 1.9 | 2.2 | 2.1 | 4.3 | 5.3 | 4.9 | 12.3 | 25.8 | 18.9 |
| 2,6-Dimethyl-Nonane | 1.6 | 2.3 | 1.9 | 0.9 | 1.4 | 1.1 | 2.4 | 2.9 | 2.7 | 0.6 | 0.8 | 0.7 | 0.8 | 1.4 | 1.1 | 12.9 | 22.7 | 18.4 |
| 2,5-Dimethyl-Nonane | 0.4 | 0.6 | 0.5 | 0.9 | 1.5 | 1.2 | 6.0 | 8.0 | 6.8 | 0.9 | 1.4 | 1.1 | 1.2 | 1.9 | 1.6 | 0.3 | 0.3 | 0.3 |
| 4-Methyl-2-Pentanone | 1.0 | 1.2 | 1.1 | 0.2 | 0.2 | 0.2 | 0.2 | 0.5 | 0.3 | 0.9 | 1.2 | 1.1 | 0.4 | 0.7 | 0.5 | 19.9 | 30.4 | 25.3 |
| 2-Methy-2-Butanol | 0.3 | 0.4 | 0.4 | 0.2 | 0.2 | 0.2 | 0.4 | 0.5 | 0.4 | 0.1 | 0.3 | 0.2 | 0.3 | 0.5 | 0.4 | 3.1 | 4.2 | 3.9 |
| 2-Methyl-Propyl Ester Acetic Acid | 1.5 | 2.1 | 1.8 | 1.6 | 1.9 | 1.7 | 9.5 | 19.2 | 14.4 | 2.8 | 5.8 | 4.2 | 0.4 | 0.6 | 0.5 | 0.7 | 1.1 | 0.9 |
| α-Pinene | 0.1 | 0.1 | 0.1 | 0.2 | 0.2 | 0.2 | 1.4 | 2.2 | 1.7 | 0.2 | 0.4 | 0.3 | 0.5 | 0.8 | 0.6 | 1.0 | 1.6 | 1.3 |
| 4,4-Dimethyl-2-Pentanone | 0.1 | 0.1 | 0.1 | 0.1 | 0.2 | 0.2 | 0.3 | 0.4 | 0.3 | 0.2 | 0.2 | 0.2 | 0.1 | 0.1 | 0.1 | 4.2 | 4.9 | 4.4 |
| 1-Penten-3-one | 0.3 | 0.4 | 0.4 | 0.2 | 0.3 | 0.3 | 4.2 | 5.2 | 4.5 | 1.7 | 2.2 | 2.0 | 0.9 | 1.3 | 1.1 | 7.6 | 10.4 | 8.6 |
| 5-Butyl-Nonane | 2.9 | 4.2 | 3.5 | 1.7 | 2.1 | 1.9 | 7.7 | 9.6 | 8.5 | 0.5 | 0.6 | 0.6 | 1.2 | 2.5 | 1.9 | 0.5 | 0.8 | 0.7 |
| 3,6-Dimethyl-Decane | 0.2 | 0.4 | 0.3 | 0.7 | 0.9 | 0.8 | 0.4 | 0.7 | 0.5 | 0.1 | 0.2 | 0.1 | 0.2 | 0.3 | 0.3 | 0.1 | 0.1 | 0.1 |
| 2-Methyl-3-Buten-2-ol | 0.4 | 0.8 | 0.6 | 1.7 | 2.6 | 2.2 | 9.7 | 19.6 | 14.9 | 0.6 | 0.7 | 0.7 | 1.4 | 2.2 | 1.7 | 0.6 | 0.8 | 0.7 |
| 5-Methyl-Decane | 1.0 | 1.9 | 1.4 | 0.9 | 1.1 | 1.0 | 1.0 | 1.4 | 1.2 | 0.8 | 1.2 | 1.0 | 0.9 | 1.5 | 1.2 | 0.3 | 0.4 | 0.3 |
| 4-Methyl-Decane | 1.0 | 2.5 | 1.8 | 0.6 | 1.0 | 0.8 | 1.8 | 2.8 | 2.1 | 0.2 | 0.3 | 0.3 | 0.8 | 1.0 | 0.9 | 0.8 | 1.2 | 1.0 |

| | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,3-Pentanedione | 11.9 | 21.7 | 16.4 | 1.0 | 1.4 | 1.2 | 2.2 | 4.1 | 3.1 | 8.1 | 10.5 | 9.3 | 0.6 | 0.8 | 0.7 | 1.7 | 3.4 | 2.6 |
| 3,3-Dimethyl-Methyl Ester Butanoic Acid | 0.8 | 1.1 | 0.9 | 1.5 | 3.4 | 2.3 | 12.6 | 27.5 | 19.0 | 0.3 | 0.3 | 0.3 | 0.7 | 1.0 | 0.8 | 0.4 | 0.4 | 0.4 |
| 2-Hexanone | 0.5 | 0.7 | 0.6 | 0.6 | 0.8 | 0.7 | 1.2 | 2.5 | 1.9 | 0.5 | 0.8 | 0.7 | 0.8 | 1.2 | 1.0 | 0.7 | 0.9 | 0.8 |
| 4-Methyl-Undecane | 0.6 | 0.8 | 0.7 | 0.5 | 0.6 | 0.5 | 4.1 | 5.4 | 4.8 | 0.9 | 1.9 | 1.4 | 1.6 | 3.0 | 2.2 | 0.6 | 0.8 | 0.7 |
| Hexanal | 6.7 | 8.8 | 7.8 | 8.5 | 13.7 | 11.3 | 40.4 | 47.9 | 45.2 | 21.3 | 37.4 | 29.5 | 0.2 | 0.7 | 0.4 | 53.2 | 75.7 | 67.3 |
| 2-Methyl-1-Propanol | 36.2 | 47.0 | 39.5 | 22.0 | 26.4 | 24.4 | 18.3 | 21.8 | 20.4 | 15.5 | 24.4 | 19.2 | 47.5 | 53.3 | 51.1 | 7.3 | 11.9 | 9.1 |
| 2-Methyl-2-Pentanol | 0.3 | 0.5 | 0.4 | 0.2 | 0.2 | 0.2 | 0.3 | 0.4 | 0.3 | 0.1 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.6 | 0.8 | 0.7 |
| Ethyl-Benzene | 28.0 | 36.5 | 31.4 | 35.4 | 45.5 | 40.5 | 72.6 | 105.6 | 87.1 | 24.3 | 30.6 | 27.5 | 3.5 | 45.1 | 23.7 | 16.4 | 19.5 | 17.7 |
| 3-Methyl Butyl Ester Acetic Acid | 7.8 | 10.9 | 8.8 | 18.2 | 26.5 | 22.6 | 18.2 | 25.7 | 22.6 | 10.4 | 13.9 | 12.2 | 1.1 | 3.6 | 2.4 | 7.8 | 11.5 | 10.0 |
| o-Xylene | 11.9 | 21.3 | 16.1 | 8.6 | 11.0 | 9.4 | 20.8 | 33.0 | 27.2 | 9.6 | 17.7 | 14.2 | 9.1 | 15.6 | 12.2 | 52.8 | 71.3 | 61.7 |
| 2-Pentanol | 0.3 | 0.5 | 0.4 | 3.3 | 5.8 | 4.4 | 63.8 | 94.3 | 80.1 | 7.7 | 8.4 | 8.0 | 6.1 | 7.9 | 7.0 | 2.0 | 3.7 | 2.7 |
| p-Xylene | 6.6 | 8.9 | 7.5 | 10.6 | 28.8 | 18.4 | 41.4 | 49.3 | 45.9 | 35.1 | 41.7 | 37.5 | 28.1 | 31.5 | 29.5 | 27.6 | 40.5 | 34.6 |
| 5-Methyl-2-Hexanone | 0.6 | 0.7 | 0.7 | 0.2 | 0.4 | 0.3 | 2.8 | 3.5 | 3.2 | 0.3 | 0.4 | 0.3 | 0.3 | 0.5 | 0.4 | 1.3 | 1.9 | 1.5 |
| 2-Ethyl Methyl Ester Pentanoic Acid | 0.3 | 0.6 | 0.5 | 14.8 | 29.1 | 21.9 | 285.3 | 471.8 | 380.6 | 8.3 | 12.0 | 10.2 | 4.2 | 6.3 | 5.1 | 20.2 | 30.5 | 24.8 |
| 1-Butanol | 0.6 | 0.7 | 0.7 | 1.3 | 2.5 | 1.8 | 12.3 | 18.9 | 15.5 | 0.4 | 0.5 | 0.4 | 11.1 | 20.2 | 15.0 | 0.3 | 0.6 | 0.4 |
| α-Phellandrene | 0.1 | 0.2 | 0.1 | 0.7 | 0.8 | 0.8 | 0.4 | 0.4 | 0.4 | 5.5 | 7.9 | 6.8 | 1.6 | 2.6 | 2.0 | 83.0 | 177.1 | 131.2 |
| 2-Methyl-3-Pentanol | 4.0 | 6.4 | 5.1 | 2.4 | 3.7 | 3.1 | 26.3 | 33.5 | 28.9 | 9.0 | 13.8 | 11.0 | 3.4 | 4.3 | 3.8 | 2.5 | 3.6 | 3.0 |
| 1-Penten-3-ol | 57.4 | 73.7 | 66.1 | 99.7 | 165.5 | 130.0 | 141.5 | 233.5 | 188.0 | 37.4 | 49.3 | 41.9 | 89.8 | 116.7 | 104.0 | 110.7 | 203.4 | 146.5 |
| α-Terpinene | 0.4 | 0.5 | 0.5 | 0.1 | 0.2 | 0.1 | 0.1 | 0.2 | 0.1 | 4.8 | 7.8 | 6.4 | 0.4 | 0.7 | 0.5 | 27.4 | 43.1 | 35.0 |
| Butyl Ester 2-Propenoic Acid | 4.3 | 6.5 | 5.3 | 1.4 | 4.9 | 3.1 | 10.0 | 20.0 | 14.7 | 3.5 | 5.1 | 4.4 | 4.5 | 7.2 | 5.5 | 8.4 | 17.5 | 12.9 |
| m-Xylene | 1.5 | 1.9 | 1.7 | 13.6 | 16.5 | 15.1 | 30.5 | 41.5 | 36.1 | 1.4 | 2.1 | 1.7 | 12.0 | 16.5 | 14.3 | 21.7 | 31.4 | 26.9 |
| 2-Heptanone | 124.9 | 187.9 | 154.5 | 731.2 | 797.7 | 763.0 | 78.5 | 116.9 | 97.4 | 139.7 | 256.6 | 185.9 | 489.0 | 626.0 | 562.5 | 268.0 | 356.7 | 329.0 |
| Heptanal | 0.3 | 0.5 | 0.4 | 9.1 | 11.2 | 10.2 | 4.8 | 8.7 | 6.6 | 0.8 | 0.9 | 0.8 | 1.2 | 1.7 | 1.5 | 4.0 | 5.5 | 4.5 |
| D-Limonene | 0.1 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 2.6 | 3.2 | 2.9 | 0.1 | 0.2 | 0.2 | 1.2 | 1.8 | 1.5 | 1.2 | 2.0 | 1.5 |
| 3-Hexanol | 0.2 | 0.3 | 0.3 | 1.7 | 2.2 | 1.9 | 0.4 | 0.6 | 0.5 | 3.1 | 3.8 | 3.3 | 1.6 | 2.0 | 1.8 | 0.5 | 0.8 | 0.6 |
| β-Phellandrene | 0.2 | 0.3 | 0.2 | 1.4 | 1.7 | 1.5 | 0.3 | 0.4 | 0.4 | 2.0 | 4.5 | 3.2 | 8.9 | 11.0 | 9.6 | 300.7 | 417.0 | 354.8 |
| Eucalyptol | 0.2 | 0.2 | 0.2 | 0.1 | 0.2 | 0.1 | 0.1 | 0.2 | 0.1 | 0.3 | 0.4 | 0.4 | 0.1 | 0.2 | 0.1 | 0.5 | 0.8 | 0.7 |
| m-Menthane | 0.1 | 0.1 | 0.1 | 0.2 | 0.2 | 0.2 | 1.5 | 2.8 | 2.1 | 0.3 | 0.4 | 0.4 | 0.5 | 0.7 | 0.6 | 2.0 | 2.6 | 2.4 |
| 4-Methyl-2-Heptanone | 0.3 | 0.3 | 0.3 | 22.6 | 31.4 | 26.0 | 2.1 | 4.1 | 3.1 | 2.1 | 2.6 | 2.3 | 1.5 | 2.0 | 1.8 | 366.4 | 452.6 | 423.2 |
| 3-Methyl-2-Pentanol | 11.2 | 20.8 | 14.9 | 79.4 | 100.0 | 89.3 | 82.1 | 89.3 | 85.2 | 4.9 | 7.3 | 6.1 | 84.7 | 101.1 | 91.3 | 1.7 | 3.9 | 2.8 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Methyl-1-Butanol | 151.8 | 250.8 | 196.0 | 179.2 | 201.1 | 191.7 | 131.3 | 263.3 | 184.0 | 79.9 | 127.9 | 101.9 | 125.9 | 185.9 | 160.9 | 16.5 | 26.4 | 21.8 |
| 3-Methyl-1-Butanol | 439.5 | 668.2 | 532.4 | 241.6 | 437.0 | 339.9 | 447.9 | 564.4 | 502.7 | 263.0 | 446.1 | 348.1 | 310.8 | 596.6 | 439.6 | 28.7 | 37.2 | 33.7 |
| o-Ethyltoluene | 1.3 | 1.9 | 1.7 | 3.8 | 5.9 | 4.9 | 7.7 | 8.5 | 8.3 | 5.2 | 6.8 | 5.9 | 2.0 | 4.0 | 2.9 | 5.9 | 6.9 | 6.4 |
| m-Ethyltoluene | 1.0 | 2.3 | 1.6 | 3.5 | 4.0 | 3.7 | 13.0 | 15.9 | 14.1 | 6.7 | 9.9 | 8.3 | 6.0 | 7.3 | 6.6 | 1.9 | 3.0 | 2.4 |
| 2-Hexanol | 57.7 | 83.0 | 68.6 | 48.1 | 70.1 | 56.6 | 1.3 | 3.1 | 2.3 | 1.5 | 3.1 | 2.4 | 5.5 | 9.0 | 7.1 | 1.8 | 2.0 | 1.8 |
| Ethylene Glycol Ethyl Ether | 0.1 | 0.2 | 0.1 | 1.2 | 1.8 | 1.5 | 2.5 | 2.9 | 2.7 | 9.1 | 20.0 | 14.1 | 1.7 | 2.7 | 2.1 | 1.3 | 2.6 | 1.8 |
| 6-Methyl-2-Heptanone | 1.6 | 3.0 | 2.2 | 1.5 | 2.3 | 1.9 | 2.2 | 3.7 | 2.9 | 1.7 | 2.0 | 1.9 | 1.4 | 2.1 | 1.7 | 6.9 | 9.3 | 7.8 |
| Pseudocumene | 2.1 | 3.3 | 2.7 | 3.8 | 6.0 | 4.9 | 7.2 | 8.1 | 7.7 | 4.3 | 5.3 | 4.8 | 2.1 | 4.1 | 3.0 | 4.5 | 5.7 | 5.0 |
| 4,6-Dimethyl-2-Heptanone | 0.7 | 0.9 | 0.8 | 0.7 | 1.0 | 0.9 | 1.1 | 1.7 | 1.4 | 0.7 | 0.9 | 0.8 | 0.3 | 0.4 | 0.4 | 39.1 | 61.2 | 51.8 |
| 2,3-Dimethyl-2-Hexanol | 0.2 | 0.4 | 0.3 | 0.2 | 0.3 | 0.2 | 1.0 | 2.4 | 1.6 | 0.2 | 0.3 | 0.2 | 0.2 | 0.4 | 0.3 | 18.3 | 21.5 | 19.6 |
| 3-Octanone | 5.1 | 6.8 | 5.9 | 15.5 | 23.4 | 19.2 | 17.3 | 24.0 | 21.1 | 0.8 | 1.0 | 0.9 | 17.0 | 21.6 | 19.3 | 0.3 | 0.4 | 0.3 |
| Styrene | 26.2 | 45.3 | 35.3 | 31.5 | 35.5 | 33.5 | 81.2 | 132.2 | 101.9 | 47.4 | 64.8 | 56.3 | 48.1 | 65.6 | 53.5 | 23.0 | 30.6 | 27.3 |
| 5-Methyl-2-Heptanone | 4.2 | 6.8 | 5.4 | 9.7 | 18.4 | 13.9 | 7.7 | 9.6 | 8.7 | 9.1 | 10.6 | 9.8 | 7.4 | 8.6 | 7.7 | 16.9 | 26.5 | 22.4 |
| 1-Pentanol | 30.0 | 52.0 | 39.6 | 27.4 | 34.2 | 30.2 | 3.9 | 4.9 | 4.5 | 27.2 | 48.2 | 38.0 | 6.3 | 8.9 | 7.7 | 4.7 | 6.0 | 5.3 |
| p-Ethyltoluene | 0.2 | 0.4 | 0.3 | 2.2 | 3.3 | 2.7 | 6.6 | 9.2 | 7.5 | 4.4 | 5.5 | 4.9 | 3.0 | 4.6 | 3.8 | 1.8 | 2.7 | 2.2 |
| p-Cymene | 1.4 | 2.1 | 1.7 | 2.2 | 2.5 | 2.3 | 3.5 | 4.0 | 3.8 | 11.4 | 18.1 | 14.5 | 3.2 | 3.7 | 3.5 | 30.9 | 52.2 | 39.5 |
| Mesitylene | 8.4 | 13.2 | 10.5 | 1.2 | 1.3 | 1.2 | 0.4 | 0.5 | 0.4 | 8.2 | 11.8 | 10.2 | 14.0 | 15.2 | 14.7 | 8.0 | 11.2 | 9.1 |
| 4-Methyl-4-Heptanol | 1.0 | 1.8 | 1.4 | 0.5 | 0.6 | 0.5 | 0.1 | 0.2 | 0.2 | 0.4 | 0.5 | 0.4 | 0.2 | 0.4 | 0.3 | 0.7 | 1.1 | 0.8 |
| 4-Heptanol | 0.4 | 0.5 | 0.4 | 2.4 | 3.0 | 2.6 | 2.8 | 3.6 | 3.2 | 3.3 | 3.9 | 3.7 | 1.4 | 2.1 | 1.7 | 10.5 | 19.7 | 14.0 |
| 2-Octanone | 21.9 | 39.4 | 30.0 | 98.8 | 117.5 | 107.3 | 11.8 | 21.1 | 16.8 | 27.7 | 43.8 | 34.5 | 67.1 | 84.0 | 77.5 | 65.4 | 96.1 | 81.6 |
| Octanal | 0.2 | 0.2 | 0.2 | 0.1 | 0.2 | 0.1 | 4.1 | 4.6 | 4.3 | 1.4 | 2.3 | 1.8 | 1.5 | 1.9 | 1.7 | 3.8 | 4.7 | 4.2 |
| 3-Hydroxy-2-Butanone | 0.2 | 0.3 | 0.2 | 0.3 | 0.5 | 0.4 | 0.1 | 0.1 | 0.1 | 0.2 | 0.3 | 0.2 | 0.2 | 0.3 | 0.2 | 0.1 | 0.1 | 0.1 |
| 1-Octen-3-one | 15.1 | 23.6 | 18.8 | 6.2 | 7.5 | 6.9 | 2.6 | 3.3 | 3.0 | 3.4 | 4.4 | 3.8 | 0.2 | 0.3 | 0.2 | 14.9 | 23.7 | 19.3 |
| trans-2-Pentenol | 10.4 | 13.4 | 11.8 | 21.7 | 24.0 | 23.2 | 22.5 | 26.2 | 23.9 | 15.6 | 26.0 | 19.6 | 14.4 | 22.7 | 18.6 | 13.7 | 17.6 | 16.0 |
| 2,2,6-Trimethyl-Cyclohexanone | 2.0 | 2.6 | 2.3 | 2.9 | 3.5 | 3.1 | 4.7 | 5.7 | 5.1 | 1.9 | 2.3 | 2.1 | 2.5 | 3.6 | 3.0 | 3.6 | 4.1 | 3.8 |
| 2-Heptanol | 503.2 | 589.8 | 553.6 | 484.5 | 631.5 | 549.0 | 260.5 | 289.9 | 273.6 | 561.6 | 665.8 | 627.5 | 595.9 | 760.8 | 692.6 | 372.6 | 475.0 | 423.5 |
| cis-2-Pentenol | 206.9 | 331.8 | 257.8 | 119.8 | 201.6 | 164.7 | 141.0 | 155.8 | 148.0 | 209.3 | 315.4 | 251.4 | 93.2 | 147.2 | 113.7 | 121.8 | 155.2 | 137.8 |
| 1-Hydroxy-2-Propanone | 20.3 | 24.7 | 22.0 | 8.9 | 11.9 | 10.1 | 5.2 | 7.1 | 6.1 | 87.3 | 126.9 | 105.8 | 4.3 | 6.1 | 5.3 | 3.6 | 4.9 | 4.3 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 5-Methyl-4-Hexen-3-one | 1.2 | 1.6 | 1.4 | 2.0 | 3.5 | 2.7 | 1.3 | 2.1 | 1.8 | 2.2 | 2.8 | 2.4 | 2.9 | 3.4 | 3.2 | 1.6 | 2.1 | 1.8 |
| Hemimellitene | 4.0 | 5.3 | 4.5 | 2.2 | 3.8 | 2.9 | 7.0 | 9.5 | 8.5 | 5.3 | 5.9 | 5.5 | 3.4 | 4.7 | 4.1 | 2.5 | 4.4 | 3.2 |
| 6-Methyl-5-Hepten-2-one | 14.1 | 21.7 | 17.4 | 9.1 | 13.3 | 11.3 | 17.1 | 25.7 | 21.1 | 10.0 | 17.0 | 12.9 | 9.2 | 14.5 | 11.4 | 40.3 | 45.9 | 42.5 |
| 2-Pentene | 272.3 | 363.4 | 306.5 | 400.7 | 459.4 | 439.3 | 92.8 | 148.2 | 119.8 | 294.2 | 457.2 | 395.5 | 475.8 | 506.7 | 486.2 | 308.2 | 435.5 | 388.6 |
| 1-Hexanol | 527.7 | 721.0 | 610.1 | 366.0 | 424.6 | 402.9 | 630.0 | 717.2 | 680.2 | 633.3 | 746.6 | 696.4 | 359.4 | 472.9 | 411.8 | 102.3 | 192.7 | 153.5 |
| 2-Cyclopenten-1-one | 0.9 | 1.3 | 1.1 | 9.6 | 12.6 | 10.6 | 7.7 | 15.8 | 11.5 | 13.3 | 16.7 | 15.0 | 1.4 | 2.1 | 1.7 | 8.1 | 15.1 | 11.5 |
| 2-Methyl-2-Cyclopenten-1-one | 0.2 | 0.3 | 0.3 | 3.0 | 3.9 | 3.4 | 2.8 | 3.4 | 3.1 | 3.1 | 3.9 | 3.5 | 0.5 | 6.4 | 3.3 | 4.0 | 5.2 | 4.6 |
| β-Methy-Styrene | 0.2 | 0.4 | 0.3 | 1.7 | 2.1 | 1.9 | 3.1 | 4.1 | 3.7 | 3.3 | 3.5 | 3.4 | 2.3 | 3.2 | 2.6 | 0.7 | 0.8 | 0.8 |
| 4-Octanol | 3.4 | 3.9 | 3.6 | 3.4 | 4.0 | 3.8 | 1.6 | 2.4 | 2.0 | 3.1 | 4.0 | 3.7 | 3.2 | 4.4 | 3.9 | 5.2 | 6.6 | 5.8 |
| cis-3-Hexen-1-ol | 9.8 | 16.5 | 13.1 | 6.8 | 9.0 | 7.8 | 8.5 | 11.1 | 10.2 | 5.2 | 7.3 | 6.3 | 4.3 | 5.2 | 4.7 | 1.5 | 1.7 | 1.6 |
| 2-Nonanone | 46.5 | 59.6 | 52.8 | 296.6 | 385.7 | 350.6 | 52.3 | 69.4 | 60.7 | 12.5 | 21.6 | 16.4 | 143.4 | 276.5 | 204.1 | 1.2 | 1.4 | 1.3 |
| Nonanal | 80.8 | 93.4 | 85.5 | 77.3 | 88.0 | 83.0 | 11.9 | 26.2 | 19.1 | 37.4 | 51.7 | 43.5 | 36.4 | 51.3 | 42.8 | 2.8 | 4.2 | 3.7 |
| Ethylene Glycol Butyl Ether | 25.6 | 28.7 | 27.5 | 2.4 | 2.9 | 2.7 | 9.9 | 17.3 | 12.7 | 21.8 | 24.0 | 23.1 | 5.1 | 5.9 | 5.4 | 1.2 | 1.8 | 1.5 |
| 1-Ethyl-1-Methyl-Cyclopentane | 1.5 | 2.3 | 1.9 | 2.9 | 4.0 | 3.5 | 11.1 | 18.5 | 15.0 | 6.1 | 7.7 | 6.9 | 3.4 | 4.7 | 4.3 | 49.4 | 70.6 | 58.2 |
| 3-Octen-2-one | 2.5 | 3.2 | 2.8 | 82.2 | 171.8 | 124.7 | 6.6 | 7.8 | 7.2 | 7.7 | 9.0 | 8.3 | 2.1 | 3.1 | 2.7 | 28.6 | 38.5 | 33.3 |
| 2-Octanol | 77.8 | 110.0 | 88.6 | 142.1 | 175.6 | 162.6 | 10.3 | 10.9 | 10.6 | 82.3 | 113.5 | 97.3 | 241.8 | 308.3 | 274.6 | 45.0 | 59.7 | 53.8 |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | 0.3 | 0.3 | 0.3 | 0.2 | 0.3 | 0.3 | 0.9 | 1.2 | 1.0 | 0.3 | 0.4 | 0.3 | 2.4 | 2.7 | 2.5 | 0.2 | 0.3 | 0.2 |
| 1,3-Bis(1,1-Dimethylethyl)-Benzene | 0.3 | 0.4 | 0.4 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.1 | 0.2 | 0.2 | 0.4 | 0.5 | 0.4 | 25.6 | 39.7 | 33.3 |
| trans-2-Octenal | 0.7 | 0.9 | 0.8 | 8.3 | 10.0 | 9.2 | 17.0 | 23.4 | 20.0 | 1.4 | 2.4 | 1.9 | 9.7 | 9.9 | 9.7 | 26.0 | 39.5 | 31.9 |
| m-Ethyl-Styrene | 9.2 | 11.4 | 10.2 | 8.3 | 10.3 | 9.2 | 1.0 | 2.2 | 1.6 | 0.4 | 0.5 | 0.4 | 2.4 | 4.0 | 3.1 | 12.2 | 23.9 | 17.7 |
| 5-Methyl-2-Heptanone | 0.6 | 0.7 | 0.7 | 0.5 | 0.6 | 0.5 | 0.7 | 0.9 | 0.8 | 0.7 | 0.8 | 0.7 | 0.4 | 0.6 | 0.5 | 13.2 | 21.7 | 16.4 |
| 2-Decanone | 1.6 | 2.5 | 2.1 | 1.7 | 2.8 | 2.3 | 1.0 | 1.8 | 1.5 | 1.5 | 1.8 | 1.7 | 6.5 | 8.4 | 7.2 | 10.2 | 20.8 | 15.2 |
| 1-Octen-3-ol | 106.6 | 148.8 | 125.8 | 98.2 | 135.5 | 120.4 | 115.7 | 153.9 | 133.6 | 146.7 | 205.4 | 183.7 | 109.3 | 159.1 | 136.3 | 251.7 | 365.9 | 296.5 |
| trans,trans-2,4-Heptadienal | 1.8 | 2.3 | 2.1 | 4.2 | 4.9 | 4.5 | 2.5 | 3.2 | 2.8 | 4.8 | 5.8 | 5.2 | 3.1 | 3.8 | 3.4 | 1.3 | 1.9 | 1.5 |
| 1-Heptanol | 48.1 | 58.9 | 52.9 | 49.8 | 55.8 | 52.6 | 51.0 | 66.3 | 56.0 | 73.1 | 89.7 | 83.5 | 79.4 | 90.7 | 85.1 | 12.8 | 18.2 | 14.8 |
| cis,cis-3,5-Octadiene | 1.6 | 2.6 | 2.0 | 2.1 | 2.3 | 2.2 | 1.0 | 1.5 | 1.2 | 0.9 | 1.1 | 0.9 | 1.8 | 2.7 | 2.2 | 0.6 | 1.0 | 0.8 |
| 2-Oxo-Methyl Ester Propanoic Acid | 130.3 | 187.5 | 157.1 | 90.8 | 122.0 | 103.8 | 14.5 | 17.4 | 15.5 | 149.4 | 213.4 | 178.9 | 98.4 | 115.8 | 103.8 | 48.4 | 58.1 | 52.3 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Dihydromyrcenol | 14.9 | 22.6 | 17.6 | 11.0 | 13.8 | 12.4 | 9.1 | 12.4 | 10.6 | 14.2 | 19.6 | 17.2 | 10.5 | 12.9 | 11.9 | 9.7 | 12.8 | 11.0 |
| trans-Menthone | 0.1 | 0.2 | 0.1 | 0.8 | 1.2 | 1.0 | 0.4 | 0.4 | 0.4 | 17.3 | 29.2 | 21.8 | 1.7 | 2.2 | 2.0 | 64.6 | 91.7 | 75.0 |
| Furfural | 59.4 | 82.0 | 70.7 | 60.3 | 89.9 | 76.5 | 52.9 | 78.2 | 65.2 | 69.4 | 82.6 | 77.3 | 78.4 | 86.4 | 83.4 | 29.6 | 36.8 | 34.2 |
| Ethanoic Acid | 1861.2 | 2563.4 | 2073.7 | 1799.1 | 2430.2 | 2178.3 | 1316.2 | 1606.0 | 1449.3 | 1896.6 | 2145.7 | 2033.9 | 511.7 | 538.4 | 528.6 | 10.9 | 19.8 | 15.7 |
| 2-Ethyl-1-Hexanol | 30.1 | 38.3 | 33.1 | 12.8 | 14.7 | 13.5 | 28.5 | 33.5 | 30.8 | 20.2 | 28.9 | 24.6 | 11.9 | 19.0 | 15.4 | 38.4 | 50.4 | 46.5 |
| Decanal | 24.3 | 33.9 | 29.3 | 39.5 | 52.8 | 47.7 | 59.9 | 68.4 | 64.1 | 56.1 | 67.6 | 62.2 | 20.6 | 26.9 | 23.4 | 37.9 | 48.1 | 42.2 |
| Furfuryl Formate | 46.8 | 58.5 | 52.2 | 44.7 | 57.7 | 51.3 | 31.4 | 32.7 | 32.1 | 59.9 | 67.4 | 64.0 | 9.7 | 16.1 | 12.3 | 8.5 | 9.9 | 9.1 |
| trans-2-Hepten-1-ol | 19.5 | 24.7 | 22.2 | 17.2 | 23.4 | 20.2 | 38.2 | 46.7 | 42.9 | 46.1 | 51.6 | 48.9 | 23.9 | 27.4 | 25.4 | 10.0 | 17.1 | 13.3 |
| 2-Nonanol | 19.6 | 25.3 | 22.6 | 328.1 | 384.4 | 361.7 | 3.7 | 4.2 | 3.9 | 21.1 | 22.4 | 21.7 | 346.0 | 421.8 | 382.4 | 45.9 | 57.1 | 49.6 |
| 1-(2-Furanyl)-Ethanone | 299.6 | 400.0 | 335.8 | 432.4 | 499.2 | 474.3 | 59.6 | 74.0 | 65.1 | 57.1 | 72.5 | 66.7 | 43.5 | 50.0 | 47.3 | 30.3 | 34.9 | 33.0 |
| 3,5-Octadien-2-one | 10.4 | 13.3 | 11.7 | 6.6 | 7.6 | 7.0 | 21.2 | 26.9 | 23.7 | 18.9 | 26.5 | 21.4 | 8.7 | 11.3 | 10.0 | 27.7 | 38.1 | 32.9 |
| Benzaldehyde | 28.4 | 35.3 | 30.5 | 21.4 | 28.1 | 25.5 | 33.3 | 44.2 | 38.1 | 22.6 | 27.1 | 24.5 | 22.3 | 27.9 | 24.3 | 32.6 | 42.2 | 37.6 |
| Furfuryl Acetate | 0.4 | 0.4 | 0.4 | 0.3 | 0.4 | 0.4 | 0.7 | 0.9 | 0.8 | 0.5 | 0.6 | 0.5 | 0.2 | 0.2 | 0.2 | 0.3 | 2.6 | 1.4 |
| Linalool | 6.4 | 7.9 | 7.0 | 4.7 | 5.5 | 5.0 | 5.8 | 6.6 | 6.2 | 1.3 | 1.7 | 1.4 | 1.0 | 1.3 | 1.2 | 0.8 | 1.1 | 1.0 |
| β-Myrcene | 0.8 | 1.0 | 0.9 | 0.9 | 1.4 | 1.1 | 1.0 | 1.6 | 1.3 | 0.2 | 0.2 | 0.2 | 1.1 | 1.3 | 1.2 | 4.6 | 5.4 | 4.9 |
| 1-Octanol | 80.4 | 101.1 | 88.2 | 64.8 | 77.7 | 69.8 | 109.5 | 137.8 | 124.2 | 90.1 | 116.3 | 99.3 | 86.1 | 113.5 | 97.8 | 31.6 | 35.8 | 33.6 |
| trans-p-2-Menthen-1-ol | 0.1 | 0.1 | 0.1 | 0.7 | 0.9 | 0.8 | 0.6 | 0.7 | 0.6 | 50.7 | 75.3 | 63.1 | 2.1 | 3.1 | 2.5 | 86.8 | 123.2 | 101.2 |
| Propanoic Acid | 4.0 | 4.9 | 4.4 | 0.8 | 1.0 | 0.9 | 1.4 | 1.6 | 1.5 | 17.0 | 20.1 | 18.5 | 0.4 | 0.6 | 0.5 | 8.3 | 11.8 | 10.0 |
| 2,3-Butanediol | 230.3 | 361.6 | 284.6 | 415.1 | 459.8 | 441.4 | 51.5 | 63.0 | 57.5 | 64.4 | 76.8 | 71.3 | 129.8 | 298.4 | 200.5 | 51.0 | 61.2 | 54.6 |
| Dimethyl Sulfoxide | 59.1 | 73.7 | 65.4 | 30.2 | 36.2 | 33.6 | 18.8 | 26.4 | 22.4 | 99.8 | 107.2 | 101.8 | 49.2 | 73.3 | 59.9 | 4.7 | 5.8 | 5.4 |
| m-Menth-3-ene | 48.7 | 62.0 | 54.0 | 43.6 | 57.4 | 49.7 | 6.2 | 8.3 | 7.1 | 31.4 | 48.4 | 38.7 | 11.7 | 14.8 | 13.3 | 6.0 | 7.1 | 6.6 |
| Trans-(2-Ethylcyclopentyl)-Methanol | 20.0 | 29.9 | 24.6 | 33.0 | 37.2 | 34.6 | 32.5 | 45.3 | 36.7 | 38.1 | 43.4 | 40.0 | 31.7 | 41.7 | 35.0 | 10.1 | 14.3 | 12.4 |
| Bornyl Acetate | 9.0 | 11.3 | 9.8 | 4.7 | 5.5 | 5.1 | 8.7 | 11.6 | 9.8 | 7.7 | 9.7 | 8.7 | 9.2 | 11.6 | 10.2 | 0.8 | 1.1 | 1.0 |
| 4-Cyclopentene-1,3-dione | 267.1 | 328.5 | 289.9 | 260.4 | 276.8 | 269.2 | 94.5 | 145.0 | 119.6 | 77.1 | 101.9 | 89.4 | 12.9 | 20.9 | 16.6 | 39.3 | 51.5 | 44.0 |
| Menthol | 2.6 | 3.7 | 3.2 | 9.1 | 11.4 | 10.4 | 0.3 | 0.5 | 0.4 | 2.7 | 3.4 | 3.1 | 2.6 | 2.6 | 2.6 | 40.0 | 45.6 | 43.8 |
| 2-Undecanone | 9.2 | 12.3 | 10.2 | 23.5 | 35.6 | 28.4 | 6.9 | 7.6 | 7.1 | 2.3 | 3.3 | 2.8 | 1.0 | 2.1 | 1.4 | 1.7 | 2.6 | 2.1 |
| 2-(2-Furanyl)-Furan | 2.3 | 3.7 | 3.0 | 3.0 | 3.6 | 3.3 | 3.6 | 4.4 | 3.9 | 1.5 | 2.5 | 1.9 | 0.8 | 1.1 | 1.0 | 0.4 | 0.6 | 0.5 |
| trans-2-Octen-1-ol | 34.2 | 50.7 | 42.0 | 43.6 | 54.5 | 50.6 | 97.3 | 105.0 | 100.3 | 63.1 | 72.6 | 67.9 | 50.6 | 56.1 | 52.0 | 13.2 | 17.0 | 15.1 |
| trans-2-Nonen-1-ol | 21.0 | 26.1 | 23.2 | 14.0 | 15.6 | 14.7 | 28.9 | 35.2 | 32.5 | 25.1 | 30.1 | 27.8 | 20.9 | 27.4 | 24.1 | 58.0 | 72.6 | 66.1 |
| Diethylene Glycol Ethyl Ether | 61.2 | 78.3 | 66.8 | 43.4 | 53.6 | 49.0 | 63.8 | 74.1 | 68.3 | 55.4 | 62.9 | 58.8 | 42.5 | 54.8 | 46.7 | 46.1 | 61.7 | 57.2 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3,5,5-Trimethyl-2-Cyclopenten-1-one | 11.2 | 19.2 | 15.1 | 10.7 | 14.8 | 12.4 | 11.1 | 21.2 | 16.4 | 16.4 | 19.3 | 17.5 | 11.5 | 18.1 | 14.4 | 11.3 | 16.6 | 14.3 |
| cis-p-2-Menthen-1-ol | 1.4 | 2.0 | 1.7 | 3.2 | 3.9 | 3.6 | 2.3 | 3.1 | 2.6 | 2.7 | 35.9 | 18.2 | 3.4 | 4.0 | 3.6 | 4.2 | 5.3 | 4.6 |
| β-Cyclocitral | 2.9 | 3.4 | 3.2 | 4.4 | 4.8 | 4.5 | 9.4 | 10.9 | 10.2 | 8.5 | 10.3 | 9.2 | 5.6 | 6.9 | 6.3 | 14.9 | 21.7 | 17.5 |
| Benzeneacetaldehyde | 86.2 | 100.6 | 92.9 | 34.8 | 39.3 | 36.6 | 16.9 | 19.5 | 18.5 | 13.9 | 18.0 | 16.2 | 11.5 | 14.0 | 13.1 | 75.7 | 82.2 | 79.1 |
| 1-Nonanol | 23.9 | 35.2 | 28.1 | 36.5 | 43.7 | 39.9 | 29.1 | 34.1 | 31.6 | 26.7 | 32.7 | 29.7 | 73.9 | 84.8 | 80.3 | 8.8 | 9.9 | 9.4 |
| Furfuryl Alcohol | 56.0 | 61.6 | 59.2 | 69.3 | 89.3 | 83.6 | 71.8 | 84.4 | 76.9 | 39.9 | 54.0 | 47.0 | 10.3 | 13.9 | 12.6 | 49.3 | 55.5 | 53.5 |
| Phoracanthol | 65.8 | 81.8 | 71.4 | 12.0 | 17.5 | 14.7 | 8.9 | 11.4 | 10.3 | 11.0 | 14.1 | 13.0 | 9.4 | 11.5 | 10.1 | 5.2 | 6.5 | 5.9 |
| cis-3-Nonen-1-ol | 17.6 | 23.2 | 19.6 | 7.7 | 10.0 | 8.9 | 10.1 | 12.5 | 11.0 | 15.6 | 22.7 | 18.9 | 12.5 | 16.7 | 14.4 | 11.4 | 16.5 | 14.0 |
| cis-Piperitol | 2.8 | 3.7 | 3.3 | 1.6 | 2.5 | 2.0 | 0.5 | 0.6 | 0.6 | 26.2 | 31.4 | 28.3 | 2.3 | 2.8 | 2.5 | 37.5 | 48.0 | 42.8 |
| p-Methoxy-Styrene | 5.3 | 7.4 | 6.0 | 1.5 | 1.7 | 1.6 | 23.0 | 30.2 | 25.6 | 4.0 | 5.6 | 4.7 | 0.3 | 0.4 | 0.4 | 2.7 | 3.6 | 3.2 |
| (2Z)-3-Ethyl-2,4-Pentadien-1-ol | 9.0 | 11.5 | 9.9 | 6.6 | 7.0 | 6.9 | 6.5 | 6.9 | 6.6 | 6.1 | 8.3 | 7.4 | 4.2 | 4.9 | 4.4 | 1.3 | 2.0 | 1.5 |
| Butylene Glycol Monobutyl Ether | 13.0 | 18.8 | 15.6 | 11.3 | 17.7 | 14.4 | 8.7 | 10.1 | 9.1 | 10.7 | 16.9 | 13.0 | 8.2 | 9.1 | 8.6 | 1.1 | 1.4 | 1.3 |
| α-Terpineol | 1.9 | 2.5 | 2.2 | 2.2 | 2.3 | 2.2 | 0.9 | 1.2 | 1.0 | 0.5 | 0.6 | 0.5 | 0.1 | 0.2 | 0.2 | 4.4 | 5.8 | 5.1 |
| 1,5-Cyclooctanedione | 2.0 | 2.2 | 2.1 | 0.5 | 4.3 | 2.4 | 1.9 | 2.2 | 2.1 | 2.1 | 2.9 | 2.6 | 2.2 | 2.9 | 2.7 | 4.1 | 5.1 | 4.5 |
| γ-Terpinene | 1.7 | 2.1 | 1.9 | 3.2 | 4.5 | 3.6 | 5.8 | 7.5 | 6.5 | 3.0 | 3.8 | 3.4 | 4.4 | 5.7 | 5.0 | 1.6 | 2.0 | 1.7 |
| trans-2-Decenol | 6.2 | 7.8 | 6.7 | 6.5 | 7.6 | 7.2 | 9.4 | 13.1 | 11.3 | 11.0 | 12.3 | 11.5 | 6.5 | 6.8 | 6.6 | 3.2 | 3.6 | 3.4 |
| 2-Propenoic Acid | 8.7 | 14.3 | 10.8 | 1.0 | 1.1 | 1.0 | 0.5 | 0.6 | 0.5 | 0.2 | 0.2 | 0.2 | 0.5 | 0.5 | 0.5 | 0.9 | 1.3 | 1.1 |
| 2-Undecanol | 4.1 | 4.9 | 4.5 | 76.1 | 87.0 | 79.7 | 2.1 | 3.7 | 2.9 | 0.9 | 1.1 | 1.0 | 21.7 | 27.5 | 24.6 | 1.6 | 2.7 | 2.2 |
| 3-Ethyl-Benzaldehyde | 5.1 | 6.6 | 5.7 | 4.2 | 5.0 | 4.6 | 5.6 | 6.5 | 6.1 | 4.9 | 5.7 | 5.3 | 3.2 | 4.4 | 3.5 | 5.9 | 7.3 | 6.5 |
| 3-Hydroxy-Benzaldehyde | 13.0 | 22.0 | 16.2 | 1.7 | 2.1 | 1.8 | 4.4 | 5.2 | 4.7 | 11.7 | 14.8 | 12.7 | 0.9 | 1.0 | 1.0 | 1.5 | 1.8 | 1.6 |
| trans-2-Nonene | 3.1 | 3.6 | 3.4 | 4.2 | 5.4 | 4.8 | 0.4 | 0.5 | 0.4 | 1.4 | 1.6 | 1.5 | 1.0 | 1.7 | 1.4 | 1.7 | 2.0 | 1.8 |
| 2-Methyl-2-Pentenal | 14.1 | 18.0 | 15.8 | 6.7 | 7.8 | 7.3 | 6.5 | 7.1 | 6.7 | 8.7 | 13.4 | 10.3 | 3.6 | 4.1 | 3.8 | 8.3 | 11.1 | 9.7 |
| cis-5-Decenol | 5.0 | 5.6 | 5.2 | 96.0 | 121.9 | 108.0 | 1.5 | 2.9 | 2.2 | 4.0 | 4.6 | 4.4 | 83.3 | 94.5 | 88.4 | 13.8 | 20.0 | 16.2 |
| trans-Piperitol | 2.0 | 2.6 | 2.3 | 4.4 | 5.6 | 5.1 | 0.8 | 1.0 | 0.9 | 19.6 | 26.7 | 22.6 | 1.9 | 2.4 | 2.1 | 30.1 | 36.1 | 33.7 |
| 4-Ethyl-Benzaldehyde | 3.4 | 4.0 | 3.6 | 2.7 | 3.4 | 3.0 | 4.9 | 5.8 | 5.4 | 3.4 | 3.5 | 3.4 | 3.1 | 3.4 | 3.3 | 3.9 | 5.0 | 4.7 |
| Naphthalene | 14.9 | 19.1 | 16.7 | 7.5 | 8.3 | 7.9 | 18.4 | 22.1 | 19.8 | 12.8 | 18.1 | 14.6 | 8.0 | 11.1 | 9.9 | 1.1 | 1.6 | 1.4 |
| 1-Decanol | 30.6 | 39.9 | 33.6 | 16.6 | 20.4 | 18.1 | 15.5 | 20.8 | 18.3 | 13.9 | 18.2 | 15.5 | 17.3 | 22.8 | 20.8 | 18.1 | 20.5 | 19.3 |
| Cyclodecane | 98.1 | 150.3 | 121.5 | 84.7 | 94.3 | 88.4 | 62.6 | 68.7 | 66.1 | 65.1 | 74.1 | 69.7 | 32.2 | 35.8 | 34.0 | 39.3 | 44.3 | 42.0 |
| trans,trans-2,4-Decadienal | 11.7 | 19.7 | 15.3 | 19.4 | 25.3 | 21.4 | 49.2 | 57.2 | 52.2 | 14.8 | 20.9 | 17.3 | 16.5 | 23.4 | 20.7 | 3.8 | 4.4 | 4.2 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,2-Cyclopentanedione | 531.1 | 662.6 | 574.6 | 417.1 | 457.3 | 439.9 | 182.0 | 207.8 | 193.8 | 554.1 | 644.1 | 596.9 | 209.6 | 247.4 | 225.7 | 212.8 | 269.4 | 240.3 |
| Cyclodecene | 2.0 | 2.6 | 2.3 | 2.0 | 2.2 | 2.1 | 1.4 | 2.0 | 1.7 | 3.1 | 3.6 | 3.3 | 1.5 | 2.0 | 1.9 | 0.5 | 0.6 | 0.5 |
| cis-4-Decenol | 1.5 | 1.9 | 1.8 | 2.9 | 3.4 | 3.1 | 0.5 | 0.7 | 0.6 | 0.7 | 0.8 | 0.8 | 1.2 | 1.6 | 1.4 | 2.6 | 3.2 | 2.8 |
| 1-Phenyl-2-Butanone | 7.3 | 9.0 | 7.9 | 6.8 | 7.7 | 7.3 | 14.3 | 16.0 | 15.2 | 5.9 | 8.3 | 6.7 | 12.5 | 13.8 | 13.0 | 7.9 | 9.3 | 8.6 |
| Phenethyl Alcohol | 11.8 | 16.4 | 13.8 | 2.1 | 2.5 | 2.3 | 5.1 | 5.8 | 5.5 | 19.6 | 24.8 | 21.3 | 4.2 | 4.3 | 4.3 | 7.6 | 9.8 | 8.8 |
| trans,cis-2,4-Decadienal | 7.9 | 10.1 | 8.9 | 12.5 | 15.9 | 14.0 | 40.3 | 47.8 | 43.4 | 11.6 | 15.3 | 12.9 | 10.8 | 17.5 | 14.1 | 2.9 | 3.3 | 3.2 |
| 2-Cyclohexenol | 73.6 | 86.0 | 79.2 | 36.9 | 48.0 | 42.2 | 4.0 | 5.0 | 4.5 | 64.0 | 77.9 | 71.7 | 10.6 | 12.5 | 11.6 | 8.1 | 9.0 | 8.4 |
| 2-Ethyl Hexanoic Acid | 20.2 | 29.3 | 24.3 | 4.1 | 4.6 | 4.3 | 48.6 | 56.2 | 52.5 | 15.0 | 22.2 | 18.6 | 1.0 | 1.2 | 1.1 | 13.5 | 17.7 | 15.7 |
| 3-Methyl-1,2-Cyclopentanedione | 26.3 | 35.9 | 30.8 | 45.8 | 53.9 | 49.7 | 8.5 | 9.9 | 8.9 | 63.2 | 73.7 | 67.3 | 2.0 | 2.8 | 2.5 | 6.7 | 7.5 | 7.2 |
| trans-Cinnamaldehyde | 9.1 | 12.1 | 10.4 | 5.5 | 5.9 | 5.8 | 7.6 | 8.9 | 8.2 | 8.7 | 9.6 | 9.2 | 4.7 | 5.1 | 4.8 | 7.4 | 8.7 | 8.0 |
| Heptanoic Acid | 72.8 | 86.5 | 80.1 | 29.8 | 37.5 | 33.7 | 72.1 | 89.4 | 83.7 | 48.1 | 61.8 | 52.7 | 1.3 | 1.9 | 1.5 | 95.5 | 116.4 | 104.7 |
| Mequinol | 26.7 | 30.6 | 28.0 | 19.7 | 25.3 | 22.2 | 78.4 | 84.5 | 82.8 | 81.7 | 132.1 | 109.9 | 44.9 | 51.4 | 46.8 | 7.3 | 8.5 | 7.7 |
| 2,4,5-Trihydroxypyrimidine | 63.6 | 72.2 | 69.0 | 9.8 | 17.0 | 13.5 | 10.0 | 11.7 | 10.6 | 7.5 | 9.1 | 8.5 | 11.1 | 17.5 | 14.1 | 14.4 | 20.2 | 16.8 |
| cis-Cinnamaldehyde | 8.2 | 9.8 | 9.1 | 8.0 | 9.2 | 8.7 | 7.3 | 8.5 | 7.8 | 8.1 | 9.0 | 8.5 | 4.0 | 5.0 | 4.5 | 7.9 | 9.2 | 8.6 |
| Benzenemethanol | 45.2 | 55.3 | 48.4 | 20.4 | 28.3 | 24.7 | 102.7 | 150.7 | 123.7 | 77.4 | 92.4 | 83.6 | 38.3 | 48.7 | 41.8 | 10.8 | 20.5 | 14.8 |
| Mesitaldehyde | 5.0 | 6.4 | 5.5 | 2.1 | 3.0 | 2.5 | 5.8 | 7.1 | 6.3 | 5.9 | 6.1 | 6.0 | 2.9 | 3.9 | 3.4 | 5.7 | 6.8 | 6.2 |
| 2-Ethylhexyl Ester Octanoic Acid | 1.0 | 1.6 | 1.3 | 2.8 | 3.2 | 3.0 | 0.7 | 0.9 | 0.8 | 8.9 | 10.0 | 9.5 | 4.2 | 5.0 | 4.5 | 3.9 | 4.4 | 4.1 |
| Benzeneethanol | 89.1 | 126.9 | 106.3 | 28.9 | 35.0 | 30.9 | 42.2 | 53.5 | 47.9 | 58.8 | 73.0 | 63.5 | 28.2 | 34.9 | 31.1 | 37.8 | 47.5 | 43.6 |
| 1,4-Butanediol | 82.3 | 97.6 | 88.6 | 64.9 | 77.5 | 68.8 | 59.3 | 65.9 | 61.5 | 62.4 | 74.8 | 68.1 | 35.7 | 43.2 | 38.9 | 47.2 | 59.5 | 51.6 |
| β-Ionone | 12.5 | 16.7 | 14.3 | 11.3 | 12.2 | 11.7 | 35.5 | 46.6 | 40.5 | 19.5 | 31.2 | 25.4 | 16.4 | 21.7 | 18.8 | 48.3 | 63.8 | 52.7 |
| 2-Methyl-1,4-Benzenediol | 20.2 | 28.5 | 23.9 | 12.8 | 19.2 | 15.9 | 3.2 | 4.1 | 3.7 | 19.6 | 28.1 | 23.1 | 0.7 | 7.3 | 3.9 | 1.4 | 2.0 | 1.8 |
| 2-Ethyl Heptanoic Acid | 0.9 | 1.2 | 1.0 | 5.2 | 5.7 | 5.3 | 1.5 | 1.7 | 1.6 | 2.4 | 3.1 | 2.7 | 9.9 | 17.2 | 12.9 | 1.5 | 2.2 | 1.8 |
| 1-Dodecanol | 9.4 | 13.9 | 11.6 | 5.0 | 6.9 | 5.9 | 10.5 | 15.5 | 13.0 | 3.0 | 3.9 | 3.5 | 5.4 | 6.2 | 5.8 | 11.4 | 13.5 | 12.6 |
| Benzalacetone | 18.1 | 19.1 | 18.5 | 8.6 | 9.6 | 9.0 | 9.4 | 12.2 | 10.5 | 8.7 | 10.3 | 9.4 | 4.9 | 5.7 | 5.2 | 10.2 | 12.1 | 11.3 |
| Maltol | 92.4 | 157.8 | 124.5 | 127.1 | 179.1 | 150.8 | 62.7 | 69.9 | 65.9 | 181.4 | 246.6 | 212.9 | 2.7 | 23.4 | 12.7 | 66.6 | 78.8 | 74.7 |
| 2-Acetylpyrrole | 17.8 | 19.5 | 18.6 | 19.7 | 21.7 | 20.4 | 0.6 | 0.7 | 0.6 | 11.4 | 14.1 | 12.8 | 0.9 | 1.2 | 1.0 | 2.0 | 2.7 | 2.4 |
| 2,4-Decadien-1-ol | 8.1 | 12.1 | 9.6 | 7.8 | 8.2 | 8.0 | 7.4 | 8.7 | 8.0 | 8.9 | 10.4 | 9.3 | 8.4 | 10.0 | 9.3 | 4.0 | 4.7 | 4.3 |
| Levoglucosenone | 8.8 | 11.6 | 9.7 | 12.5 | 17.1 | 14.6 | 7.9 | 9.3 | 8.7 | 13.5 | 17.1 | 16.0 | 0.9 | 1.5 | 1.2 | 3.8 | 4.4 | 4.2 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Phenol | 32.4 | 51.1 | 41.4 | 36.3 | 47.1 | 42.9 | 48.8 | 67.1 | 57.5 | 20.3 | 29.0 | 24.6 | 35.9 | 44.6 | 40.0 | 35.3 | 40.4 | 38.6 |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | 40.8 | 50.8 | 47.0 | 22.5 | 28.8 | 25.7 | 4.1 | 5.3 | 4.8 | 9.2 | 10.2 | 9.8 | 24.0 | 27.2 | 25.3 | 5.9 | 7.1 | 6.5 |
| 4,6-Dimethyl-Dodecane | 18.9 | 29.1 | 22.9 | 30.3 | 32.5 | 31.1 | 3.3 | 4.0 | 3.6 | 24.2 | 31.3 | 28.0 | 1.3 | 2.0 | 1.6 | 9.9 | 12.6 | 11.3 |
| Ethyl Ester Decanoic Acid | 5.3 | 6.8 | 6.0 | 5.1 | 6.0 | 5.5 | 4.9 | 5.5 | 5.2 | 5.8 | 7.4 | 6.5 | 8.9 | 10.0 | 9.6 | 1.4 | 2.0 | 1.6 |
| 1-Methyl-4-Piperidinone | 1.2 | 1.8 | 1.5 | 0.5 | 0.6 | 0.6 | 0.3 | 0.4 | 0.4 | 1.3 | 1.9 | 1.7 | 0.6 | 0.7 | 0.7 | 4.1 | 4.8 | 4.5 |
| 2,2-Dimethyl-3-Heptanone | 2.5 | 3.2 | 2.8 | 100.3 | 112.5 | 107.6 | 3.7 | 4.2 | 4.0 | 98.3 | 198.8 | 143.2 | 1.0 | 1.5 | 1.2 | 36.2 | 40.9 | 38.0 |
| Octanoic Acid | 29.8 | 43.1 | 34.8 | 1.3 | 1.6 | 1.4 | 15.4 | 19.7 | 18.1 | 10.7 | 18.1 | 15.0 | 1.4 | 1.8 | 1.6 | 15.6 | 21.7 | 18.0 |
| 1,3-Dihydroxy-2-Propanone | 78.0 | 102.4 | 87.6 | 36.4 | 43.4 | 41.1 | 1.1 | 2.1 | 1.7 | 126.7 | 185.1 | 158.3 | 1.1 | 1.3 | 1.2 | 1.2 | 1.6 | 1.4 |
| 2-Phenoxy-Ethanol | 6.8 | 8.2 | 7.3 | 5.3 | 6.5 | 5.9 | 13.6 | 18.1 | 16.5 | 16.2 | 17.9 | 17.3 | 11.6 | 14.7 | 13.5 | 49.1 | 56.2 | 52.7 |
| Isophthalaldehyde | 4.1 | 5.3 | 4.7 | 4.3 | 5.0 | 4.6 | 4.5 | 5.5 | 5.1 | 3.5 | 4.3 | 4.0 | 3.0 | 3.7 | 3.4 | 5.9 | 6.5 | 6.3 |
| Cyclotetradecane | 8.5 | 10.3 | 9.0 | 2.1 | 2.9 | 2.5 | 4.6 | 5.1 | 4.9 | 7.1 | 8.0 | 7.5 | 1.9 | 3.1 | 2.6 | 2.8 | 3.3 | 3.1 |
| Nonanoic Acid | 14.2 | 21.7 | 17.6 | 1.4 | 1.8 | 1.6 | 40.0 | 49.2 | 44.8 | 13.2 | 16.6 | 14.5 | 1.2 | 1.3 | 1.2 | 50.4 | 58.3 | 54.1 |
| 2-Ethyl-Phenol | 14.4 | 21.3 | 17.7 | 11.9 | 15.9 | 13.7 | 24.8 | 28.4 | 26.5 | 28.1 | 36.4 | 34.2 | 22.7 | 30.2 | 24.8 | 10.9 | 14.1 | 12.5 |
| 2-Methoxy-4-Vinyl-Phenol | 60.8 | 67.4 | 63.3 | 50.9 | 59.8 | 54.3 | 26.6 | 32.4 | 30.7 | 72.7 | 85.5 | 80.4 | 64.2 | 72.3 | 67.0 | 4.1 | 4.6 | 4.4 |
| 4-Methylimidazole | 1.0 | 1.3 | 1.1 | 17.8 | 24.2 | 20.8 | 24.0 | 32.6 | 26.6 | 13.2 | 21.4 | 17.9 | 8.6 | 11.7 | 9.8 | 89.3 | 110.5 | 101.7 |
| m-tert-Butyl-Toluene | 15.0 | 18.9 | 16.7 | 16.2 | 18.4 | 17.1 | 16.6 | 19.6 | 18.3 | 11.7 | 15.0 | 13.3 | 9.5 | 11.5 | 10.4 | 15.9 | 16.9 | 16.3 |
| Syringol | 18.8 | 24.7 | 21.4 | 17.7 | 19.6 | 18.6 | 12.3 | 14.0 | 13.4 | 19.8 | 24.5 | 22.3 | 10.8 | 13.8 | 12.1 | 13.6 | 14.7 | 14.0 |
| Decanoic Acid | 27.9 | 35.2 | 32.7 | 5.2 | 6.6 | 5.7 | 27.0 | 34.4 | 31.3 | 27.4 | 32.5 | 30.2 | 1.4 | 1.9 | 1.7 | 30.2 | 39.7 | 34.1 |
| 3-Hydroxy-2,3-Dihydro-Maltol | 57.6 | 66.2 | 61.2 | 17.8 | 19.2 | 18.7 | 33.2 | 43.9 | 40.0 | 19.0 | 26.0 | 21.8 | 1.0 | 1.4 | 1.3 | 4.4 | 5.8 | 4.9 |
| 5-Hydroxy-Maltol | 34.3 | 39.4 | 36.8 | 67.0 | 72.7 | 70.1 | 27.5 | 43.9 | 36.0 | 30.1 | 39.6 | 34.3 | 1.3 | 1.8 | 1.5 | 43.8 | 49.6 | 45.9 |
| Triethylene Glycol | 0.9 | 1.2 | 1.1 | 0.9 | 1.4 | 1.2 | 5.3 | 6.1 | 5.7 | 11.6 | 14.8 | 13.5 | 1.5 | 2.1 | 1.9 | 4.2 | 5.2 | 4.8 |
| Benzoic Acid | 12.5 | 20.4 | 16.7 | 5.9 | 6.8 | 6.4 | 5.2 | 5.7 | 5.4 | 12.1 | 15.1 | 13.9 | 19.1 | 21.9 | 20.4 | 2.9 | 3.4 | 3.2 |
| 2-Methyl-Benzaldehyde | 190.8 | 224.3 | 201.6 | 124.6 | 192.5 | 158.7 | 216.0 | 268.2 | 242.7 | 470.7 | 610.9 | 533.6 | 515.4 | 623.5 | 573.5 | 15.4 | 21.7 | 19.1 |
| Undecanoic Acid | 28.3 | 35.1 | 32.1 | 4.7 | 5.8 | 5.1 | 28.1 | 31.6 | 30.4 | 22.0 | 29.9 | 27.0 | 1.5 | 2.0 | 1.7 | 63.3 | 75.3 | 70.1 |
| 4-Pyridinol | 91.6 | 133.0 | 104.5 | 4.4 | 5.5 | 5.1 | 37.0 | 46.4 | 43.0 | 83.6 | 98.8 | 91.0 | 16.9 | 19.1 | 17.8 | 61.2 | 76.0 | 69.3 |
| 4-Amino-Phenol | 48.4 | 55.5 | 50.9 | 5.7 | 6.4 | 6.0 | 1.5 | 2.1 | 1.8 | 35.7 | 42.0 | 39.0 | 13.1 | 18.4 | 16.0 | 3.7 | 5.0 | 4.3 |

**Table S12. VOCs from regional cultivars samples previously identified in others SC-based products.**

| Volatile Organic Compound | Sugarcane Based-Products | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **SCH** [1] | **Juice** [2–7] | **Sugar** [6,8–11] | **Treacle** [12] | **Molasses** [13–15] | **Syrup** [1,6,16–18] | **Rum** [19–25] | **Infusion** [26] | **Alcoholic Fermented Beverage** [27,28] | **All Products** |
| Pentane | | | | | | | | | | 0 |
| 1-Pentene | | | | | | | | | | 0 |
| 2-Methyl-Pentane | | | | | | | | | | 0 |
| Hexane | | | | | | | | | | 0 |
| Ethyl Ether | | | | | | | | | | 0 |
| cis-4-Methyl-2-Pentene | | | | | | | | | | 0 |
| cis-Piperylene | | | | | | | | | | 0 |
| 2-Methyl-1-Pentene | | | | | | | | | | 0 |
| cis-3-Methyl-2-Pentene | | | | | | | | | | 0 |
| 3-Methyl-Hexane | | | | | | | | | | 0 |
| 1,4-Pentadiene | | | | | | | | | | 0 |
| Methanethiol | | | | | | | | | | 0 |
| trans-Piperylene | | | | | | | | | | 0 |
| Heptane | | | | | | | | | | 0 |
| tert-Butyl Ethyl Ether | | | | | | | | | | 0 |
| Ethanal | X | | X | | | X | X | | | 4 |
| Dimethyl Sulfide | X | X | X | X | | X | | | | 5 |
| 4-Methyl-Heptane | | | | | | | | | | 0 |
| Octane | | | | | | | | | | 0 |
| Propanal | | | | | | X | X | | | 2 |
| Furan | X | | | | | X | | | | 2 |
| 2,4-Dimethyl-Heptane | | | | | | | | | | 0 |
| 2-Methyl-Propanal | X | | X | X | | X | | | | 4 |
| 2-Propanone | | X | | | | | | | | 1 |
| Methyl Ester Acetic Acid | | | | | | | | | | 0 |
| 2-Methyl-2-Heptene | | | | | | | | | | 0 |
| Crotonal | | | | | | | | | | 0 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 2,3-Dimethyl-Heptane | | | | | | | | 0 |
| 4-Methyl-Octane | | | | | | | | 0 |
| 2-Methyl-Furan | X | X | | | | X | | 3 |
| 2,4-Dimethyl-1-Heptene | | | | | | | | 0 |
| Ethyl Ester Acetic Acid | X | X | | | | X | X | 4 |
| Nonane | | | | | | | | 0 |
| 2-Butanone | X | | | X | | X | | 3 |
| 2-Methyl-Butanal | X | | X | X | X | X | X | 6 |
| 3-Methyl-Butanal | X | X | X | X | X | X | X | 7 |
| Ethyl Alcohol | X | X | X | X | | X | X | 6 |
| Benzene | | | | | | | | 0 |
| 3-Ethyl-Heptane | | | | | | | | 0 |
| 2-Ethyl-Furan | | | | | | | | 0 |
| Ethyl Ester Propanoic Acid | X | | | | | X | | 2 |
| 2-Methyl Ethyl Ester Propanoic Acid | | | | | | | | 0 |
| 2-Methyl-Crotonal | | | | | | | | 0 |
| Propyl Ester Acetic Acid | | | | | | | | 0 |
| 3-Pentanone | | | | | | | | 0 |
| Pentanal | | X | | | | X | X | 3 |
| 2,3-Butanedione | X | X | X | | X | X | X | 6 |
| 2,3,4-Trimethyl-Hexane | | | | | | | | 0 |
| Decane | | | | | | | | 0 |
| 2,6-Dimethyl-Nonane | | | | | | | | 0 |
| 2,5-Dimethyl-Nonane | | | | | | | | 0 |
| 4-Methyl-2-Pentanone | | | | | | | | 0 |
| 2-Methy-2-Butanol | | | | | | | | 0 |
| 2-Methyl-Propyl Ester Acetic Acid | | | | | | | | 0 |
| α-Pinene | | | | | | | | 0 |
| 4,4-Dimethyl-2-Pentanone | | | | | | | | 0 |
| 1-Penten-3-one | | X | | | | | | 1 |
| 5-Butyl-Nonane | | | | | | | | 0 |
| 3,6-Dimethyl-Decane | | | | | | | | 0 |
| 2-Methyl-3-Buten-2-ol | X | | | X | | X | | 3 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 5-Methyl-Decane | | | | | | | | | 0 |
| 4-Methyl-Decane | | | | | | | | | 0 |
| 2,3-Pentanedione | X | | | | | X | | | 2 |
| 3,3-Dimethyl-Methyl Ester Butanoic Acid | | | | | | | | | 0 |
| 2-Hexanone | | | | | | | | | 0 |
| 4-Methyl-Undecane | | | | | | | | | 0 |
| Hexanal | X | X | X | | | X | X | | 5 |
| 2-Methyl-1-Propanol | X | X | | X | X | X | X | X | 7 |
| 2-Methyl-2-Pentanol | | | | | | | | | 0 |
| Ethyl-Benzene | | | | | | | | | 0 |
| 3-Methyl Butyl Ester Acetic Acid | | | | | | | | | 0 |
| o-Xylene | | | | | | | | | 0 |
| 2-Pentanol | | X | | | | | | | 1 |
| p-Xylene | | | | | | | | | 0 |
| 5-Methyl-2-Hexanone | | | | | | | | | 0 |
| 2-Ethyl Methyl Ester Pentanoic Acid | | | | | | | | | 0 |
| 1-Butanol | X | | | | | X | X | | 3 |
| α-Phellandrene | | | | | | | | | 0 |
| 2-Methyl-3-Pentanol | | | | | | | X | | 1 |
| 1-Penten-3-ol | | | | | | | | | 0 |
| α-Terpinene | | | | | | | | | 0 |
| Butyl Ester 2-Propenoic Acid | | | | | | | | | 0 |
| m-Xylene | | X | X | | | X | | | 3 |
| 2-Heptanone | | X | | | | | | | 1 |
| Heptanal | X | X | | | | X | X | | 4 |
| D-Limonene | | X | X | | | | | | 2 |
| 3-Hexanol | | | | | | | | | 0 |
| β-Phellandrene | | | | | | | | | 0 |
| Eucalyptol | | | | | | | | | 0 |
| m-Menthane | | | | | | | | | 0 |
| 4-Methyl-2-Heptanone | | | | | | | | | 0 |
| 3-Methyl-2-Pentanol | | | | | | | | | 0 |
| 2-Methyl-1-Butanol | X | | | X | X | X | X | X | 6 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 3-Methyl-1-Butanol | X | X | | X | X | X | X | X | 7 |
| o-Ethyltoluene | | | | | | | | | 0 |
| m-Ethyltoluene | | | | | | | | | 0 |
| 2-Hexanol | | | | | | | | | 0 |
| Ethylene Glycol Ethyl Ether | | | | | | | | | 0 |
| 6-Methyl-2-Heptanone | | | | | | | | | 0 |
| Pseudocumene | | | | | | | | | 0 |
| 4,6-Dimethyl-2-Heptanone | | | | | | | | | 0 |
| 2,3-Dimethyl-2-Hexanol | | | | | | | | | 0 |
| 3-Octanone | | | | | | | | | 0 |
| Styrene | | X | X | | | X | | | 3 |
| 5-Methyl-2-Heptanone | | | | | | | | | 0 |
| 1-Pentanol | | X | X | | | | | | 2 |
| p-Ethyltoluene | | | | | | | | | 0 |
| p-Cymene | X | X | X | | | X | | | 4 |
| Mesitylene | | | | | | | | | 0 |
| 4-Methyl-4-Heptanol | | | | | | | | | 0 |
| 4-Heptanol | | | | | | | | | 0 |
| 2-Octanone | | | | | | | | | 0 |
| Octanal | X | X | | | | X | | | 3 |
| 3-Hydroxy-2-Butanone | | X | X | X | X | X | | | 5 |
| 1-Octen-3-one | | | | | X | | X | | 2 |
| trans-2-Pentenol | | X | | | | | | | 1 |
| 2,2,6-Trimethyl-Cyclohexanone | | | | | | | | | 0 |
| 2-Heptanol | | X | | | | | X | | 2 |
| cis-2-Pentenol | | X | | | | | | | 1 |
| 1-Hydroxy-2-Propanone | X | X | X | X | | X | | | 5 |
| 5-Methyl-4-Hexen-3-one | | | | | | | | | 0 |
| Hemimellitene | | | | | | | | | 0 |
| 6-Methyl-5-Hepten-2-one | | | | | | | | | 0 |
| 2-Pentene | | X | | | | | | | 1 |
| 1-Hexanol | X | X | | | | | X | | 3 |
| 2-Cyclopenten-1-one | | | | | | | X | | 1 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 2-Methyl-2-Cyclopenten-1-one | | | | | | X | | | 1 |
| β-Methy-Styrene | | | | | | | | | 0 |
| 4-Octanol | | | | | | | | | 0 |
| cis-3-Hexen-1-ol | | X | | | | | | | 1 |
| 2-Nonanone | | | | | | | | | 0 |
| Nonanal | X | X | X | | | X | X | | 5 |
| Ethylene Glycol Butyl Ether | | | | | | | | | 0 |
| 1-Ethyl-1-Methyl-Cyclopentane | | | | | | | | | 0 |
| 3-Octen-2-one | | | | | | | | | 0 |
| 2-Octanol | | X | | | | | X | | 2 |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | | | | | | | | | 0 |
| 1,3-Bis(1,1-Dimethylethyl)-Benzene | | | | | | | | | 0 |
| trans-2-Octenal | | X | | | | | | | 1 |
| m-Ethyl-Styrene | | | | | | | | | 0 |
| 5-Methyl-2-Heptanone | | | | | | | | | 0 |
| 2-Decanone | | | | | | | | | 0 |
| 1-Octen-3-ol | | X | | | | | X | | 2 |
| trans,trans-2,4-Heptadienal | | X | | | | | | | 1 |
| 1-Heptanol | | | | | | | X | | 1 |
| cis,cis-3,5-Octadiene | | | | | | | | | 0 |
| 2-Oxo-Methyl Ester Propanoic Acid | | | | | | | | | 0 |
| Dihydromyrcenol | | | | | | | | | 0 |
| trans-Menthone | | | | | | | | | 0 |
| Furfural | X | X | X | X | | X | X | X | 7 |
| Ethanoic Acid | X | X | X | X | X | X | X | | 7 |
| 2-Ethyl-1-Hexanol | | X | X | | | | | | 2 |
| Decanal | X | | | | | X | X | | 3 |
| Furfuryl Formate | | | | | | | | | 0 |
| trans-2-Hepten-1-ol | | | | | | | | | 0 |
| 2-Nonanol | | X | | | | | | | 1 |
| 1-(2-Furanyl)-Ethanone | X | | X | | X | X | | | 3 |
| 3,5-Octadien-2-one | | | | | | | | | 0 |
| Benzaldehyde | X | X | X | | | X | | | 4 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Furfuryl Acetate | X | | | | | X | | | | 2 |
| Linalool | | X | | | X | | X | | | 3 |
| β-Myrcene | | X | | | | | | | | 1 |
| 1-Octanol | | X | X | | | X | X | | X | 5 |
| trans-p-2-Menthen-1-ol | | | | | | | | | | 0 |
| Propanoic Acid | | | X | X | | | X | X | | 4 |
| 2,3-Butanediol | | X | X | | | X | | | | 3 |
| Dimethyl Sulfoxide | | X | X | | | X | | | | 3 |
| m-Menth-3-ene | | | | | | | | | | 0 |
| Trans-(2-Ethylcyclopentyl)-Methanol | | | | | | | | | | 0 |
| Bornyl Acetate | | | | | | | | | | 0 |
| 4-Cyclopentene-1,3-dione | | | | | | | | | | 0 |
| Menthol | | | | | | | X | | | 1 |
| 2-Undecanone | | | | | | | | | | 0 |
| 2-(2-Furanyl)-Furan | | | | | | | | | | 0 |
| trans-2-Octen-1-ol | | X | | | | | | | | 1 |
| trans-2-Nonen-1-ol | | | | | | | | | | 0 |
| Diethylene Glycol Ethyl Ether | | | | | | | | | | 0 |
| 3,5,5-Trimethyl-2-Cyclopenten-1-one | | | | | | | | | | 0 |
| cis-p-2-Menthen-1-ol | | | | | | | | | | 0 |
| β-Cyclocitral | | | | | | | | | | 0 |
| Benzeneacetaldehyde | X | X | | | | X | | | | 3 |
| 1-Nonanol | | | | | | | X | | | 1 |
| Furfuryl Alcohol | X | X | X | X | X | X | | X | | 7 |
| Phoracanthol | | | | | | | | | | 0 |
| cis-3-Nonen-1-ol | | | | | | | X | | | 1 |
| cis-Piperitol | | | | | | | | | | 0 |
| p-Methoxy-Styrene | | | | | | | | | | 0 |
| (2Z)-3-Ethyl-2,4-Pentadien-1-ol | | | | | | | | | | 0 |
| Butylene Glycol Monobutyl Ether | | | | | | | | | | 0 |
| α-Terpineol | | X | | | | | | | | 1 |
| 1,5-Cyclooctanedione | | | | | | | | | | 0 |
| γ-Terpinene | | | | | | | | | | 0 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| trans-2-Decenol | | | | | | | 0 |
| 2-Propenoic Acid | | | X | | | | 1 |
| 2-Undecanol | | | | | | | 0 |
| 3-Ethyl-Benzaldehyde | | | | | | | 0 |
| 3-Hydroxy-Benzaldehyde | | | | | | | 0 |
| trans-2-Nonene | | | | | | | 0 |
| 2-Methyl-2-Pentenal | | | | | | | 0 |
| cis-5-Decenol | | | | | | | 0 |
| trans-Piperitol | | | | | | | 0 |
| 4-Ethyl-Benzaldehyde | | | | | | | 0 |
| Naphthalene | | | | | | | 0 |
| 1-Decanol | | | | | | X | 1 |
| Cyclodecane | | | | | | | 0 |
| trans,trans-2,4-Decadienal | | | | X | | X | 2 |
| 1,2-Cyclopentanedione | | | | | | | 0 |
| Cyclodecene | | | | | | | 0 |
| cis-4-Decenol | | | | | | | 0 |
| 1-Phenyl-2-Butanone | | | | | | | 0 |
| Phenethyl Alcohol | | | | | | | 0 |
| trans,cis-2,4-Decadienal | | | | | | | 0 |
| 2-Cyclohexenol | | | | | | | 0 |
| 2-Ethyl Hexanoic Acid | | | | | | | 0 |
| 3-Methyl-1,2-Cyclopentanedione | | | X | | | | 1 |
| trans-Cinnamaldehyde | | | | | | | 0 |
| Heptanoic Acid | | | | | | | 0 |
| Mequinol | X | X | X | X | X | X | 6 |
| 2,4,5-Trihydroxypyrimidine | | | | | | | 0 |
| cis-Cinnamaldehyde | | | | | | | 0 |
| Benzenemethanol | X | X | X | X | X | | 5 |
| Mesitaldehyde | | | | | | | 0 |
| 2-Ethylhexyl Ester Octanoic Acid | | | | | | | 0 |
| Benzeneethanol | X | X | | X | X | X | 5 |
| 1,4-Butanediol | | | | | | | 0 |

| | | | | | | |
|---|---|---|---|---|---|---|
| β-Ionone | | X | | | X | 2 |
| 2-Methyl-1,4-Benzenediol | | | | | | 0 |
| 2-Ethyl Heptanoic Acid | | | | | | 0 |
| 1-Dodecanol | | | | | | 0 |
| Benzalacetone | | | | | | 0 |
| Maltol | | | | | | 0 |
| 2-Acetylpyrrole | | | | | | 0 |
| 2,4-Decadien-1-ol | | | | | | 0 |
| Levoglucosenone | | | | | | 0 |
| Phenol | X | X | | X | | 3 |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | | | | | | 0 |
| 4,6-Dimethyl-Dodecane | | | | | | 0 |
| Ethyl Ester Decanoic Acid | | | | | X | 1 |
| 1-Methyl-4-Piperidinone | | | | | | 0 |
| 2,2-Dimethyl-3-Heptanone | | | | | | 0 |
| Octanoic Acid | | | X | | X | 2 |
| 1,3-Dihydroxy-2-Propanone | | | | | | 0 |
| 2-Phenoxy-Ethanol | | | | | | 0 |
| Isophthalaldehyde | | | | | | 0 |
| Cyclotetradecane | | | | | | 0 |
| Nonanoic Acid | | X | | | | 1 |
| 2-Ethyl-Phenol | | | | X | X | 2 |
| 2-Methoxy-4-Vinyl-Phenol | | X | X | X | X | 4 |
| 4-Methylimidazole | | | | | | 0 |
| m-tert-Butyl-Toluene | | | | | | 0 |
| Syringol | | | | | | 0 |
| Decanoic Acid | | | | X | X | 2 |
| 3-Hydroxy-2,3-Dihydro-Maltol | | X | X | | | 2 |
| 5-Hydroxy-Maltol | | | | | | 0 |
| Triethylene Glycol | | | | | | 0 |
| Benzoic Acid | | | X | X | | 2 |
| 2-Methyl-Benzaldehyde | | | | | | 0 |
| Undecanoic Acid | | | | | | 0 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 4-Pyridinol | | | | | | | | | | 0 |
| 4-Amino-Phenol | | | | | | | | | | 0 |
| **Total** | **37** | **56** | **34** | **16** | **20** | **45** | **42** | **3** | **4** | **87** |

X – Identified in sugarcane based-product.

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**Table S13. Summary of number of VOCs identified, relative peak areas and total relative peak areas (%) values of main chemical classes identified in SC samples.**

| Main Chemical Class | Abbreviation | Harvest Year | Sugarcane Varieties | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | AMA | | | RAD | | | ROX | | | VER | | | VIO | | | CAN | | |
| | | | N°[1] | RPA[2] | TRPA[3] (%) | N°[1] | RPA[2] | TRPA[3] (%) | N°[1] | RPA[2] | TRPA[3] (%) | N°[1] | RPA[2] | TRPA[3] (%) | N°[1] | RPA[2] | TRPA[3] (%) | N°[1] | RPA[2] | TRPA[3] (%) |
| Alcohol | ALC | 2015 | 49 | 3665.7 | 31.2 | 49 | 4513.9 | 33.5 | 49 | 3860.5 | 36.1 | 49 | 3604.2 | 28.8 | 49 | 4264.6 | 45.6 | 49 | 2044.7 | 21.6 |
| | | 2017 | 49 | 4496.0 | 33.5 | 49 | 4904.7 | 34.8 | 49 | 3919.4 | 35.7 | 49 | 4064.3 | 30.2 | 49 | 5265.1 | 49.4 | 49 | 1971.6 | 21.2 |
| Aldehyde | ALD | 2015 | 19 | 422.2 | 3.6 | 19 | 415.9 | 3.1 | 19 | 545.4 | 5.1 | 19 | 555.7 | 4.4 | 19 | 204.8 | 2.2 | 19 | 486.7 | 5.1 |
| | | 2017 | 19 | 521.1 | 3.9 | 19 | 413.6 | 2.9 | 19 | 467.3 | 4.3 | 19 | 536.3 | 4.0 | 19 | 214.9 | 2.0 | 19 | 424.3 | 4.6 |
| Benzene | BNZ | 2015 | 33 | 701.4 | 6.0 | 33 | 497.2 | 3.7 | 33 | 952.3 | 8.9 | 33 | 981.7 | 7.8 | 33 | 882.5 | 9.4 | 33 | 582.5 | 6.2 |
| | | 2017 | 33 | 788.7 | 5.9 | 33 | 548.6 | 3.9 | 33 | 982.2 | 9.0 | 33 | 1120.1 | 8.3 | 33 | 1027.2 | 9.6 | 33 | 589.4 | 6.3 |
| Carboxylic Acid | CAC | 2015 | 10 | 2113.8 | 18.0 | 10 | 2030.3 | 15.1 | 10 | 1630.1 | 15.2 | 10 | 2091.9 | 16.7 | 10 | 544.2 | 5.8 | 10 | 332.3 | 3.5 |
| | | 2017 | 10 | 2509.2 | 18.7 | 10 | 2444.2 | 17.3 | 10 | 1797.4 | 16.4 | 10 | 2334.4 | 17.3 | 10 | 558.4 | 5.2 | 10 | 318.5 | 3.4 |
| Ester | EST | 2015 | 14 | 202.4 | 1.7 | 14 | 178.0 | 1.3 | 14 | 921.2 | 8.6 | 14 | 280.2 | 2.2 | 14 | 156.1 | 1.7 | 14 | 167.8 | 1.8 |
| | | 2017 | 14 | 262.8 | 2.0 | 14 | 218.7 | 1.6 | 14 | 1306.6 | 11.9 | 14 | 343.8 | 2.6 | 14 | 158.4 | 1.5 | 14 | 162.6 | 1.8 |
| Ether | ETH | 2015 | 6 | 168.7 | 1.4 | 6 | 143.5 | 1.1 | 6 | 141.1 | 1.3 | 6 | 260.6 | 2.1 | 6 | 143.6 | 1.5 | 6 | 321.1 | 3.4 |
| | | 2017 | 6 | 115.3 | 0.9 | 6 | 66.6 | 0.5 | 6 | 94.5 | 0.9 | 6 | 120.0 | 0.9 | 6 | 61.5 | 0.6 | 6 | 374.4 | 4.0 |
| Furan | FUR | 2015 | 10 | 554.2 | 4.7 | 10 | 759.1 | 5.6 | 10 | 284.6 | 2.7 | 10 | 282.9 | 2.3 | 10 | 203.3 | 2.2 | 10 | 162.1 | 1.7 |
| | | 2017 | 10 | 631.7 | 4.7 | 10 | 746.7 | 5.3 | 10 | 283.3 | 2.6 | 10 | 324.4 | 2.4 | 10 | 213.1 | 2.0 | 10 | 165.2 | 1.8 |
| Hydrocarbon | HYD | 2015 | 38 | 555.7 | 4.7 | 38 | 747.6 | 5.5 | 38 | 485.4 | 4.5 | 38 | 854.7 | 6.8 | 38 | 702.8 | 7.5 | 38 | 1181.7 | 12.5 |
| | | 2017 | 38 | 602.1 | 4.5 | 38 | 653.9 | 4.6 | 38 | 384.5 | 3.5 | 38 | 549.7 | 4.1 | 38 | 615.5 | 5.8 | 38 | 1371.2 | 14.8 |
| Ketone | KET | 2015 | 39 | 1780.6 | 15.2 | 39 | 3034.6 | 22.5 | 39 | 960.0 | 9.0 | 39 | 2102.8 | 16.8 | 39 | 1349.7 | 14.4 | 39 | 2447.5 | 25.9 |

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 2017 | 39 | 1769.0 | 13.2 | 39 | 3016.8 | 21.4 | 39 | 855.9 | 7.8 | 39 | 2251.7 | 16.7 | 39 | 1479.0 | 13.9 | 39 | 2357.0 | 25.4 |
| Naphthalene | NPH | 2015 | 1 | 16.4 | 0.1 | 1 | 7.5 | 0.1 | 1 | 19.1 | 0.2 | 1 | 13.2 | 0.1 | 1 | 10.7 | 0.1 | 1 | 1.3 | 0.0 |
| | | 2017 | 1 | 17.0 | 0.1 | 1 | 8.3 | 0.1 | 1 | 20.4 | 0.2 | 1 | 16.0 | 0.1 | 1 | 9.0 | 0.1 | 1 | 1.4 | 0.0 |
| Nitrogen | NIT | 2015 | 5 | 180.2 | 1.5 | 5 | 56.8 | 0.4 | 5 | 81.6 | 0.8 | 5 | 126.4 | 1.0 | 5 | 46.5 | 0.5 | 5 | 192.5 | 2.0 |
| | | 2017 | 5 | 209.1 | 1.6 | 5 | 64.0 | 0.5 | 5 | 80.7 | 0.7 | 5 | 137.2 | 1.0 | 5 | 40.4 | 0.4 | 5 | 196.9 | 2.1 |
| Phenol | PHE | 2015 | 7 | 228.0 | 1.9 | 7 | 150.2 | 1.1 | 7 | 223.4 | 2.1 | 7 | 299.8 | 2.4 | 7 | 198.4 | 2.1 | 7 | 81.7 | 0.9 |
| | | 2017 | 7 | 249.9 | 1.9 | 7 | 168.8 | 1.2 | 7 | 211.5 | 1.9 | 7 | 346.2 | 2.6 | 7 | 216.8 | 2.0 | 7 | 84.8 | 0.9 |
| Pyran | PYR | 2015 | 3 | 192.1 | 1.6 | 3 | 218.6 | 1.6 | 3 | 149.4 | 1.4 | 3 | 243.7 | 1.9 | 3 | 5.3 | 0.1 | 3 | 129.2 | 1.4 |
| | | 2017 | 3 | 252.8 | 1.9 | 3 | 260.7 | 1.8 | 3 | 134.4 | 1.2 | 3 | 294.3 | 2.2 | 3 | 25.7 | 0.2 | 3 | 121.9 | 1.3 |
| Sulfur | SUL | 2015 | 3 | 850.9 | 7.2 | 3 | 619.5 | 4.6 | 3 | 351.2 | 3.3 | 3 | 592.4 | 4.7 | 3 | 547.5 | 5.9 | 3 | 242.0 | 2.6 |
| | | 2017 | 3 | 879.1 | 6.5 | 3 | 457.7 | 3.2 | 3 | 325.9 | 3.0 | 3 | 698.5 | 5.2 | 3 | 678.3 | 6.4 | 3 | 307.5 | 3.3 |
| Terpene / Terpenoid | TER | 2015 | 23 | 108.0 | 0.9 | 23 | 111.8 | 0.8 | 23 | 102.9 | 1.0 | 23 | 240.8 | 1.9 | 23 | 93.1 | 1.0 | 23 | 1094.1 | 11.6 |
| | | 2017 | 23 | 122.5 | 0.9 | 23 | 125.7 | 0.9 | 23 | 100.1 | 0.9 | 23 | 329.8 | 2.4 | 23 | 95.8 | 0.9 | 23 | 842.3 | 9.1 |

[1]Number of volatile organic compounds identified.
[2]Relative Peak Areas values.
[3]Total Relative Peak Areas percentage values.

**Table S14. One-way ANOVA with Post-hoc Tukey test results based on the relative peak areas of the identified VOCs in sugarcane samples.**

| Volatile Organic Compounds | One-way ANOVA Test | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | All Samples | | Tukey Test[3] ($\alpha < 0.05$) | | | | | |
| | F[1] | P[2] | AMA (A) | RAD (B) | ROX (C) | VER (D) | VIO (E) | CAN (F) |
| Pentane | 48.39 | ≤1.00E-07 | B; C; E | A; C; D; F | A; B; D; E; F | B; C | A; C | B; C |
| 1-Pentene | 30.91 | ≤1.00E-07 | C; E; F | C; E; F | A; B; D; E | C; E | A; B; C; F | A; B; D; E |
| 2-Methyl-Pentane | 43.08 | ≤1.00E-07 | C; D | C; D; F | A; B; D; E; F | A; B; C; E; F | C; D | B; C; D |
| Hexane | 37.75 | ≤1.00E-07 | F | F | F | F | F | A; B; C; D; E |
| Ethyl Ether | 4.64 | 2.96E-03 | D | | F | A; F | | C; D |
| cis-4-Methyl-2-Pentene | 5.00 | 1.90E-03 | C | C | A; B; E; F | | C | C |
| cis-Piperylene | 27.39 | ≤1.00E-07 | C; D | C | A; B; D; E; F | A; C; E; F | C; D | C; D |
| 2-Methyl-1-Pentene | 4.53 | 3.40E-03 | F | | F | | F | A; C; E |
| cis-3-Methyl-2-Pentene | 30.80 | ≤1.00E-07 | B; D | A; C; D; E; F | B; E | A; B; C | B | B |
| 3-Methyl-Hexane | 106.12 | ≤1.00E-07 | C; D, E; F | E; F | A; F | A; E; F | A; B; D; F | A; B; C; D; E |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 1,4-Pentadiene | 5.68 | 8.45E-04 | C | | A; D; E; F | C | C | C |
| Methanethiol | 65.91 | ≤1.00E-07 | B; C; E | A; C; E; F | A; B; D; E; F | C; E | A; B; C; D; F | B; C; E |
| trans-Piperylene | 16.68 | ≤1.00E-07 | D; E | C | B; D; E; F | A; C | A; C | C |
| Heptane | 46.55 | ≤1.00E-07 | B; C; D; F | A; C; D; F | A, B; D; E | A; B; C; E; F | C; D; F | A; B; D; E |
| tert-Butyl Ethyl Ether | 26.94 | ≤1.00E-07 | F | F | F | F | F | A; B; C; D; E |
| Ethanal | 55.79 | ≤1.00E-07 | B; C; E | A; D; E; F | A; D; E; F | B; C; D | A; B; C; D; F | B; C; E |
| Dimethyl Sulfide | 61.07 | ≤1.00E-07 | B; C; D; E; F | A; C | A; B; D; E | A; C; F | A; C; F | A; B; D; E |
| 4-Methyl-Heptane | 22.08 | ≤1.00E-07 | F | F | F | F | F | A; B; C; D; E |
| Octane | 92.54 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B; D; E | A, B; C; F | A; B; C; F | A; B; D; E |
| Propanal | 35.24 | ≤1.00E-07 | E; F | F | E; F | F | A; C; F | A; B; C; D; E |
| Furan | 18.66 | ≤1.00E-07 | D; E; F | E; F | E; F | A; E; F | A; B; C; D | A; B; C; D |
| 2,4-Dimethyl-Heptane | 11.84 | 2.00E-06 | C | C; F | A; B; D; E; F | C; F | C | B; C; D |
| 2-Methyl-Propanal | 165.43 | ≤1.00E-07 | B; C; D | A; C; D; E; F | A; B; D; E; F | A; B; C; E; F | B; C; D | B; C; D |
| 2-Propanone | 214.47 | ≤1.00E-07 | B; C; D; E; F | A; C; E; F | A; B; C; F | A; C; E; F | A; B; D; F | A; B; C; D; E |
| Methyl Ester Acetic Acid | 5.30 | 1.32E-03 | C | C | A; B; E; F | | C | C |
| 2-Methyl-2-Heptene | 155.28 | ≤1.00E-07 | F | F | F | F | F | A; B; C; D; E |
| Crotonal | 24.32 | ≤1.00E-07 | B; C; D; E | A; D; E | A; F | A; B; F | A; B; F | C; D; E |
| 2,3-Dimethyl-Heptane | 11.25 | 4.00E-06 | C | C | A; B; E; F | E; F | C; D | C; D |
| 4-Methyl-Octane | 102.07 | ≤1.00E-07 | C; F | C | A; B; D; E; F | C; F | C; F | A; C; D; E |
| 2-Methyl-Furan | 29.72 | ≤1.00E-07 | B; C | A; C; D; E; F | A; B | B | B | B |
| 2,4-Dimethyl-1-Heptene | 324.27 | ≤1.00E-07 | F | F | F | F | F | A; B; C; D; E |
| Ethyl Ester Acetic Acid | 217.48 | ≤1.00E-07 | C | C | A; B; D; E; F | C; E | C; D | C |
| Nonane | 31.19 | ≤1.00E-07 | B; C; E; F | A; C; D | A; B; D; E | B; C; F | A; C; F | A; B; D; E |
| 2-Butanone | 143.17 | ≤1.00E-07 | B; C; D; E; F | A; C; D; F | A; B; E; F | A; B; E; F | A; C; D; F | A; B; C; D; E |
| 2-Methyl-Butanal | 81.36 | ≤1.00E-07 | B; C; E; F | A; D; E | A; D; E | B; C; E | A; B; C; D; F | A; D; E |
| 3-Methyl-Butanal | 33.25 | ≤1.00E-07 | B; C; E | A; D; E; F | A; D; E; F | B; C; E | A; B; C; D; F | B; C; E |
| Ethyl Alcohol | 112.86 | ≤1.00E-07 | B; C; D; E; F | A; C; D; F | A; B; D; E; F | A; B; C; E; F | A; C; D; F | A; B; C; D; E |
| Benzene | 27.31 | ≤1.00E-07 | B; C; D; E | A; C; F | A; B; E; F | A; E; F | A; C; D | B; C; D |
| 3-Ethyl-Heptane | 97.26 | ≤1.00E-07 | B; D; E; F | A; C; F | B; D; E; F | A; C; F | A; C; F | A; B; C; D; E |
| 2-Ethyl-Furan | 5.61 | 9.20E-04 | B; C; D | A | A | A | | |
| Ethyl Ester Propanoic Acid | 76.40 | ≤1.00E-07 | C | C | A; B; D; E; F | C | C | C |
| 2-Methyl Ethyl Ester Propanoic Acid | 115.73 | ≤1.00E-07 | C | C | A; B; D; E; F | C | C | C |
| 2-Methyl-Crotonal | 350.13 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E | A; B; D; E; F | A; B; C; E; F | A; B; C; D; F | A; C; D; E |

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|---|---|---|---|---|---|---|---|---|
| Propyl Ester Acetic Acid | 77.02 | ≤1.00E-07 | C | C | A; B; D; E; F | C | C | C |
| 3-Pentanone | 53.64 | ≤1.00E-07 | B; C; D; F | A; E; F | A; D; E; F | A; C; E; F | B; C; D; F | A; B; C; D; E |
| Pentanal | 288.09 | ≤1.00E-07 | C; F | C; F | A; B; D; E; F | C; F | C; F | A; B; C; D; E |
| 2,3-Butanedione | 134.31 | ≤1.00E-07 | B; C; D; E; F | A; E; F | A; E; F | A; E; F | A; B; C; D; F | A; B; C; D; E |
| 2,3,4-Trimethyl-Hexane | 285.58 | ≤1.00E-07 | F | F | F | F | F | A; B; C; D; E |
| Decane | 59.20 | ≤1.00E-07 | E; F | E; F | F | F | A; B; F | A; B; C; D; E |
| 2,6-Dimethyl-Nonane | 92.65 | ≤1.00E-07 | F | F | F | F | F | A; B; C; D; E |
| 2,5-Dimethyl-Nonane | 216.67 | ≤1.00E-07 | C; E | C; F | A; B; D; E; F | C; F | A; C; F | B; C; D; E |
| 4-Methyl-2-Pentanone | 159.02 | ≤1.00E-07 | F | F | F | F | F | A; B; C; D; E |
| 2-Methy-2-Butanol | 342.89 | ≤1.00E-07 | F | F | F | F | F | A; B; C; D; E |
| 2-Methyl-Propyl Ester Acetic Acid | 33.42 | ≤1.00E-07 | C | C | A; B; D; E; F | C | C | C |
| α-Pinene | 54.12 | ≤1.00E-07 | C; E; F | C; E; F | A; B; D; E | C; F | A; B; C; F | A; B; D; E |
| 4,4-Dimethyl-2-Pentanone | 1684.33 | ≤1.00E-07 | C; F | F | A; E; F | F | C; F | A; B; C; D; E |
| 1-Penten-3-one | 229.25 | ≤1.00E-07 | C; D; F | C; D; F | A; B; D; E; F | A; B; C; F | C; F | A; B; C; D; E |
| 5-Butyl-Nonane | 195.21 | ≤1.00E-07 | B; C; D; E; F | A; C; D; F | A; B; D; E; F | A; B; C; E | A; C; D; F | A; B; C; E |
| 3,6-Dimethyl-Decane | 121.28 | ≤1.00E-07 | B; C; D; F | A; C; D; E; F | A; B; D; E; F | A; B; C; E | A; B; C; D; F | A; B; C; E |
| 2-Methyl-3-Buten-2-ol | 69.73 | ≤1.00E-07 | C | C | A; B; D; E; F | C | C | C |
| 5-Methyl-Decane | 18.07 | ≤1.00E-07 | B; D; F | A; F | F | A; F | F | A; B; C; D; E |
| 4-Methyl-Decane | 19.34 | ≤1.00E-07 | B; D; E; F | A; C | B; D; E; F | A; C; F | A; C | A; C; D |
| 2,3-Pentanedione | 66.15 | ≤1.00E-07 | B; C; D; E; F | A; D | A; D | A; B; C; E; F | A; D | A; D |
| 3,3-Dimethyl-Methyl Ester Butanoic Acid | 38.31 | ≤1.00E-07 | C | C | A; B; D; E; F | C | C | C |
| 2-Hexanone | 19.88 | ≤1.00E-07 | C | C | A; B; D; E; F | C | C | C |
| 4-Methyl-Undecane | 98.06 | ≤1.00E-07 | C; D; E | C; D; E | A; B; D; E; F | A; B; C; E; F | A; B; C; D; F | C; D; E |
| Hexanal | 133.72 | ≤1.00E-07 | C; D; F | C; D; E; F | A; B; D; E; F | A; B; C; E; F | B; C; D; F | A; B; C; D; E |
| 2-Methyl-1-Propanol | 190.36 | ≤1.00E-07 | B; C; D; E; F | A; D; E; F | A; E; F | A; B; E; F | A; B; C; D; F | A; B; C; D; E |
| 2-Methyl-2-Pentanol | 162.43 | ≤1.00E-07 | B; D; E; F | A; C; F | B; D; E; F | A; C; F | A; C; F | A; B; C; D; E |
| Ethyl-Benzene | 28.80 | ≤1.00E-07 | C | C; F | A; B; D; E; F | C | C | B; C |
| 3-Methyl Butyl Ester Acetic Acid | 98.57 | ≤1.00E-07 | B; C; E | A; D; E; F | A; D; E; F | B; C; E | A; B; C; D; F | B; C; E |
| o-Xylene | 95.67 | ≤1.00E-07 | C; F | C; F | A; B; D; E; F | C; F | C; F | A; B; C; D; E |
| 2-Pentanol | 209.29 | ≤1.00E-07 | C | C | A; B; D; E; F | C | C | C |
| p-Xylene | 56.17 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B; E; F | A; B;  E | A; B; C; D | A; B; C |
| 5-Methyl-2-Hexanone | 274.44 | ≤1.00E-07 | B; C; D; F | A; C; F | A; B; D; E; F | A; C; F | C; F | A; B; C; D; E |
| 2-Ethyl Methyl Ester Pentanoic Ester | 78.94 | ≤1.00E-07 | C | C | A; B; D; E; F | C | C | C |

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| 1-Butanol | 72.01 | ≤1.00E-07 | C; E | C; E | A; B; D; E | C; E | A; B; D; F | C; E |
| α-Phellandrene | 43.64 | ≤1.00E-07 | F | F | F | F | F | A; B; C; D; E |
| 2-Methyl-3-Pentanol | 214.21 | ≤1.00E-07 | C; D | C; D | A; B; D; E; F | A; B; C; E; F | C; D | C; D |
| 1-Penten-3-ol | 26.15 | ≤1.00E-07 | B; C; F | A; C; D | A; B; D; E | B; C; E; F | C; D | A; D |
| α-Terpinene | 162.78 | ≤1.00E-07 | D; F | D; F | D; F | A; B; C; E; F | D; F | A; B; C; D; E |
| Butyl Ester 2-Propenoic Acid | 17.37 | ≤1.00E-07 | C; F | C; F | A; B; D; E | C; F | C; F | A; B; D; E |
| m-Xylene | 141.47 | ≤1.00E-07 | B; C; E; F | A; C; D; F | A; B; D; E; F | B; C; E; F | A; C; D; F | A; B; C; D; E |
| 2-Heptanone | 266.55 | ≤1.00E-07 | B; E; F | A; C; D; E; F | B; D; E; F | B; C; E; F | A; B; C; D; F | A; B; C; D; E |
| Heptanal | 130.47 | ≤1.00E-07 | B; C; F | A; C; D; E; F | A; B; D; E; F | B; C; E; F | B; C; F | A; B; C; D; E |
| D-Limonene | 241.25 | ≤1.00E-07 | C; E; F | C; E; F | A; B; D; E; F | C; E; F | A; B; C; D | A; B; C; D |
| 3-Hexanol | 248.12 | ≤1.00E-07 | B; D; E; F | A; C; D; F | B; D; E | A; B; C; E; F | A; C; D; F | A; B; D; E |
| β-Phellandrene | 22.59 | ≤1.00E-07 | F | F | F | F | F | A; B; C; D; E |
| Eucalyptol | 58.70 | ≤1.00E-07 | D; F | D; F | D; F | A; B; C; E; F | D; F | A; B; C; D; E |
| m-Menthane | 76.50 | ≤1.00E-07 | C; E; F | C; F | A; B; D; E | C; F | A; C; F | A; B; D; E |
| 4-Methyl-2-Heptanone | 1066.87 | ≤1.00E-07 | B; F | A; C; D; E; F | B; F | B; F | B; F | A; B; C; D; E |
| 3-Methyl-2-Pentanol | 504.97 | ≤1.00E-07 | B; C; D; E; F | A; D; F | A; D; F | A; B; C; E | A; D; F | A; B; C; E |
| 2-Methyl-1-Butanol | 26.64 | ≤1.00E-07 | D; F | D; F | D; F | A; B; C; E; F | D; F | A; B; C; D; E |
| 3-Methyl-1-Butanol | 23.35 | ≤1.00E-07 | B; D; F | A; F | F | A; F | F | A; B; C; D; E |
| o-Ethyltoluene | 69.98 | ≤1.00E-07 | B; C; D; E; F | A; C; E; F | A; B; D; E; F | A; C; E | A; B; C; D; F | A; B; C; E |
| m-Ethyltoluene | 157.66 | ≤1.00E-07 | B; C; D; E | A; C; D; E | A; B; D; E; F | A; B; C; E; F | A; B; C; D; F | C; D; E |
| 2-Hexanol | 171.88 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B | A; B | A; B | A; B |
| Ethylene Glycol Ethyl Ether | 32.70 | ≤1.00E-07 | D | D | D | A; B; C; E; F | D | D |
| 6-Methyl-2-Heptanone | 106.44 | ≤1.00E-07 | F | C; F | B; D; E; F | C; F | C; F | A; B; C; D; E |
| Pseudocumene | 38.50 | ≤1.00E-07 | B; C; D; F | A; C; E; F | A; B; D; E; F | A; C; E | B; C; D; F | A; C; E |
| 4,6-Dimethyl-2-Heptanone | 179.79 | ≤1.00E-07 | F | F | F | F | F | A; B; C; D; E |
| 2,3-Dimethyl-2-Hexanol | 1243.14 | ≤1.00E-07 | C; F | C; F | A; B; D; E; F | C; F | C; F | A; B; C; D; E |
| 3-Octanone | 137.45 | ≤1.00E-07 | B; C; D; E; F | A; D; F | A; D; F | A; B; C; E | A; D; F | A; B; C; E |
| Styrene | 34.57 | ≤1.00E-07 | C; D | C; D; E | A; B; D; E; F | A; B; C; F | B; C; F | C; D; E |
| 5-Methyl-2-Heptanone | 33.99 | ≤1.00E-07 | B; F | A; C; E; F | B; F | F | B; F | A; B; C; D; E |
| 1-Pentanol | 49.63 | ≤1.00E-07 | C; E; F | C; E; F | A; B; D | C; E; F | A; B; D | A; B; D |
| p-Ethyltoluene | 92.19 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; | A; B; D; E; F | A; B; C; F | A; B; C; F | A; C; D; E |
| p-Cymene | 94.51 | ≤1.00E-07 | D; F | D; F | D; F | A; B; C; E; F | D; F | A; B; C; D; E |
| Mesitylene | 112.91 | ≤1.00E-07 | B; C; E | A; D; E; F | A; D; E; F | B; C; E | A; B; C; D; F | B; C; E |

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| 4-Methyl-4-Heptanol | 41.36 | ≤1.00E-07 | B; C; D; E; F | A; C; F | A; B; F | A; F | A; F | A; B; C; D; E |
| 4-Heptanol | 50.36 | ≤1.00E-07 | D; F | F | F | A; F | F | A; B; C; D; E |
| 2-Octanone | 130.90 | ≤1.00E-07 | B; E; F | A; C; D; E; F | B; D; E; F | B; C; E; F | A; B; C; D | A; B; C; D |
| Octanal | 289.51 | ≤1.00E-07 | C; D; E; F | C; D; E; F | A; B; D; E | A; B; C; F | A; B; C; F | A; B; D; E |
| 3-Hydroxy-2-Butanone | 34.07 | ≤1.00E-07 | B; C; F | A; C; D; E; F | A; B; D; E | B; C; F | B; C; F | A; B; D; E |
| 1-Octen-3-one | 69.53 | ≤1.00E-07 | B; C; D; E | A; E; F | A; F | A; F | A; B; F | B; C; D; E |
| trans-2-Pentenol | 15.06 | ≤1.00E-07 | B; C; D; E | A; F | A; F | A | A | B; C |
| 2,2,6-Trimethyl-Cyclohexanone | 83.07 | ≤1.00E-07 | B; C; E; F | A; C; D; F | A; B; D; E; F | B; C; E; F | A; C; D; F | A; B; C; D; E |
| 2-Heptanol | 67.77 | ≤1.00E-07 | C; E; F | C; E; F | A; B; D; E; F | C; F | A; B; C; F | A; B; C; D; E |
| cis-2-Pentenol | 20.15 | ≤1.00E-07 | B; C; E; F | A; D | A; D | B; C; E; F | A; D | A; D |
| 1-Hydroxy-2-Propanone | 192.90 | ≤1.00E-07 | C; D; E; F | D | A; D | A; B; C; E; F | A; D | A; D |
| 5-Methyl-4-Hexen-3-one | 28.36 | ≤1.00E-07 | B; D; E | A; C; F | B; D; E | A; C; E; F | A; C; D; F | B; D; E |
| Hemimellitene | 56.95 | ≤1.00E-07 | B; C; F | A; C; D; E | A; B; D; E; F | B; C; E; F | B; C; D | A; C; D |
| 6-Methyl-5-Hepten-2-one | 98.82 | ≤1.00E-07 | B; E; F | A; C; F | B; D; E; F | C; F | A; C; F | A; B; C; D; E |
| 2-Pentene | 63.40 | ≤1.00E-07 | B; C; D; E; F | A; C | A; B; D; E; F | A; C; E | A; C; E; F | A; C; E |
| 1-Hexanol | 102.15 | ≤1.00E-07 | B; E; F | A; C; D; F | B; E; F | B; E; F | A; C; D; F | A; B; C; D; E |
| 2-Cyclopenten-1-one | 52.26 | ≤1.00E-07 | B; C; D; F | A; D; E | A; D; E | A; B; C; E; F | B; C; D; F | A; D; E |
| 2-Methyl-2-Cyclopenten-1-one | 7.91 | 7.60E-05 | B; C; D; E; F | A | A | A | A | A |
| β-Methy-Styrene | 218.18 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B; E; F | A; B; E; F | A; B; C; D; F | A; B; C; D; E |
| 4-Octanol | 52.41 | ≤1.00E-07 | C; F | C; F | A; B; D; E; F | C; F | C; F | A; B; C; D; E |
| cis-3-Hexen-1-ol | 62.26 | ≤1.00E-07 | B; C; D; E; F | A; C; E; F | A; B; D; E; F | A; C; F | A; B; C; F | A; B; C; D; E |
| 2-Nonanone | 129.63 | ≤1.00E-07 | B; E; F | A; C; D; E; F | B; E; F | B; E | A; B; C; D; F | A; B; C; E |
| Nonanal | 250.24 | ≤1.00E-07 | C; D; E; F | C; D; E; F | A; B; D; E; F | A; B; C; F | A; B; C; F | A; B; C; D; E |
| Ethylene Glycol Butyl Ether | 349.45 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E | A; B; D; E; F | A; B; C; E; F | A; B; C; D; F | A; C; D; E |
| 1-Ethyl-1-Methyl-Cyclopentane | 230.15 | ≤1.00E-07 | C; F | C; F | A; B; D; E; F | C; F | C; F | A; B; C; D; E |
| 3-Octen-2-one | 42.77 | ≤1.00E-07 | B | A; C; D; E; F | B | B | B | B |
| 2-Octanol | 229.83 | ≤1.00E-07 | B; C; E; F | A; C; D; E; F | A; B; D; E; F | B; C; E; F | A; B; C; D; F | A; B; C; D; E |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | 1111.23 | ≤1.00E-07 | C; F | C; F | A; B; D; E; F | C; F | C; F | A; B; C; D; E |
| 1,3-Bis(1,1-Dimethylethyl)-Benzene | 249.95 | ≤1.00E-07 | F | F | F | F | F | A; B; C; D; E |
| trans-2-Octenal | 151.75 | ≤1.00E-07 | B; C; E; F | A; C; D; F | A; B; D; E; F | B; C; E; F | A; C; D; F | A; B; C; D; E |
| m-Ethyl-Styrene | 61.93 | ≤1.00E-07 | C; D; E; F | C; D; E; F | A; B; F | A; B; F | A; B; F | A; B; C; D; E |
| 5-Methyl-2-Heptanone | 124.37 | ≤1.00E-07 | F | F | F | F | F | A; B; C; D; E |
| 2-Decanone | 61.19 | ≤1.00E-07 | E; F | E; F | E; F | E; F | A; B; C; D; F | A; B; C; D; E |

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| 1-Octen-3-ol | 47.02 | ≤1.00E-07 | D; F | D; F | D; F | A; B; C; E; F | D; F | A; B; C; D; E |
| trans,trans-2,4-Heptadienal | 140.74 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B; D; E; F | A; B; C; E; F | A; B; C; D; F | A; B; C; D; E |
| 1-Heptanol | 187.71 | ≤1.00E-07 | D; E; F | D; E; F | D; E; F | A; B; C; F | A; B; C; F | A; B; C; D; E |
| cis,cis-3,5-Octadiene | 37.74 | ≤1.00E-07 | C; D; F | C; D; F | A; B; E | A; B; E | C; D; F | A; B; E |
| 2-Oxo-Methyl Ester Propanoic Acid | 91.88 | ≤1.00E-07 | B; C; E; F | A; C; D; F | A; B; D; E; F | B; C; E; F | A; C; D; F | A; B; C; D; E |
| Dihydromyrcenol | 17.40 | ≤1.00E-07 | B; C; E; F | A; D | A; D | B; C; E; F | A; D | A; D |
| trans-Menthone | 252.21 | ≤1.00E-07 | D; F | D; F | D; F | A; B; C; E; F | D; F | A; B; C; D; E |
| Furfural | 2.79 | 3.49E-02 | | | F | | | C |
| Ethanoic Acid | 166.51 | ≤1.00E-07 | C; E; F | C; E; F | A; B; D; E; F | C; E; F | A; B; C; D; F | A; B; C; D; E |
| 2-Ethyl-1-Hexanol | 90.74 | ≤1.00E-07 | B; D; E; F | A; C; D; F | B; E; F | A; B; E; F | A; C; D; F | A; B; C; D; E |
| Decanal | 80.40 | ≤1.00E-07 | B; C; D; F | A; C; D; E | A; B; E; F | A; B; E; F | B; C; D; F | A; C; D; E |
| Furfuryl Formate | 266.49 | ≤1.00E-07 | C; D; E; F | C; D; E; F | A; B; D; E; F | A; B; C; E; F | A; B; C; D | A; B; C; D |
| trans-2-Hepten-1-ol | 181.36 | ≤1.00E-07 | C; D; F | C; D; E; F | A; B; D; E; F | A; B; C; E; F | B; C; D; F | A; B; C; D; E |
| 2-Nonanol | 695.37 | ≤1.00E-07 | B; E | A; C; D; F | B; E; F | B; E | A; C; D; F | B; C; E |
| 1-(2-Furanyl)-Ethanone | 560.99 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B | A; B | A; B | A; B |
| 3,5-Octadien-2-one | 101.41 | ≤1.00E-07 | B; C; D; F | A; C; D; F | A; B; E; F | A; B; E; F | C; D; F | A; B; C; D; E |
| Benzaldehyde | 21.35 | ≤1.00E-07 | C; D; E; F | C; F | A; B; D; E | A; C; F | A; C; F | A; B; D; E |
| Furfuryl Acetate | 4.82 | 2.36E-03 | F | F | | F | F | A; B; D; E |
| Linalool | 384.56 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B; D; E; F | A; B; C | A; B; C | A; B; C |
| β-Myrcene | 526.99 | ≤1.00E-07 | C; D; E; F | D; F | A; D; F | A; B; C; E; F | A; D; F | A; B; C; D; E |
| 1-Octanol | 84.42 | ≤1.00E-07 | B; C; F | A; C; D; E; F | A; B; D; E; F | B; C; F | B; C; F | A; B; C; D; E |
| trans-p-2-Menthen-1-ol | 218.39 | ≤1.00E-07 | D; F | D; F | D; F | A; B; C; E; F | D; F | A; B; C; D; E |
| Propanoic Acid | 582.46 | ≤1.00E-07 | B; C; D; E; F | A; D; F | A; D; F | A; B; C; E; F | A; D; F | A; B; C; D; E |
| 2,3-Butanediol | 90.14 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B; E | A; B; E | A; B; C; D; F | A; B; E |
| Dimethyl Sulfoxide | 252.84 | ≤1.00E-07 | B; C; D; F | A; C; D; E; F | A; B; D; E; F | A; B; C; E; F | B; C; D; F | A; B; C; D; E |
| m-Menth-3-ene | 127.78 | ≤1.00E-07 | C; D; E; F | C; D; E; F | A; B; D | A; B; C; E; F | A; B; D | A; B; D |
| Trans-(2-Ethylcyclopentyl)-Methanol | 49.21 | ≤1.00E-07 | B; C; D; E; F | A; F | A; F | A; F | A; F | A; B; C; D; E |
| Bornyl Acetate | 119.13 | ≤1.00E-07 | B; F | A; C; D; E; F | B; F | B; E; F | B; D; F | A; B; C; D; E |
| 4-Cyclopentene-1,3-dione | 365.04 | ≤1.00E-07 | C; D; E; F | C; D; E; F | A; B; D; E; F | A; B; C; E; F | A; B; C; D; F | A; B; C; D; E |
| Menthol | 1781.56 | ≤1.00E-07 | B; C; F | A; C; D; E; F | A; B; D; E; F | B; C; F | B; C; F | A; B; C; D; E |
| 2-Undecanone | 153.94 | ≤1.00E-07 | B; D; E; F | A; C; D; E; F | B; D; E; F | A; B; C | A; B; C | A; B; C |
| 2-(2-Furanyl)-Furan | 82.05 | ≤1.00E-07 | C; D; E; F | D; E; F | A; D; E; F | A; B; C; E; F | A; B; C; D | A; B; C; D |
| trans-2-Octen-1-ol | 255.47 | ≤1.00E-07 | B; C; D; E; F | A; C; D; F | A; B; D; E; F | A; B; C; E; F | A; C; D; F | A; B; C; D; E |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| trans-2-Nonen-1-ol | 270.13 | ≤1.00E-07 | B; C; F | A; C; D; E; F | A; B; E; F | B; E; F | B; C; F | A; B; C; D; E |
| Diethylene Glycol Ethyl Ether | 17.81 | ≤1.00E-07 | B; E; F | A; C; D | B; E, F | B; E | A; C; D; F | A; C; E |
| 3,5,5-Trimethyl-2-Cyclopenten-1-one | 2.42 | 5.91E-02 | | D | | B | | |
| cis-p-2-Menthen-1-ol | 4.76 | 2.56E-03 | D | D | D | A; B; C; E; F | D | D |
| β-Cyclocitral | 112.59 | ≤1.00E-07 | C; D, E; F | C; D; F | A; B; E; F | A; B; E; F | A; C; E; F | A; B; C; D; E |
| Benzeneacetaldehyde | 1009.48 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B; E; F | A; B; F | A; B; C; F | A; B; C; D; E |
| 1-Nonanol | 298.22 | ≤1.00E-07 | B; E; F | A; C; D; E; F | B; E; F | B; E; F | A; B; C; D; F | A; B; C; D; E |
| Furfuryl Alcohol | 175.76 | ≤1.00E-07 | B; C; D; E | A; D; E; F | A; D; E; F | A; B; C; E | A; B; C; D; F | B; C; E |
| Phoracanthol | 432.85 | ≤1.00E-07 | B; C; D; E; F | A; F | A | A; F | A | A; B; D |
| cis-3-Nonen-1-ol | 31.73 | ≤1.00E-07 | B; C; E; F | A; D; E; F | A; D; E | B; C; E; F | A; B; C; D | A; B; D |
| cis-Piperitol | 596.97 | ≤1.00E-07 | D; F | D; F | D; F | A; B; C; E; F | D; F | A; B; C; D; E |
| p-Methoxy-Styrene | 285.67 | ≤1.00E-07 | B; C; E; F | A; C; D | A; B; D; E; F | B; C; E | A; C; D; F | A; C; E |
| (2Z)-3-Ethyl-2,4-Pentadien-1-ol | 165.69 | ≤1.00E-07 | B; C; D; E; F | A; E; F | A; E; F | A; E; F | A; B; C; D; F | A; B; C; D; E |
| Butylene Glycol Monobutyl Ether | 49.14 | ≤1.00E-07 | C; E; F | C; E; F | A; B; D; F | C; E; F | A; B; D; F | A; B; C; D; E |
| α-Terpineol | 250.62 | ≤1.00E-07 | C; D; E; F | C; D; E; F | A; B; D; E; F | A; B; C; F | A; B; C; F | A; B; C; D; E |
| 1,5-Cyclooctanedione | 6.47 | 3.44E-04 | F | F | F | F | F | A; B; C; D; E |
| γ-Terpinene | 101.61 | ≤1.00E-07 | B; C; D; E | A; C; E; F | A; B; D; E; F | A; C; E; F | A; B; C; D; F | B; C; D; E |
| trans-2-Decenol | 127.16 | ≤1.00E-07 | C; D; F | C; D; F | A; B; E; F | A; B; E; F | C; D; F | A; B; C; D; E |
| 2-Propenoic Acid | 107.28 | ≤1.00E-07 | B; C; D; E; F | A | A | A | A | A |
| 2-Undecanol | 1153.59 | ≤1.00E-07 | B; E | A; C; D; E; F | B; E | B; E | A; B; C; D; F | B; E |
| 3-Ethyl-Benzaldehyde | 36.39 | ≤1.00E-07 | B; E; F | A; C; E; F | B; E | E; F | A; B; C; D; F | A; B; D; E |
| 3-Hydroxy-Benzaldehyde | 90.20 | ≤1.00E-07 | B; C; D; E; F | A; D | A; D; E; F | A; B; C; E; F | A, C; D | A, C; D |
| trans-2-Nonene | 293.65 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B; D; E; F | A; B; C | A; B; C; F | A; B; C; E |
| 2-Methyl-2-Pentenal | 86.36 | ≤1.00E-07 | B; C; D; E; F | A; D; E; F | A; D; E; F | A; B; C; E | A; B; C; D; F | A; B; C; E |
| cis-5-Decenol | 706.67 | ≤1.00E-07 | B; E; F | A; C; D; E; F | B; E; F | B; E; F | A; B; C; D; F | A; B; C; D; E |
| trans-Piperitol | 481.52 | ≤1.00E-07 | B; D; F | A; C; D; E; F | B; D; F | A; B; C; E; F | B; D; F | A; B; C; D; E |
| 4-Ethyl-Benzaldehyde | 56.90 | ≤1.00E-07 | B; C; F | A; C; F | A; B; D; E; F | C; F | C; F | A; B; C; D; E |
| Naphthalene | 149.55 | ≤1.00E-07 | B; C; E; F | A; C; D; F | A; B; D; E; F | B; C; D; F | A; C; D; F | A; B; C; D; E |
| 1-Decanol | 52.83 | ≤1.00E-07 | B; C; D; E; F | A | A | A; E | A; D | A |
| Cyclodecane | 97.31 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B; E; F | A; B; E; F | A; B; C; D | A; B; C; D |
| trans,trans-2,4-Decadienal | 216.56 | ≤1.00E-07 | B; C; E; F | A; C; F | A; B; D; E; F | C; F | A; C; F | A; B; C; D; E |
| 1,2-Cyclopentanedione | 237.96 | ≤1.00E-07 | B; C; E; F | A; C; D; E; F | A; B; D | B; C; E; F | A; B; D | A; B; D |
| Cyclodecene | 176.38 | ≤1.00E-07 | C; D; E; F | C; D; F | A; B; D; F | A; B; C; E; F | A; D; F | A; B; C; D; E |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| cis-4-Decenol | 327.97 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E | A; B; E; F | A; B; E; F | A; B; C; D; F | A; C; D; E |
| 1-Phenyl-2-Butanone | 112.81 | ≤1.00E-07 | C; E | C; E | A; B; D; E; F | C; E; F | A; B; C; D; F | C; D; E |
| Phenethyl Alcohol | 246.86 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B; D; F | A; B; C; E; F | A; B; D; F | A; B; C; D; E |
| trans,cis-2,4-Decadienal | 223.31 | ≤1.00E-07 | B; C; D; E; F | A; C; F | A; B; D; E; F | A; C; F | A; C; F | A; B; C; D; E |
| 2-Cyclohexenol | 443.59 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B; D; E | A; B; C; E; F | A; B; C; D | A; B; D |
| 2-Ethyl Hexanoic Acid | 264.43 | ≤1.00E-07 | B; C; D; E; F | A; C; D; F | A; B; D; E; F | A; B; C; E | A; C; D; F | A; B; C; E |
| 3-Methyl-1,2-Cyclopentanedione | 544.81 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B; D; E | A; B; C; E; F | A; B; C; D | A; B; D |
| trans-Cinnamaldehyde | 60.02 | ≤1.00E-07 | B; C; D; E; F | A; C; D; F | A; B; D | A; B; E; F | A; C; D; F | A; B; D; E |
| Heptanoic Acid | 289.77 | ≤1.00E-07 | B; D; E; F | A; C; D; E; F | B; D; E; F | A; B; C; E; F | A; B; C; D; F | A; B; C; D; E |
| Mequinol | 105.13 | ≤1.00E-07 | C; D; E; F | C; D; E | A; B; D; E; F | A; B; C; E; F | A; B; C; D; F | A; C; D; E |
| 2,4,5-Trihydroxypyrimidine | 637.12 | ≤1.00E-07 | B; C; D; E; F | A; D | A; F | A; B; E; F | A; D | A, C; D |
| cis-Cinnamaldehyde | 74.15 | ≤1.00E-07 | C; E | C; E | A; B; D; E; F | C; E | A; B; C; D; F | C; E |
| Benzenemethanol | 99.47 | ≤1.00E-07 | B; C; D; F | A; C; D | A; B; D; E; F | A; B; C; E; F | C; D; F | A; C; D; E |
| Mesitaldehyde | 73.47 | ≤1.00E-07 | B; E | A; C; D; E; F | B; E | B; E | A; B; C; D; F | B; E |
| 2-Ethylhexyl Ester Octanoic Acid | 873.20 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B; D; E; F | A; B; C; E; F | A; B; C; D | A; B; C; D |
| Benzeneethanol | 109.24 | ≤1.00E-07 | B; C; D; E; F | A; C; D; F | A; B; D; E | A; B; C; E; F | A; C; D; F | A; B; D; E |
| 1,4-Butanediol | 76.56 | ≤1.00E-07 | B; C; D; E; F | A; C; E; F | A; B; E | A; E; F | A; B; C; D; F | A; B; D; E |
| β-Ionone | 116.48 | ≤1.00E-07 | C; D; F | C; D; E; F | A; B; D; E; F | A; B; C; E; F | B; C; D; F | A; B; C; D; E |
| 2-Methyl-1,4-Benzenediol | 80.72 | ≤1.00E-07 | B; C; E; F | A; C; D; E; F | A; B; D | B; C; E; F | A; B; D | A; B; D |
| 2-Ethyl Heptanoic Acid | 85.33 | ≤1.00E-07 | B; E | A; C; D; E; F | B; E | B; E | A; B; C; D; F | B; E |
| 1-Dodecanol | 64.66 | ≤1.00E-07 | B; D; E | A; C; D; F | B; D; E | A; B; C; E; F | A; C; D; F | B; D; E |
| Benzalacetone | 246.67 | ≤1.00E-07 | B; C; D; E; F | A; C; E; F | A; B; E | A; E; F | A; B; C; D; F | A; B; D; E |
| Maltol | 71.61 | ≤1.00E-07 | C; D; E; F | C; D; E; F | A; B; D; E | A; B; C; E; F | A; B; C; D; F | A; B; D, E |
| 2-Acetylpyrrole | 1508.90 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B; D; F | A; B; C; E; F | A; B; D; F | A; B; C; D; E |
| 2,4-Decadien-1-ol | 35.84 | ≤1.00E-07 | B; C; F | A; F | A; F | F | F | A; B; C; D; E |
| Levoglucosenone | 154.19 | ≤1.00E-07 | B; D; E; F | A; C; E; F | B; D; E; F | A; C; E; F | A; B; C; D; F | A; B; C; D; E |
| Phenol | 26.92 | ≤1.00E-07 | C; D | C; D | A; B; D; E; F | A; B; C; E; F | C; D | C; D |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | 356.33 | ≤1.00E-07 | B; C; D; E; F | A; C; D; F | A; B; D; E | A; B; C; E | A; C; D; F | A; B; E |
| 4,6-Dimethyl-Dodecane | 274.61 | ≤1.00E-07 | B; C; D; E; F | A; C; E; F | A; B; D; F | A; C; E; F | A; B; D; F | A; B; C; D; E |
| Ethyl Ester Decanoic Acid | 215.54 | ≤1.00E-07 | C; E; F | D; E; F | A; D; E; F | B; C; D; F | A; B; C; D; F | A; B; C; D; E |
| 1-Methyl-4-Piperidinone | 558.99 | ≤1.00E-07 | B; C; E; F | A; D; F | A; D; E; F | B; C; E; F | A; C; D; F | A; B; C; D; E |
| 2,2-Dimethyl-3-Heptanone | 65.10 | ≤1.00E-07 | B; D; F | A; C; D; E; F | B; D; F | A; B; C; E; F | B; D; F | A; B; C; D; E |
| Octanoic Acid | 113.84 | ≤1.00E-07 | B; C; D; E; F | A; C; D; F | A; B; E | A; B; E | A; C; D; F | A; B; E |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 1,3-Dihydroxy-2-Propanone | 198.54 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E; F | A; B; D | A; B; C; E; F | A; B; D | A; B; D |
| 2-Phenoxy-Ethanol | 592.27 | ≤1.00E-07 | C; D; E; F | C; D; E; F | A; B; E; F | A; B; E; F | A; B; C; D; F | A; B; C; D; E |
| Isophthalaldehyde | 58.32 | ≤1.00E-07 | D; E; F | D; E; F | D; E; F | A; B; C; E; F | A; B; C; D; F | A; B; C; D; E |
| Cyclotetradecane | 237.95 | ≤1.00E-07 | B; C; D; E; F | A; C; D | A; B; D; E; F | A; B; C; E; F | A; C; D | A; C; D |
| Nonanoic Acid | 534.87 | ≤1.00E-07 | B; C; E; F | A; C; D; F | A; B; D; E; F | B; C; E; F | A; C; D; F | A; B; C; D; E |
| 2-Ethyl-Phenol | 73.25 | ≤1.00E-07 | C; D; E; F | C; D; E | A; B; D; F | A; B; C; E; F | A; B; D; F | A; C; D; E |
| 2-Methoxy-4-Vinyl-Phenol | 531.37 | ≤1.00E-07 | B; C; D; F | A; C; D; E; F | A; B; D; E; F | A; B; C; E; F | B; C; D; F | A; B; C; D; E |
| 4-Methylimidazole | 543.79 | ≤1.00E-07 | B; C; D; E; F | A; E; F | A; D; E; F | A; C; E; F | A; B; C; D; F | A; B; C; D; E |
| m-tert-Butyl-Toluene | 38.56 | ≤1.00E-07 | D; E | D; E | D; E | A; B; C; E; F | A; B; C; D; F | D; E |
| Syringol | 72.89 | ≤1.00E-07 | B; C; E; F | A; C; D; E; F | A; B; D | B; C; E; F | A; B; D | A; B; D |
| Decanoic Acid | 253.85 | ≤1.00E-07 | B; E | A; C; D; E; F | B; E | B; E | A; B; C; D; F | B; E |
| 3-Hydroxy-2,3-Dihydro-Maltol | 492.74 | ≤1.00E-07 | B; C; D; E; F | A; C; E; F | A; B; D; E; F | A; C; E; F | A; B; C; D | A; B; C; D |
| 5-Hydroxy-Maltol | 269.56 | ≤1.00E-07 | B; E; F | A; C; D; E; F | B; E; F | B; E; F | A; B; C; D; F | A; B; C; D; E |
| Triethylene Glycol | 304.57 | ≤1.00E-07 | C; D; F | C; D; F | A; B; D; E | A; B; C; E; F | C; D; F | A; B; D; E |
| Benzoic Acid | 116.38 | ≤1.00E-07 | B; C; E; F | A; D; E; F | A; D; E | B; C; E; F | A; B; C; D; F | A; B; D; E |
| 2-Methyl-Benzaldehyde | 255.45 | ≤1.00E-07 | D; E; F | C; D; E; F | B; D; E; F | A; B; C; F | A; B; C; F | A; B; C; D; E |
| Undecanoic Acid | 561.56 | ≤1.00E-07 | B; D; E; F | A; C; D; F | B; E; F | A; B; E; F | A; C; D; F | A; B; C; D; E |
| 4-Pyridinol | 160.11 | ≤1.00E-07 | B; C; E; F | A; C; D; F | A; B; D; E; F | B; C; E; F | A; C; D; F | A; B; C; D; E |
| 4-Amino-Phenol | 886.23 | ≤1.00E-07 | B; C; D; E; F | A; C; D; E | A; B; D; E | A; B; C; E; F | A; B; C; D; F | A; D; E |

[1]F Value - Fischer value from One-way ANOVA test.
[2]P Value - Probability value from One-way ANOVA test.
[3]Samples with significantly different relative peak area values determined by one-way ANOVA with Post-hoc Tukey test ($\alpha < 0.05$).

**Table S15. Information summary of PCA and PLS based on the relative peak areas of the identified VOCs in SC samples.**

| Analysis | Component | $R^2X$ | Eigenvalues | $R^2Y$ | $Q^2$ | Significance | Iterations |
|---|---|---|---|---|---|---|---|
| PCA | 1 | 0.320 | 86.86 | n.a. | 0.266 | S | 16 |
| | 2 | 0.219 | 59.46 | n.a. | 0.183 | S | 9 |
| | 3 | 0.159 | 43.10 | n.a. | 0.279 | S | 6 |
| | 4 | 0.113 | 30.70 | n.a. | 0.315 | S | 10 |
| | 5 | 0.085 | 23.11 | n.a. | 0.418 | S | 5 |
| | 6 | 0.024 | 6.63 | n.a. | 0.009 | S | 31 |
| | 7 | 0.020 | 5.40 | n.a. | 0.152 | S | 5 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | 8 | 0.015 | 3.99 | n.a. | 0.096 | S | 26 |
| | 9 | 0.013 | 3.40 | n.a. | 0.011 | S | 29 |
| | 10 | 0.012 | 3.16 | n.a. | 0.180 | S | 23 |
| | 11 | 0.010 | 2.67 | n.a. | 0.469 | S | 4 |
| | 12 | 0.003 | 0.81 | n.a. | 0.240 | S | 6 |
| | 13 | 0.001 | 0.29 | n.a. | 0.045 | S | 7 |
| | 14 | 0.001 | 0.21 | n.a. | -0.053 | UNKNOWN | 17 |
| PLS | 1 | 0.328 | 86.95 | 0.091 | 0.014 | S | 14 |
| | 2 | 0.225 | 59.56 | 0.091 | 0.029 | S | 8 |
| | 3 | 0.163 | 43.19 | 0.090 | 0.042 | S | 9 |
| | 4 | 0.116 | 30.80 | 0.091 | 0.059 | S | 10 |
| | 5 | 0.088 | 23.21 | 0.091 | 0.073 | S | 4 |
| | 6 | 0.021 | 5.57 | 0.090 | 0.051 | S | 8 |
| | 7 | 0.016 | 4.31 | 0.091 | 0.089 | S | 6 |
| | 8 | 0.011 | 2.92 | 0.087 | 0.107 | S | 10 |
| | 9 | 0.009 | 2.32 | 0.090 | 0.168 | S | 16 |
| | 10 | 0.008 | 2.08 | 0.088 | 0.331 | S | 21 |
| | 11 | 0.006 | 1.60 | 0.089 | 0.851 | S | 4 |
| | 12 | 0.003 | 0.70 | 0.008 | 0.607 | S | 4 |
| | 13 | 0.001 | 0.21 | 0.002 | 0.176 | S | 7 |
| | 14 | 0.001 | 0.17 | 0.001 | -0.072 | S | 50 |
| | 15 | 0.001 | 0.18 | 0.001 | 0.036 | S | 13 |
| | 16 | 0.001 | 0.18 | 0.000 | 0.072 | S | 50 |
| | 17 | 0.001 | 0.12 | 0.000 | 0.100 | S | 14 |
| | 18 | 0.000 | 0.14 | 0.000 | 0.152 | S | 13 |

**Table S16. Loading results and variable importance in projection scores of variables from PCA and PLS based on the relative peak areas of the identified VOCs in SC samples.**

| ID Number | Volatile Organic Compound | Abbreviation | PCA | | | | PLS | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | 3 | VIP[1] | 1 | 2 | 3 | VIP[1] |

| | | | | | | Importance | Power (x 100) | | | | Importance | Power (x 100) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Pentane | PTANE | 0.198 | 0.827 | -0.155 | 185 | 99.52 | 0.019 | 0.107 | 0.024 | 64 | 6.42 |
| 2 | 1-Pentene | PT1ENE | -0.591 | 0.507 | 0.264 | 219 | 99.20 | -0.065 | 0.064 | -0.040 | 46 | 7.13 |
| 3 | 2-Methyl-Pentane | M2PTANE | 0.364 | 0.806 | 0.320 | 42 | 99.93 | 0.037 | 0.106 | -0.047 | 127 | 5.35 |
| 4 | Hexane | HEXANE | -0.935 | -0.006 | 0.063 | 30 | 99.94 | -0.100 | -0.003 | -0.009 | 91 | 5.98 |
| 5 | Ethyl Ether | EETHR | -0.482 | -0.275 | 0.022 | 195 | 99.47 | -0.051 | -0.037 | -0.005 | 2 | 13.71 |
| 6 | cis-4-Methyl-2-Pentene | CM4PT2ENE | 0.205 | 0.638 | 0.273 | 176 | 99.60 | 0.020 | 0.084 | -0.040 | 11 | 9.87 |
| 7 | cis-Piperylene | CPIPERLNE | 0.156 | 0.767 | 0.303 | 94 | 99.82 | 0.015 | 0.100 | -0.044 | 31 | 7.88 |
| 8 | 2-Methyl-1-Pentene | M2PT1ENE | -0.556 | -0.223 | -0.041 | 92 | 99.83 | -0.059 | -0.030 | 0.006 | 7 | 11.84 |
| 9 | cis-3-Methyl-2-Pentene | CM3PT2ENE | 0.183 | -0.250 | -0.287 | 122 | 99.77 | 0.020 | -0.033 | 0.042 | 13 | 9.66 |
| 10 | 3-Methyl-Hexane | M3HXANE | -0.921 | 0.010 | -0.259 | 178 | 99.59 | -0.099 | -0.002 | 0.040 | 149 | 5.20 |
| 11 | 1,4-Pentadiene | PT14DIENE | 0.098 | 0.507 | 0.240 | 111 | 99.80 | 0.009 | 0.066 | -0.037 | 10 | 10.63 |
| 12 | Methanethiol | METHIOL | 0.026 | 0.782 | 0.312 | 149 | 99.69 | 0.001 | 0.102 | -0.047 | 54 | 6.67 |
| 13 | trans-Piperylene | TPIPERLNE | -0.004 | 0.487 | 0.493 | 184 | 99.53 | -0.002 | 0.064 | -0.076 | 17 | 8.91 |
| 14 | Heptane | HPTANE | -0.574 | 0.406 | 0.072 | 188 | 99.51 | -0.063 | 0.051 | -0.012 | 56 | 6.64 |
| 15 | tert-Butyl Ethyl Ether | BEETHR | -0.894 | -0.214 | -0.015 | 123 | 99.77 | -0.095 | -0.030 | 0.002 | 61 | 6.47 |
| 16 | Ethanal | ETAL | -0.307 | -0.300 | 0.820 | 48 | 99.92 | -0.032 | -0.038 | -0.125 | 41 | 7.26 |
| 17 | Dimethyl Sulfide | DMSULFI | 0.647 | -0.564 | 0.224 | 248 | 98.87 | 0.071 | -0.071 | -0.035 | 52 | 6.80 |
| 18 | 4-Methyl-Heptane | M4HPTANE | -0.844 | -0.197 | 0.048 | 17 | 99.96 | -0.090 | -0.028 | -0.007 | 28 | 7.99 |
| 19 | Octane | OCTANE | -0.597 | 0.379 | 0.218 | 155 | 99.67 | -0.065 | 0.048 | -0.034 | 119 | 5.41 |
| 20 | Propanal | PPAL | -0.903 | -0.103 | 0.261 | 225 | 99.15 | -0.096 | -0.015 | -0.040 | 139 | 5.26 |
| 21 | Furan | FUR | 0.449 | 0.057 | 0.616 | 241 | 98.98 | 0.048 | 0.010 | -0.095 | 15 | 9.23 |
| 22 | 2,4-Dimethyl-Heptane | DM24HPTANE | 0.492 | 0.688 | 0.204 | 259 | 98.59 | 0.051 | 0.091 | -0.029 | 19 | 8.78 |
| 23 | 2-Methyl-Propanal | MPPAL | 0.231 | 0.386 | 0.375 | 77 | 99.86 | 0.024 | 0.052 | -0.055 | 88 | 5.99 |
| 24 | 2-Propanone | PP2ONE | -0.650 | -0.550 | 0.161 | 116 | 99.79 | -0.068 | -0.073 | -0.026 | 205 | 4.63 |
| 25 | Methyl Ester Acetic Acid | MESTAA | 0.182 | 0.651 | 0.290 | 7 | 99.97 | 0.018 | 0.085 | -0.043 | 9 | 10.64 |
| 26 | 2-Methyl-2-Heptene | M2HPTENE | -0.967 | -0.095 | -0.015 | 1 | 99.99 | -0.103 | -0.015 | 0.002 | 206 | 4.63 |
| 27 | Crotonal | CROTNAL | 0.270 | 0.469 | -0.462 | 159 | 99.66 | 0.028 | 0.061 | 0.073 | 12 | 9.83 |
| 28 | 2,3-Dimethyl-Heptane | DM23HPTANE | 0.426 | 0.584 | 0.447 | 90 | 99.83 | 0.044 | 0.078 | -0.067 | 34 | 7.81 |
| 29 | 4-Methyl-Octane | M4OCTANE | 0.306 | 0.890 | 0.217 | 192 | 99.48 | 0.030 | 0.117 | -0.031 | 145 | 5.22 |
| 30 | 2-Methyl-Furan | M2FUR | 0.273 | -0.389 | -0.347 | 240 | 99.01 | 0.030 | -0.051 | 0.050 | 25 | 8.19 |
| 31 | 2,4-Dimethyl-1-Heptene | DM24HPT1ENE | -0.977 | -0.116 | -0.016 | 4 | 99.98 | -0.104 | -0.018 | 0.002 | 243 | 4.09 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 32 | Ethyl Ester Acetic Acid | EESTAA | 0.012 | 0.951 | 0.274 | 32 | 99.94 | -0.001 | 0.124 | -0.040 | 233 | 4.26 |
| 33 | Nonane | NNANE | -0.632 | 0.556 | -0.231 | 180 | 99.57 | -0.069 | 0.070 | 0.036 | 30 | 7.97 |
| 34 | 2-Butanone | BT2ONE | -0.867 | 0.042 | 0.351 | 209 | 99.34 | -0.093 | 0.004 | -0.052 | 217 | 4.52 |
| 35 | 2-Methyl-Butanal | M2BTAL | -0.013 | -0.341 | 0.861 | 137 | 99.74 | -0.001 | -0.042 | -0.132 | 65 | 6.42 |
| 36 | 3-Methyl-Butanal | M3BTAL | -0.166 | -0.395 | 0.840 | 210 | 99.34 | -0.017 | -0.050 | -0.129 | 48 | 7.11 |
| 37 | Ethyl Alcohol | ETOL | 0.747 | 0.298 | -0.547 | 224 | 99.15 | 0.079 | 0.039 | 0.084 | 213 | 4.56 |
| 38 | Benzene | BNZ | 0.169 | 0.672 | -0.089 | 234 | 99.06 | 0.016 | 0.088 | 0.015 | 23 | 8.24 |
| 39 | 3-Ethyl-Heptane | E3HPTANE | -0.912 | 0.063 | 0.143 | 170 | 99.63 | -0.098 | 0.006 | -0.022 | 173 | 5.00 |
| 40 | 2-Ethyl-Furan | E2FUR | 0.152 | 0.314 | -0.082 | 257 | 98.61 | 0.015 | 0.041 | 0.014 | 5 | 13.06 |
| 41 | Ethyl Ester Propanoic Acid | EESTPA | 0.081 | 0.937 | 0.169 | 11 | 99.96 | 0.006 | 0.122 | -0.024 | 140 | 5.25 |
| 42 | 2-Methyl Ethyl Ester Propanoic Acid | M2EESTPA | 0.056 | 0.949 | 0.199 | 27 | 99.94 | 0.003 | 0.123 | -0.029 | 189 | 4.86 |
| 43 | 2-Methyl-Crotonal | M2CROTNAL | 0.301 | 0.541 | 0.329 | 95 | 99.82 | 0.031 | 0.072 | -0.047 | 94 | 5.84 |
| 44 | Propyl Ester Acetic Acid | PESTAA | 0.081 | 0.931 | 0.229 | 3 | 99.98 | 0.006 | 0.121 | -0.033 | 138 | 5.27 |
| 45 | 3-Pentanone | PT3ONE | -0.769 | -0.013 | 0.191 | 242 | 98.97 | -0.082 | -0.003 | -0.029 | 98 | 5.77 |
| 46 | Pentanal | PTNAL | -0.991 | 0.031 | 0.036 | 26 | 99.95 | -0.106 | 0.001 | -0.005 | 260 | 3.70 |
| 47 | 2,3-Butanedione | BT23DONE | 0.693 | 0.388 | -0.066 | 247 | 98.88 | 0.073 | 0.052 | 0.011 | 146 | 5.21 |
| 48 | 2,3,4-Trimethyl-Hexane | TM234HXANE | -0.979 | -0.091 | -0.013 | 28 | 99.94 | -0.105 | -0.014 | 0.002 | 244 | 4.07 |
| 49 | Decane | DCANE | -0.935 | -0.022 | -0.114 | 167 | 99.63 | -0.100 | -0.006 | 0.018 | 147 | 5.21 |
| 50 | 2,6-Dimethyl-Nonane | DM26NNANE | -0.955 | -0.081 | 0.027 | 68 | 99.88 | -0.102 | -0.013 | -0.004 | 165 | 5.07 |
| 51 | 2,5-Dimethyl-Nonane | DM25NNANE | 0.188 | 0.974 | 0.066 | 29 | 99.94 | 0.017 | 0.127 | -0.008 | 245 | 4.05 |
| 52 | 4-Methyl-2-Pentanone | M4PT2ONE | -0.967 | -0.170 | 0.025 | 10 | 99.97 | -0.103 | -0.024 | -0.004 | 237 | 4.20 |
| 53 | 2-Methy-2-Butanol | M2BT2OL | -0.976 | -0.118 | -0.003 | 6 | 99.98 | -0.104 | -0.018 | 0.000 | 246 | 4.01 |
| 54 | 2-Methyl-Propyl Ester Acetic Acid | M2PESTAA | 0.145 | 0.873 | 0.321 | 117 | 99.79 | 0.013 | 0.114 | -0.047 | 73 | 6.28 |
| 55 | α-Pinene | APNENE | -0.551 | 0.772 | -0.047 | 133 | 99.75 | -0.061 | 0.098 | 0.009 | 111 | 5.51 |
| 56 | 4,4-Dimethyl-2-Pentanone | DM44PT2ONE | -0.986 | -0.116 | 0.004 | 50 | 99.92 | -0.105 | -0.018 | -0.001 | 264 | 3.56 |
| 57 | 1-Penten-3-one | PT1E3ONE | -0.925 | 0.302 | 0.104 | 144 | 99.70 | -0.100 | 0.037 | -0.015 | 253 | 3.88 |
| 58 | 5-Butyl-Nonane | B5NONANE | 0.237 | 0.832 | 0.246 | 2 | 99.98 | 0.023 | 0.109 | -0.037 | 221 | 4.46 |
| 59 | 3,6-Dimethyl-Decane | DM36DCANE | 0.429 | 0.297 | -0.219 | 135 | 99.75 | 0.045 | 0.039 | 0.031 | 90 | 5.98 |
| 60 | 2-Methyl-3-Buten-2-ol | M3BT2OL | 0.070 | 0.922 | 0.088 | 86 | 99.84 | 0.005 | 0.120 | -0.012 | 93 | 5.85 |
| 61 | 5-Methyl-Decane | M5DCANE | 0.813 | 0.117 | 0.173 | 140 | 99.74 | 0.087 | 0.018 | -0.026 | 43 | 7.24 |
| 62 | 4-Methyl-Decane | M4DCANE | 0.031 | 0.486 | 0.357 | 253 | 98.78 | 0.002 | 0.063 | -0.054 | 18 | 8.83 |
| 63 | 2,3-Pentanedione | PTDONE | 0.292 | -0.372 | 0.813 | 98 | 99.82 | 0.032 | -0.046 | -0.124 | 99 | 5.76 |
| 64 | 3,3-Dimethyl-Methyl Ester Butanoic Acid | DM33MESTBA | 0.099 | 0.908 | 0.159 | 35 | 99.94 | 0.008 | 0.118 | -0.023 | 80 | 6.16 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 65 | 2-Hexanone | HX2ONE | -0.059 | 0.828 | -0.098 | 161 | 99.66 | -0.008 | 0.107 | 0.016 | 21 | 8.45 |
| 66 | 4-Methyl-Undecane | M4UNCANE | 0.154 | 0.926 | -0.023 | 88 | 99.84 | 0.014 | 0.120 | 0.006 | 87 | 6.03 |
| 67 | Hexanal | HXAL | -0.834 | 0.351 | 0.287 | 82 | 99.85 | -0.090 | 0.044 | -0.043 | 198 | 4.72 |
| 68 | 2-Methyl-1-Propanol | M2PP1OL | 0.619 | -0.214 | -0.349 | 191 | 99.50 | 0.067 | -0.027 | 0.053 | 100 | 5.75 |
| 69 | 2-Methyl-2-Pentanol | M2PT2OL | -0.906 | -0.062 | 0.273 | 124 | 99.77 | -0.097 | -0.010 | -0.042 | 196 | 4.73 |
| 70 | Ethyl-Benzene | ETBNZ | 0.266 | 0.833 | 0.189 | 45 | 99.92 | 0.026 | 0.109 | -0.028 | 36 | 7.66 |
| 71 | 3-Methyl Butyl Ester Acetic Acid | M3BESTAA | 0.094 | 0.468 | 0.183 | 264 | 98.14 | 0.009 | 0.061 | -0.029 | 72 | 6.29 |
| 72 | o-Xylene | OXYLNE | -0.958 | 0.095 | 0.115 | 25 | 99.95 | -0.103 | 0.010 | -0.017 | 208 | 4.61 |
| 73 | 2-Pentanol | PT2OL | 0.067 | 0.957 | 0.148 | 5 | 99.98 | 0.005 | 0.124 | -0.021 | 172 | 5.01 |
| 74 | p-Xylene | PXYLNE | -0.321 | 0.701 | -0.080 | 119 | 99.78 | -0.036 | 0.090 | 0.015 | 82 | 6.12 |
| 75 | 5-Methyl-2-Hexanone | M5HX2AONE | -0.347 | 0.855 | 0.248 | 84 | 99.85 | -0.040 | 0.110 | -0.037 | 202 | 4.65 |
| 76 | 2-Ethyl Methyl Ester Pentanoic Acid | E2MESTPTA | 0.018 | 0.945 | 0.179 | 55 | 99.91 | -0.001 | 0.123 | -0.026 | 143 | 5.22 |
| 77 | 1-Butanol | BT1OL | 0.236 | 0.728 | -0.449 | 179 | 99.58 | 0.023 | 0.094 | 0.070 | 101 | 5.74 |
| 78 | α-Phellandrene | APHELDNE | -0.928 | -0.154 | 0.011 | 37 | 99.94 | -0.099 | -0.022 | -0.002 | 95 | 5.82 |
| 79 | 2-Methyl-3-Pentanol | M2PT3OL | 0.160 | 0.915 | 0.351 | 126 | 99.76 | 0.015 | 0.120 | -0.051 | 238 | 4.20 |
| 80 | 1-Penten-3-ol | PT1E3OL | -0.415 | 0.626 | -0.264 | 168 | 99.63 | -0.046 | 0.079 | 0.040 | 44 | 7.22 |
| 81 | α-Terpinene | ATERPNNE | -0.948 | -0.186 | 0.064 | 31 | 99.94 | -0.101 | -0.026 | -0.010 | 235 | 4.23 |
| 82 | Butyl Ester 2-Propenoic Acid | BTESTPPEA | -0.552 | 0.632 | 0.171 | 76 | 99.87 | -0.061 | 0.081 | -0.024 | 33 | 7.86 |
| 83 | m-Xylene | MXYLNE | -0.513 | 0.753 | -0.225 | 129 | 99.76 | -0.057 | 0.096 | 0.035 | 148 | 5.20 |
| 84 | 2-Heptanone | HPT2ONE | 0.101 | -0.345 | -0.812 | 181 | 99.57 | 0.012 | -0.046 | 0.122 | 130 | 5.34 |
| 85 | Heptanal | HPTAL | -0.117 | 0.310 | -0.311 | 99 | 99.81 | -0.013 | 0.039 | 0.046 | 60 | 6.49 |
| 86 | D-Limonene | DLIMNENE | -0.349 | 0.856 | -0.170 | 163 | 99.66 | -0.040 | 0.110 | 0.028 | 195 | 4.73 |
| 87 | 3-Hexanol | HX3OL | 0.372 | -0.222 | -0.207 | 139 | 99.74 | 0.041 | -0.028 | 0.033 | 105 | 5.64 |
| 88 | β-Phellandrene | BPHELDNE | -0.885 | -0.143 | -0.014 | 78 | 99.86 | -0.095 | -0.021 | 0.002 | 47 | 7.12 |
| 89 | Eucalyptol | EUCPTOL | -0.826 | -0.260 | 0.247 | 120 | 99.78 | -0.088 | -0.035 | -0.037 | 108 | 5.60 |
| 90 | m-Menthane | MMTHANE | -0.751 | 0.592 | 0.033 | 21 | 99.95 | -0.082 | 0.075 | -0.004 | 158 | 5.14 |
| 91 | 4-Methyl-2-Heptanone | M4HPT2ONE | -0.976 | -0.163 | -0.023 | 14 | 99.96 | -0.104 | -0.024 | 0.003 | 261 | 3.69 |
| 92 | 3-Methyl-2-Pentanol | M2PT2OL | 0.445 | 0.478 | -0.666 | 156 | 99.67 | 0.047 | 0.061 | 0.101 | 184 | 4.91 |
| 93 | 2-Methyl-1-Butanol | M2BT1OL | 0.797 | 0.184 | 0.003 | 142 | 99.73 | 0.085 | 0.026 | -0.001 | 66 | 6.40 |
| 94 | 3-Methyl-1-Butanol | M3BT1OL | 0.814 | 0.248 | 0.178 | 118 | 99.79 | 0.086 | 0.035 | -0.027 | 51 | 6.89 |
| 95 | o-Ethyltoluene | OETOLENE | -0.385 | 0.708 | 0.094 | 172 | 99.62 | -0.043 | 0.091 | -0.013 | 55 | 6.67 |
| 96 | m-Ethyltoluene | METOLENE | 0.261 | 0.896 | 0.023 | 24 | 99.95 | 0.026 | 0.117 | -0.001 | 215 | 4.54 |
| 97 | 2-Hexanol | HX2OL | 0.425 | -0.510 | 0.213 | 100 | 99.81 | 0.047 | -0.065 | -0.036 | 156 | 5.15 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 98 | Ethylene Glycol Ethyl Ether | ENGOLEETHR | 0.187 | -0.012 | 0.272 | 38 | 99.94 | 0.020 | 0.000 | -0.039 | 35 | 7.79 |
| 99 | 6-Methyl-2-Heptanone | M6HPT2ONE | -0.985 | -0.018 | 0.072 | 151 | 99.69 | -0.106 | -0.005 | -0.011 | 262 | 3.65 |
| 100 | Pseudocumene | PSEUDCUMNE | -0.194 | 0.787 | 0.169 | 201 | 99.42 | -0.023 | 0.102 | -0.024 | 38 | 7.59 |
| 101 | 4,6-Dimethyl-2-Heptanone | DM46HPT2ONE | -0.964 | -0.141 | 0.004 | 20 | 99.95 | -0.103 | -0.021 | -0.001 | 220 | 4.50 |
| 102 | 2,3-Dimethyl-2-Hexanol | DM23HX2OL | -0.991 | -0.091 | 0.013 | 8 | 99.97 | -0.106 | -0.014 | -0.002 | 265 | 3.54 |
| 103 | 3-Octanone | OCT3ONE | 0.452 | 0.526 | -0.567 | 49 | 99.92 | 0.047 | 0.068 | 0.086 | 114 | 5.44 |
| 104 | Styrene | STYNE | 0.298 | 0.878 | 0.126 | 198 | 99.44 | 0.030 | 0.115 | -0.017 | 112 | 5.48 |
| 105 | 5-Methyl-2-Heptanone | M5HPTAONE | -0.805 | -0.118 | -0.180 | 148 | 99.69 | -0.086 | -0.018 | 0.027 | 39 | 7.54 |
| 106 | 1-Pentanol | PT1OL | 0.545 | -0.574 | 0.502 | 13 | 99.96 | 0.060 | -0.072 | -0.078 | 107 | 5.61 |
| 107 | p-Ethyltoluene | PETOLENE | 0.148 | 0.872 | -0.073 | 96 | 99.82 | 0.013 | 0.113 | 0.014 | 188 | 4.87 |
| 108 | p-Cymene | PCYMNE | -0.905 | -0.158 | 0.095 | 64 | 99.90 | -0.097 | -0.023 | -0.014 | 201 | 4.68 |
| 109 | Mesitylene | MESTLNE | -0.025 | -0.538 | -0.106 | 60 | 99.90 | -0.001 | -0.070 | 0.017 | 57 | 6.51 |
| 110 | 4-Methyl-4-Heptanol | M4HPT4OL | -0.173 | -0.621 | 0.448 | 81 | 99.85 | -0.017 | -0.080 | -0.071 | 20 | 8.65 |
| 111 | 4-Heptanol | HPT4OL | -0.933 | -0.036 | -0.001 | 61 | 99.90 | -0.100 | -0.007 | 0.001 | 123 | 5.38 |
| 112 | 2-Octanone | OCT2ONE | -0.250 | -0.433 | -0.732 | 207 | 99.37 | -0.026 | -0.059 | 0.109 | 131 | 5.34 |
| 113 | Octanal | OCTAL | -0.682 | 0.661 | 0.050 | 91 | 99.83 | -0.075 | 0.084 | -0.005 | 240 | 4.14 |
| 114 | 3-Hydroxy-2-Butanone | HXY3BT2ONE | 0.577 | -0.444 | -0.309 | 214 | 99.29 | 0.063 | -0.057 | 0.045 | 22 | 8.41 |
| 115 | 1-Octen-3-one | OCT3E1ONE | -0.532 | -0.472 | 0.493 | 36 | 99.94 | -0.056 | -0.062 | -0.077 | 89 | 5.99 |
| 116 | trans-2-Pentenol | TPT1E2OL | 0.214 | 0.568 | -0.309 | 243 | 98.97 | 0.021 | 0.073 | 0.048 | 14 | 9.33 |
| 117 | 2,2,6-Trimethyl-Cyclohexanone | TM226CHXONE | -0.362 | 0.843 | -0.109 | 256 | 98.67 | -0.041 | 0.108 | 0.017 | 171 | 5.01 |
| 118 | 2-Heptanol | HPT2OL | 0.417 | -0.680 | -0.334 | 252 | 98.79 | 0.047 | -0.088 | 0.051 | 74 | 6.24 |
| 119 | cis-2-Pentenol | CPT1E2OL | 0.379 | -0.363 | 0.751 | 229 | 99.10 | 0.041 | -0.044 | -0.114 | 53 | 6.78 |
| 120 | 1-Hydroxy-2-Propanone | HXY1PP2ONE | 0.300 | -0.218 | 0.447 | 12 | 99.96 | 0.033 | -0.026 | -0.066 | 132 | 5.33 |
| 121 | 5-Methyl-4-Hexen-3-one | M5HX3E4ONE | 0.253 | -0.106 | -0.770 | 230 | 99.10 | 0.027 | -0.015 | 0.118 | 26 | 8.17 |
| 122 | Hemimellitene | HEMIMLTNE | 0.218 | 0.801 | 0.372 | 211 | 99.31 | 0.021 | 0.105 | -0.054 | 77 | 6.20 |
| 123 | 6-Methyl-5-Hepten-2-one | M6HPT2E5ONE | -0.918 | 0.072 | 0.215 | 72 | 99.88 | -0.099 | 0.007 | -0.033 | 168 | 5.05 |
| 124 | 2-Pentene | PT2ENE | -0.005 | -0.723 | -0.564 | 173 | 99.61 | 0.001 | -0.095 | 0.085 | 71 | 6.29 |
| 125 | 1-Hexanol | HX1OL | 0.738 | 0.326 | 0.528 | 132 | 99.76 | 0.078 | 0.045 | -0.079 | 204 | 4.64 |
| 126 | 2-Cyclopenten-1-one | CY2PT1EONE | -0.288 | 0.261 | 0.194 | 222 | 99.19 | -0.032 | 0.034 | -0.029 | 50 | 6.91 |
| 127 | 2-Methyl-2-Cyclopenten-1-one | M2CY2PT1EONE | -0.444 | 0.120 | -0.373 | 101 | 99.81 | -0.048 | 0.014 | 0.058 | 1 | 14.64 |
| 128 | β-Methy-Styrene | BMSTYNE | 0.364 | 0.692 | -0.160 | 200 | 99.42 | 0.037 | 0.091 | 0.027 | 153 | 5.18 |
| 129 | 4-Octanol | OCT4OL | -0.676 | -0.635 | -0.174 | 227 | 99.12 | -0.071 | -0.084 | 0.026 | 67 | 6.39 |
| 130 | cis-3-Hexen-1-ol | CHX1E3OL | 0.634 | 0.125 | 0.502 | 223 | 99.16 | 0.068 | 0.019 | -0.078 | 32 | 7.87 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 131 | 2-Nonanone | NON2ONE | 0.437 | -0.123 | -0.678 | 125 | 99.76 | 0.047 | -0.017 | 0.101 | 86 | 6.04 |
| 132 | Nonanal | NONAL | 0.715 | -0.530 | 0.081 | 85 | 99.84 | 0.078 | -0.067 | -0.015 | 212 | 4.57 |
| 133 | Ethylene Glycol Butyl Ether | ENGOLBETHR | 0.486 | -0.137 | 0.778 | 146 | 99.70 | 0.052 | -0.015 | -0.118 | 113 | 5.45 |
| 134 | 1-Ethyl-1-Methyl-Cyclopentane | E1M1CYPTANE | -0.987 | 0.042 | 0.034 | 41 | 99.93 | -0.106 | 0.003 | -0.005 | 256 | 3.85 |
| 135 | 3-Octen-2-one | OCT2E3ONE | 0.025 | -0.212 | -0.312 | 22 | 99.95 | 0.003 | -0.028 | 0.045 | 16 | 9.03 |
| 136 | 2-Octanol | OCT2OL | 0.394 | -0.396 | -0.770 | 114 | 99.79 | 0.043 | -0.052 | 0.117 | 141 | 5.23 |
| 137 | 3-Ethyl-2-Methyl-1,3-Hexadiene | E3M2HX13DENE | 0.258 | 0.278 | -0.685 | 154 | 99.68 | 0.027 | 0.035 | 0.106 | 128 | 5.35 |
| 138 | 1,3-Bis(1,1-Dimethylethyl)-Benzene | BI13DME11BNZ | -0.968 | -0.154 | -0.007 | 109 | 99.80 | -0.103 | -0.023 | 0.001 | 241 | 4.14 |
| 139 | trans-2-Octenal | TOCT2EAL | -0.875 | 0.372 | -0.192 | 52 | 99.91 | -0.095 | 0.045 | 0.030 | 210 | 4.58 |
| 140 | m-Ethyl-Styrene | MESTYNE | -0.680 | -0.447 | 0.037 | 136 | 99.74 | -0.072 | -0.060 | -0.008 | 92 | 5.97 |
| 141 | 5-Methyl-2-Heptanone | M5HPT2ONE | -0.969 | -0.140 | 0.016 | 73 | 99.88 | -0.104 | -0.021 | -0.002 | 234 | 4.23 |
| 142 | 2-Decanone | DEC2ONE | -0.844 | -0.199 | -0.311 | 215 | 99.23 | -0.090 | -0.029 | 0.047 | 97 | 5.78 |
| 143 | 1-Octen-3-ol | OCT3E1OL | -0.893 | -0.179 | 0.079 | 232 | 99.09 | -0.095 | -0.025 | -0.011 | 170 | 5.02 |
| 144 | trans,trans-2,4-Heptadienal | TTHPT22DEAL | 0.605 | -0.075 | -0.158 | 107 | 99.81 | 0.065 | -0.008 | 0.025 | 102 | 5.72 |
| 145 | 1-Heptanol | HPT1OL | 0.805 | 0.049 | -0.190 | 203 | 99.41 | 0.086 | 0.008 | 0.031 | 203 | 4.65 |
| 146 | cis,cis-3,5-Octadiene | CCOCT35DENE | 0.589 | -0.246 | -0.444 | 261 | 98.28 | 0.064 | -0.032 | 0.066 | 24 | 8.19 |
| 147 | 2-Oxo-Methyl Ester Propanoic Acid | OM2ESTPPA | 0.509 | -0.710 | 0.283 | 160 | 99.66 | 0.056 | -0.090 | -0.043 | 193 | 4.80 |
| 148 | Dihydromyrcenol | DHMYRCNOL | 0.440 | -0.498 | 0.581 | 269 | 97.64 | 0.048 | -0.062 | -0.088 | 45 | 7.15 |
| 149 | trans-Menthone | TMTHONE | -0.926 | -0.198 | 0.085 | 79 | 99.86 | -0.099 | -0.028 | -0.013 | 248 | 4.01 |
| 150 | Furfural | FURAL | -0.515 | -0.127 | -0.059 | 33 | 99.94 | -0.055 | -0.018 | 0.009 | 6 | 12.44 |
| 151 | Ethanoic Acid | ETNOIC | 0.753 | -0.112 | 0.451 | 250 | 98.80 | 0.081 | -0.012 | -0.070 | 214 | 4.56 |
| 152 | 2-Ethyl-1-Hexanol | E2HX1OL | -0.758 | 0.035 | 0.558 | 187 | 99.51 | -0.081 | 0.004 | -0.085 | 157 | 5.15 |
| 153 | Decanal | DECAL | 0.000 | 0.527 | 0.408 | 228 | 99.12 | -0.001 | 0.069 | -0.061 | 70 | 6.34 |
| 154 | Furfuryl Formate | FURYLFMTE | 0.640 | -0.231 | 0.558 | 70 | 99.88 | 0.069 | -0.027 | -0.086 | 187 | 4.88 |
| 155 | trans-2-Hepten-1-ol | THPT1E2OL | 0.466 | 0.499 | 0.337 | 190 | 99.50 | 0.049 | 0.067 | -0.049 | 154 | 5.17 |
| 156 | 2-Nonanol | NON2OL | 0.299 | -0.230 | -0.891 | 16 | 99.96 | 0.033 | -0.031 | 0.135 | 169 | 5.03 |
| 157 | 1-(2-Furanyl)-Ethanone | FURYLETONE | 0.432 | -0.417 | 0.062 | 54 | 99.91 | 0.047 | -0.053 | -0.013 | 125 | 5.36 |
| 158 | 3,5-Octadien-2-one | OCT35DE2ONE | -0.791 | 0.293 | 0.360 | 162 | 99.66 | -0.086 | 0.037 | -0.053 | 192 | 4.81 |
| 159 | Benzaldehyde | BENZAL | -0.606 | 0.436 | 0.340 | 270 | 97.53 | -0.066 | 0.055 | -0.052 | 29 | 7.99 |
| 160 | Furfuryl Acetate | FURYLACTE | -0.599 | 0.146 | 0.165 | 128 | 99.76 | -0.065 | 0.018 | -0.025 | 8 | 11.39 |
| 161 | Linalool | LINOL | 0.435 | 0.212 | 0.455 | 141 | 99.73 | 0.046 | 0.029 | -0.071 | 178 | 4.93 |
| 162 | β-Myrcene | BMYRCNE | -0.967 | -0.055 | -0.124 | 51 | 99.92 | -0.103 | -0.010 | 0.019 | 250 | 3.93 |
| 163 | 1-Octanol | OCT1OL | 0.725 | 0.573 | 0.145 | 245 | 98.95 | 0.076 | 0.077 | -0.020 | 211 | 4.57 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 164 | trans-p-2-Menthen-1-ol | TMNTH1E2OL | -0.781 | -0.225 | 0.192 | 43 | 99.92 | -0.083 | -0.031 | -0.028 | 216 | 4.52 |
| 165 | Propanoic Acid | PPANOIC | -0.241 | -0.281 | 0.489 | 59 | 99.91 | -0.025 | -0.036 | -0.073 | 137 | 5.28 |
| 166 | 2,3-Butanediol | BT23DIOL | 0.493 | -0.449 | -0.259 | 169 | 99.63 | 0.054 | -0.058 | 0.036 | 63 | 6.43 |
| 167 | Dimethyl Sulfoxide | DMSULFO | 0.660 | -0.352 | 0.237 | 165 | 99.65 | 0.072 | -0.043 | -0.035 | 144 | 5.22 |
| 168 | m-Menth-3-ene | MMTH3ENE | 0.589 | -0.607 | 0.353 | 58 | 99.91 | 0.065 | -0.077 | -0.056 | 199 | 4.71 |
| 169 | Trans-(2-Ethylcyclopentyl)-Methanol | T2ECYPTMTOL | 0.805 | 0.336 | -0.115 | 239 | 99.01 | 0.085 | 0.046 | 0.019 | 152 | 5.18 |
| 170 | Bornyl Acetate | BORNYLACTE | 0.817 | 0.263 | 0.130 | 189 | 99.51 | 0.087 | 0.037 | -0.018 | 224 | 4.41 |
| 171 | 4-Cyclopentene-1,3-dione | CYPT4E13DONE | 0.445 | -0.299 | 0.402 | 39 | 99.94 | 0.048 | -0.037 | -0.064 | 167 | 5.06 |
| 172 | Menthol | MNTHOL | -0.942 | -0.255 | -0.065 | 65 | 99.89 | -0.100 | -0.036 | 0.009 | 257 | 3.84 |
| 173 | 2-Undecanone | UNDEC2ONE | 0.356 | -0.159 | -0.103 | 186 | 99.52 | 0.039 | -0.020 | 0.013 | 69 | 6.36 |
| 174 | 2-(2-Furanyl)-Furan | FURYLFUR | 0.578 | 0.403 | 0.382 | 255 | 98.70 | 0.061 | 0.054 | -0.059 | 116 | 5.43 |
| 175 | trans-2-Octen-1-ol | TOCT1E2OL | 0.577 | 0.771 | 0.151 | 183 | 99.55 | 0.060 | 0.102 | -0.021 | 236 | 4.22 |
| 176 | trans-2-Nonen-1-ol | TNON1E2OL | -0.959 | 0.068 | 0.128 | 196 | 99.45 | -0.103 | 0.007 | -0.019 | 251 | 3.89 |
| 177 | Diethylene Glycol Ethyl Ether | DENGOLEETHR | -0.040 | 0.292 | 0.811 | 258 | 98.60 | -0.005 | 0.039 | -0.123 | 27 | 8.06 |
| 179 | cis-p-2-Menthen-1-ol | CMNTH1E2OL | 0.109 | -0.092 | 0.218 | 71 | 99.88 | 0.012 | -0.011 | -0.031 | 4 | 13.10 |
| 180 | β-Cyclocitral | BCYCITAL | -0.893 | 0.239 | 0.049 | 121 | 99.78 | -0.096 | 0.029 | -0.006 | 225 | 4.40 |
| 181 | Benzeneacetaldehyde | BENZACETAL | -0.441 | -0.515 | 0.459 | 212 | 99.31 | -0.046 | -0.067 | -0.072 | 197 | 4.73 |
| 182 | 1-Nonanol | NON1OL | 0.571 | 0.027 | -0.709 | 80 | 99.85 | 0.061 | 0.004 | 0.109 | 182 | 4.92 |
| 183 | Furfuryl Alcohol | FURFOL | 0.007 | 0.269 | 0.420 | 246 | 98.94 | 0.000 | 0.035 | -0.066 | 84 | 6.09 |
| 184 | Phoracanthol | PHOCATHOL | 0.358 | -0.430 | 0.572 | 18 | 99.95 | 0.039 | -0.054 | -0.089 | 191 | 4.81 |
| 185 | cis-3-Nonen-1-ol | ZNONE3OL | 0.130 | -0.424 | 0.565 | 263 | 98.22 | 0.015 | -0.053 | -0.085 | 81 | 6.12 |
| 186 | cis-Piperitol | CPIPETOL | -0.770 | -0.274 | 0.211 | 19 | 99.95 | -0.082 | -0.037 | -0.031 | 230 | 4.32 |
| 187 | p-Methoxy-Styrene | PMTXYESTYNE | 0.058 | 0.890 | 0.401 | 193 | 99.48 | 0.004 | 0.116 | -0.060 | 229 | 4.33 |
| 188 | (2Z)-3-Ethyl-2,4-Pentadien-1-ol | E3PT1DE24OL | 0.796 | -0.094 | 0.536 | 236 | 99.06 | 0.086 | -0.009 | -0.082 | 231 | 4.31 |
| 189 | Butylene Glycol Monobutyl Ether | BNGOLBTHR | 0.864 | -0.231 | 0.301 | 235 | 99.06 | 0.093 | -0.027 | -0.047 | 161 | 5.09 |
| 190 | α-Terpineol | ATERPINOL | -0.835 | -0.284 | 0.162 | 63 | 99.90 | -0.089 | -0.039 | -0.027 | 218 | 4.51 |
| 191 | 1,5-Cyclooctanedione | CYOCTD15ONE | -0.687 | -0.169 | -0.128 | 194 | 99.47 | -0.073 | -0.024 | 0.020 | 3 | 13.60 |
| 192 | γ-Terpinene | GTERPINE | 0.410 | 0.823 | -0.334 | 204 | 99.40 | 0.042 | 0.107 | 0.053 | 209 | 4.58 |
| 193 | trans-2-Decenol | TDECE2OL | 0.616 | 0.497 | 0.328 | 237 | 99.04 | 0.065 | 0.067 | -0.048 | 160 | 5.10 |
| 194 | 2-Propenoic Acid | PPE2NOIC | 0.215 | -0.430 | 0.559 | 46 | 99.92 | 0.024 | -0.054 | -0.087 | 104 | 5.69 |
| 195 | 2-Undecanol | UNDEC2OL | 0.316 | -0.219 | -0.568 | 62 | 99.90 | 0.035 | -0.029 | 0.084 | 109 | 5.57 |
| 196 | 3-Ethyl-Benzaldehyde | E3BNZAL | -0.571 | 0.193 | 0.678 | 260 | 98.55 | -0.062 | 0.025 | -0.103 | 42 | 7.26 |
| 197 | 3-Hydroxy-Benzaldehyde | HXY3BENZAL | 0.395 | -0.298 | 0.829 | 93 | 99.83 | 0.043 | -0.036 | -0.126 | 162 | 5.09 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 198 | trans-2-Nonene | TNONENE | 0.231 | -0.649 | -0.050 | 231 | 99.10 | 0.027 | -0.084 | 0.004 | 155 | 5.15 |
| 199 | 2-Methyl-2-Pentenal | M2PNTE2AL | -0.017 | -0.478 | 0.832 | 206 | 99.39 | -0.001 | -0.060 | -0.128 | 179 | 4.93 |
| 200 | cis-5-Decenol | CDEC5E1OL | 0.271 | -0.241 | -0.848 | 175 | 99.61 | 0.030 | -0.033 | 0.128 | 164 | 5.08 |
| 201 | trans-Piperitol | TPIPETOL | -0.760 | -0.287 | 0.181 | 34 | 99.94 | -0.081 | -0.038 | -0.027 | 223 | 4.46 |
| 202 | 4-Ethyl-Benzaldehyde | E4BNZAL | -0.552 | 0.702 | 0.299 | 244 | 98.97 | -0.061 | 0.090 | -0.044 | 177 | 4.94 |
| 203 | Naphthalene | NPHNE | 0.683 | 0.452 | 0.511 | 157 | 99.67 | 0.072 | 0.062 | -0.076 | 200 | 4.70 |
| 204 | 1-Decanol | DEC1OL | 0.188 | -0.398 | 0.379 | 233 | 99.07 | 0.021 | -0.051 | -0.059 | 68 | 6.38 |
| 205 | Cyclodecane | CDECANE | 0.474 | -0.303 | 0.637 | 221 | 99.19 | 0.052 | -0.037 | -0.099 | 174 | 4.99 |
| 206 | trans,trans-2,4-Decadienal | TTDEC24DENAL | 0.410 | 0.895 | 0.056 | 171 | 99.62 | 0.042 | 0.117 | -0.007 | 242 | 4.10 |
| 207 | 1,2-Cyclopentanedione | CPT12DONE | 0.469 | -0.612 | 0.564 | 83 | 99.85 | 0.052 | -0.077 | -0.087 | 232 | 4.29 |
| 208 | Cyclodecene | CDECENE | 0.784 | -0.180 | 0.295 | 202 | 99.41 | 0.085 | -0.020 | -0.044 | 207 | 4.62 |
| 209 | cis-4-Decenol | CDEC4E1OL | -0.427 | -0.543 | -0.288 | 199 | 99.42 | -0.044 | -0.072 | 0.041 | 134 | 5.32 |
| 210 | 1-Phenyl-2-Butanone | PHYLBT2ONE | 0.045 | 0.799 | -0.295 | 226 | 99.13 | 0.003 | 0.103 | 0.047 | 76 | 6.20 |
| 211 | Phenethyl Alcohol | MBNZMETOL | 0.081 | -0.321 | 0.709 | 145 | 99.70 | 0.009 | -0.039 | -0.106 | 176 | 4.94 |
| 212 | trans,cis-2,4-Decadienal | TCDEC24DENAL | 0.321 | 0.937 | 0.073 | 75 | 99.87 | 0.032 | 0.122 | -0.009 | 247 | 4.01 |
| 213 | 2-Cyclohexenol | CHEX2E1OL | 0.508 | -0.607 | 0.587 | 53 | 99.91 | 0.056 | -0.076 | -0.090 | 228 | 4.34 |
| 214 | 2-Ethyl Hexanoic Acid | E2HEXOIC | -0.020 | 0.751 | 0.638 | 67 | 99.88 | -0.004 | 0.098 | -0.096 | 226 | 4.39 |
| 215 | 3-Methyl-1,2-Cyclopentanedione | M3CPT12DONE | 0.454 | -0.394 | 0.369 | 74 | 99.87 | 0.050 | -0.049 | -0.057 | 150 | 5.20 |
| 216 | trans-Cinnamaldehyde | TCINAMAL | -0.047 | -0.086 | 0.962 | 138 | 99.74 | -0.005 | -0.009 | -0.146 | 83 | 6.10 |
| 217 | Heptanoic Acid | HEPTOIC | -0.624 | 0.170 | 0.717 | 166 | 99.64 | -0.067 | 0.022 | -0.109 | 219 | 4.51 |
| 218 | Mequinol | MEQNOL | 0.452 | 0.445 | 0.288 | 131 | 99.76 | 0.047 | 0.060 | -0.041 | 120 | 5.39 |
| 219 | 2,4,5-Trihydroxypyrimidine | THDXYPYMNE | 0.175 | -0.459 | 0.511 | 205 | 99.40 | 0.020 | -0.058 | -0.080 | 151 | 5.18 |
| 220 | cis-Cinnamaldehyde | CCINAMAL | -0.160 | -0.219 | 0.734 | 268 | 97.65 | -0.017 | -0.027 | -0.113 | 106 | 5.64 |
| 221 | Benzenemethanol | BENZMTOL | 0.378 | 0.760 | 0.404 | 254 | 98.72 | 0.038 | 0.100 | -0.059 | 185 | 4.90 |
| 222 | Mesitaldehyde | MESIAL | -0.400 | 0.287 | 0.752 | 249 | 98.82 | -0.044 | 0.038 | -0.112 | 121 | 5.39 |
| 223 | 2-Ethylhexyl Ester Octanoic Acid | EHESTOA | 0.012 | -0.331 | -0.031 | 134 | 99.75 | 0.002 | -0.042 | 0.007 | 115 | 5.44 |
| 224 | Benzeneethanol | BENZETOL | 0.223 | -0.317 | 0.827 | 164 | 99.65 | 0.025 | -0.039 | -0.126 | 175 | 4.98 |
| 225 | 1,4-Butanediol | BT14DIOL | 0.364 | -0.299 | 0.760 | 262 | 98.25 | 0.040 | -0.036 | -0.118 | 136 | 5.29 |
| 226 | β-Ionone | BIONNE | -0.852 | 0.417 | 0.155 | 197 | 99.44 | -0.093 | 0.052 | -0.022 | 227 | 4.39 |
| 227 | 2-Methyl-1,4-Benzenediol | M2BNZ14DIOL | 0.571 | -0.530 | 0.559 | 103 | 99.81 | 0.063 | -0.066 | -0.086 | 126 | 5.35 |
| 228 | 2-Ethyl Heptanoic Acid | EHPTOIC | 0.288 | -0.086 | -0.857 | 238 | 99.02 | 0.031 | -0.012 | 0.131 | 75 | 6.23 |
| 229 | 1-Dodecanol | DODEC1OL | -0.520 | 0.331 | 0.355 | 217 | 99.22 | -0.057 | 0.042 | -0.055 | 59 | 6.49 |
| 230 | Benzalacetone | BNZONE | -0.040 | -0.273 | 0.808 | 220 | 99.19 | -0.004 | -0.034 | -0.125 | 135 | 5.32 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 231 | Maltol | MALTOL | 0.294 | -0.349 | 0.553 | 23 | 99.95 | 0.032 | -0.043 | -0.085 | 85 | 6.09 |
| 232 | 2-Acetylpyrrole | ACTLPYROLE | 0.467 | -0.615 | 0.320 | 127 | 99.76 | 0.052 | -0.078 | -0.052 | 190 | 4.82 |
| 233 | 2,4-Decadien-1-ol | DEC24DIE1OL | 0.907 | -0.062 | 0.116 | 218 | 99.22 | 0.097 | -0.005 | -0.017 | 103 | 5.69 |
| 234 | Levoglucosenone | LEVGLCONE | 0.425 | -0.135 | 0.463 | 213 | 99.31 | 0.046 | -0.015 | -0.071 | 58 | 6.51 |
| 235 | Phenol | PHEOL | 0.003 | 0.609 | -0.067 | 267 | 97.78 | -0.001 | 0.078 | 0.010 | 37 | 7.64 |
| 236 | 1-(2-Furanyl)-2-Hydroxy-Ethanone | FURYLHXYEONE | 0.488 | -0.594 | 0.072 | 87 | 99.84 | 0.054 | -0.076 | -0.014 | 122 | 5.38 |
| 237 | 4,6-Dimethyl-Dodecane | DM45DODCANE | 0.299 | -0.590 | 0.371 | 153 | 99.68 | 0.034 | -0.075 | -0.058 | 124 | 5.37 |
| 238 | Ethyl Ester Decanoic Acid | EESDECA | 0.799 | -0.032 | -0.382 | 113 | 99.79 | 0.086 | -0.003 | 0.059 | 222 | 4.46 |
| 239 | 1-Methyl-4-Piperidinone | M1PIP4DIONE | -0.890 | -0.362 | 0.204 | 152 | 99.69 | -0.094 | -0.049 | -0.031 | 258 | 3.83 |
| 240 | 2,2-Dimethyl-3-Heptanone | DM22HPT3ONE | 0.154 | -0.289 | 0.104 | 104 | 99.81 | 0.017 | -0.037 | -0.016 | 49 | 6.91 |
| 241 | Octanoic Acid | OCTOIC | -0.113 | -0.098 | 0.881 | 216 | 99.22 | -0.012 | -0.011 | -0.134 | 142 | 5.23 |
| 242 | 1,3-Dihydroxy-2-Propanone | DHYPPAONE | 0.429 | -0.422 | 0.581 | 177 | 99.59 | 0.047 | -0.052 | -0.088 | 186 | 4.89 |
| 243 | 2-Phenoxy-Ethanol | PHENXYOL | -0.969 | 0.011 | 0.024 | 105 | 99.81 | -0.104 | -0.001 | -0.003 | 259 | 3.77 |
| 244 | Isophthalaldehyde | ISOPHTAL | -0.821 | 0.078 | 0.307 | 271 | 96.23 | -0.088 | 0.008 | -0.048 | 183 | 4.92 |
| 245 | Cyclotetradecane | CTTDECANE | 0.352 | -0.184 | 0.869 | 66 | 99.89 | 0.038 | -0.021 | -0.132 | 163 | 5.09 |
| 246 | Nonanoic Acid | NONOIC | -0.785 | 0.441 | 0.411 | 97 | 99.82 | -0.085 | 0.056 | -0.062 | 252 | 3.88 |
| 247 | 2-Ethyl-Phenol | E2PHEOL | 0.480 | 0.349 | 0.188 | 265 | 98.11 | 0.050 | 0.047 | -0.025 | 129 | 5.35 |
| 248 | 2-Methoxy-4-Vinyl-Phenol | MXY2VYL4PHEOL | 0.862 | -0.335 | 0.011 | 143 | 99.72 | 0.093 | -0.041 | -0.001 | 254 | 3.86 |
| 249 | 4-Methylimidazole | M4IMDZOLE | -0.968 | 0.025 | -0.029 | 150 | 99.69 | -0.104 | 0.001 | 0.005 | 255 | 3.86 |
| 250 | m-tert-Butyl-Toluene | MTBTLNE | -0.184 | 0.249 | 0.526 | 251 | 98.80 | -0.020 | 0.032 | -0.082 | 40 | 7.27 |
| 251 | Syringol | SYNGOL | 0.390 | -0.520 | 0.602 | 266 | 97.81 | 0.043 | -0.065 | -0.093 | 62 | 6.46 |
| 252 | Decanoic Acid | DECOIC | -0.421 | 0.130 | 0.872 | 208 | 99.36 | -0.046 | 0.018 | -0.132 | 180 | 4.92 |
| 253 | 3-Hydroxy-2,3-Dihydro-Maltol | HX3DH23MALTOL | 0.409 | 0.076 | 0.778 | 112 | 99.79 | 0.044 | 0.012 | -0.119 | 194 | 4.78 |
| 254 | 5-Hydroxy-Maltol | HX5MALTOL | -0.171 | -0.157 | 0.246 | 158 | 99.67 | -0.018 | -0.021 | -0.040 | 79 | 6.16 |
| 255 | Triethylene Glycol | TETYNEGLOL | -0.034 | 0.166 | 0.398 | 56 | 99.91 | -0.004 | 0.023 | -0.058 | 118 | 5.42 |
| 256 | Benzoic Acid | BNZOIC | 0.599 | -0.370 | -0.107 | 182 | 99.56 | 0.065 | -0.046 | 0.017 | 78 | 6.18 |
| 257 | 2-Methyl-Benzaldehyde | M2BNZAL | 0.604 | 0.023 | -0.252 | 115 | 99.79 | 0.065 | 0.004 | 0.041 | 159 | 5.12 |
| 258 | Undecanoic Acid | UNDECOIC | -0.852 | -0.004 | 0.506 | 130 | 99.76 | -0.091 | -0.002 | -0.077 | 249 | 3.94 |
| 259 | 4-Pyridinol | PYRDINOL | -0.132 | -0.288 | 0.864 | 102 | 99.81 | -0.013 | -0.036 | -0.131 | 166 | 5.06 |
| 260 | 4-Amino-Phenol | AMIPHEOL | 0.447 | -0.551 | 0.574 | 44 | 99.92 | 0.049 | -0.069 | -0.088 | 181 | 4.92 |

[1]VIP - Variable Importance in Projection scores.

**Table S17. Loading results of samples and variables from PCA and PLS based on the relative peak areas of the identified VOCs in sugarcane samples.**

| ID Sample Code | ID Variety Code | PCA | | | PLS | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 1 | 2 | 3 |
| AMA15 | AMA | 0.13 | -0.28 | 0.31 | n.a. | n.a. | n.a. |
| AMA17 | AMA | 0.22 | -0.29 | 0.46 | n.a. | n.a. | n.a. |
| RAD15 | RAD | 0.13 | -0.13 | -0.25 | n.a. | n.a. | n.a. |
| RAD17 | RAD | 0.20 | -0.14 | -0.22 | n.a. | n.a. | n.a. |
| ROX15 | ROX | 0.00 | 0.61 | 0.11 | n.a. | n.a. | n.a. |
| ROX17 | ROX | 0.06 | 0.69 | 0.15 | n.a. | n.a. | n.a. |
| VER15 | VER | 0.12 | -0.11 | 0.18 | n.a. | n.a. | n.a. |
| VER17 | VER | 0.18 | -0.08 | 0.29 | n.a. | n.a. | n.a. |
| VIO15 | VIO | 0.12 | -0.06 | -0.50 | n.a. | n.a. | n.a. |
| VIO17 | VIO | 0.17 | 0.01 | -0.52 | n.a. | n.a. | n.a. |
| CAN15 | CAN | -0.68 | -0.11 | 0.01 | n.a. | n.a. | n.a. |
| CAN17 | CAN | -0.64 | -0.10 | -0.02 | n.a. | n.a. | n.a. |
| Centroid (AMA) | AMA | n.a. | n.a. | n.a. | 0.03 | -0.05 | -0.09 |
| Centroid (RAD) | RAD | n.a. | n.a. | n.a. | 0.03 | -0.03 | 0.05 |
| Centroid (ROX) | ROX | n.a. | n.a. | n.a. | 0.00 | 0.12 | -0.03 |
| Centroid (VER) | VER | n.a. | n.a. | n.a. | 0.02 | -0.02 | -0.05 |
| Centroid (VIO) | VIO | n.a. | n.a. | n.a. | 0.02 | -0.01 | 0.12 |
| Centroid (CAN) | CAN | n.a. | n.a. | n.a. | -0.10 | -0.02 | 0.00 |

n.a. – not available

**Table S18. Scores results of all cases from PCA and PLS based on the relative peak areas of the identified VOCs in SC samples.**

| ID Replicate Number | ID Replicate Code | PCA | | | PLS | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 1 | 2 | 3 |
| 1 | AMA15A | 3.97 | -7.19 | 6.70 | 4.16 | -7.00 | -6.97 |
| 2 | AMA15B | 3.93 | -7.08 | 6.55 | 4.11 | -6.90 | -6.81 |
| 3 | AMA15C | 3.95 | -7.13 | 6.63 | 4.14 | -6.95 | -6.89 |
| 4 | AMA17A | 5.87 | -6.99 | 8.23 | 6.02 | -6.75 | -8.40 |
| 5 | AMA17B | 7.32 | -7.44 | 11.42 | 7.47 | -7.13 | -11.54 |
| 6 | AMA17C | 6.60 | -7.22 | 9.83 | 6.75 | -6.94 | -9.97 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 7 | RAD15A | 4.04 | -3.45 | -5.10 | 4.15 | -3.48 | 4.88 |
| 8 | RAD15B | 4.14 | -3.41 | -5.69 | 4.24 | -3.45 | 5.47 |
| 9 | RAD15C | 4.09 | -3.43 | -5.39 | 4.20 | -3.46 | 5.17 |
| 10 | RAD17A | 6.31 | -3.60 | -4.66 | 6.39 | -3.57 | 4.46 |
| 11 | RAD17B | 5.76 | -3.65 | -4.78 | 5.85 | -3.62 | 4.57 |
| 12 | RAD17C | 6.03 | -3.62 | -4.72 | 6.12 | -3.60 | 4.51 |
| 13 | ROX15A | 0.04 | 13.93 | 1.46 | -0.29 | 13.99 | -1.35 |
| 14 | ROX15B | -0.10 | 16.75 | 3.47 | -0.50 | 16.81 | -3.29 |
| 15 | ROX15C | -0.03 | 15.34 | 2.46 | -0.39 | 15.40 | -2.32 |
| 16 | ROX17A | 1.51 | 16.07 | 2.58 | 1.10 | 16.14 | -2.40 |
| 17 | ROX17B | 2.11 | 18.60 | 3.80 | 1.63 | 18.68 | -3.55 |
| 18 | ROX17C | 1.81 | 17.33 | 3.19 | 1.37 | 17.41 | -2.98 |
| 19 | VER15A | 3.86 | -2.76 | 4.27 | 3.93 | -2.57 | -4.16 |
| 20 | VER15B | 3.27 | -2.92 | 3.34 | 3.36 | -2.76 | -3.26 |
| 21 | VER15C | 3.56 | -2.84 | 3.80 | 3.65 | -2.67 | -3.71 |
| 22 | VER17A | 5.42 | -2.23 | 5.81 | 5.45 | -2.00 | -5.62 |
| 23 | VER17B | 5.77 | -1.96 | 6.47 | 5.80 | -1.72 | -6.22 |
| 24 | VER17C | 5.59 | -2.10 | 6.14 | 5.62 | -1.86 | -5.92 |
| 25 | VIO15A | 3.59 | -1.54 | -10.65 | 3.65 | -1.61 | 10.74 |
| 26 | VIO15B | 3.53 | -1.41 | -10.70 | 3.58 | -1.48 | 10.77 |
| 27 | VIO15C | 3.56 | -1.48 | -10.67 | 3.62 | -1.54 | 10.75 |
| 28 | VIO17A | 5.12 | 0.26 | -11.24 | 5.12 | 0.16 | 11.35 |
| 29 | VIO17B | 5.16 | 0.22 | -11.16 | 5.16 | 0.13 | 11.28 |
| 30 | VIO17C | 5.14 | 0.24 | -11.20 | 5.14 | 0.15 | 11.32 |
| 31 | CAN15A | -19.48 | -2.89 | -0.21 | -19.41 | -3.30 | 0.18 |
| 32 | CAN15B | -22.09 | -2.36 | 0.73 | -22.02 | -2.82 | -0.71 |
| 33 | CAN15C | -20.78 | -2.63 | 0.26 | -20.72 | -3.06 | -0.26 |
| 34 | CAN17A | -19.37 | -2.57 | -0.61 | -19.32 | -2.99 | 0.56 |
| 35 | CAN17B | -19.67 | -2.36 | -0.05 | -19.63 | -2.78 | 0.02 |
| 36 | CAN17C | -19.52 | -2.46 | -0.33 | -19.48 | -2.89 | 0.29 |

**Table S19. CDF Coefficients and Highest Probability Classification results of samples from LDA after matrix reduction method obtained from One-way ANOVA test based on the relative peak areas of identified VOCs in SC samples.**

| ID Replicate Code | ID Variety Code | LDA | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | CDF[1] | | | CDF[1] Class Mean | | | Highest Probability Classification | | |
| | | 1 | 2 | 3 | 1 | 2 | 3 | First | Second | Third |
| AMA15A | AMA | 4761.06 | 1257.08 | 2488.92 | 4760.20 | 1257.23 | 2488.64 | AMA | ROX | VER |
| AMA15B | | 4761.10 | 1257.14 | 2488.90 | | | | AMA | ROX | VER |
| AMA15C | | 4758.43 | 1257.46 | 2488.07 | | | | AMA | ROX | VER |
| AMA17A | | 4761.10 | 1257.78 | 2488.49 | | | | AMA | ROX | VER |
| AMA17B | | 4761.12 | 1257.82 | 2488.43 | | | | AMA | ROX | VER |
| AMA17C | | 4758.39 | 1256.10 | 2489.02 | | | | AMA | ROX | VER |
| RAD15A | RAD | 3911.76 | 2210.37 | -309.59 | 3910.84 | 2210.20 | -309.34 | RAD | ROX | VER |
| RAD15B | | 3911.79 | 2210.40 | -309.69 | | | | RAD | ROX | VER |
| RAD15C | | 3908.97 | 2209.85 | -308.73 | | | | RAD | ROX | VER |
| RAD17A | | 3911.93 | 2210.73 | -309.64 | | | | RAD | ROX | VER |
| RAD17B | | 3911.99 | 2210.78 | -309.62 | | | | RAD | ROX | VER |
| RAD17C | | 3908.57 | 2209.08 | -308.77 | | | | RAD | ROX | VER |
| ROX15A | ROX | -3224.84 | 839.81 | 1128.66 | -3225.08 | 840.17 | 1127.53 | ROX | RAD | VER |
| ROX15B | | -3224.85 | 839.81 | 1128.66 | | | | ROX | RAD | VER |
| ROX15C | | -3225.53 | 840.91 | 1125.26 | | | | ROX | RAD | VER |
| ROX17A | | -3225.31 | 840.37 | 1128.06 | | | | ROX | RAD | VER |
| ROX17B | | -3225.32 | 840.33 | 1128.10 | | | | ROX | RAD | VER |
| ROX17C | | -3224.60 | 839.81 | 1126.45 | | | | ROX | RAD | VER |
| VER15A | VER | -1884.33 | 3365.55 | -2672.50 | -1884.36 | 3364.28 | -2672.69 | VER | ROX | RAD |
| VER15B | | -1884.34 | 3365.57 | -2672.54 | | | | VER | ROX | RAD |
| VER15C | | -1884.38 | 3361.76 | -2673.06 | | | | VER | ROX | RAD |
| VER17A | | -1883.76 | 3363.48 | -2673.56 | | | | VER | ROX | RAD |
| VER17B | | -1883.76 | 3363.52 | -2673.63 | | | | VER | ROX | RAD |
| VER17C | | -1885.60 | 3365.81 | -2670.84 | | | | VER | ROX | RAD |
| VIO15A | VIO | 4543.55 | -5357.89 | -1357.82 | 4543.66 | -5357.13 | -1357.94 | VIO | ROX | VER |
| VIO15B | | 4543.59 | -5357.81 | -1357.92 | | | | VIO | ROX | VER |
| VIO15C | | 4543.82 | -5355.68 | -1358.06 | | | | VIO | ROX | VER |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| VIO17A | | 4544.39 | -5357.78 | -1356.69 | | | | VIO | ROX | VER |
| VIO17B | | 4544.36 | -5357.80 | -1356.61 | | | | VIO | ROX | VER |
| VIO17C | | 4542.25 | -5355.81 | -1360.55 | | | | VIO | ROX | VER |
| CAN15A | | -8105.75 | -2314.18 | 723.82 | | | | CAN | ROX | VER |
| CAN15B | | -8105.77 | -2314.20 | 723.84 | | | | CAN | ROX | VER |
| CAN15C | CAN | -8104.27 | -2315.90 | 723.73 | -8105.26 | -2314.76 | 723.80 | CAN | ROX | VER |
| CAN17A | | -8105.18 | -2313.94 | 724.55 | | | | CAN | ROX | VER |
| CAN17B | | -8105.18 | -2313.94 | 724.55 | | | | CAN | ROX | VER |
| CAN17C | | -8105.42 | -2316.39 | 722.29 | | | | CAN | ROX | VER |

[1]CDF - Canonical Discriminant Function Coefficients.

**Table S20. Information summary of PLS based only on the relative peak areas of the 23 most predictive VOCs identified in SC samples.**

| Analysis | Component | $R^2X$ | Eigenvalues | $R^2Y$ | $Q^2$ | Significance | Iterations |
|---|---|---|---|---|---|---|---|
| PLS | 1 | 0,4137 | 11,997 | 0,0908 | 0,0292 | S | 10 |
| | 2 | 0,2058 | 5,969 | 0,0909 | 0,0287 | S | 23 |
| | 3 | 0,1638 | 4,750 | 0,0909 | 0,0365 | S | 20 |
| | 4 | 0,1281 | 3,714 | 0,0908 | 0,0571 | S | 7 |
| | 5 | 0,0806 | 2,337 | 0,0909 | 0,0856 | S | 3 |
| | 6 | 0,0023 | 0,062 | 0,0694 | 0,0410 | S | 12 |
| | 7 | 0,0019 | 0,055 | 0,0803 | 0,1272 | S | 7 |
| | 8 | 0,0010 | 0,029 | 0,0854 | 0,1699 | S | 16 |
| | 9 | 0,0006 | 0,018 | 0,0777 | 0,1586 | S | 14 |
| | 10 | 0,0004 | 0,013 | 0,0788 | 0,2370 | S | 9 |
| | 11 | 0,0005 | 0,010 | 0,0503 | -0,0589 | S | 15 |
| | 12 | 0,0003 | 0,009 | 0,0446 | 0,3147 | S | 5 |
| | 13 | 0,0002 | 0,005 | 0,0115 | -0,0270 | S | 21 |
| | 14 | 0,0002 | 0,005 | 0,0079 | 0,0002 | S | 9 |

**Table S21. Results of variables from LDA after matrix reduction method to 20 % of original dimension according with higher on the VIP scores values from the PLS analysis based on the relative peak areas of the identified VOCs in SC samples.**

| Volatile Organic Compounds | Abbreviations | PLS | | LDA | |
|---|---|---|---|---|---|
| | | VIP[1] | | W[2] | F[3] |
| | | Importance | Power (x 100) | | |
| 2-Methyl-2-Cyclopenten-1-one | M2CY2PT1EONE | 1 | 14.64 | Removed from analysis. | |
| Ethyl Ether | EETHR | 2 | 13.71 | 3.82E-67 | 5.90E+66 |
| 1.5-Cyclooctanedione | CYOCTD15ONE | 3 | 13.60 | Removed from analysis. | |
| cis-p-2-Menthen-1-ol | CMNTH1E2OL | 4 | 13.10 | Removed from analysis. | |
| 2-Ethyl-Furan | E2FUR | 5 | 13.06 | 7.33E-73 | 4.55E+72 |
| Furfural | FURAL | 6 | 12.44 | Removed from analysis. | |
| 2-Methyl-1-Pentene | M2PT1ENE | 7 | 11.84 | Removed from analysis. | |
| Furfuryl Acetate | FURYLACTE | 8 | 11.39 | Removed from analysis. | |
| Methyl Ester Acetic Acid | MESTAA | 9 | 10.64 | 2.54E-66 | 8.85E+65 |
| 1.4-Pentadiene | PT14DIENE | 10 | 10.63 | 1.93E-66 | 1.16E+66 |
| cis-4-Methyl-2-Pentene | CM4PT2ENE | 11 | 9.87 | Removed from analysis. | |
| Crotonal | CROTNAL | 12 | 9.83 | 2.02E-59 | 7.93E+58 |
| cis-3-Methyl-2-Pentene | CM3PT2ENE | 13 | 9.66 | 1.67E-66 | 1.35E+66 |
| trans-2-Pentenol | TPT1E2OL | 14 | 9.33 | Removed from analysis. | |
| Furan | FUR | 15 | 9.23 | 1.40E-66 | 1.60E+66 |
| 3-Octen-2-one | OCT2E3ONE | 16 | 9.03 | Removed from analysis. | |
| trans-Piperylene | TPIPERLNE | 17 | 8.91 | 3.22E-73 | 1.04E+73 |
| 4-Methyl-Decane | M4DCANE | 18 | 8.83 | 5.05E-73 | 6.60E+72 |
| 2.4-Dimethyl-Heptane | DM24HPTANE | 19 | 8.78 | Removed from analysis. | |
| 4-Methyl-4-Heptanol | M4HPT4OL | 20 | 8.65 | Removed from analysis. | |
| 2-Hexanone | HX2ONE | 21 | 8.45 | 1.01E-72 | 3.31E+72 |
| 3-Hydroxy-2-Butanone | HXY3BT2ONE | 22 | 8.41 | Removed from analysis. | |
| Benzene | BNZ | 23 | 8.24 | 2.43E-66 | 9.26E+65 |
| cis.cis-3.5-Octadiene | CCOCT35DENE | 24 | 8.19 | 1.25E-66 | 1.79E+66 |
| 2-Methyl-Furan | M2FUR | 25 | 8.19 | Removed from analysis. | |
| 5-Methyl-4-Hexen-3-one | M5HX3E4ONE | 26 | 8.17 | Removed from analysis. | |
| Diethylene Glycol Ethyl Ether | DENGOLEETHR | 27 | 8.06 | Removed from analysis. | |

| | | | | | |
|---|---|---|---|---|---|
| 4-Methyl-Heptane | M4HPTANE | 28 | 7.99 | 2.38E-59 | 6.72E+58 |
| Benzaldehyde | BENZAL | 29 | 7.99 | Removed from analysis. | |
| Nonane | NNANE | 30 | 7.97 | 4.70E-60 | 3.40E+59 |
| cis-Piperylene | CPIPERLNE | 31 | 7.88 | 1.27E-59 | 1.26E+59 |
| cis-3-Hexen-1-ol | CHX1E3OL | 32 | 7.87 | Removed from analysis. | |
| Butyl Ester 2-Propenoic Acid | BTESTPPEA | 33 | 7.86 | 5.45E-66 | 4.13E+65 |
| 2.3-Dimethyl-Heptane | DM23HPTANE | 34 | 7.81 | 3.98E-66 | 5.66E+65 |
| Ethylene Glycol Ethyl Ether | ENGOLEETHR | 35 | 7.79 | 1.29E-59 | 1.24E+59 |
| Ethyl-Benzene | ETBNZ | 36 | 7.66 | Removed from analysis. | |
| Phenol | PHEOL | 37 | 7.64 | Removed from analysis. | |
| Pseudocumene | PSEUDCUMNE | 38 | 7.59 | Removed from analysis. | |
| 5-Methyl-2-Heptanone | M5HPTAONE | 39 | 7.54 | Removed from analysis. | |
| m-tert-Butyl-Toluene | MTBTLNE | 40 | 7.27 | Removed from analysis. | |
| Ethanal | ETAL | 41 | 7.26 | 3.09E-66 | 7.28E+65 |
| 3-Ethyl-Benzaldehyde | E3BNZAL | 42 | 7.26 | Removed from analysis. | |
| 5-Methyl-Decane | M5DCANE | 43 | 7.24 | Removed from analysis. | |
| 1-Penten-3-ol | PT1E3OL | 44 | 7.22 | 2.94E-59 | 5.45E+58 |
| Dihydromyrcenol | DHMYRCNOL | 45 | 7.15 | Removed from analysis. | |
| 1-Pentene | PT1ENE | 46 | 7.13 | Removed from analysis. | |
| β-Phellandrene | BPHELDNE | 47 | 7.12 | 2.07E-59 | 7.74E+58 |
| 3-Methyl-Butanal | M3BTAL | 48 | 7.11 | 1.67E-59 | 9.58E+58 |
| 2.2-Dimethyl-3-Heptanone | DM22HPT3ONE | 49 | 6.91 | Removed from analysis. | |
| 2-Cyclopenten-1-one | CY2PT1EONE | 50 | 6.91 | Removed from analysis. | |
| 3-Methyl-1-Butanol | M3BT1OL | 51 | 6.89 | 7.19E-59 | 2.22E+58 |
| Dimethyl Sulfide | DMSULFI | 52 | 6.80 | Removed from analysis. | |

[1]F - Fischer value from One-way ANOVA test.
[2]W - Wilks value from Linear Discriminant Analysis.
[3]F - Fischer value from Linear Discriminant Analysis.
[4]CDF - Canonical Discriminant Function Coefficients.

**Table S22. ID replicate number, ID replicate code, ID sample code, ID stage code, processing year, processing stage description and producer name of samples from SCH processing stages during 2015-2018 production years.**

| ID Replicate Number | ID Replicate Code | ID Sample Code | ID Stage Code | Processing Year | Processing Stage Description | Producer Name |
|---|---|---|---|---|---|---|
| 1 | S1-15A | S1-15 | S1 | 2015 | Stage 1 - Sugarcane juice, "*guarapa*", extracted by mechanical pressing of sugarcane stalks. Temperature: > 40 ºC | Fábrica de Mel-de-Cana do Ribeiro Seco (Madeira Island, Portugal) |
| 2 | S1-15B | | | | | |
| 3 | S1-15C | | | | | |
| 4 | S1-16A | S1-16 | | 2016 | | |
| 5 | S1-16B | | | | | |
| 6 | S1-16C | | | | | |
| 7 | S1-17A | S1-17 | | 2017 | | |
| 8 | S1-17B | | | | | |
| 9 | S1-17C | | | | | |
| 10 | S1-18A | S1-18 | | 2018 | | |
| 11 | S1-18B | | | | | |
| 12 | S1-18C | | | | | |
| 13 | S2-15A | S2-15 | S2 | 2015 | Stage 2 - Sugarcane juice is directly conducted to a first and heated filtering process. Temperature: > 80 ºC | |
| 14 | S2-15B | | | | | |
| 15 | S2-15C | | | | | |
| 16 | S2-16A | S2-16 | | 2016 | | |
| 17 | S2-16B | | | | | |
| 18 | S2-16C | | | | | |
| 19 | S2-17A | S2-17 | | 2017 | | |
| 20 | S2-17B | | | | | |
| 21 | S2-17C | | | | | |
| 22 | S2-18A | S2-18 | | 2018 | | |
| 23 | S2-18B | | | | | |
| 24 | S2-18C | | | | | |
| 25 | S3-15A | S3-15 | S3 | 2015 | Stage 3 - Filtered sugarcane juice is heated for 24h into evaporator and led to a second heated filtering process. Temperature: > 100 ºC | |
| 26 | S3-15B | | | | | |
| 27 | S3-15C | | | | | |
| 28 | S3-16A | S3-16 | | 2016 | | |
| 29 | S3-16B | | | | | |
| 30 | S3-16C | | | | | |
| 31 | S3-17A | S3-17 | | 2017 | | |
| 32 | S3-17B | | | | | |
| 33 | S3-17C | | | | | |
| 34 | S3-18A | S3-18 | | 2018 | | |
| 35 | S3-18B | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 36 | S3-18C | | | | |
| 37 | S4-15A | S4-15 | S4 | 2015 | Stage 4 - Primary syrup is heated for 10h into evaporator and led to a third filtering process. Temperature: > 120 ºC |
| 38 | S4-15B | | | | |
| 39 | S4-15C | | | | |
| 40 | S4-16A | S4-16 | | 2016 | |
| 41 | S4-16B | | | | |
| 42 | S4-16C | | | | |
| 43 | S4-17A | S4-17 | | 2017 | |
| 44 | S4-17B | | | | |
| 45 | S4-17C | | | | |
| 46 | S4-18A | S4-18 | | 2018 | |
| 47 | S4-18B | | | | |
| 48 | S4-18C | | | | |
| 49 | S5-15A | S5-15 | S5 | 2015 | Stage 5 - Final syrup is placed in a reservoir for 6 months, where it cools down naturally. Temperature: 20 ºC (Room Air) |
| 50 | S5-15B | | | | |
| 51 | S5-15C | | | | |
| 52 | S5-16A | S5-16 | | 2016 | |
| 53 | S5-16B | | | | |
| 54 | S5-16C | | | | |
| 55 | S5-17A | S5-17 | | 2017 | |
| 56 | S5-17B | | | | |
| 57 | S5-17C | | | | |
| 58 | S5-18A | S5-18 | | 2018 | |
| 59 | S5-18B | | | | |
| 60 | S5-18C | | | | |

**Table S23. ID number, retention time, main ions (m/z), target ion, match percent, IUPAC name, NIST database, abbreviation, CAS number, molecular formula and main chemical class of identified VOCs in samples from SCH processing stages during 2015-2018 production years.**

| ID Number | RT (min)[a] | m/z | Target Ion | Match Percent (%) | IUPAC Name | NIST Database Name | Abbreviations | CAS Number | Molecular Formula | Main Chemical Class |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 4,253 | 43; 42; 41 | 43 | 86 | pentane | Pentane | PTANE | 109-66-0 | C5H12 | Hydrocarbon |
| 2 | 4,518 | 57; 41; 56 | 57 | 84 | hexane | Hexane | HXANE | 110-54-3 | C6H14 | Hydrocarbon |
| 3 | 4,544 | 59; 45; 74 | 59 | 86 | ethoxyethane | Ethyl Ether | EETHR | 60-29-7 | C4H10O | Ether |
| 4 | 4,586 | 67; 68; 53 | 67 | 90 | penta-1,4-diene | 1,4-Pentadiene | PT14DIENE | 591-93-5 | C5H8 | Hydrocarbon |
| 5 | 4,709 | 47; 48; 45 | 47 | 87 | methanethiol | Methanethiol | METHIOL | 74-93-1 | CH4S | Sulfur |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 6 | 4,903 | 44; 43; 42 | 44 | 88 | acetaldehyde | Ethanal | ETAL | 75-07-0 | C2H4O | Aldehyde |
| 7 | 5,282 | 47; 62; 45 | 47 | 97 | methylsulfanylmethane | Dimethyl Sulfide | DMSULFI | 75-18-3 | C2H6S | Sulfur |
| 8 | 5,713 | 58; 57; 59 | 58 | 79 | propanal | Propanal | PPAL | 123-38-6 | C3H6O | Aldehyde |
| 9 | 5,830 | 68; 39; 40 | 68 | 91 | furan | Furan | FUR | 110-00-9 | C4H4O | Furan |
| 10 | 6,041 | 43; 41; 72 | 72 | 86 | 2-methylpropanal | 2-Methyl-Propanal | MPPAL | 78-84-2 | C4H8O | Aldehyde |
| 11 | 6,255 | 31; 45; 74 | 31 | 80 | ethyl formate | Ethyl Formate | EESTFA | 109-94-4 | C3H6O2 | Ester |
| 12 | 6,632 | 56; 55; 37 | 56 | 78 | prop-2-enal | 2-Propenal | PPENAL | 107-02-8 | C3H4O | Aldehyde |
| 13 | 7,199 | 82; 53; 81 | 82 | 94 | 2-methylfuran | 2-Methyl-Furan | M2FUR | 534-22-5 | C5H6O | Furan |
| 14 | 7,591 | 43; 61; 70 | 43 | 90 | ethyl acetate | Ethyl Acetate | EESTAA | 141-78-6 | C4H8O2 | Ester |
| 15 | 7,906 | 43; 72; 57 | 72 | 78 | butan-2-one | 2-Butanone | BT2ONE | 78-93-3 | C4H8O | Ketone |
| 16 | 8,338 | 57; 41; 58 | 57 | 86 | 2-methylbutanal | 2-Methyl-Butanal | M2BTAL | 96-17-3 | C5H10O | Aldehyde |
| 17 | 8,494 | 44; 41, 43 | 41 | 93 | 3-methylbutanal | 3-Methyl-Butanal | M3BTAL | 590-86-3 | C5H10O | Aldehyde |
| 18 | 8,946 | 31; 45; 46 | 31 | 78 | ethanol | Ethanol | ETOL | 64-17-5 | C2H6O | Alcohol |
| 19 | 9,379 | 78; 77; 52 | 78 | 83 | Benzene | Benzene | BNZ | 71-43-2 | C6H6 | Benzene |
| 20 | 9,569 | 55; 43; 70 | 55 | 80 | but-3-en-2-one | 3-Buten-2-one | BT3ONE | 78-94-4 | C4H6O | Ketone |
| 21 | 10,027 | 81; 53; 96 | 81 | 93 | 2-ethylfuran | 2-Ethyl-Furan | E2FUR | 3208-16-0 | C6H8O | Furan |
| 22 | 10,058 | 96; 95; 43 | 96 | 94 | 2,5-dimethylfuran | 2,5-Dimethyl-Furan | DM25FUR | 625-86-5 | C6H8O | Furan |
| 23 | 10,190 | 57; 75; 102 | 57 | 82 | ethyl propanoate | Ethyl Propanoate | EESTPA | 105-37-3 | C5H10O2 | Ester |
| 24 | 11,053 | 57; 86; 42 | 57 | 79 | pentan-3-one | 3-Pentanone | PT3ONE | 96-22-0 | C5H10O | Ketone |
| 25 | 11,132 | 44; 58; 57 | 58 | 84 | pentanal | Pentanal | PTNAL | 110-62-3 | C5H10O | Aldehyde |
| 26 | 11,412 | 43; 86; 41 | 86 | 80 | butane-2,3-dione | 2,3-Butanedione | BT23DONE | 431-03-8 | C4H6O2 | Ketone |
| 27 | 13,594 | 55; 84; 57 | 55 | 79 | pent-1-en-3-one | 1-Penten-3-one | PT1E3ONE | 1629-58-9 | C5H8O | Ketone |
| 28 | 14,801 | 31; 59; 42 | 31 | 80 | propan-1-ol | 1-Propanol | P1POL | 71-23-8 | C3H8O | Alcohol |
| 29 | 14,903 | 95; 110; 43 | 95 | 86 | 2-ethyl-5-methylfuran | 2-Ethyl-5-Methyl-Furan | E2M5FUR | 1703-52-2 | C7H10O | Furan |
| 30 | 15,111 | 91; 92; 65 | 91 | 94 | toluene | Toluene | TOLNE | 108-88-3 | C7H8 | Benzene |
| 31 | 15,327 | 71; 43; 59 | 71 | 78 | 2-methylbut-3-en-2-ol | 2-Methyl-3-Buten-2-ol | M3BT2OL | 115-18-4 | C5H10O | Alcohol |
| 32 | 16,166 | 101; 55; 73 | 101 | 82 | nonomethyl succinate | Nonomethyl Succinate | METESTBA | 3878-55-5 | C5H8O4 | Ester |
| 33 | 17,382 | 43; 57; 100 | 57 | 83 | pentane-2,3-dione | 2,3-Pentanedione | PTDONE | 600-14-6 | C5H8O2 | Ketone |
| 34 | 18,081 | 94; 45; 79 | 94 | 90 | (methyldisulfanyl)methane | Dimethyl Disulfide | DMDSFD | 624-92-0 | C2H6S2 | Sulfur |
| 35 | 18,284 | 94; 65; 39 | 94 | 78 | 2-ethenylfuran | 2-Ethenyl-Furan | ENYL2FUR | 1487-18-9 | C6H6O | Furan |
| 36 | 18,905 | 44; 56; 43 | 44 | 94 | hexanal | Hexanal | HXAL | 66-25-1 | C6H12O | Aldehyde |
| 37 | 21,231 | 43; 42; 41 | 43 | 90 | 2-methylpropan-1-ol | 2-Methyl-1-Propanol | M2PP1OL | 78-83-1 | C4H10O | Alcohol |
| 38 | 25,434 | 87; 43; 102 | 87 | 82 | methyl 2-ethyl-2-methylpentanoate | Methyl 2-Ethylpentanoate | EMESTPTA | 816-16-0 | C8H16O2 | Ester |

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|---|---|---|---|---|---|---|---|---|---|---|
| 39 | 25,551 | 85; 41; 56 | 85 | 80 | 5-butyloxolan-2-one | 5-Butyl-Dihydro-2(3H)-Furanone (γ-Octalactone) | BDH2FURONE | 104-50-7 | C8H14O2 | Furan |
| 40 | 27,262 | 108; 107; 77 | 108 | 80 | 3-methylphenol | m-Cresol | MCREOL | 108-39-4 | C7H8O | Phenol |
| 41 | 27,966 | 56; 31; 41 | 56 | 80 | butan-1-ol | 1-Butanol | BT1OL | 71-36-3 | C4H10O | Alcohol |
| 42 | 28,085 | 85; 56; 41 | 85 | 82 | 5-propyloxolan-2-one | 5-Propyl-Dihydro-2(3H)-Furanone (γ-Heptalactone) | PDH2FURONE | 105-21-5 | C7H12O2 | Furan |
| 43 | 29,054 | 94; 39; 65 | 94 | 87 | 3-methylpyridazine | 3-Methyl-Pyridazine | M3PYRDZNE | 1632-76-4 | C5H6N2 | Nitrogen |
| 44 | 29,147 | 57; 41: 43 | 57 | 84 | pent-1-en-3-ol | 1-Penten-3-ol | PT1E3OL | 616-25-1 | C5H10O | Alcohol |
| 45 | 29,851 | 43; 58; 71 | 58 | 91 | heptan-2-one | 2-Heptanone | HPT2ONE | 110-43-0 | C7H14O | Ketone |
| 46 | 30,151 | 44; 70; 43; | 70 | 80 | heptanal | Heptanal | HPTAL | 111-71-7 | C7H14O | Aldehyde |
| 47 | 32,080 | 95; 138; 67 | 95 | 85 | 1-methyl-3-propan-2-ylcyclohexane | m-Menthane | MMTHANE | 16580-24-8 | C10H20 | Terpenoid |
| 48 | 32,436 | 80; 53; 52 | 80 | 80 | pyrimidine | 1,3-Diazine | D13ZINE | 289-95-2 | C4H4N2 | Nitrogen |
| 49 | 32,630 | 57; 41; 56 | 57 | 83 | 2-methylbutan-1-ol | 2-Methyl-1-Butanol | M2BT1OL | 137-32-6 | C5H12O | Alcohol |
| 50 | 33,174 | 82; 53; 81 | 82 | 90 | 2-propylfuran | 2-Propyl-Furan | PP2FUR | 4229-91-8 | C7H10O | Furan |
| 51 | 33,353 | 55; 42; 70 | 55 | 83 | 3-methylbutan-1-ol | 3-Methyl-1-Butanol | M3BT1OL | 123-51-3 | C5H12O | Alcohol |
| 52 | 34,394 | 81; 82; 138 | 81 | 94 | 2-pentylfuran | 2-Pentyl-Furan | PT2FUR | 3777-69-3 | C9H14O | Furan |
| 53 | 36,114 | 43; 57; 99 | 43 | 94 | octan-3-one | 3-Octanone | OCT3ONE | 106-68-3 | C8H16O | Ketone |
| 54 | 36,151 | 42; 55; 70 | 55 | 90 | pentan-1-ol | 1-Pentanol | PT1OL | 71-41-0 | C5H12O | Alcohol |
| 55 | 36,565 | 94; 67; 53 | 94 | 81 | 2-methylpyrazine | 2-Methyl-Pyrazine | MPYZNE | 109-08-0 | C5H6N | Nitrogen |
| 56 | 37,622 | 43; 72; 100 | 72 | 91 | 2-methyloxolan-3-one | 2-Methyl-Dihydro-2(3H)-Furanone | MDH2FURONE | 3188-00-9 | C5H8O2 | Furan |
| 57 | 37,261 | 119; 134; 91 | 119 | 84 | 1-methyl-4-propan-2-ylbenzene | p-Cymene | PCYMNE | 99-87-6 | C10H14 | Terpenoid |
| 58 | 37,369 | 105; 120; 77 | 105 | 95 | 1,3,5-trimethylbenzene | Mesitylene | MESTLNE | 108-67-8 | C9H12 | Benzene |
| 59 | 38,007 | 122; 107; 121 | 122 | 80 | 3,5-dimethylphenol | 3,5-Xylenol | XYL35NOL | 108-68-9 | C8H10O | Phenol |
| 60 | 38,238 | 45; 43; 88 | 45 | 90 | 3-hydroxybutan-2-one | 3-Hydroxy-2-Butanone | HXY3BT2ONE | 513-86-0 | C4H8O2 | Ketone (Alcohol) |
| 61 | 38,261 | 86; 42; 58 | 86 | 82 | 1,3-dioxol-2-one | Vinylene Carbonate | VYLESTCA | 96-49-1 | C3H4O3 | Ester (Ketone) |
| 62 | 38,738 | 122; 107; 121 | 122 | 82 | 2,6-dimethylphenol | 2,6-Xylenol | XYL26NOL | 576-26-1 | C8H10O | Phenol |
| 63 | 38,659 | 43; 44; 41 | 43 | 83 | octanal | Octanal | OCTAL | 124-13-0 | C8H16O | Aldehyde |
| 64 | 39,324 | 43; 31; 74 | 43 | 90 | 1-hydroxypropan-2-one | 1-Hydroxy-2-Propanone | HXY1PP2ONE | 116-09-6 | C3H6O2 | Ketone (Alcohol) |
| 65 | 40,467 | 41; 55; 83 | 55 | 84 | (Z)-hept-2-enal | cis-2-Heptanal | CH2PTAL | 57266-86-1 | C7H12O | Aldehyde |

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|---|---|---|---|---|---|---|---|---|---|---|
| 66 | 40,500 | 108; 42; 40 | 108 | 80 | 2,5-dimethylpyrazine | 2,5-Dimethyl-Pyrazine | DM25PYZNE | 123-32-0 | C6H8N2 | Nitrogen |
| 67 | 40,755 | 57; 41; 39 | 57 | 79 | (Z)-pent-2-en-1-ol | cis-2-Pentenol | CPT1E2OL | 1576-95-0 | C5H10O | Alcohol |
| 68 | 40,910 | 108; 42; 40 | 108 | 90 | 2,6-dimethylpyrazine | 2,6-Dimethyl-Pyrazine | DM26PYZNE | 108-50-9 | C6H8N2 | Nitrogen |
| 69 | 40,969 | 45; 55; 83 | 45 | 83 | heptan-2-ol | 2-Heptanol | HPT2OL | 543-49-7 | C7H16O | Alcohol |
| 70 | 42,220 | 55; 42; 70 | 55 | 83 | pent-2-ene | 2-Pentene | PT2ENE | 109-68-2 | C5H10 | Hydrocarbon |
| 71 | 42,422 | 82; 39; 54 | 82 | 91 | cyclopent-2-en-1-one | 2-Cyclopenten-1-one | CY2PT1EONE | 930-30-3 | C5H6O | Ketone |
| 72 | 42,918 | 56; 43; 55 | 56 | 78 | hexan-1-ol | 1-Hexanol | HX1OL | 111-27-3 | C6H14O | Alcohol |
| 73 | 43,239 | 67; 96; 53 | 67 | 83 | 2-methylcyclopent-2-en-1-one | 2-Methyl-2-Cyclopenten-1-one | M2CY2PT1EONE | 1120-73-6 | C6H8O | Ketone |
| 74 | 43,444 | 95; 43; 96 | 95 | 80 | (5-methylfuran-2-yl)methanethiol | 5-Methyl-2-Furanmethanethiol | M2FURTHOL | 59303-05-8 | C6H8OS | Furan (Sulfur) |
| 75 | 43,682 | 57; 88; 56 | 57 | 79 | 1-hydroxybutan-2-one | 1-Hydroxy-2-Butanone | H1BT2ONE | 5077-67-8 | C4H8O2 | Ketone (Alcohol) |
| 76 | 44,389 | 121; 122; 39 | 121 | 80 | 2-ethyl-6-methylpyrazine | 2-Ethyl-6-Methyl-Pyrazine | E6MPYZNE | 13925-03-6 | C7H10N2 | Nitrogen |
| 77 | 45,234 | 57; 41; 43 | 57 | 93 | nonanal | Nonanal | NONAL | 124-19-6 | C9H18O | Aldehyde |
| 78 | 45,421 | 83; 55; 41 | 83 | 78 | 1-ethyl-1-methylcyclopentane | 1-Ethyl-1-Methyl-Cyclopentane | E1M1CYPTANE | 3726-47-4 | C8H16 | Hydrocarbon |
| 79 | 45,956 | 67; 95; 124 | 67 | 81 | (3E)-3-ethyl-2-methylhexa-1,3-diene | 3-Ethyl-2-Methyl-1,3-Hexadiene | E3M2HX13DENE | 61142-36-7 | C9H16 | Terpene |
| 80 | 46,595 | 45; 55; 41 | 45 | 90 | octan-2-ol | 2-Octanol | OCT2OL | 123-96-6 | C8H18O | Alcohol |
| 81 | 46,726 | 68; 96; 40 | 68 | 82 | cyclohex-2-en-1-one | 2-Cyclohexen-1-one | C2HEXONE | 930-68-7 | C6H8O | Ketone |
| 82 | 46,820 | 41; 55; 70 | 41 | 83 | (E)-oct-2-enal | trans-2-Octenal | TOCT2EAL | 2548-87-0 | C8H14O | Aldehyde |
| 83 | 46,901 | 55; 43; 98 | 55 | 87 | 2-methyl-2H-furan-5-one | 5-Methyl-2(3H)-Furanone (β-Angelica Lactone) | M5FURONE | 591-12-8 | C5H6O2 | Furan |
| 84 | 47,214 | 98; 42; 69 | 98 | 84 | 4-methyl-1,3-dihydroimidazol-2-one | 1,3-Dihydro-4-Methyl-2H-Imidazol-2-one | M4IMDZONE | 214-751-9 | C4H6N2O | Nitrogen (Ketone) |
| 85 | 47,861 | 159; 174; 131 | 159 | 94 | 1,2,3,4-tetrahydro-1,1,6-trimethylnaphthalene | 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | T116TNP | 475-03-6 | C13H18 | Naphthalene |
| 86 | 48,068 | 57; 43; 72; | 57 | 78 | oct-1-en-3-ol | 1-Octen-3-ol | OCT3E1OL | 3391-86-4 | C8H16O | Alcohol |
| 87 | 48,282 | 70; 56; 55 | 70 | 90 | heptan-1-ol | 1-Heptanol | HPT1OL | 111-70-6 | C7H16O | Alcohol |
| 88 | 48,559 | 96; 95; 39 | 96 | 96 | 2-furanaldehyde | Furfural | FURAL | 98-01-1 | C5H4O2 | Furan (Aldehyde) |
| 89 | 49,502 | 43; 45; 60 | 43 | 90 | Acetic Acid | Ethanoic Acid | ETNOIC | 64-19-7 | C2H4O2 | Carboxylic Acid |
| 90 | 49,561 | 69; 84; 41 | 69 | 80 | non-2-en-4-one | 2-Nonen-4-one | NON2ONE | 32064-72-5 | C9H16O | Ketone |
| 91 | 49,783 | 159; 174; 131 | 159 | 96 | 1,2,3,4-tetrahydro-1,6,8-trimethylnaphthalene | 1,2,3,4-Tetrahydro-1,6,8-Trimethyl-Naphthalene | T168TNP | 30316-36-0 | C13H18 | Naphthalene |
| 92 | 50,004 | 57; 41; 55 | 57 | 82 | 2-ethylhexan-1-ol | 2-Ethyl-1-Hexanol | E2HX1OL | 104-76-7 | C8H18O | Alcohol |
| 93 | 50,015 | 81; 110; 53 | 81 | 80 | (2E,4E)-hepta-2,4-dienal | trans,trans-2,4-Heptadienal | TTHPT24DAL | 4313-03-5 | C7H10O | Aldehyde |

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|---|---|---|---|---|---|---|---|---|---|---|
| 94 | 50,131 | 110; 109; 53 | 110 | 92 | 3-methyl-2-furanaldehyde | 3-Methyl-Furfural | M3FURAL | 33342-48-2 | C6H6O2 | Furan (Aldehyde) |
| 95 | 50,259 | 81; 53; 126 | 81 | 82 | furan-2-ylmethyl formate | Furfuryl Formate | FURYLFMTE | 13493-97-5 | C6H6O3 | Furan (Ester) |
| 96 | 50,530 | 95; 110; 39 | 95 | 91 | 1-(furan-2-yl)ethanone | 1-(2-Furanyl)-Ethanone | FURYLONE | 1192-62-7 | C6H6O2 | Furan (Ketone) |
| 97 | 50,655 | 57; 43; 55 | 57 | 93 | decanal | Decanal | DECAL | 112-31-2 | C10H2O | Aldehyde |
| 98 | 51,329 | 106; 105; 77 | 106 | 95 | benzaldehyde | Benzaldehyde | BENZAL | 100-52-7 | C7H6O | Benzene (Aldehyde) |
| 99 | 51,771 | 81; 98; 52 | 81 | 95 | furan-2-ylmethyl acetate | Furfuryl Acetate | FURYLACTE | 623-17-6 | C7H8O3 | Furan (Ester) |
| 100 | 52,336 | 74; 45; 73 | 74 | 90 | propanoic acid | Propanoic Acid | PPANOIC | 79-09-4 | C3H6O2 | Carboxylic Acid |
| 101 | 53,002 | 56; 55; 70 | 56 | 86 | octan-1-ol | 1-Octanol | OCT1OL | 111-87-5 | C8H18O | Alcohol |
| 102 | 53,078 | 63; 78; 45 | 63 | 91 | methylsulfinylmethane | Dimethyl Sulfoxide | DMSULFO | 67-68-5 | C2H6OS | Sulfur |
| 103 | 53,245 | 159; 174; 131 | 159 | 94 | 1,2,3,4-tetrahydro-1,5,8-trimethylnaphthalene | 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | T158TNP | 21693-51-6 | C13H18 | Naphthalene |
| 104 | 53,657 | 110; 109; 53 | 110 | 94 | 5-methyl-2-furanaldehyde | 5-Methyl-Furfural | M5FURAL | 620-02-0 | C6H6O2 | Furan (Aldehyde) |
| 105 | 54,207 | 96; 42; 68 | 96 | 91 | cyclopent-4-ene-1,3-dione | 4-Cyclopentene-1,3-dione | CPT4E13DONE | 930-60-9 | C5H4O2 | Ketone |
| 106 | 54,861 | 131; 132; 103 | 131 | 97 | 2-methyl-1-benzofuran | 2-Methyl-Benzofuran | M2BNZFUR | 4265-25-2 | C9H8O | Benzofuran |
| 107 | 55,678 | 109; 124; 81 | 109 | 80 | 1-(5-methylfuran-2-yl)ethanone | 1-(5-Methyl-2-Furanyl)-Ethanone | M5FURYLONE | 1193-79-9 | C7H8O2 | Furan (Ketone) |
| 108 | 55,337 | 57; 41; 54 | 57 | 79 | (E)-oct-2-en-1-ol | trans-2-Octenol | TOCTE2OL | 18409-17-1 | C8H16O | Alcohol |
| 109 | 55,835 | 45; 59; 72 | 45 | 90 | 2-(2-ethoxyethoxy)ethanol | Diethylene Glycol Ethyl Ether | DENGOLEETHR | 111-90-0 | C6H14O3 | Ether (Alcohol) |
| 110 | 56,251 | 42; 41; 56 | 42 | 82 | 3-methyloxolan-3-one | 3-Methyl-Dihydro-2(3H)-Furanone | M3DHFURONE | 1679-47-6 | C5H8O2 | Furan (Lactone) |
| 111 | 56,693 | 159; 174; 128 | 159 | 86 | 3,3,5,7-tetramethyl-1,2-dihydroindene | 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | DHT1146MIDNE | 941-60-6 | C13H18 | Indene |
| 112 | 57,065 | 91; 92; 120 | 91 | 90 | 2-phenylacetaldehyde | Benzeneacetaldehyde | BENZACETAL | 122-78-1 | C8H8O | Benzene (Aldehyde) |
| 113 | 57,117 | 69; 41; 112 | 91 | 87 | 2,4-dimethyl-2H-furan-5-one | 3,5-Dimethyl-Dihydro-2-Furanone | DM35DHFURONE | 5584-69-0 | C6H8O2 | Furan (Lactone) |
| 114 | 57,239 | 91; 119; 120 | 119 | 96 | 3-methylbenzaldehyde | 3-Methyl-Benzaldehyde | M3BENZAL | 620-23-5 | C8H8O | Benzene (Aldehyde) |
| 115 | 57,323 | 72; 55; 45 | 72 | 78 | prop-2-enoic acid | 2-Propenoic Acid | PPE2NOIC | 79-10-7 | C3H4O2 | Carboxylic Acid |
| 116 | 57,354 | 105; 77; 51 | 105 | 87 | 1-phenylethanone | Acetophenone | ACETPHONE | 98-86-2 | C8H8O | Benzene (Ketone) |
| 117 | 57,744 | 98; 41; 81 | 98 | 98 | furan-2-ylmethanol | 2-Furanmethanol | FUR2OL | 98-00-0 | C5H6O2 | Furan (Alcohol) |
| 118 | 57,981 | 98; 41; 97 | 97 | 93 | furan-3-ylmethanol | 3-Furanmethanol | FUR3OL | 4412-91-3 | C5H6O2 | Furan (Alcohol) |

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|---|---|---|---|---|---|---|---|---|---|---|
| 119 | 58,675 | 159; 128; 144 | 159 | 86 | 3,3,5,6-tetramethyl-1,2-dihydroindene | 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | DHT1156MIDNE | 942-43-8 | C13H18 | Indene |
| 120 | 58,897 | 162; 91; 43 | 162 | 91 | 2-(2-furylmethyl)-5-methylfuran | 2-(2-Furanylmethyl)-5-Methyl-Furan | FURYLMFUR | 13678-51-8 | C10H10O2 | Furan |
| 121 | 60,229 | 41; 69; 98 | 41 | 83 | 4-methyl-2H-furan-5-one | 3-Methyl-2(5H)-Furanone | M3FURONE | 22122-36-7 | C5H6O2 | Furan (Lactone) |
| 122 | 60,456 | 95; 112; 43 | 95 | 93 | (5-methylfuran-2-yl)methanol | 5-Methyl-2-Furanmethanol | M5FUR2OL | 3857-25-8 | C6H8O2 | Furan (Alcohol) |
| 123 | 60,947 | 108; 91; 90 | 108 | 75 | benzyl acetate | Phenylmethyl Acetate | PMESTAA | 140-11-4 | C9H10O2 | Benzene (Ester) |
| 124 | 61,403 | 128; 129; 127 | 128 | 81 | naphthalene | Naphthalene | NPHNE | 91-20-3 | C10H8 | Naphthalene |
| 125 | 61,749 | 55; 84; 54 | 55 | 80 | 2H-furan-5-one | 2(5H)-Furanone | FURONE | 497-23-4 | C4H4O2 | Furan (Lactone) |
| 126 | 62,073 | 176; 43; 161 | 176 | 96 | 2-methyl-5-[(5-methylfuran-2-yl)methyl]furan | 2,2'-Methylenebis[5-Methyl-Furan | MNEB5MFUR | 13679-43-1 | C10H10O2 | Furan |
| 127 | 62,421 | 98; 55; 42 | 98 | 90 | cyclopentane-1,2-dione | 1,2-Cyclopentanedione | CPT12DONE | 3008-40-0 | C5H6O2 | Ketone |
| 128 | 63,612 | 45; 57; 41 | 57 | 80 | 2-(2-butoxyethoxy)ethanol | Diethylene Glycol Monobutyl Ether | DETNGOLBTHR | 112-34-5 | C8H18O3 | Ether (Alcohol) |
| 129 | 63,971 | 70; 39; 41 | 70 | 84 | cyclohex-2-en-1-ol | 2-Cyclohexenol | CHEX2E1OL | 822-67-3 | C6H10O | Alcohol |
| 130 | 64,539 | 104; 43; 91 | 104 | 84 | 2-phenylethyl acetate | 2-Phenylethyl Acetate | PEESTAA | 103-45-7 | C10H12O2 | Benzene (Ester) |
| 131 | 64,803 | 112; 69; 41 | 112 | 93 | 3-methylcyclopentane-1,2-dione | 3-Methyl-1,2-Cyclopentanedione | M3CPT12DONE | 765-70-8 | C6H8O2 | Ketone |
| 132 | 64,922 | 69; 121; 41 | 69 | 96 | 1-(2,6,6-trimethylcyclohexa-1,3-dien-1-yl)but-2-en-1-one | β-Damascenone | DAMSNONE | 23726-93-4 | C13H18O | Terpenoid (Ketone) |
| 133 | 65,660 | 43; 41; 73 | 43 | 79 | 2-methylpropanoic acid | 2-Methyl-Propanoic Acid | M2PPOICA | 79-31-2 | C4H8O2 | Carboxylic Acid |
| 134 | 65,701 | 121; 150; 77 | 121 | 78 | 4-butan-2-ylphenol | 4-(1-Methylpropyl)-Phenol | MPPYLPHEOL | 99-71-8 | C10H14O | Phenol |
| 135 | 65,986 | 128; 57; 85 | 128 | 77 | 1,3-diazinane-2,4,6-trione | 2,4,6-Trihydroxypyrimidine | THDXYPYMNE | 67-52-7 | C4H4N2O3 | Nitrogen |
| 136 | 66,118 | 109; 124, 81 | 109 | 90 | 4-methoxyphenol | Mequinol | MEQNOL | 150-76-5 | C7H8O2 | Phenol (Ether) |
| 137 | 66,384 | 114; 58; 57 | 114 | 84 | 2,2-diethyl-3-methyl-1,3-oxazolidine | 2,2-Diethyl-3-Methyl-Oxazolidine | DEMOXZDNE | | C8H17NO | Nitrogen |
| 138 | 66,461 | 109; 152, 52 | 109 | 82 | 1,7-dihydropyrazolo[3,4-d]pyrimidine-4,6-dione | Oxypurinol | OXYPUROL | 2465-59-0 | C5H4N4O2 | Nitrogen |
| 139 | 66,688 | 79; 108; 77 | 79 | 92 | phenylmethanol | Benzenemethanol | BENZMTOL | 100-51-6 | C7H8O | Benzene (Alcohol) |
| 140 | 67,106 | 69; 41; 39 | 69 | 87 | 3-methyl-2H-furan-5-one | 4-Methyl-2(5H)-Furanone | M4FUR2ONE | 6124-79-4 | C5H6O2 | Furan (Lactone) |

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|---|---|---|---|---|---|---|---|---|---|---|
| 141 | 67,293 | 126; 55; 83 | 126 | 95 | 3-ethyl-2-hydroxycyclopent-2-en-1-one | 3-Ethyl-2-Hydroxy-2-Cyclopenten-1-one | E3H2C2PT1ONE | 21835-01-8 | C7H10O2 | Ketone (Alcohol) |
| 142 | 68,036 | 91; 92; 122 | 91 | 78 | 2-phenylethanol | Benzeneethanol | BENZETOL | 60-12-8 | C8H10O | Benzene (Alcohol) |
| 143 | 68,135 | 42; 44, 31; 71 | 42 | 79 | butane-1,4-diol | 1,4-Butanediol | BT14DIOL | 110-63-4 | C4H10O2 | Alcohol |
| 144 | 68,580 | 44; 71; 55 | 44 | 80 | prop-2-enamide | Acrylamide | ACRYLMDE | 79-06-1 | C3H5NO | Nitrogen |
| 145 | 68,698 | 61; 44; 43 | 61 | 79 | (2S,3R)-butane-1,2,3,4-tetrol | Erythritol | ERYTOL | 149-32-6 | C4H10O4 | Alcohol (Polyol) |
| 146 | 68,890 | 112; 111; 39 | 112 | 80 | 2,3-dimethyl-1H-pyrazol-5-one | 2,3-Dimethyl-3-Pyrazolin-5-one | DM23PYZLONE | 3201-28-3 | C5H8N2O | Nitrogen |
| 147 | 69,323 | 136; 121; 65 | 136 | 87 | (E)-4-(furan-2-yl)but-3-en-2-one | Furfural Acetone | FURALTONE | 623-15-4 | C8H8O2 | Furan (Ketone) |
| 148 | 69,469 | 112; 69; 55 | 112 | 85 | 2-hydroxy-3-methylcyclopent-2-en-1-one | Cyclotene | CYTENE | 80-71-7 | C6H8O2 | Ketone (Alcohol) |
| 149 | 69,557 | 124; 95; 107 | 124 | 80 | 2-methylbenzene-1,4-diol | 2-Methyl-1,4-Benzenediol | M2BNZ14DIOL | 95-71-6 | C7H8O2 | Benzene (Alcohol) |
| 150 | 69,883 | 126; 71; 43 | 126 | 95 | 3-hydroxy-2-methylpyran-4-one | Maltol | MALTOL | 118-71-8 | C6H6O3 | Pyran |
| 151 | 70,149 | 94; 109; 66 | 94 | 95 | 1-(1H-pyrrol-2-yl)ethanone | 2-Acetylpyrrole | ACTLPYROLE | 1072-83-9 | C6H7NO | Nitrogen (Pyrrole) |
| 152 | 70,504 | 124; 123; 95 | 124 | 91 | furan-2,5-dicarbaldehyde | 2,5-Furandicarboxaldehyde | FUR25DIAL | 823-82-5 | C6H4O3 | Furan (Aldehyde) |
| 153 | 70,953 | 112; 55; 84 | 112 | 80 | 3H-pyran-2,6-dione | 2H-Pyran-2,6(3H)-Dione | PYR26DIONE | 5926-95-4 | C5H4O3 | Pyran |
| 154 | 71,427 | 95; 126; 67 | 95 | 84 | 1,3-bis(furan-2-yl)-1,3-dihydroxypropan-2-one | 1-(2-Furanyl)-2-Hydroxy-Ethanone | H2FURYLONE | 17678-19-2 | C6H6O3 | Furan (Ketone) |
| 155 | 71,638 | 94; 66; 65 | 94 | 89 | phenol | Phenol | PHEOL | 108-95-2 | C6H6O | Phenol |
| 156 | 72,019 | 95; 94; 66 | 95 | 84 | 1H-pyrrole-2-carbaldehyde | 1H-Pyrrole-2-Carboxaldehyde | PYRLE2AL | 1003-29-8 | C5H5NO | Nitrogen (Pyrrole) |
| 157 | 72,070 | 126; 69; 85 | 126 | 79 | benzene-1,3,5-triol | Phloroglucinol | PHLOGLNOL | 108-73-6 | C6H6O3 | Phenol |
| 158 | 72,219 | 43; 57; 128 | 43 | 91 | 4-hydroxy-2,5-dimethylfuran-3-one | Furaneol | FUREOL | 3658-77-3 | C6H8O3 | Furan (Ketone) |
| 159 | 72,823 | 60; 73; 43 | 60 | 84 | octanoic acid | Octanoic Acid | OCTOIC | 124-07-2 | C8H16O2 | Carboxylic Acid |
| 160 | 73,300 | 85; 43; 57 | 85 | 78 | 5-acetyloxolan-2-one | 5-Acetyl-Dihydro-2(3H)-Furanone (Solerone) | ACYLDHFURONE | 29393-32-6 | C6H8O3 | Furan (Lactone) |
| 161 | 73,838 | 81; 140; 53 | 81 | 80 | 3-(furan-2-yl)propanoic acid | 2-Furanpropionic Acid | FURPPIONIC | 935-13-7 | C7H8O3 | Furan (Acid) |
| 162 | 74,038 | 31; 43; 42, 60 | 31 | 83 | 1,3-dihydroxypropan-2-one | 1,3-Dihydroxy-2-Propanone | DHYPPAONE | 96-26-4 | C3H6O3 | Ketone (Alcohol) |
| 163 | 74,258 | 85; 43; 41 | 85 | 82 | [(2S,5R)-5-methyloxolan-2-yl]methanol | Tetrahydro-5-Methyl-2-Furanmethanol | TEHYMFUROL | 6126-49-4 | C6H12O2 | Furan (Alcohol) |

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|---|---|---|---|---|---|---|---|---|---|---|
| 164 | 74,965 | 43; 55; 114 | 55 | 79 | 4,5-dimethyl-1,3-dioxol-2-one | 4,5-Dimethyl Vinylene Carbonate | DM45VYLESTCA | 37830-90-3 | C5H6O3 | Ester (Ketone) |
| 165 | 76,832 | 57; 58; 44 | 57 | 83 | 3-hydroxyoxolan-2-one | 2-Hydroxy-Dihydro-2(3H)-Furanone | HY2DHFURONE | 19444-84-9 | C4H6O3 | Furan (Lactone) |
| 166 | 77,073 | 107; 122; 77 | 107 | 82 | 2-ethylphenol | 2-Ethyl-Phenol | E2PHEOL | 90-00-6 | C8H10O | Phenol |
| 167 | 77,493 | 126; 43; 79 | 126 | 87 | (5-formylfuran-2-yl)methyl acetate | 5-Acetoxymethyl-2-Furfural A | ACTYMFURALA | 10551-58-3 | C8H8O4 | Furan (Aldehyde / Ether) |
| 168 | 77,713 | 126; 43; 79 | 126 | 90 | (5-formylfuran-2-yl)methyl acetate | 5-Acetoxymethyl-2-Furfural B | ACTYMFURALB | 10551-58-3 | C8H8O4 | Furan (Aldehyde / Ether) |
| 169 | 77,842 | 135; 150; 77 | 135 | 86 | 4-ethenyl-2-methoxyphenol | 2-Methoxy-4-Vinyl-Phenol | MXY2VYL4PHEOL | 7786-61-0 | C9H10O2 | Phenol (Ether) |
| 170 | 78,094 | 56; 114; 42 | 56 | 82 | 3-methyloxolane-2,4-dione | 3-Methyl-2,4(3H,5H)-Furandione | M3FURDIONE | 616-02-4 | C5H4O3 | Furan (Lactone) |
| 171 | 79,890 | 43; 42; 144 | 43 | 94 | 3,5-dihydroxy-6-methyl-2,3-dihydropyran-4-one | 3-Hydroxy-2,3-Dihydro-Maltol | HX3DH23MALTOL | 28564-83-2 | C6H8O4 | Pyran (Alcohol / Ether) |
| 172 | 80,260 | 60; 73; 41 | 60 | 91 | decanoic acid | Decanoic Acid | DECOIC | 334-48-5 | C10H20O2 | Carboxylic Acid |
| 173 | 80,469 | 142; 43; 68 | 142 | 83 | 3,5-dihydroxy-2-methylpyran-4-one | 5-Hydroxy-Maltol | HX5MALTOL | 1073-96-7 | C6H6O4 | Pyran (Ether) |
| 174 | 83,557 | 120; 91; 119 | 120 | 82 | 2,3-dihydro-1-benzofuran | 2,3-Dihydro-Benzofuran | DHBNZFUR | 496-16-2 | C8H8O | Benzofuran |
| 175 | 83,819 | 69; 57; 41 | 69 | 97 | (1R,3R,6R,7R,9R)-2,5,8-Trioxatricyclo[4.2.1.0~3,7~]nonan-9-ol | 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | GLUPYROSE | 4451-31-4 | C6H8O4 | Pyran (Derivative) |
| 176 | 84,222 | 95; 39; 68 | 95 | 90 | 1H-pyridin-4-one | 4-Pyridinol | PYRDINOL | 626-64-2 | C5H5NO | Nitrogen |
| 177 | 84,511 | 109; 80; 53 | 109 | 80 | 4-aminophenol | 4-Amino-Phenol | AMIPHEOL | 123-30-8 | C6H7NO | Phenol (Amine) |
| 178 | 85,024 | 105; 122; 77 | 105 | 95 | benzoic acid | Benzoic Acid | BNZOIC | 65-85-0 | C7H6O2 | Benzene (Acid) |
| 179 | 85,202 | 55; 84; 128 | 55 | 78 | N-methyl-N-(pentan-3-ylideneamino)methanamine | Dimethylhydrazone 3-Pentanone | DMHDZPTONE | 16795-73-6 | C7H16N2 | Nitrogen (Amine) |
| 180 | 85,552 | 60; 73; 43 | 60 | 82 | undecanoic acid | Undecanoic Acid | UNDECOIC | 112-37-8 | C11H22O2 | Carboxylic Acid |
| 181 | 86,034 | 85; 86; 57 | 85 | 91 | 5-(hydroxymethyl)oxolan-2-one | 5-(Hydroxymethyl)-Dihydro-2(3H)-Furanone | HM5FURONE | 10374-51-3 | C5H8O3 | Furan (Lactone) |
| 182 | 86,387 | 105; 77; 182 | 105 | 86 | diphenylmethanone | Benzophenone | BENZPONE | 119-61-9 | C13H10O | Benzene (Ketone) |
| 183 | 86,481 | 60; 73; 43 | 60 | 82 | dodecanoic acid | Dodecanoic Acid | DODECOIC | 143-07-7 | C12H24O2 | Carboxylic Acid |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 184 | 86,680 | 97; 126; 41 | 97 | 98 | 5-(hydroxymethyl)furan-2-carbaldehyde | 5-(Hydroxymethyl)-2-Furfural | HM5FURAL | 67-47-0 | C6H6O3 | Furan (Aldehyde) |
| 185 | 87,210 | 140; 125; 97 | 140 | 80 | 3-methoxybenzene-1,2-diol | 3-Methoxy-1,2-Benzenediol | M3BNZDIOL | 934-00-9 | C7H8O3 | Benzene (Alcohol / Ether) |
| 186 | 89,065 | 97; 41; 128 | 97 | 84 | 1-(furan-2-yl)ethane-1,2-diol | 1-(2-Furanyl)-1,2-Ethanediol | FURYLETDIOL | 19377-75-4 | C6H8O3 | Furan (Alcohol) |
| 187 | 89,906 | 44; 74; 102 | 44 | 82 | 4-hydroxyoxolan-2-one | 4-Hydroxy-Dihydro-2(3H)-Furanone | DHYHYFURONE | 5469-16-9 | C4H6O | Furan (Lactone) |

**Table S24. Mean and relative standard deviation values of identified VOCs in samples from SCH processing stages during 2015-2018 production years.**

| NIST Database Name | Production Year | Stage 1 | | Stage 2 | | Stage 3 | | Stage 4 | | Stage 5 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Relative Peak Areas (x $10^3$) | | Relative Peak Areas (x $10^3$) | | Relative Peak Areas (x $10^3$) | | Relative Peak Areas (x $10^3$) | | Relative Peak Areas (x $10^3$) | |
| | | Mean | RSD[1] (%) | Mean | RSD[1] (%) | Mean | RSD[1] (%) | Mean | RSD[1] (%) | Mean | RSD[1] (%) |
| Pentane | 2015 | 13.8 | 11.1 | 29.84 | 10.4 | 0.0 | | 0.0 | | 19.0 | 11.8 |
| | 2016 | 15.0 | 11.2 | 12.51 | 2.6 | 0.0 | | 0.0 | | 52.2 | 1.8 |
| | 2017 | 53.9 | 4.6 | 6.65 | 5.6 | 0.0 | | 0.0 | | 47.9 | 6.2 |
| | 2018 | 62.3 | 7.2 | 11.37 | 5.6 | 0.0 | | 0.0 | | 60.5 | 4.4 |
| Hexane | 2015 | 6.2 | 11.3 | 54.8 | 7.5 | 46.3 | 7.6 | 196.0 | 9.7 | 77.8 | 1.6 |
| | 2016 | 4.3 | 3.3 | 14.6 | 9.2 | 66.0 | 1.2 | 131.2 | 8.7 | 142.7 | 2.6 |
| | 2017 | 16.9 | 1.4 | 28.2 | 6.9 | 198.9 | 8.6 | 119.3 | 6.1 | 99.3 | 5.7 |
| | 2018 | 51.6 | 9.8 | 9.2 | 8.1 | 57.2 | 3.8 | 66.8 | 0.4 | 167.5 | 1.9 |
| Ethyl Ether | 2015 | 10.8 | 4.6 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 3.3 | 6.0 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 4.7 | 4.3 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 2.5 | 4.5 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 1,4-Pentadiene | 2015 | 11.4 | 8.6 | 3.9 | 9.2 | 6.9 | 1.2 | 9.1 | 6.8 | 0.0 | |
| | 2016 | 1.9 | 5.4 | 5.3 | 5.3 | 5.8 | 2.6 | 7.2 | 1.3 | 0.0 | |
| | 2017 | 28.8 | 2.9 | 4.0 | 2.5 | 4.7 | 9.1 | 6.3 | 8.2 | 0.0 | |
| | 2018 | 17.2 | 6.0 | 3.0 | 7.3 | 4.2 | 6.4 | 3.0 | 5.8 | 0.0 | |
| Methanethiol | 2015 | 0.0 | | 0.0 | | 21.8 | 13.3 | 52.8 | 5.8 | 208.9 | 11.3 |
| | 2016 | 0.0 | | 0.0 | | 38.3 | 0.9 | 43.1 | 7.4 | 163.4 | 2.9 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2017 | 0.0 | | 0.0 | | 12.0 | 3.3 | 18.4 | 0.4 | 448.0 | 7.4 |
| | 2018 | 0.0 | | 0.0 | | 21.2 | 2.4 | 41.2 | 7.9 | 318.0 | 3.3 |
| | 2015 | 24.9 | 12.7 | 59.2 | 11.5 | 220.5 | 6.3 | 790.9 | 8.9 | 3942.1 | 1.7 |
| Ethanal | 2016 | 6.7 | 12.4 | 61.4 | 3.1 | 392.4 | 3.3 | 672.5 | 1.7 | 8786.9 | 3.9 |
| | 2017 | 28.9 | 4.9 | 19.4 | 8.5 | 421.9 | 5.5 | 480.8 | 5.5 | 8939.0 | 9.4 |
| | 2018 | 61.6 | 10.8 | 71.2 | 4.8 | 471.5 | 7.8 | 665.4 | 10.7 | 12257.1 | 9.3 |
| | 2015 | 252.3 | 8.8 | 8832.7 | 7.6 | 236.3 | 9.9 | 96.4 | 8.8 | 894.2 | 5.3 |
| Dimethyl Sulfide | 2016 | 233.1 | 5.9 | 9477.0 | 3.3 | 78.3 | 9.3 | 21.3 | 10.5 | 1378.0 | 7.3 |
| | 2017 | 866.4 | 2.5 | 9680.8 | 0.4 | 107.0 | 2.2 | 8.4 | 4.0 | 2272.4 | 8.0 |
| | 2018 | 1899.9 | 11.1 | 7881.9 | 8.9 | 212.1 | 13.9 | 12.4 | 8.8 | 1569.8 | 6.2 |
| | 2015 | 26.2 | 11.3 | 38.3 | 11.7 | 72.2 | 0.7 | 129.1 | 8.6 | 293.4 | 11.0 |
| Propanal | 2016 | 17.6 | 12.2 | 15.3 | 9.2 | 80.2 | 11.7 | 70.3 | 1.2 | 753.7 | 4.3 |
| | 2017 | 28.2 | 10.7 | 32.7 | 10.5 | 99.1 | 4.7 | 34.5 | 7.9 | 495.0 | 12.5 |
| | 2018 | 14.6 | 2.1 | 19.3 | 12.9 | 93.5 | 0.3 | 108.6 | 6.3 | 1390.6 | 11.5 |
| | 2015 | 0.0 | | 115.7 | 4.7 | 434.9 | 10.0 | 208.2 | 11.1 | 593.1 | 1.0 |
| Furan | 2016 | 0.0 | | 136.0 | 11.6 | 608.4 | 4.6 | 67.3 | 3.0 | 2149.9 | 12.7 |
| | 2017 | 0.0 | | 140.0 | 8.5 | 351.9 | 3.5 | 39.1 | 5.9 | 6029.2 | 0.2 |
| | 2018 | 0.0 | | 89.4 | 6.5 | 687.3 | 10.0 | 53.5 | 4.5 | 4240.4 | 7.2 |
| | 2015 | 17.0 | 5.0 | 131.1 | 1.5 | 1479.8 | 13.7 | 1549.0 | 2.6 | 6454.5 | 3.5 |
| 2-Methyl-Propanal | 2016 | 55.2 | 12.5 | 180.4 | 12.0 | 2208.9 | 9.4 | 807.4 | 6.7 | 11410.9 | 5.8 |
| | 2017 | 44.0 | 11.0 | 13.9 | 0.7 | 2099.2 | 6.7 | 424.2 | 4.8 | 17659.5 | 7.9 |
| | 2018 | 180.7 | 11.6 | 167.0 | 8.8 | 2518.7 | 12.6 | 1059.2 | 11.2 | 21889.5 | 8.7 |
| | 2015 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 894.4 | 5.3 |
| Ethyl Formate | 2016 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 7155.3 | 5.1 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 2667.3 | 2.1 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 2.0 | 8.5 | 12.8 | 4.1 | 58.7 | 10.5 | 59.7 | 9.4 | 400.3 | 0.3 |
| 2-Propenal | 2016 | 4.6 | 1.0 | 20.2 | 0.8 | 94.3 | 0.7 | 37.4 | 5.7 | 572.5 | 1.0 |
| | 2017 | 34.5 | 4.3 | 8.8 | 2.0 | 23.4 | 7.5 | 27.8 | 4.6 | 310.2 | 6.9 |
| | 2018 | 15.8 | 8.0 | 5.4 | 1.0 | 28.8 | 10.0 | 36.9 | 8.5 | 353.4 | 13.2 |
| | 2015 | 6.6 | 11.2 | 15.0 | 6.0 | 1413.8 | 3.8 | 1514.8 | 12.6 | 708.2 | 9.7 |
| 2-Methyl-Furan | 2016 | 21.8 | 11.9 | 47.8 | 0.2 | 1319.5 | 8.7 | 569.0 | 8.9 | 2031.0 | 11.0 |
| | 2017 | 27.8 | 4.5 | 99.7 | 13.2 | 1411.4 | 1.2 | 366.3 | 7.5 | 2646.0 | 10.7 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2018 | 20.7 | 8.1 | 42.8 | 13.4 | 1886.2 | 6.3 | 151.1 | 1.0 | 6988.8 | 6.3 |
| | 2015 | 410.7 | 6.0 | 63.2 | 1.7 | 6.8 | 3.9 | 16.4 | 7.1 | 2801.0 | 5.8 |
| Ethyl Acetate | 2016 | 66.0 | 11.3 | 216.2 | 1.0 | 7.4 | 13.5 | 18.5 | 1.1 | 25389.2 | 1.8 |
| | 2017 | 51.2 | 13.6 | 177.2 | 10.7 | 4.1 | 7.4 | 15.5 | 2.9 | 13187.9 | 7.0 |
| | 2018 | 116.2 | 9.3 | 27.5 | 12.4 | 2.0 | 5.1 | 16.8 | 9.1 | 280.0 | 4.6 |
| | 2015 | 0.0 | | 11.2 | 6.7 | 58.3 | 5.9 | 32.8 | 8.9 | 404.9 | 3.7 |
| 2-Butanone | 2016 | 0.0 | | 17.1 | 10.1 | 53.5 | 13.9 | 40.2 | 7.5 | 217.2 | 12.9 |
| | 2017 | 0.0 | | 16.4 | 7.6 | 36.3 | 5.0 | 22.7 | 1.2 | 1133.4 | 7.4 |
| | 2018 | 0.0 | | 14.5 | 10.2 | 66.5 | 3.3 | 44.9 | 0.6 | 988.7 | 1.6 |
| | 2015 | 39.3 | 4.5 | 158.2 | 11.2 | 6215.2 | 9.7 | 2894.0 | 5.1 | 12966.1 | 3.7 |
| 2-Methyl-Butanal | 2016 | 58.9 | 5.6 | 279.9 | 1.9 | 7642.6 | 13.5 | 1394.4 | 2.5 | 19612.8 | 1.2 |
| | 2017 | 105.5 | 10.9 | 132.6 | 3.1 | 5826.5 | 4.8 | 880.8 | 7.5 | 30163.3 | 8.7 |
| | 2018 | 319.1 | 8.4 | 161.3 | 8.9 | 8792.8 | 4.4 | 2211.4 | 8.2 | 37630.2 | 9.5 |
| | 2015 | 34.7 | 1.9 | 275.9 | 13.0 | 9778.3 | 5.6 | 3576.7 | 4.9 | 7073.4 | 9.5 |
| 3-Methyl-Butanal | 2016 | 35.0 | 12.8 | 505.0 | 4.1 | 12036.5 | 8.1 | 1746.8 | 8.1 | 14668.8 | 5.7 |
| | 2017 | 247.1 | 13.6 | 210.4 | 11.3 | 9846.5 | 5.8 | 1437.3 | 9.1 | 31870.8 | 4.7 |
| | 2018 | 289.4 | 8.8 | 246.6 | 7.7 | 11066.0 | 9.8 | 1962.1 | 5.8 | 41914.2 | 13.0 |
| | 2015 | 839.1 | 10.8 | 535.3 | 9.7 | 185.5 | 9.0 | 1271.0 | 6.0 | 107855.0 | 4.4 |
| Ethanol | 2016 | 3305.8 | 3.7 | 967.1 | 3.4 | 272.9 | 3.1 | 677.3 | 12.5 | 115261.9 | 3.6 |
| | 2017 | 1022.3 | 3.6 | 1488.6 | 4.3 | 490.7 | 9.7 | 754.9 | 4.4 | 145024.3 | 1.6 |
| | 2018 | 733.4 | 1.9 | 782.0 | 10.6 | 991.0 | 5.0 | 741.7 | 7.3 | 159606.9 | 2.9 |
| | 2015 | 20.4 | 12.6 | 2.1 | 11.2 | 18.8 | 5.0 | 13.0 | 8.5 | 53.8 | 1.5 |
| Benzene | 2016 | 6.1 | 12.8 | 11.8 | 2.3 | 11.1 | 2.9 | 12.1 | 1.7 | 101.2 | 9.1 |
| | 2017 | 26.9 | 11.4 | 11.7 | 3.8 | 11.2 | 5.5 | 34.7 | 7.1 | 84.4 | 5.9 |
| | 2018 | 12.4 | 2.8 | 6.1 | 2.5 | 8.8 | 5.6 | 11.6 | 6.0 | 200.4 | 4.3 |
| | 2015 | 0.0 | | 15.0 | 11.8 | 63.8 | 2.9 | 45.6 | 13.5 | 341.5 | 3.4 |
| 3-Buten-2-one | 2016 | 0.0 | | 49.6 | 4.7 | 44.3 | 11.6 | 218.5 | 5.5 | 872.8 | 5.1 |
| | 2017 | 0.0 | | 34.2 | 1.1 | 56.1 | 7.8 | 25.3 | 8.7 | 5111.2 | 3.4 |
| | 2018 | 0.0 | | 21.9 | 12.7 | 55.4 | 10.8 | 42.7 | 11.7 | 5047.9 | 5.4 |
| | 2015 | 0.0 | | 147.5 | 11.1 | 0.0 | | 0.0 | | 0.0 | |
| 2-Ethyl-Furan | 2016 | 0.0 | | 63.6 | 9.4 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 0.0 | | 362.9 | 2.3 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 0.0 | | 82.4 | 9.9 | 0.0 | | 0.0 | | 0.0 | |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,5-Dimethyl-Furan | 2015 | 0.0 | | 0.0 | | 209.1 | 10.8 | 39.2 | 8.9 | 880.9 | 6.2 |
| | 2016 | 0.0 | | 0.0 | | 250.7 | 8.5 | 61.7 | 2.5 | 3919.7 | 9.0 |
| | 2017 | 0.0 | | 0.0 | | 238.0 | 5.3 | 4.9 | 10.4 | 2021.6 | 6.6 |
| | 2018 | 0.0 | | 0.0 | | 197.4 | 9.6 | 35.4 | 12.6 | 1956.1 | 4.6 |
| Ethyl Propanoate | 2015 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 132.7 | 11.3 |
| | 2016 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 1881.4 | 4.4 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 307.1 | 8.6 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 3-Pentanone | 2015 | 195.2 | 7.6 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 203.2 | 5.6 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 29.8 | 13.5 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 64.9 | 5.8 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Pentanal | 2015 | 0.0 | | 239.8 | 12.2 | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 0.0 | | 227.6 | 7.4 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 0.0 | | 286.2 | 8.4 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 0.0 | | 152.3 | 10.8 | 0.0 | | 0.0 | | 0.0 | |
| 2,3-Butanedione | 2015 | 0.0 | | 560.9 | 2.3 | 975.1 | 0.6 | 3962.0 | 10.1 | 2814.3 | 7.2 |
| | 2016 | 0.0 | | 140.0 | 9.9 | 2016.1 | 3.0 | 3610.1 | 9.2 | 1397.2 | 13.2 |
| | 2017 | 0.0 | | 4.8 | 10.9 | 2051.6 | 7.8 | 32.1 | 6.4 | 33123.4 | 11.0 |
| | 2018 | 0.0 | | 59.8 | 5.4 | 405.0 | 5.2 | 1711.2 | 1.5 | 49665.1 | 11.3 |
| 1-Penten-3-one | 2015 | 16.5 | 11.9 | 12.5 | 10.9 | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 6.5 | 6.9 | 25.1 | 5.9 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 190.7 | 4.0 | 16.8 | 2.0 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 49.7 | 9.7 | 3.6 | 8.3 | 0.0 | | 0.0 | | 0.0 | |
| 1-Propanol | 2015 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 89.0 | 2.2 |
| | 2016 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 38.8 | 13.4 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 92.1 | 7.1 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2-Ethyl-5-Methyl-Furan | 2015 | 0.0 | | 0.0 | | 10.9 | 12.4 | 4.2 | 14.0 | 240.6 | 10.8 |
| | 2016 | 0.0 | | 0.0 | | 5.1 | 8.7 | 8.7 | 1.2 | 544.9 | 9.3 |
| | 2017 | 0.0 | | 0.0 | | 4.5 | 1.1 | 7.4 | 4.9 | 350.0 | 11.4 |
| | 2018 | 0.0 | | 0.0 | | 16.3 | 9.3 | 3.6 | 1.7 | 340.4 | 0.4 |
| Toluene | 2015 | 76.1 | 3.4 | 331.5 | 12.8 | 70.5 | 2.3 | 32.8 | 0.5 | 4721.7 | 9.8 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2016 | 18.1 | 5.9 | 60.5 | 5.3 | 50.3 | 5.4 | 20.7 | 2.3 | 19603.0 | 8.9 |
| | 2017 | 146.3 | 1.3 | 282.4 | 5.1 | 59.1 | 2.1 | 49.2 | 6.8 | 53948.0 | 9.8 |
| | 2018 | 35.4 | 2.4 | 63.7 | 14.1 | 38.4 | 6.7 | 16.5 | 10.8 | 651.6 | 2.2 |
| | 2015 | 57.5 | 3.0 | 2.3 | 4.8 | 75.6 | 13.4 | 0.0 | | 0.0 | |
| 2-Methyl-3-Buten-2-ol | 2016 | 15.6 | 4.2 | 29.3 | 1.1 | 37.0 | 11.0 | 0.0 | | 0.0 | |
| | 2017 | 191.5 | 4.4 | 43.2 | 3.0 | 63.4 | 6.4 | 0.0 | | 0.0 | |
| | 2018 | 97.3 | 9.3 | 33.6 | 11.2 | 45.9 | 10.7 | 0.0 | | 0.0 | |
| | 2015 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 26.1 | 2.0 |
| Nonomethyl Succinate | 2016 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 477.6 | 11.6 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 1202.6 | 5.2 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 209.6 | 12.4 | 30.0 | 5.1 | 917.1 | 0.9 | 1736.8 | 12.6 | 2025.1 | 11.2 |
| 2,3-Pentanedione | 2016 | 11.5 | 2.3 | 283.6 | 7.1 | 1951.0 | 6.6 | 1613.0 | 1.0 | 886.0 | 6.1 |
| | 2017 | 13.3 | 7.7 | 14.2 | 0.4 | 1805.8 | 5.5 | 33.8 | 9.0 | 3204.1 | 12.5 |
| | 2018 | 15.4 | 11.1 | 146.9 | 3.2 | 418.3 | 2.5 | 1057.5 | 5.4 | 17911.1 | 2.4 |
| | 2015 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 46.6 | 0.8 |
| Dimethyl Disulfide | 2016 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 322.5 | 1.0 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 302.9 | 1.5 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 0.0 | | 0.0 | | 155.5 | 1.8 | 101.2 | 5.7 | 27.9 | 9.2 |
| 2-Ethenyl-Furan | 2016 | 0.0 | | 0.0 | | 168.6 | 0.4 | 12.0 | 3.7 | 106.8 | 4.6 |
| | 2017 | 0.0 | | 0.0 | | 96.2 | 10.3 | 12.7 | 9.2 | 263.5 | 5.5 |
| | 2018 | 0.0 | | 0.0 | | 146.8 | 6.4 | 18.3 | 5.0 | 185.8 | 1.6 |
| | 2015 | 32.6 | 12.4 | 246.9 | 8.1 | 9.9 | 13.9 | 21.0 | 6.1 | 0.0 | |
| Hexanal | 2016 | 31.0 | 13.8 | 157.6 | 7.1 | 26.6 | 9.3 | 11.1 | 5.3 | 0.0 | |
| | 2017 | 455.6 | 13.4 | 503.5 | 0.6 | 6.6 | 9.5 | 5.5 | 4.6 | 0.0 | |
| | 2018 | 226.1 | 8.2 | 137.5 | 11.8 | 25.5 | 8.1 | 5.4 | 8.7 | 0.0 | |
| | 2015 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 23.1 | 13.4 |
| 2-Methyl-1-Propanol | 2016 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 19137.9 | 10.8 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 2101.6 | 1.1 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 25.4 | 8.2 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Methyl 2-Ethylpentanoate | 2016 | 28.2 | 4.8 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2017 | 320.0 | 8.4 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 58.3 | 5.9 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 5-Butyl-Dihydro-2(3H)-Furanone | 2015 | 0.0 | | 386.3 | 13.3 | 119.5 | 8.1 | 4.3 | 12.3 | 506.1 | 1.7 |
| | 2016 | 0.0 | | 254.7 | 11.6 | 92.1 | 10.3 | 4.2 | 10.3 | 1645.1 | 1.4 |
| | 2017 | 0.0 | | 1245.5 | 0.2 | 105.4 | 7.5 | 14.5 | 7.4 | 1942.4 | 6.1 |
| | 2018 | 0.0 | | 262.3 | 9.6 | 117.1 | 7.1 | 4.7 | 6.2 | 1114.9 | 9.6 |
| m-Cresol | 2015 | 3.9 | 2.9 | 6.5 | 6.2 | 182.1 | 3.6 | 206.6 | 6.3 | 269.3 | 4.1 |
| | 2016 | 4.1 | 12.2 | 17.1 | 8.0 | 226.8 | 6.5 | 73.5 | 8.8 | 368.4 | 15.0 |
| | 2017 | 5.0 | 7.9 | 13.8 | 4.0 | 163.6 | 3.6 | 3.8 | 6.2 | 2300.9 | 5.2 |
| | 2018 | 6.0 | 9.0 | 11.5 | 1.0 | 94.7 | 14.0 | 49.2 | 3.4 | 3490.7 | 8.4 |
| 1-Butanol | 2015 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 34.9 | 1.0 |
| | 2016 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 1044.9 | 5.3 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 408.2 | 14.4 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 105.6 | 4.6 |
| 5-Propyl-Dihydro-2(3H)-Furanone | 2015 | 0.0 | | 235.7 | 10.1 | 58.4 | 8.9 | 2.9 | 1.7 | 274.4 | 0.8 |
| | 2016 | 0.0 | | 144.7 | 8.3 | 41.6 | 9.1 | 3.6 | 6.9 | 1009.7 | 1.5 |
| | 2017 | 0.0 | | 643.3 | 2.4 | 59.5 | 4.7 | 12.4 | 4.0 | 1047.0 | 7.3 |
| | 2018 | 0.0 | | 129.8 | 10.5 | 38.2 | 12.3 | 6.8 | 3.5 | 536.6 | 5.0 |
| 3-Methyl-Pyridazine | 2015 | 0.0 | | 15.3 | 2.7 | 70.9 | 10.5 | 741.4 | 8.9 | 2183.3 | 13.2 |
| | 2016 | 0.0 | | 60.0 | 1.3 | 305.6 | 8.0 | 571.5 | 7.4 | 3201.6 | 8.1 |
| | 2017 | 0.0 | | 9.7 | 2.1 | 422.2 | 7.8 | 10.9 | 4.7 | 4764.7 | 11.2 |
| | 2018 | 0.0 | | 53.0 | 5.1 | 328.4 | 2.9 | 168.7 | 6.5 | 8754.7 | 4.1 |
| 1-Penten-3-ol | 2015 | 89.6 | 8.0 | 17.3 | 1.6 | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 178.5 | 4.9 | 3.1 | 1.5 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 282.2 | 3.8 | 57.6 | 11.0 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 267.0 | 0.5 | 26.3 | 9.7 | 0.0 | | 0.0 | | 0.0 | |
| 2-Heptanone | 2015 | 5.7 | 7.8 | 86.4 | 13.3 | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 66.6 | 13.9 | 68.1 | 4.8 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 114.1 | 12.9 | 110.5 | 0.3 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 1558.9 | 2.2 | 16.7 | 2.1 | 0.0 | | 0.0 | | 0.0 | |
| Heptanal | 2015 | 0.0 | | 49.1 | 10.5 | 16.9 | 5.4 | 0.0 | | 0.0 | |
| | 2016 | 0.0 | | 39.4 | 6.7 | 2.3 | 7.8 | 0.0 | | 0.0 | |
| | 2017 | 0.0 | | 119.7 | 4.4 | 5.8 | 5.2 | 0.0 | | 0.0 | |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2018 | 0.0 | | 7.2 | 5.7 | 11.0 | 5.5 | 0.0 | | 0.0 | |
| | 2015 | 0.0 | | 33.6 | 9.3 | 14.4 | 0.9 | 16.1 | 11.7 | 7.1 | 9.7 |
| | 2016 | 0.0 | | 3.9 | 6.8 | 3.3 | 6.9 | 8.0 | 2.3 | 16.9 | 2.2 |
| m-Menthane | 2017 | 0.0 | | 27.8 | 5.7 | 4.9 | 11.9 | 5.5 | 0.5 | 27.3 | 16.0 |
| | 2018 | 0.0 | | 3.4 | 4.8 | 5.6 | 7.5 | 4.5 | 6.0 | 63.7 | 10.2 |
| | 2015 | 0.0 | | 40.6 | 2.7 | 4.0 | 9.9 | 46.0 | 13.2 | 27.2 | 11.1 |
| | 2016 | 0.0 | | 13.0 | 7.9 | 6.2 | 12.8 | 18.7 | 3.1 | 325.7 | 12.0 |
| 1,3-Diazine | 2017 | 0.0 | | 3.6 | 0.7 | 44.3 | 6.0 | 8.7 | 7.4 | 62.5 | 12.3 |
| | 2018 | 0.0 | | 49.1 | 3.4 | 3.4 | 2.9 | 16.0 | 7.3 | 150.1 | 2.9 |
| | 2015 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 4709.4 | 1.8 |
| | 2016 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 21874.3 | 8.6 |
| 2-Methyl-1-Butanol | 2017 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 14512.1 | 11.9 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 76.4 | 8.7 | 185.6 | 3.0 | 46.3 | 2.5 | 162.0 | 6.9 | 7982.1 | 6.9 |
| | 2016 | 142.4 | 4.6 | 158.6 | 10.5 | 46.6 | 9.2 | 65.2 | 10.5 | 9422.0 | 10.5 |
| 2-Propyl-Furan | 2017 | 8.0 | 9.6 | 7.0 | 2.0 | 34.7 | 11.4 | 11.5 | 7.7 | 11776.4 | 7.7 |
| | 2018 | 12.4 | 7.1 | 10.2 | 8.6 | 22.2 | 10.3 | 191.1 | 2.5 | 11826.9 | 2.5 |
| | 2015 | 32.2 | 11.0 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 300.3 | 4.1 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 3-Methyl-1-Butanol | 2017 | 192.6 | 8.7 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 221.3 | 10.7 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 35.4 | 2.9 | 240.0 | 12.1 | 45.0 | 2.9 | 21.1 | 10.9 | 110.9 | 5.8 |
| | 2016 | 17.4 | 11.1 | 14.3 | 10.6 | 21.3 | 3.8 | 3.8 | 9.9 | 13.0 | 5.8 |
| 2-Pentyl-Furan | 2017 | 263.2 | 9.8 | 167.3 | 7.0 | 20.5 | 8.8 | 6.4 | 1.7 | 19.4 | 1.9 |
| | 2018 | 216.3 | 3.3 | 137.8 | 8.5 | 38.4 | 6.3 | 6.2 | 3.8 | 12.0 | 10.3 |
| | 2015 | 32.7 | 2.4 | 20.4 | 8.7 | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 117.1 | 3.7 | 2.9 | 5.7 | 0.0 | | 0.0 | | 0.0 | |
| 3-Octanone | 2017 | 91.2 | 5.7 | 28.0 | 3.0 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 60.5 | 4.4 | 3.9 | 8.8 | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 46.1 | 5.8 | 54.1 | 13.8 | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 57.8 | 8.6 | 34.3 | 7.9 | 0.0 | | 0.0 | | 0.0 | |
| 1-Pentanol | 2017 | 142.0 | 5.7 | 67.4 | 1.5 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 50.0 | 11.1 | 40.3 | 12.4 | 0.0 | | 0.0 | | 0.0 | |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Methyl-Pyrazine | 2015 | 3.7 | 3.4 | 114.8 | 12.0 | 550.8 | 1.7 | 270.7 | 10.4 | 1014.2 | 6.9 |
| | 2016 | 18.1 | 0.8 | 112.0 | 3.5 | 566.1 | 1.5 | 162.8 | 7.7 | 1080.1 | 3.1 |
| | 2017 | 5.9 | 11.7 | 2.0 | 1.1 | 274.7 | 6.4 | 39.6 | 10.6 | 2077.3 | 10.6 |
| | 2018 | 864.4 | 6.9 | 203.1 | 7.8 | 449.7 | 2.8 | 233.7 | 8.0 | 454.2 | 2.2 |
| 2-Methyl-Dihydro-2(3H)-Furanone | 2015 | 11.0 | 5.3 | 6.7 | 5.4 | 1161.0 | 1.9 | 437.4 | 12.5 | 11415.6 | 8.6 |
| | 2016 | 3.8 | 8.5 | 152.1 | 1.6 | 1645.6 | 2.3 | 577.1 | 8.8 | 15831.7 | 7.7 |
| | 2017 | 22.8 | 4.4 | 1.5 | 1.1 | 1015.8 | 6.8 | 153.8 | 4.6 | 21675.5 | 7.5 |
| | 2018 | 26.6 | 8.3 | 67.2 | 6.2 | 1178.3 | 1.0 | 817.3 | 11.9 | 19081.9 | 11.8 |
| p-Cymene | 2015 | 12.0 | 2.8 | 5.7 | 4.2 | 16.3 | 0.9 | 7.3 | 2.0 | 49.6 | 10.4 |
| | 2016 | 2.9 | 2.6 | 0.6 | 1.4 | 11.5 | 5.1 | 2.6 | 2.2 | 120.3 | 0.5 |
| | 2017 | 4.0 | 7.2 | 2.5 | 14.6 | 10.9 | 7.5 | 0.4 | 7.1 | 20.7 | 5.8 |
| | 2018 | 195.4 | 6.0 | 2.2 | 13.1 | 2.9 | 2.9 | 4.8 | 1.4 | 58.5 | 7.3 |
| Mesitylene | 2015 | 8.2 | 11.8 | 25.9 | 11.8 | 24.6 | 4.8 | 10.5 | 8.0 | 3.5 | 9.4 |
| | 2016 | 11.3 | 2.2 | 2.0 | 2.4 | 21.1 | 9.8 | 13.4 | 8.3 | 3436.8 | 11.6 |
| | 2017 | 31.5 | 1.7 | 23.3 | 10.2 | 19.6 | 6.0 | 17.2 | 8.0 | 14.9 | 9.7 |
| | 2018 | 1532.1 | 4.6 | 21.5 | 4.5 | 31.2 | 6.9 | 8.9 | 8.2 | 10.2 | 5.3 |
| 3,5-Xylenol | 2015 | 0.0 | | 0.0 | | 41.8 | 7.9 | 18.5 | 8.1 | 97.3 | 8.5 |
| | 2016 | 0.0 | | 0.0 | | 39.9 | 12.6 | 3.4 | 3.6 | 158.9 | 5.7 |
| | 2017 | 0.0 | | 0.0 | | 61.1 | 10.4 | 2.9 | 11.6 | 286.1 | 9.3 |
| | 2018 | 0.0 | | 0.0 | | 40.0 | 13.7 | 22.1 | 6.9 | 350.1 | 13.2 |
| 3-Hydroxy-2-Butanone | 2015 | 116.5 | 7.8 | 132.0 | 5.6 | 141.9 | 6.9 | 306.1 | 10.1 | 1477.8 | 7.2 |
| | 2016 | 101.6 | 1.0 | 155.5 | 6.2 | 184.8 | 9.4 | 266.0 | 8.7 | 2171.8 | 13.4 |
| | 2017 | 15.8 | 0.1 | 24.6 | 6.3 | 121.0 | 6.4 | 77.8 | 5.0 | 3354.1 | 8.4 |
| | 2018 | 82.9 | 9.0 | 107.8 | 5.1 | 209.5 | 7.2 | 360.6 | 2.4 | 5088.3 | 6.7 |
| Vinylene Carbonate | 2015 | 0.0 | | 0.0 | | 330.7 | 4.4 | 2070.1 | 0.5 | 9172.5 | 9.7 |
| | 2016 | 0.0 | | 0.0 | | 758.3 | 2.8 | 1901.9 | 9.5 | 16120.0 | 4.0 |
| | 2017 | 0.0 | | 0.0 | | 1035.4 | 4.5 | 717.3 | 4.3 | 19420.9 | 12.7 |
| | 2018 | 0.0 | | 0.0 | | 1079.4 | 8.7 | 2090.4 | 6.6 | 21659.4 | 10.7 |
| 2,6-Xylenol | 2015 | 0.0 | | 0.0 | | 378.5 | 8.5 | 116.3 | 13.0 | 480.3 | 4.2 |
| | 2016 | 0.0 | | 0.0 | | 392.7 | 6.0 | 38.9 | 2.0 | 648.1 | 3.0 |
| | 2017 | 0.0 | | 0.0 | | 504.5 | 9.1 | 21.9 | 0.5 | 1249.9 | 8.2 |
| | 2018 | 0.0 | | 0.0 | | 350.5 | 7.2 | 44.8 | 9.3 | 1624.2 | 3.4 |
| Octanal | 2015 | 0.0 | | 19.2 | 4.3 | 48.6 | 5.8 | 0.0 | | 0.0 | |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2016 | 0.0 | | 40.1 | 9.7 | 61.5 | 3.4 | 0.0 | | 0.0 | |
| | 2017 | 0.0 | | 26.9 | 7.9 | 54.5 | 8.9 | 0.0 | | 0.0 | |
| | 2018 | 0.0 | | 34.1 | 8.6 | 53.1 | 9.5 | 0.0 | | 0.0 | |
| 1-Hydroxy-2-Propanone | 2015 | 2960.0 | 10.5 | 1458.7 | 10.3 | 1659.9 | 1.1 | 5867.8 | 9.3 | 6411.6 | 1.6 |
| | 2016 | 1247.7 | 7.5 | 1545.6 | 11.3 | 2414.8 | 6.1 | 3062.3 | 9.9 | 13091.7 | 5.4 |
| | 2017 | 804.1 | 5.0 | 1722.8 | 3.1 | 2379.5 | 7.8 | 6784.9 | 3.3 | 28531.5 | 7.0 |
| | 2018 | 843.2 | 7.9 | 1274.6 | 6.1 | 1946.2 | 4.9 | 3316.1 | 0.3 | 21972.9 | 10.8 |
| | 2015 | 12.7 | 3.3 | 13.0 | 11.4 | 0.0 | | 0.0 | | 0.0 | |
| cis-2-Heptanal | 2016 | 15.1 | 7.7 | 7.3 | 12.2 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 32.7 | 11.8 | 22.4 | 3.8 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 1707.7 | 3.3 | 15.1 | 10.2 | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 0.0 | | 0.0 | | 330.7 | 11.1 | 23.5 | 10.0 | 41.8 | 12.8 |
| 2,5-Dimethyl-Pyrazine | 2016 | 0.0 | | 0.0 | | 464.0 | 1.5 | 15.7 | 2.7 | 1053.3 | 4.8 |
| | 2017 | 0.0 | | 0.0 | | 196.7 | 10.8 | 23.2 | 9.4 | 149.4 | 2.2 |
| | 2018 | 0.0 | | 0.0 | | 78.5 | 0.7 | 10.8 | 9.0 | 1178.3 | 13.8 |
| | 2015 | 39.1 | 9.3 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| cis-2-Pentenol | 2016 | 107.8 | 10.8 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 124.7 | 10.4 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 205.1 | 4.3 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 0.0 | | 0.0 | | 431.4 | 4.4 | 152.6 | 3.1 | 1374.8 | 1.1 |
| 2,6-Dimethyl-Pyrazine | 2016 | 0.0 | | 0.0 | | 484.3 | 2.7 | 77.0 | 6.5 | 1075.6 | 5.0 |
| | 2017 | 0.0 | | 0.0 | | 183.9 | 4.1 | 64.0 | 2.6 | 1368.4 | 5.3 |
| | 2018 | 0.0 | | 0.0 | | 333.6 | 0.4 | 62.4 | 13.3 | 1308.0 | 2.8 |
| | 2015 | 12.2 | 4.9 | 33.0 | 10.3 | 0.0 | | 0.0 | | 0.0 | |
| 2-Heptanol | 2016 | 40.2 | 2.7 | 8.3 | 12.3 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 387.9 | 12.8 | 34.0 | 6.4 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 1452.9 | 4.2 | 13.4 | 12.0 | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 7.8 | 5.4 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2-Pentene | 2016 | 25.6 | 8.2 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 197.7 | 11.5 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 590.3 | 8.6 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2-Cyclopenten-1-one | 2015 | 118.0 | 8.3 | 56.1 | 10.2 | 181.9 | 6.2 | 294.6 | 14.5 | 1692.7 | 1.4 |
| | 2016 | 107.5 | 3.6 | 197.2 | 3.1 | 207.6 | 2.2 | 245.2 | 8.1 | 1387.8 | 1.8 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2017 | 108.8 | 13.5 | 53.5 | 4.5 | 219.2 | 9.4 | 224.5 | 5.1 | 3467.5 | 0.5 |
| | 2018 | 48.4 | 13.2 | 130.5 | 13.2 | 240.0 | 7.6 | 334.2 | 0.4 | 3582.4 | 12.3 |
| | 2015 | 91.3 | 1.1 | 74.2 | 6.8 | 0.0 | | 0.0 | | 0.0 | |
| 1-Hexanol | 2016 | 552.6 | 9.4 | 53.2 | 6.8 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 516.7 | 5.2 | 93.2 | 0.4 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 747.3 | 7.8 | 49.7 | 6.5 | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 22.1 | 6.6 | 10.4 | 10.1 | 119.9 | 3.9 | 119.9 | 3.9 | 485.5 | 2.9 |
| 2-Methyl-2-Cyclopenten-1-one | 2016 | 5.3 | 1.5 | 17.7 | 6.0 | 115.8 | 7.2 | 115.8 | 7.2 | 1094.2 | 11.9 |
| | 2017 | 5.4 | 7.4 | 8.7 | 1.3 | 127.5 | 7.1 | 183.8 | 6.5 | 1534.2 | 7.8 |
| | 2018 | 12.3 | 4.1 | 26.8 | 13.3 | 133.5 | 1.8 | 133.5 | 1.8 | 1830.1 | 5.4 |
| | 2015 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 1428.4 | 1.3 |
| 5-Methyl-2-Furanmethanethiol | 2016 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 8526.8 | 0.9 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 2656.3 | 5.7 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 27.9 | 9.2 |
| | 2015 | 314.3 | 7.6 | 140.1 | 12.3 | 257.6 | 12.0 | 976.6 | 10.9 | 3674.1 | 1.9 |
| 1-Hydroxy-2-Butanone | 2016 | 96.8 | 11.4 | 169.0 | 2.9 | 497.1 | 9.2 | 649.8 | 4.9 | 656.2 | 4.7 |
| | 2017 | 29.1 | 7.3 | 37.1 | 2.0 | 404.5 | 10.1 | 849.4 | 1.1 | 7972.4 | 1.6 |
| | 2018 | 76.4 | 6.8 | 77.5 | 11.4 | 429.0 | 10.5 | 635.9 | 8.5 | 9836.8 | 10.8 |
| | 2015 | 0.0 | | 0.0 | | 47.4 | 4.1 | 10.6 | 4.2 | 138.2 | 2.5 |
| 2-Ethyl-6-Methyl-Pyrazine | 2016 | 0.0 | | 0.0 | | 55.8 | 3.8 | 11.5 | 0.9 | 130.3 | 11.7 |
| | 2017 | 0.0 | | 0.0 | | 26.3 | 2.2 | 4.1 | 10.9 | 181.4 | 6.5 |
| | 2018 | 0.0 | | 0.0 | | 43.2 | 4.3 | 11.2 | 1.9 | 144.0 | 6.9 |
| | 2015 | 18.6 | 1.1 | 51.2 | 2.6 | 53.2 | 4.1 | 134.8 | 10.5 | 508.3 | 7.2 |
| Nonanal | 2016 | 8.4 | 7.3 | 43.2 | 5.2 | 75.8 | 12.1 | 101.1 | 8.9 | 681.2 | 5.2 |
| | 2017 | 10.6 | 7.4 | 104.2 | 5.3 | 76.0 | 1.1 | 220.8 | 3.4 | 1376.7 | 15.2 |
| | 2018 | 13.7 | 11.2 | 63.2 | 7.8 | 94.3 | 8.6 | 70.3 | 3.9 | 2511.5 | 5.6 |
| | 2015 | 7.8 | 4.2 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 1-Ethyl-1-Methyl-Cyclopentane | 2016 | 5.2 | 2.4 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 86.1 | 4.4 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 35.2 | 4.7 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 9.9 | 6.0 | 73.1 | 5.5 | 0.0 | | 0.0 | | 0.0 | |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | 2016 | 12.7 | 10.7 | 27.6 | 10.0 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 240.9 | 5.5 | 92.7 | 0.6 | 0.0 | | 0.0 | | 0.0 | |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Octanol | 2018 | 66.6 | 13.2 | 33.0 | 14.5 | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 3.0 | 3.6 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 9.3 | 9.8 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 75.9 | 2.3 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 383.3 | 5.4 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2-Cyclohexen-1-one | 2015 | 9.6 | 5.5 | 7.2 | 14.0 | 22.5 | 6.5 | 66.3 | 9.9 | 56.4 | 6.1 |
| | 2016 | 9.8 | 10.0 | 10.0 | 6.7 | 35.6 | 9.4 | 49.3 | 10.9 | 587.2 | 3.1 |
| | 2017 | 19.2 | 13.3 | 7.2 | 7.3 | 40.5 | 7.9 | 6.4 | 2.6 | 746.9 | 6.2 |
| | 2018 | 6.6 | 5.7 | 2.9 | 8.1 | 54.0 | 7.7 | 70.1 | 2.4 | 31.8 | 13.7 |
| trans-2-Octenal | 2015 | 6.6 | 12.7 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 2.9 | 14.5 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 340.8 | 4.6 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 63.4 | 3.6 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 5-Methyl-2(3H)-Furanone | 2015 | 0.0 | | 114.2 | 11.7 | 308.8 | 8.2 | 1260.0 | 11.6 | 5683.0 | 3.9 |
| | 2016 | 0.0 | | 167.5 | 8.8 | 577.9 | 9.3 | 1356.4 | 7.1 | 8085.5 | 2.0 |
| | 2017 | 0.0 | | 36.3 | 9.3 | 706.7 | 8.6 | 1163.4 | 4.4 | 10002.6 | 1.5 |
| | 2018 | 0.0 | | 177.0 | 7.0 | 695.3 | 6.0 | 1308.0 | 5.4 | 8980.7 | 5.3 |
| 1,3-Dihydro-4-Methyl-2H-Imidazol-2-one | 2015 | 31.4 | 9.9 | 33.5 | 6.8 | 102.9 | 11.2 | 597.6 | 9.3 | 1816.1 | 7.9 |
| | 2016 | 26.8 | 7.9 | 58.1 | 1.8 | 293.8 | 5.2 | 475.4 | 12.3 | 3910.9 | 1.8 |
| | 2017 | 17.6 | 7.7 | 18.1 | 2.0 | 358.1 | 6.4 | 589.6 | 2.9 | 4005.1 | 1.2 |
| | 2018 | 39.8 | 11.0 | 76.3 | 7.3 | 335.4 | 3.1 | 544.2 | 2.5 | 6696.1 | 9.9 |
| 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | 2015 | 0.0 | | 0.0 | | 78.3 | 7.4 | 18.6 | 7.2 | 192.8 | 2.0 |
| | 2016 | 0.0 | | 0.0 | | 64.8 | 8.5 | 5.6 | 7.2 | 483.1 | 2.7 |
| | 2017 | 0.0 | | 0.0 | | 73.1 | 8.7 | 7.3 | 1.9 | 694.6 | 4.7 |
| | 2018 | 0.0 | | 0.0 | | 108.3 | 6.7 | 3.0 | 3.4 | 370.7 | 8.4 |
| 1-Octen-3-ol | 2015 | 151.6 | 3.2 | 98.9 | 2.6 | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 460.6 | 1.9 | 69.0 | 7.4 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 447.2 | 5.9 | 129.4 | 1.1 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 348.1 | 2.7 | 46.3 | 12.4 | 0.0 | | 0.0 | | 0.0 | |
| 1-Heptanol | 2015 | 7.3 | 9.0 | 13.5 | 1.7 | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 34.0 | 2.4 | 7.3 | 13.8 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 43.6 | 8.9 | 12.4 | 1.4 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 35.7 | 9.1 | 6.0 | 14.2 | 0.0 | | 0.0 | | 0.0 | |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| Furfural | 2015 | 8369.4 | 8.4 | 8940.0 | 1.0 | 14841.3 | 0.9 | 18300.5 | 5.2 | 24513.0 | 6.4 |
| | 2016 | 9343.6 | 4.1 | 10268.8 | 1.5 | 17582.7 | 0.2 | 17116.0 | 6.0 | 26387.8 | 10.5 |
| | 2017 | 5340.1 | 3.4 | 6632.6 | 0.6 | 15302.5 | 7.0 | 18128.9 | 2.7 | 32952.1 | 2.7 |
| | 2018 | 8732.3 | 10.0 | 9144.1 | 0.3 | 16086.3 | 1.1 | 18062.7 | 2.0 | 34806.3 | 14.1 |
| Ethanoic Acid | 2015 | 8277.6 | 6.3 | 8487.5 | 6.6 | 11058.8 | 3.9 | 19837.7 | 2.1 | 66429.6 | 5.0 |
| | 2016 | 8609.0 | 3.1 | 8815.0 | 8.7 | 15822.9 | 8.8 | 18791.3 | 3.9 | 76709.6 | 9.1 |
| | 2017 | 2514.7 | 1.5 | 2973.5 | 5.3 | 19983.3 | 8.1 | 19701.2 | 5.5 | 191576.4 | 0.8 |
| | 2018 | 4124.4 | 13.8 | 6653.4 | 9.3 | 13462.7 | 1.6 | 31012.7 | 4.5 | 194203.0 | 2.0 |
| 2-Nonen-4-one | 2015 | 0.0 | | 24.7 | 9.1 | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 0.0 | | 42.4 | 2.3 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 0.0 | | 18.8 | 0.8 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 0.0 | | 32.5 | 2.5 | 0.0 | | 0.0 | | 0.0 | |
| 1,2,3,4-Tetrahydro-1,6,8-Trimethyl-Naphthalene | 2015 | 0.0 | | 0.0 | | 67.4 | 0.2 | 47.1 | 10.2 | 447.6 | 1.0 |
| | 2016 | 0.0 | | 0.0 | | 53.9 | 5.1 | 19.0 | 4.8 | 670.1 | 2.8 |
| | 2017 | 0.0 | | 0.0 | | 62.1 | 2.3 | 9.6 | 4.5 | 1265.3 | 15.7 |
| | 2018 | 0.0 | | 0.0 | | 96.9 | 11.1 | 19.5 | 6.6 | 606.5 | 5.1 |
| 2-Ethyl-1-Hexanol | 2015 | 41.3 | 5.8 | 51.1 | 1.5 | 62.8 | 3.5 | 108.2 | 10.0 | 392.4 | 12.2 |
| | 2016 | 50.1 | 8.3 | 32.8 | 2.0 | 56.5 | 3.3 | 83.9 | 6.6 | 1777.5 | 0.0 |
| | 2017 | 25.5 | 10.3 | 34.1 | 3.2 | 81.7 | 7.9 | 42.3 | 2.8 | 2997.0 | 4.4 |
| | 2018 | 21.5 | 4.1 | 50.1 | 2.4 | 88.7 | 3.2 | 109.0 | 2.9 | 855.9 | 8.7 |
| trans,trans-2,4-Heptadienal | 2015 | 0.0 | | 42.7 | 13.3 | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 0.0 | | 20.0 | 3.4 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 0.0 | | 23.3 | 7.0 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 0.0 | | 48.0 | 11.1 | 0.0 | | 0.0 | | 0.0 | |
| 3-Methyl-Furfural | 2015 | 439.1 | 9.7 | 571.0 | 10.0 | 1342.7 | 2.7 | 3975.3 | 3.5 | 275.2 | 5.0 |
| | 2016 | 312.3 | 9.1 | 690.2 | 4.1 | 2852.6 | 5.0 | 2506.2 | 9.2 | 514.6 | 4.3 |
| | 2017 | 83.5 | 3.4 | 145.6 | 2.8 | 2526.2 | 3.5 | 1840.5 | 5.9 | 455.5 | 10.0 |
| | 2018 | 124.0 | 8.4 | 153.2 | 1.1 | 1670.3 | 3.6 | 1820.7 | 6.9 | 848.6 | 7.2 |
| Furfuryl Formate | 2015 | 97.4 | 10.9 | 118.0 | 11.4 | 246.2 | 0.2 | 429.5 | 10.7 | 1820.2 | 10.4 |
| | 2016 | 80.5 | 1.3 | 126.7 | 3.4 | 179.1 | 8.9 | 395.4 | 5.4 | 3999.8 | 8.9 |
| | 2017 | 85.1 | 4.6 | 167.3 | 1.7 | 161.3 | 10.3 | 282.6 | 5.6 | 2991.8 | 0.5 |
| | 2018 | 58.1 | 8.1 | 127.9 | 8.0 | 159.0 | 5.2 | 384.1 | 10.2 | 4359.7 | 11.4 |
| 1-(2-Furanyl)-Ethanone | 2015 | 1064.0 | 6.9 | 1357.5 | 7.7 | 3309.3 | 2.7 | 5147.5 | 12.0 | 10890.1 | 3.1 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2016 | 770.8 | 7.2 | 1531.5 | 9.0 | 6772.3 | 5.1 | 5929.1 | 11.7 | 14842.7 | 4.5 |
| | 2017 | 849.9 | 2.4 | 1049.3 | 2.9 | 5290.8 | 2.8 | 5333.7 | 4.0 | 14116.0 | 5.9 |
| | 2018 | 409.6 | 8.5 | 533.6 | 10.1 | 3979.8 | 4.0 | 4075.8 | 9.7 | 15542.0 | 13.8 |
| | 2015 | 25.5 | 9.8 | 29.2 | 12.9 | 54.1 | 13.8 | 56.4 | 11.8 | 250.3 | 0.8 |
| Decanal | 2016 | 17.7 | 7.4 | 5.3 | 10.1 | 91.8 | 3.4 | 107.1 | 7.1 | 1242.0 | 8.6 |
| | 2017 | 19.8 | 12.9 | 58.8 | 12.1 | 10.1 | 1.5 | 48.8 | 4.6 | 2215.3 | 13.5 |
| | 2018 | 9.3 | 10.8 | 13.7 | 5.3 | 16.8 | 8.0 | 6.3 | 8.9 | 3199.5 | 10.7 |
| | 2015 | 90.3 | 5.7 | 221.4 | 8.2 | 228.4 | 10.4 | 206.3 | 8.1 | 611.7 | 7.8 |
| Benzaldehyde | 2016 | 110.9 | 1.6 | 248.5 | 10.9 | 219.9 | 10.4 | 150.3 | 7.8 | 675.0 | 1.2 |
| | 2017 | 264.5 | 6.9 | 114.9 | 6.5 | 238.0 | 0.4 | 124.7 | 13.3 | 1375.2 | 5.9 |
| | 2018 | 91.3 | 6.0 | 133.4 | 13.8 | 183.5 | 2.7 | 165.8 | 6.0 | 1623.6 | 1.8 |
| | 2015 | 23.7 | 7.3 | 29.1 | 2.5 | 28.5 | 4.1 | 243.4 | 9.4 | 1123.8 | 6.1 |
| Furfuryl Acetate | 2016 | 27.2 | 6.5 | 39.2 | 7.6 | 89.3 | 11.5 | 200.2 | 10.1 | 2237.2 | 8.4 |
| | 2017 | 11.4 | 1.4 | 12.5 | 4.9 | 87.9 | 7.4 | 156.3 | 4.6 | 2016.1 | 5.0 |
| | 2018 | 23.6 | 7.4 | 24.3 | 13.8 | 92.2 | 4.5 | 239.3 | 10.7 | 3456.7 | 1.1 |
| | 2015 | 0.0 | | 0.0 | | 23.9 | 0.3 | 773.1 | 13.2 | 2314.0 | 6.0 |
| Propanoic Acid | 2016 | 0.0 | | 0.0 | | 83.6 | 13.1 | 693.4 | 3.6 | 6815.4 | 7.8 |
| | 2017 | 0.0 | | 0.0 | | 192.3 | 7.7 | 693.4 | 3.6 | 299.8 | 5.8 |
| | 2018 | 0.0 | | 0.0 | | 7.6 | 10.3 | 485.4 | 7.5 | 701.6 | 13.0 |
| | 2015 | 28.0 | 3.5 | 34.8 | 4.6 | 0.0 | | 0.0 | | 0.0 | |
| 1-Octanol | 2016 | 60.8 | 10.0 | 34.1 | 3.7 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 71.6 | 7.2 | 17.8 | 1.7 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 65.2 | 4.1 | 29.3 | 11.0 | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 6.1 | 8.0 | 191.9 | 2.3 | 29.5 | 5.4 | 58.2 | 5.5 | 435.3 | 3.3 |
| Dimethyl Sulfoxide | 2016 | 5.6 | 10.0 | 365.1 | 15.0 | 24.5 | 11.2 | 15.9 | 6.4 | 441.0 | 4.4 |
| | 2017 | 8.9 | 2.3 | 6.7 | 3.9 | 65.5 | 5.4 | 8.0 | 3.1 | 514.9 | 8.1 |
| | 2018 | 6.0 | 4.3 | 282.6 | 14.3 | 41.6 | 6.2 | 65.7 | 5.6 | 267.6 | 12.3 |
| | 2015 | 0.0 | | 0.0 | | 65.4 | 5.8 | 23.8 | 1.4 | 169.3 | 1.5 |
| 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | 2016 | 0.0 | | 0.0 | | 52.4 | 0.3 | 5.7 | 3.6 | 417.8 | 11.7 |
| | 2017 | 0.0 | | 0.0 | | 63.3 | 1.7 | 12.8 | 8.8 | 571.3 | 10.9 |
| | 2018 | 0.0 | | 0.0 | | 79.8 | 2.8 | 4.5 | 3.6 | 118.3 | 4.3 |
| | 2015 | 2072.4 | 8.2 | 2040.9 | 7.5 | 2463.7 | 2.2 | 7971.7 | 8.7 | 17003.7 | 4.2 |
| 5-Methyl-Furfural | 2016 | 2018.7 | 1.2 | 3172.0 | 4.0 | 4953.3 | 11.7 | 5627.7 | 6.2 | 17848.8 | 5.6 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| 4-Cyclopentene-1,3-dione | 2017 | 875.8 | 2.9 | 1429.0 | 2.0 | 1864.1 | 2.2 | 2230.6 | 7.1 | 18869.5 | 2.1 |
| | 2018 | 1620.3 | 12.0 | 1814.7 | 1.7 | 3940.3 | 0.7 | 5491.2 | 13.0 | 22090.1 | 11.1 |
| | 2015 | 517.0 | 2.5 | 462.5 | 10.7 | 1416.1 | 1.9 | 8184.9 | 13.0 | 13308.5 | 8.6 |
| | 2016 | 397.1 | 9.5 | 699.4 | 13.1 | 4026.0 | 2.2 | 6619.5 | 11.8 | 17196.2 | 6.4 |
| | 2017 | 111.9 | 7.5 | 152.9 | 2.7 | 2690.9 | 9.0 | 4404.3 | 3.4 | 20881.1 | 2.1 |
| | 2018 | 399.1 | 10.2 | 594.2 | 4.6 | 4026.4 | 3.4 | 7007.1 | 7.5 | 21389.0 | 8.8 |
| 2-Methyl-Benzofuran | 2015 | 0.0 | | 0.0 | | 753.9 | 0.3 | 193.1 | 11.0 | 2345.0 | 6.0 |
| | 2016 | 0.0 | | 0.0 | | 974.2 | 11.6 | 107.4 | 3.2 | 8254.9 | 1.6 |
| | 2017 | 0.0 | | 0.0 | | 1154.6 | 16.1 | 74.9 | 1.3 | 9803.4 | 6.9 |
| | 2018 | 0.0 | | 0.0 | | 654.3 | 11.7 | 97.7 | 9.0 | 8989.3 | 0.6 |
| 1-(5-Methyl-2-Furanyl)-Ethanone | 2015 | 53.7 | 0.1 | 46.1 | 5.7 | 72.5 | 7.0 | 177.1 | 11.3 | 1012.7 | 5.4 |
| | 2016 | 39.6 | 13.0 | 77.2 | 7.2 | 133.9 | 7.5 | 156.0 | 12.9 | 2278.6 | 3.5 |
| | 2017 | 44.5 | 9.6 | 35.5 | 1.7 | 100.0 | 9.4 | 120.5 | 0.4 | 2243.6 | 8.0 |
| | 2018 | 52.2 | 4.8 | 48.7 | 8.6 | 129.7 | 11.2 | 150.9 | 3.3 | 2693.8 | 5.3 |
| trans-2-Octenol | 2015 | 4.3 | 3.0 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 6.7 | 3.0 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 70.2 | 2.8 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 11.8 | 4.6 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Diethylene Glycol Ethyl Ether | 2015 | 77.0 | 7.4 | 257.9 | 13.5 | 318.9 | 3.6 | 421.9 | 0.6 | 2017.9 | 5.4 |
| | 2016 | 85.8 | 8.9 | 205.0 | 7.6 | 397.0 | 3.4 | 423.8 | 1.6 | 1868.5 | 11.4 |
| | 2017 | 151.7 | 2.0 | 2.6 | 13.7 | 397.6 | 9.2 | 414.3 | 1.7 | 5243.0 | 10.1 |
| | 2018 | 181.7 | 2.8 | 140.4 | 11.2 | 353.8 | 3.1 | 498.9 | 1.5 | 5155.3 | 13.4 |
| 3-Methyl-Dihydro-2(3H)-Furanone | 2015 | 55.3 | 2.4 | 38.8 | 3.7 | 67.9 | 2.4 | 251.3 | 9.0 | 863.8 | 7.4 |
| | 2016 | 37.8 | 6.0 | 50.3 | 6.8 | 142.5 | 9.9 | 139.9 | 7.9 | 1738.1 | 2.1 |
| | 2017 | 15.5 | 11.6 | 9.6 | 11.0 | 186.2 | 0.6 | 208.5 | 2.5 | 1413.1 | 8.4 |
| | 2018 | 43.4 | 3.9 | 30.3 | 12.4 | 198.5 | 2.1 | 230.3 | 7.0 | 1932.1 | 7.7 |
| 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | 2015 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 31.7 | 7.2 |
| | 2016 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 81.9 | 4.4 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 130.8 | 4.4 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 81.7 | 7.6 |
| Benzeneacetaldehyde | 2015 | 8.0 | 1.7 | 88.0 | 8.1 | 675.2 | 7.9 | 1028.7 | 7.6 | 3591.8 | 4.3 |
| | 2016 | 6.2 | 2.7 | 124.9 | 3.5 | 1095.6 | 4.5 | 947.1 | 5.6 | 8725.4 | 5.7 |
| | 2017 | 46.7 | 2.3 | 20.6 | 1.5 | 403.4 | 4.6 | 200.1 | 1.4 | 9758.5 | 6.4 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| 3,5-Dimethyl-Dihydro-2-Furanone | 2018 | 190.8 | 12.9 | 168.0 | 2.4 | 793.6 | 1.0 | 842.5 | 2.1 | 12558.9 | 11.9 |
| | 2015 | 100.2 | 10.0 | 51.6 | 10.0 | 85.2 | 14.1 | 128.4 | 7.9 | 614.7 | 10.6 |
| | 2016 | 43.0 | 7.7 | 74.7 | 7.7 | 108.0 | 11.1 | 88.3 | 3.3 | 540.0 | 3.0 |
| | 2017 | 28.7 | 6.3 | 4.3 | 6.3 | 100.6 | 5.1 | 229.6 | 2.2 | 3382.9 | 1.0 |
| | 2018 | 66.1 | 11.8 | 63.2 | 11.8 | 95.2 | 0.2 | 88.8 | 2.0 | 1552.4 | 8.3 |
| 3-Methyl-Benzaldehyde | 2015 | 11.0 | 9.1 | 2.4 | 8.3 | 38.5 | 4.1 | 1036.0 | 4.9 | 0.0 | |
| | 2016 | 5.9 | 5.4 | 54.4 | 5.6 | 1108.7 | 8.1 | 990.3 | 6.2 | 0.0 | |
| | 2017 | 5.9 | 9.3 | 82.8 | 8.2 | 728.9 | 2.5 | 51.9 | 4.6 | 0.0 | |
| | 2018 | 213.4 | 8.8 | 21.1 | 9.3 | 873.5 | 1.4 | 905.5 | 0.4 | 0.0 | |
| 2-Propenoic Acid | 2015 | 0.0 | | 0.0 | | 555.2 | 14.4 | 1486.6 | 5.5 | 3090.4 | 8.7 |
| | 2016 | 0.0 | | 0.0 | | 1273.2 | 4.1 | 1405.4 | 13.1 | 13197.2 | 2.3 |
| | 2017 | 0.0 | | 0.0 | | 348.5 | 7.3 | 541.9 | 1.6 | 6314.2 | 1.4 |
| | 2018 | 0.0 | | 0.0 | | 1169.4 | 0.8 | 911.8 | 2.2 | 11803.3 | 8.6 |
| Acetophenone | 2015 | 78.3 | 6.4 | 147.0 | 11.0 | 22.3 | 1.7 | 41.4 | 5.9 | 184.2 | 12.3 |
| | 2016 | 12.4 | 3.3 | 53.4 | 5.7 | 34.4 | 5.4 | 34.2 | 0.5 | 313.8 | 12.7 |
| | 2017 | 5.0 | 1.1 | 17.1 | 12.3 | 16.0 | 3.8 | 42.9 | 6.5 | 300.7 | 3.0 |
| | 2018 | 14.5 | 10.9 | 33.5 | 10.7 | 28.1 | 3.2 | 32.9 | 6.3 | 786.4 | 12.5 |
| 2-Furanmethanol | 2015 | 4746.7 | 8.5 | 3626.8 | 9.1 | 3947.7 | 10.4 | 18003.1 | 9.2 | 18617.5 | 2.7 |
| | 2016 | 3256.0 | 4.9 | 4241.9 | 10.8 | 12212.7 | 8.3 | 15412.9 | 5.6 | 21685.3 | 7.5 |
| | 2017 | 2271.0 | 1.3 | 1447.7 | 2.7 | 4929.0 | 1.7 | 7715.6 | 9.1 | 23273.4 | 11.9 |
| | 2018 | 2939.5 | 11.9 | 2491.9 | 0.3 | 9591.7 | 10.7 | 17009.6 | 5.6 | 52489.4 | 8.4 |
| 3-Furanmethanol | 2015 | 1196.3 | 9.4 | 1264.3 | 9.0 | 1973.8 | 4.7 | 19884.2 | 10.9 | 22481.4 | 7.7 |
| | 2016 | 1835.1 | 13.3 | 1644.0 | 2.6 | 4921.9 | 7.8 | 17916.1 | 6.9 | 16348.3 | 6.7 |
| | 2017 | 1633.5 | 5.3 | 1357.8 | 2.7 | 3784.5 | 1.7 | 9522.2 | 11.6 | 18357.0 | 11.2 |
| | 2018 | 1416.8 | 4.9 | 1814.9 | 3.9 | 4876.1 | 4.5 | 14989.8 | 5.8 | 64212.9 | 7.2 |
| 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | 2015 | 0.0 | | 0.0 | | 64.0 | 10.7 | 60.6 | 10.8 | 287.5 | 1.9 |
| | 2016 | 0.0 | | 0.0 | | 49.7 | 2.2 | 14.4 | 5.6 | 271.4 | 11.2 |
| | 2017 | 0.0 | | 0.0 | | 41.4 | 12.1 | 8.6 | 3.0 | 469.1 | 4.3 |
| | 2018 | 0.0 | | 0.0 | | 81.3 | 12.2 | 3.8 | 12.2 | 529.9 | 7.7 |
| 2-(2-Furanylmethyl)-5-Methyl-Furan | 2015 | 0.0 | | 0.0 | | 24.3 | 7.2 | 52.5 | 12.2 | 353.0 | 1.7 |
| | 2016 | 0.0 | | 0.0 | | 38.8 | 10.7 | 49.1 | 8.4 | 708.5 | 2.5 |
| | 2017 | 0.0 | | 0.0 | | 37.3 | 0.6 | 11.7 | 1.0 | 479.6 | 10.0 |
| | 2018 | 0.0 | | 0.0 | | 31.6 | 0.6 | 43.4 | 8.8 | 995.9 | 12.7 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| 3-Methyl-2(5H)-Furanone | 2015 | 66.5 | 5.7 | 31.4 | 12.9 | 81.6 | 4.5 | 116.0 | 11.2 | 579.3 | 3.8 |
| | 2016 | 29.2 | 3.9 | 47.0 | 8.7 | 91.8 | 13.3 | 120.9 | 9.0 | 681.4 | 9.7 |
| | 2017 | 23.6 | 1.6 | 9.4 | 9.6 | 101.6 | 6.0 | 123.8 | 7.7 | 976.3 | 4.6 |
| | 2018 | 40.2 | 5.9 | 29.8 | 10.1 | 86.4 | 2.1 | 107.0 | 6.3 | 985.7 | 3.5 |
| 5-Methyl-2-Furanmethanol | 2015 | 57.1 | 3.0 | 30.7 | 8.0 | 303.8 | 5.3 | 648.6 | 6.3 | 1929.1 | 6.4 |
| | 2016 | 31.7 | 11.0 | 84.0 | 11.6 | 470.4 | 13.5 | 492.2 | 8.8 | 2637.3 | 11.0 |
| | 2017 | 2.0 | 8.4 | 9.2 | 5.5 | 330.8 | 9.0 | 456.2 | 3.3 | 4174.9 | 0.4 |
| | 2018 | 65.6 | 9.0 | 44.7 | 3.2 | 398.0 | 5.9 | 492.3 | 0.9 | 5391.7 | 12.7 |
| Phenylmethyl Acetate | 2015 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 366.5 | 7.7 |
| | 2016 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 289.6 | 10.6 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 236.9 | 15.0 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Naphthalene | 2015 | 48.8 | 2.1 | 121.8 | 2.2 | 30.4 | 13.5 | 0.0 | | 0.0 | |
| | 2016 | 35.8 | 5.9 | 14.6 | 3.1 | 30.5 | 5.4 | 0.0 | | 0.0 | |
| | 2017 | 21.3 | 6.3 | 24.2 | 11.0 | 29.7 | 11.4 | 0.0 | | 0.0 | |
| | 2018 | 21.5 | 4.5 | 11.6 | 1.6 | 29.7 | 7.0 | 0.0 | | 0.0 | |
| 2(5H)-Furanone | 2015 | 1190.9 | 3.7 | 832.0 | 3.6 | 1179.3 | 7.0 | 5773.8 | 10.2 | 19058.4 | 5.4 |
| | 2016 | 929.3 | 2.7 | 964.6 | 0.9 | 3184.0 | 11.3 | 5739.1 | 3.0 | 7999.2 | 4.7 |
| | 2017 | 256.6 | 8.5 | 311.9 | 3.1 | 3285.7 | 5.8 | 4014.6 | 4.0 | 37096.8 | 2.6 |
| | 2018 | 298.6 | 2.6 | 780.4 | 7.8 | 2558.6 | 10.9 | 4698.0 | 7.9 | 27152.0 | 3.0 |
| 2,2'-Methylenebis[5-Methyl-Furan | 2015 | 0.0 | | 2.9 | 14.5 | 79.9 | 5.8 | 37.9 | 9.9 | 377.1 | 2.2 |
| | 2016 | 0.0 | | 7.4 | 4.4 | 71.2 | 6.8 | 32.2 | 10.3 | 681.3 | 7.6 |
| | 2017 | 0.0 | | 7.5 | 1.9 | 114.5 | 11.0 | 24.7 | 5.5 | 1462.2 | 8.4 |
| | 2018 | 0.0 | | 2.6 | 1.4 | 84.5 | 8.3 | 27.2 | 5.8 | 1018.0 | 10.4 |
| 1,2-Cyclopentanedione | 2015 | 97.1 | 8.2 | 594.3 | 12.4 | 2263.9 | 5.3 | 7863.1 | 0.1 | 26782.4 | 0.9 |
| | 2016 | 370.4 | 11.9 | 949.4 | 10.4 | 4865.7 | 7.4 | 8094.2 | 6.9 | 24006.4 | 5.9 |
| | 2017 | 326.1 | 9.7 | 170.1 | 3.0 | 4881.9 | 9.2 | 7315.3 | 5.7 | 33818.8 | 4.7 |
| | 2018 | 364.5 | 10.0 | 755.6 | 4.2 | 4664.4 | 13.3 | 6971.0 | 7.0 | 39417.0 | 8.6 |
| Diethylene Glycol Monobutyl Ether | 2015 | 71.4 | 12.8 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 8.7 | 9.9 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 2.6 | 7.0 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 22.0 | 10.6 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2-Cyclohexenol | 2015 | 403.6 | 6.5 | 347.2 | 5.0 | 471.0 | 7.0 | 2139.5 | 13.3 | 7666.5 | 5.0 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2016 | 382.4 | 5.2 | 510.7 | 10.2 | 1024.6 | 12.6 | 1816.8 | 6.7 | 9665.4 | 2.5 |
| | 2017 | 93.3 | 7.3 | 126.6 | 1.9 | 1091.5 | 8.4 | 1642.0 | 4.4 | 15789.5 | 3.1 |
| | 2018 | 356.8 | 7.2 | 386.0 | 1.1 | 1133.3 | 6.4 | 1756.8 | 6.0 | 16990.4 | 4.8 |
| 2-Phenylethyl Acetate | 2015 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 2664.2 | 6.6 |
| | 2016 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 6220.2 | 1.5 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 2687.3 | 12.4 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 364.5 | 4.9 |
| | 2015 | 501.5 | 11.1 | 313.1 | 1.4 | 619.3 | 2.0 | 2212.6 | 9.9 | 9727.3 | 4.3 |
| 3-Methyl-1,2-Cyclopentanedione | 2016 | 310.6 | 2.6 | 421.1 | 9.6 | 1102.0 | 10.5 | 1813.8 | 7.7 | 11541.9 | 7.6 |
| | 2017 | 84.4 | 4.5 | 117.9 | 2.2 | 1254.6 | 11.2 | 1859.1 | 7.0 | 18549.0 | 0.9 |
| | 2018 | 314.6 | 10.1 | 311.9 | 8.1 | 1222.6 | 10.0 | 1860.6 | 7.0 | 21664.8 | 11.6 |
| | 2015 | 0.0 | | 54.2 | 4.7 | 88.7 | 7.6 | 784.5 | 10.0 | 3300.4 | 9.6 |
| β-Damascenone | 2016 | 0.0 | | 101.5 | 12.1 | 56.4 | 11.8 | 18.7 | 6.4 | 1127.0 | 5.7 |
| | 2017 | 0.0 | | 47.8 | 10.4 | 65.5 | 7.7 | 10.4 | 4.2 | 292.9 | 4.0 |
| | 2018 | 0.0 | | 65.6 | 6.6 | 58.5 | 6.2 | 471.3 | 9.0 | 10703.7 | 5.0 |
| | 2015 | 117.9 | 3.4 | 87.4 | 5.0 | 198.7 | 2.5 | 1196.2 | 6.7 | 3305.0 | 7.8 |
| 2-Methyl-Propanoic Acid | 2016 | 71.8 | 1.7 | 125.8 | 9.2 | 469.7 | 13.5 | 916.4 | 9.0 | 6630.5 | 9.8 |
| | 2017 | 11.9 | 11.8 | 5.1 | 10.2 | 569.7 | 6.7 | 655.7 | 4.3 | 7936.8 | 6.8 |
| | 2018 | 54.7 | 13.3 | 68.3 | 6.0 | 517.6 | 7.3 | 828.1 | 2.5 | 12086.5 | 10.5 |
| | 2015 | 0.0 | | 17.3 | 4.1 | 0.0 | | 0.0 | | 0.0 | |
| 4-(1-Methylpropyl)-Phenol | 2016 | 0.0 | | 11.8 | 10.1 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 0.0 | | 9.6 | 1.5 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 0.0 | | 16.2 | 13.1 | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 1515.8 | 11.1 | 1095.6 | 8.1 | 1222.0 | 12.3 | 9430.6 | 13.2 | 17663.8 | 8.2 |
| 2,4,6-Trihydroxypyrimidine | 2016 | 1307.1 | 9.4 | 1719.0 | 3.4 | 4108.4 | 7.0 | 10220.5 | 6.6 | 27315.9 | 11.7 |
| | 2017 | 194.2 | 11.1 | 1160.3 | 2.6 | 2396.9 | 11.4 | 5641.7 | 4.8 | 25867.3 | 3.7 |
| | 2018 | 849.9 | 7.9 | 1039.8 | 9.0 | 3538.2 | 4.1 | 7281.2 | 10.6 | 26105.2 | 7.7 |
| | 2015 | 25.3 | 8.5 | 19.9 | 13.6 | 124.5 | 2.8 | 186.7 | 0.2 | 931.4 | 3.3 |
| Mequinol | 2016 | 15.9 | 2.9 | 37.2 | 3.4 | 171.9 | 3.3 | 154.5 | 11.4 | 1039.0 | 3.1 |
| | 2017 | 16.0 | 4.1 | 13.5 | 6.7 | 162.5 | 14.8 | 137.2 | 7.8 | 1573.3 | 3.2 |
| | 2018 | 38.1 | 6.1 | 24.8 | 9.3 | 158.1 | 7.7 | 120.1 | 3.1 | 2222.2 | 9.7 |
| | 2015 | 373.1 | 3.0 | 374.7 | 3.7 | 239.6 | 4.7 | 1228.9 | 13.3 | 3790.2 | 1.9 |
| 2,2-Diethyl-3-Methyl-Oxazolidine | 2016 | 276.5 | 9.1 | 408.4 | 8.2 | 599.3 | 9.6 | 1372.6 | 11.0 | 7490.0 | 11.4 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| Oxypurinol | 2017 | 203.8 | 1.4 | 369.5 | 2.5 | 609.3 | 7.0 | 915.7 | 4.9 | 9522.3 | 4.3 |
| | 2018 | 168.3 | 10.8 | 208.2 | 10.8 | 507.1 | 7.5 | 898.9 | 7.0 | 13662.4 | 2.5 |
| | 2015 | 554.5 | 3.7 | 353.9 | 5.9 | 294.7 | 0.3 | 1943.1 | 4.8 | 7792.4 | 12.8 |
| | 2016 | 349.5 | 8.9 | 503.7 | 2.0 | 842.2 | 6.4 | 1842.1 | 9.0 | 8884.9 | 6.7 |
| | 2017 | 758.5 | 1.6 | 526.2 | 2.4 | 816.7 | 11.1 | 986.7 | 3.4 | 12480.4 | 4.6 |
| | 2018 | 233.5 | 7.1 | 272.0 | 0.6 | 776.7 | 0.5 | 1430.8 | 9.0 | 12342.7 | 8.5 |
| Benzenemethanol | 2015 | 0.0 | | 0.0 | | 0.0 | | 41.8 | 11.0 | 805.1 | 10.2 |
| | 2016 | 0.0 | | 0.0 | | 0.0 | | 38.6 | 4.0 | 704.4 | 10.5 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 36.1 | 6.6 | 604.8 | 0.1 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 27.8 | 8.0 | 261.2 | 9.7 |
| 4-Methyl-2(5H)-Furanone | 2015 | 256.8 | 11.3 | 132.8 | 10.0 | 210.6 | 0.1 | 426.5 | 9.2 | 2280.4 | 11.8 |
| | 2016 | 124.4 | 10.5 | 186.0 | 8.8 | 318.2 | 8.4 | 450.8 | 11.4 | 3179.6 | 9.7 |
| | 2017 | 137.4 | 3.3 | 118.9 | 2.2 | 325.0 | 6.6 | 452.0 | 1.0 | 4120.6 | 7.5 |
| | 2018 | 127.3 | 7.7 | 120.0 | 13.1 | 317.4 | 9.2 | 440.2 | 0.9 | 6962.8 | 10.5 |
| 3-Ethyl-2-Hydroxy-2-Cyclopenten-1-one | 2015 | 47.2 | 6.5 | 19.4 | 3.6 | 100.5 | 8.6 | 322.3 | 3.7 | 1543.9 | 9.2 |
| | 2016 | 26.9 | 4.8 | 45.7 | 8.4 | 166.5 | 8.6 | 279.2 | 9.0 | 2151.0 | 12.2 |
| | 2017 | 3.3 | 10.6 | 2.4 | 11.6 | 185.4 | 3.5 | 213.9 | 6.4 | 3124.1 | 9.3 |
| | 2018 | 29.0 | 4.5 | 45.6 | 6.3 | 194.0 | 10.8 | 269.5 | 6.9 | 3729.0 | 10.2 |
| Benzeneethanol | 2015 | 10.2 | 12.0 | 46.5 | 10.4 | 35.8 | 6.7 | 20.2 | 6.6 | 194.6 | 5.4 |
| | 2016 | 202.2 | 5.4 | 92.7 | 13.1 | 51.2 | 6.4 | 19.4 | 2.8 | 464.1 | 12.7 |
| | 2017 | 20.0 | 5.6 | 30.8 | 2.5 | 17.9 | 5.6 | 19.0 | 3.2 | 318.8 | 5.0 |
| | 2018 | 59.4 | 4.9 | 68.8 | 7.1 | 19.5 | 5.0 | 20.6 | 1.6 | 178.5 | 4.3 |
| 1,4-Butanediol | 2015 | 81.1 | 13.4 | 62.4 | 10.7 | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 60.7 | 5.7 | 65.8 | 3.2 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 13.6 | 3.9 | 3.0 | 7.9 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 54.9 | 4.0 | 46.1 | 4.5 | 0.0 | | 0.0 | | 0.0 | |
| Acrylamide | 2015 | 0.0 | | 143.3 | 10.9 | 126.9 | 11.0 | 798.3 | 10.4 | 2951.1 | 8.9 |
| | 2016 | 0.0 | | 133.8 | 10.3 | 327.2 | 16.0 | 753.0 | 6.1 | 6052.4 | 5.0 |
| | 2017 | 0.0 | | 115.4 | 2.5 | 307.6 | 4.6 | 536.4 | 5.1 | 6188.3 | 6.0 |
| | 2018 | 0.0 | | 133.6 | 11.1 | 400.7 | 2.5 | 643.4 | 5.2 | 6777.6 | 10.7 |
| Erythritol | 2015 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 4625.2 | 11.4 |
| | 2016 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 8245.1 | 5.2 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 13061.5 | 1.1 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 17525.1 | 7.7 |
| 2,3-Dimethyl-3-Pyrazolin-5-one | 2015 | 29.6 | 4.0 | 22.1 | 4.0 | 55.3 | 12.9 | 177.4 | 14.1 | 838.8 | 5.9 |
| | 2016 | 18.6 | 6.7 | 33.9 | 10.8 | 94.5 | 9.8 | 157.6 | 4.1 | 1175.7 | 6.9 |
| | 2017 | 21.8 | 0.1 | 30.2 | 2.2 | 107.9 | 7.4 | 164.7 | 7.9 | 1585.9 | 12.1 |
| | 2018 | 17.5 | 6.4 | 25.1 | 10.9 | 105.2 | 8.2 | 161.5 | 1.2 | 1934.6 | 12.1 |
| Furfural Acetone | 2015 | 97.4 | 11.3 | 71.3 | 3.0 | 62.9 | 9.2 | 213.1 | 9.9 | 782.5 | 10.6 |
| | 2016 | 67.1 | 3.4 | 79.3 | 0.4 | 88.4 | 11.9 | 187.6 | 12.0 | 1097.1 | 10.8 |
| | 2017 | 86.8 | 3.0 | 89.3 | 2.9 | 102.2 | 4.0 | 116.7 | 1.4 | 1524.1 | 0.8 |
| | 2018 | 65.9 | 4.6 | 65.4 | 0.1 | 98.4 | 2.2 | 167.6 | 5.8 | 2071.1 | 7.9 |
| | 2015 | 0.0 | | 0.0 | | 0.0 | | 638.5 | 12.6 | 3217.2 | 5.3 |
| Cyclotene | 2016 | 0.0 | | 0.0 | | 0.0 | | 554.6 | 6.1 | 4823.6 | 8.3 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 383.5 | 3.8 | 5438.5 | 5.0 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 619.2 | 7.2 | 7902.0 | 4.7 |
| | 2015 | 77.7 | 6.9 | 49.4 | 10.2 | 118.0 | 11.7 | 462.0 | 11.8 | 1131.4 | 4.6 |
| 2-Methyl-1,4-Benzenediol | 2016 | 64.2 | 7.8 | 53.0 | 0.6 | 254.2 | 9.6 | 340.1 | 13.0 | 2171.6 | 11.0 |
| | 2017 | 54.7 | 14.7 | 17.4 | 2.9 | 188.3 | 8.3 | 308.7 | 3.7 | 2983.8 | 3.5 |
| | 2018 | 68.6 | 3.1 | 54.1 | 3.9 | 194.0 | 8.4 | 336.6 | 12.0 | 6209.2 | 5.4 |
| | 2015 | 526.6 | 11.8 | 827.0 | 11.4 | 774.0 | 1.3 | 2844.9 | 6.1 | 12514.7 | 6.2 |
| Maltol | 2016 | 669.6 | 3.3 | 1127.1 | 1.4 | 1424.1 | 6.9 | 2700.6 | 12.6 | 15762.4 | 7.3 |
| | 2017 | 866.1 | 3.1 | 899.0 | 2.7 | 1576.3 | 4.6 | 2446.3 | 2.9 | 17409.2 | 5.4 |
| | 2018 | 487.1 | 4.2 | 632.9 | 1.8 | 1408.0 | 6.5 | 2472.8 | 9.9 | 20498.4 | 10.8 |
| | 2015 | 10.6 | 12.6 | 38.7 | 6.1 | 1239.5 | 0.7 | 1377.3 | 2.0 | 7404.8 | 5.7 |
| 2-Acetylpyrrole | 2016 | 12.5 | 12.5 | 42.7 | 8.0 | 1969.3 | 0.3 | 1104.9 | 0.7 | 9360.2 | 7.7 |
| | 2017 | 24.7 | 5.5 | 19.1 | 3.4 | 1493.6 | 5.7 | 1345.9 | 1.7 | 14430.4 | 5.7 |
| | 2018 | 40.8 | 10.6 | 28.0 | 11.2 | 1522.3 | 4.6 | 1658.0 | 1.0 | 14092.6 | 9.3 |
| | 2015 | 884.9 | 9.3 | 1672.1 | 7.0 | 1409.5 | 0.3 | 3391.1 | 5.7 | 16453.0 | 3.7 |
| 2,5-Furandicarboxaldehyde | 2016 | 1824.8 | 11.2 | 2231.3 | 8.6 | 2169.0 | 9.3 | 3258.5 | 12.8 | 20916.9 | 14.1 |
| | 2017 | 1485.0 | 9.4 | 1398.5 | 3.9 | 1928.1 | 3.6 | 1716.8 | 2.2 | 31055.1 | 1.6 |
| | 2018 | 1030.0 | 13.5 | 1361.4 | 1.4 | 2306.5 | 7.9 | 2539.7 | 11.6 | 33001.5 | 6.5 |
| | 2015 | 6.7 | 4.9 | 10.7 | 11.2 | 87.8 | 2.7 | 1426.3 | 10.5 | 6873.8 | 11.2 |
| 2H-Pyran-2,6(3H)-Dione | 2016 | 2.1 | 8.1 | 35.6 | 8.4 | 772.5 | 2.4 | 1935.2 | 8.1 | 14810.2 | 5.9 |
| | 2017 | 3.8 | 5.2 | 7.5 | 4.5 | 770.3 | 2.2 | 1808.7 | 5.0 | 13451.8 | 6.9 |
| | 2018 | 1.1 | 8.2 | 5.0 | 5.0 | 701.3 | 5.1 | 1180.5 | 10.6 | 16447.7 | 6.4 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | 2015 | 624.1 | 2.9 | 1534.6 | 5.0 | 1125.8 | 5.5 | 9209.5 | 5.0 | 20822.3 | 12.7 |
| | 2016 | 522.6 | 0.3 | 1479.7 | 4.1 | 4403.7 | 8.3 | 11155.4 | 10.0 | 57419.4 | 0.3 |
| | 2017 | 559.5 | 2.2 | 1833.6 | 2.6 | 2218.4 | 7.5 | 5546.3 | 3.3 | 17626.4 | 1.2 |
| | 2018 | 265.2 | 5.7 | 387.5 | 9.2 | 3101.1 | 3.5 | 6118.9 | 6.3 | 29062.9 | 6.3 |
| Phenol | 2015 | 145.0 | 1.2 | 117.3 | 1.0 | 199.3 | 2.0 | 527.7 | 1.9 | 2987.2 | 8.8 |
| | 2016 | 107.2 | 6.6 | 146.1 | 6.8 | 327.2 | 8.7 | 472.0 | 8.1 | 4626.4 | 8.3 |
| | 2017 | 101.7 | 2.2 | 93.9 | 2.2 | 315.1 | 5.6 | 274.2 | 8.7 | 5719.0 | 12.4 |
| | 2018 | 127.8 | 3.5 | 111.0 | 11.7 | 371.7 | 3.1 | 503.4 | 7.3 | 8204.7 | 11.4 |
| 1H-Pyrrole-2-Carboxaldehyde | 2015 | 0.0 | | 56.4 | 11.6 | 129.4 | 5.8 | 187.4 | 3.6 | 911.5 | 3.4 |
| | 2016 | 0.0 | | 60.9 | 4.1 | 169.4 | 5.7 | 195.6 | 4.7 | 835.0 | 11.1 |
| | 2017 | 0.0 | | 17.1 | 1.8 | 123.2 | 4.6 | 117.4 | 12.0 | 5732.3 | 9.3 |
| | 2018 | 0.0 | | 45.1 | 10.2 | 134.3 | 6.5 | 202.5 | 1.0 | 5897.6 | 4.1 |
| Phloroglucinol | 2015 | 0.0 | | 129.8 | 8.6 | 171.9 | 9.3 | 1713.4 | 10.4 | 5238.3 | 12.2 |
| | 2016 | 0.0 | | 214.9 | 11.2 | 898.2 | 3.4 | 1814.0 | 7.1 | 14692.0 | 6.2 |
| | 2017 | 0.0 | | 11.8 | 4.4 | 790.2 | 5.8 | 1179.2 | 4.1 | 12492.0 | 0.3 |
| | 2018 | 0.0 | | 94.2 | 0.3 | 663.8 | 8.2 | 1342.3 | 9.4 | 16640.6 | 7.7 |
| Furaneol | 2015 | 552.9 | 2.1 | 348.1 | 11.3 | 929.6 | 11.6 | 7750.0 | 12.0 | 18232.8 | 7.9 |
| | 2016 | 256.9 | 5.2 | 619.8 | 11.9 | 2669.8 | 13.5 | 7059.2 | 3.2 | 13267.4 | 1.5 |
| | 2017 | 149.2 | 6.0 | 171.8 | 2.0 | 2337.9 | 10.1 | 3697.5 | 2.7 | 15414.6 | 0.6 |
| | 2018 | 389.5 | 8.0 | 574.4 | 4.4 | 3731.6 | 6.6 | 6292.6 | 6.6 | 15728.2 | 3.8 |
| Octanoic Acid | 2015 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 403.5 | 3.0 |
| | 2016 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 203.2 | 14.5 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 330.1 | 7.0 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 383.4 | 8.7 |
| 5-Acetyl-Dihydro-2(3H)-Furanone | 2015 | 873.1 | 4.8 | 833.2 | 5.4 | 1063.0 | 1.2 | 6381.1 | 8.2 | 11865.3 | 5.9 |
| | 2016 | 626.5 | 7.8 | 985.9 | 3.2 | 2759.2 | 10.5 | 4280.4 | 9.5 | 11931.0 | 7.9 |
| | 2017 | 237.1 | 7.0 | 206.8 | 0.4 | 2298.0 | 11.6 | 3598.1 | 3.9 | 17076.3 | 7.3 |
| | 2018 | 757.2 | 6.8 | 743.2 | 3.5 | 3089.9 | 4.0 | 5304.9 | 5.7 | 15308.2 | 7.6 |
| 2-Furanpropionic Acid | 2015 | 64.7 | 6.8 | 127.1 | 8.0 | 117.9 | 4.8 | 1284.7 | 12.2 | 4640.8 | 5.7 |
| | 2016 | 60.1 | 1.0 | 118.7 | 5.2 | 562.2 | 0.6 | 1329.2 | 8.8 | 10089.4 | 8.5 |
| | 2017 | 35.6 | 7.2 | 56.2 | 1.4 | 379.6 | 9.0 | 635.6 | 5.0 | 9669.9 | 1.3 |
| | 2018 | 52.0 | 9.2 | 68.5 | 1.8 | 485.0 | 0.7 | 956.3 | 6.1 | 11266.7 | 6.0 |
| 1,3-Dihydroxy-2-Propanone | 2015 | 17624.6 | 1.1 | 22942.2 | 7.2 | 35662.6 | 7.2 | 126088.9 | 8.3 | 325658.0 | 3.0 |

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| | 2016 | 17290.0 | 2.6 | 24784.6 | 4.1 | 55866.8 | 3.5 | 117789.9 | 5.9 | 350592.8 | 3.7 |
| | 2017 | 15662.3 | 3.6 | 17036.2 | 1.3 | 30861.4 | 4.6 | 93703.1 | 3.4 | 417470.4 | 1.4 |
| | 2018 | 13268.3 | 10.0 | 17417.2 | 0.5 | 51992.6 | 3.0 | 127263.4 | 3.6 | 432011.6 | 0.0 |
| Tetrahydro-5-Methyl-2-Furanmethanol | 2015 | 2499.9 | 5.3 | 2333.3 | 9.3 | 3673.2 | 10.2 | 4829.2 | 9.9 | 13027.6 | 3.1 |
| | 2016 | 2798.6 | 5.6 | 2727.5 | 7.1 | 4774.1 | 3.2 | 2533.1 | 9.4 | 9247.3 | 1.3 |
| | 2017 | 3215.6 | 0.1 | 1925.4 | 3.3 | 3137.4 | 6.0 | 5003.7 | 8.8 | 16415.9 | 2.4 |
| | 2018 | 2585.0 | 9.4 | 2152.4 | 6.4 | 3689.2 | 0.5 | 5406.5 | 3.0 | 1093.5 | 2.5 |
| | 2015 | 43.8 | 1.7 | 164.9 | 11.1 | 551.7 | 6.3 | 2265.0 | 12.1 | 9842.0 | 5.9 |
| 4,5-Dimethyl Vinylene Carbonate | 2016 | 133.1 | 6.5 | 356.0 | 9.0 | 1487.2 | 6.4 | 1833.6 | 7.7 | 6807.3 | 2.1 |
| | 2017 | 12.1 | 7.7 | 42.1 | 3.8 | 910.8 | 9.4 | 1945.6 | 6.3 | 16353.7 | 2.5 |
| | 2018 | 228.9 | 6.5 | 355.8 | 8.5 | 1142.8 | 3.2 | 1809.9 | 1.2 | 16034.3 | 10.2 |
| | 2015 | 10996.3 | 5.9 | 7438.6 | 2.5 | 11553.6 | 0.0 | 17038.1 | 8.6 | 30587.2 | 1.2 |
| 2-Hydroxy-Dihydro-2(3H)-Furanone | 2016 | 8224.9 | 6.2 | 8189.2 | 4.5 | 14056.2 | 0.8 | 15148.1 | 2.5 | 22563.2 | 3.5 |
| | 2017 | 2994.5 | 4.4 | 1787.8 | 0.6 | 14134.9 | 7.8 | 15092.2 | 8.2 | 5312.8 | 1.4 |
| | 2018 | 8892.6 | 8.3 | 8715.0 | 6.5 | 14379.4 | 6.3 | 19027.7 | 3.1 | 5574.3 | 9.1 |
| | 2015 | 0.0 | 0.0 | 28.4 | 7.2 | 0.0 | | 0.0 | | 0.0 | |
| 2-Ethyl-Phenol | 2016 | 93.5 | 1.8 | 36.7 | 11.1 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 126.8 | 7.6 | 20.7 | 3.6 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 25.1 | 8.0 | 31.9 | 6.9 | 0.0 | | 0.0 | | 0.0 | |
| | 2015 | 1829.7 | 4.5 | 2188.9 | 9.4 | 4680.0 | 0.2 | 8624.5 | 10.0 | 12051.8 | 10.6 |
| 5-Acetoxymethyl-2-Furfural A | 2016 | 2131.0 | 2.3 | 2829.0 | 2.4 | 2744.8 | 10.3 | 8318.0 | 8.9 | 9644.0 | 2.8 |
| | 2017 | 3245.2 | 2.6 | 3102.3 | 2.7 | 2020.7 | 10.2 | 6020.4 | 5.8 | 17759.4 | 6.7 |
| | 2018 | 1195.7 | 9.1 | 1393.6 | 12.1 | 2532.2 | 3.6 | 4627.7 | 8.7 | 16129.7 | 11.1 |
| | 2015 | 1446.3 | 9.6 | 1638.2 | 1.4 | 3098.5 | 0.4 | 6700.1 | 12.2 | 15313.4 | 5.4 |
| 5-Acetoxymethyl-2-Furfural B | 2016 | 1647.6 | 3.1 | 2131.9 | 3.5 | 2421.3 | 9.8 | 6542.8 | 8.5 | 17830.9 | 5.1 |
| | 2017 | 2203.5 | 0.4 | 1924.3 | 1.6 | 2378.1 | 8.1 | 5585.8 | 4.1 | 21514.3 | 2.0 |
| | 2018 | 1091.9 | 12.5 | 1316.6 | 0.6 | 2416.1 | 2.6 | 4508.0 | 4.9 | 18481.1 | 9.1 |
| | 2015 | 39.3 | 3.3 | 190.0 | 2.4 | 920.8 | 5.8 | 581.0 | 8.4 | 1441.2 | 1.6 |
| 2-Methoxy-4-Vinyl-Phenol | 2016 | 55.0 | 6.0 | 268.6 | 8.5 | 1148.8 | 0.1 | 456.9 | 11.0 | 3060.6 | 13.6 |
| | 2017 | 83.2 | 1.1 | 133.6 | 3.1 | 724.6 | 6.8 | 282.1 | 10.0 | 3382.6 | 12.2 |
| | 2018 | 60.3 | 12.8 | 159.9 | 12.5 | 564.1 | 6.5 | 580.1 | 4.7 | 6340.0 | 9.2 |
| | 2015 | 58.4 | 0.4 | 83.1 | 4.3 | 251.9 | 3.2 | 1249.5 | 5.6 | 5296.3 | 3.7 |
| 3-Methyl-2,4(3H,5H)-Furandione | 2016 | 85.0 | 8.8 | 137.1 | 11.3 | 559.7 | 8.0 | 1035.5 | 7.2 | 6246.8 | 9.6 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2017 | 36.8 | 12.9 | 51.4 | 3.9 | 686.6 | 7.9 | 315.8 | 2.5 | 9340.2 | 6.1 |
| | 2018 | 106.2 | 6.9 | 115.0 | 9.3 | 618.3 | 8.7 | 987.9 | 7.5 | 10253.6 | 10.0 |
| | 2015 | 253.7 | 6.2 | 390.4 | 12.9 | 512.5 | 7.2 | 3794.4 | 9.1 | 10080.8 | 9.0 |
| 3-Hydroxy-2,3-Dihydro-Maltol | 2016 | 293.9 | 3.7 | 575.3 | 3.9 | 1558.5 | 7.1 | 4156.8 | 8.0 | 9991.1 | 8.6 |
| | 2017 | 56.3 | 0.7 | 77.2 | 4.6 | 1136.9 | 5.6 | 3075.5 | 5.1 | 13316.2 | 13.9 |
| | 2018 | 278.3 | 13.0 | 273.0 | 10.5 | 1508.0 | 1.6 | 2868.8 | 9.7 | 13223.8 | 0.8 |
| | 2015 | 28.3 | 7.6 | 0.0 | | 0.0 | | 149.0 | 6.2 | 1697.1 | 3.0 |
| Decanoic Acid | 2016 | 133.4 | 11.8 | 0.0 | | 0.0 | | 45.2 | 12.1 | 408.7 | 12.0 |
| | 2017 | 7.2 | 3.1 | 0.0 | | 0.0 | | 175.4 | 8.2 | 211.6 | 9.6 |
| | 2018 | 33.3 | 8.7 | 0.0 | | 0.0 | | 131.3 | 12.8 | 799.9 | 1.9 |
| | 2015 | 0.0 | | 0.0 | | 709.9 | 1.5 | 5793.5 | 13.0 | 22443.4 | 3.7 |
| 5-Hydroxy-Maltol | 2016 | 0.0 | | 0.0 | | 2174.6 | 13.3 | 5284.1 | 12.8 | 20736.5 | 8.9 |
| | 2017 | 0.0 | | 0.0 | | 1947.8 | 3.6 | 3068.4 | 3.1 | 34672.7 | 4.3 |
| | 2018 | 0.0 | | 0.0 | | 2500.5 | 4.2 | 4872.2 | 8.7 | 38102.8 | 9.9 |
| | 2015 | 39.6 | 4.5 | 448.7 | 6.2 | 621.4 | 0.6 | 612.0 | 4.8 | 1486.6 | 1.8 |
| 2,3-Dihydro-Benzofuran | 2016 | 104.9 | 11.1 | 509.9 | 7.0 | 734.5 | 6.7 | 523.2 | 12.5 | 1690.0 | 2.3 |
| | 2017 | 47.2 | 2.8 | 185.9 | 2.0 | 486.9 | 10.0 | 291.4 | 7.2 | 2987.3 | 6.2 |
| | 2018 | 95.6 | 3.0 | 355.5 | 13.1 | 405.8 | 9.0 | 603.7 | 0.7 | 5430.7 | 9.4 |
| | 2015 | 287.6 | 6.3 | 317.1 | 12.0 | 409.9 | 10.8 | 784.9 | 11.9 | 4890.1 | 3.8 |
| 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | 2016 | 180.4 | 7.5 | 437.6 | 3.2 | 454.4 | 0.7 | 877.1 | 4.6 | 4620.5 | 9.6 |
| | 2017 | 198.2 | 5.5 | 114.2 | 2.0 | 585.9 | 5.2 | 320.8 | 7.5 | 8321.9 | 4.2 |
| | 2018 | 222.1 | 7.1 | 277.7 | 9.8 | 557.2 | 11.0 | 625.8 | 3.0 | 7118.6 | 6.5 |
| | 2015 | 60.5 | 10.9 | 167.0 | 5.0 | 394.6 | 5.6 | 1350.9 | 12.8 | 6563.0 | 3.9 |
| 4-Pyridinol | 2016 | 110.1 | 11.6 | 240.7 | 10.8 | 713.3 | 7.2 | 1240.2 | 4.0 | 8979.0 | 4.2 |
| | 2017 | 157.1 | 2.8 | 160.9 | 2.7 | 703.8 | 10.6 | 880.2 | 4.9 | 12385.3 | 8.3 |
| | 2018 | 92.8 | 11.7 | 204.3 | 9.4 | 713.0 | 5.7 | 1225.3 | 3.0 | 13378.4 | 8.4 |
| | 2015 | 0.0 | | 0.0 | | 120.8 | 3.1 | 868.9 | 10.2 | 3681.8 | 4.6 |
| 4-Amino-Phenol | 2016 | 0.0 | | 0.0 | | 117.6 | 4.1 | 849.1 | 4.1 | 4643.1 | 0.4 |
| | 2017 | 0.0 | | 0.0 | | 118.1 | 8.2 | 373.5 | 4.3 | 7835.5 | 6.7 |
| | 2018 | 0.0 | | 0.0 | | 460.6 | 11.6 | 887.3 | 8.4 | 10392.8 | 11.8 |
| | 2015 | 0.0 | | 0.0 | | 16.0 | 10.3 | 712.2 | 7.7 | 1746.9 | 3.7 |
| Benzoic Acid | 2016 | 0.0 | | 0.0 | | 15.4 | 2.0 | 391.4 | 8.1 | 1495.7 | 5.6 |
| | 2017 | 0.0 | | 0.0 | | 37.5 | 6.4 | 241.1 | 4.8 | 2990.6 | 2.7 |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| | 2018 | 0.0 | | 0.0 | | 22.6 | 6.8 | 887.7 | 0.2 | 2896.9 | 2.6 |
| Dimethylhydrazone 3-Pentanone | 2015 | 155.4 | 10.6 | 305.1 | 13.3 | 416.5 | 9.0 | 3409.1 | 10.1 | 7770.4 | 5.0 |
| | 2016 | 215.7 | 1.9 | 420.5 | 3.0 | 687.1 | 2.8 | 2582.7 | 12.9 | 5269.3 | 0.2 |
| | 2017 | 33.6 | 11.4 | 7.7 | 3.2 | 173.2 | 4.2 | 2415.4 | 5.8 | 22368.8 | 0.3 |
| | 2018 | 194.4 | 11.0 | 151.0 | 10.0 | 242.2 | 2.5 | 2113.2 | 11.7 | 15247.3 | 12.2 |
| Undecanoic Acid | 2015 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 1775.2 | 3.1 |
| | 2016 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 161.6 | 4.5 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 766.0 | 1.6 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 221.6 | 13.9 |
| 5-(Hydroxymethyl)-Dihydro-2(3H)-Furanone | 2015 | 1313.6 | 7.8 | 932.8 | 1.5 | 1854.7 | 3.7 | 11615.3 | 9.7 | 31683.7 | 8.0 |
| | 2016 | 940.6 | 9.7 | 1350.0 | 10.5 | 5291.8 | 11.1 | 10209.4 | 3.5 | 41433.5 | 3.5 |
| | 2017 | 1287.2 | 8.1 | 1411.4 | 3.0 | 6758.3 | 4.4 | 9091.5 | 4.9 | 20401.6 | 4.4 |
| | 2018 | 1242.6 | 8.2 | 1065.9 | 1.9 | 5951.6 | 7.6 | 9804.9 | 7.2 | 75799.6 | 11.3 |
| Benzophenone | 2015 | 51.2 | 7.9 | 132.4 | 3.4 | 0.0 | | 0.0 | | 0.0 | |
| | 2016 | 15.4 | 6.2 | 24.6 | 0.2 | 0.0 | | 0.0 | | 0.0 | |
| | 2017 | 14.6 | 2.2 | 28.6 | 2.8 | 0.0 | | 0.0 | | 0.0 | |
| | 2018 | 9.3 | 10.5 | 11.4 | 7.0 | 0.0 | | 0.0 | | 0.0 | |
| Dodecanoic Acid | 2015 | 0.0 | | 0.0 | | 0.0 | | 57.2 | 1.2 | 1125.4 | 3.8 |
| | 2016 | 0.0 | | 0.0 | | 0.0 | | 68.1 | 11.8 | 1307.2 | 6.3 |
| | 2017 | 0.0 | | 0.0 | | 0.0 | | 85.5 | 5.5 | 3671.4 | 5.8 |
| | 2018 | 0.0 | | 0.0 | | 0.0 | | 46.6 | 9.2 | 2390.5 | 13.6 |
| 5-(Hydroxymethyl)-2-Furfural | 2015 | 1888.0 | 9.4 | 25302.3 | 5.9 | 29204.2 | 6.8 | 100308.5 | 4.6 | 164599.0 | 4.5 |
| | 2016 | 2600.4 | 5.2 | 28637.3 | 5.3 | 38075.5 | 0.4 | 101861.5 | 1.9 | 198276.1 | 10.3 |
| | 2017 | 1800.5 | 4.6 | 15739.2 | 3.7 | 44507.0 | 4.3 | 51156.7 | 5.8 | 165006.0 | 1.3 |
| | 2018 | 2529.5 | 1.8 | 25265.0 | 2.1 | 38742.5 | 5.2 | 92091.6 | 1.0 | 172268.3 | 5.2 |
| 3-Methoxy-1,2-Benzenediol | 2015 | 202.3 | 6.8 | 167.0 | 11.9 | 140.5 | 6.5 | 905.9 | 12.7 | 3640.6 | 1.4 |
| | 2016 | 157.1 | 5.1 | 206.0 | 1.7 | 333.9 | 4.8 | 1177.6 | 5.9 | 5633.7 | 9.9 |
| | 2017 | 36.3 | 10.3 | 40.9 | 3.2 | 392.4 | 8.9 | 855.5 | 5.8 | 7682.9 | 3.9 |
| | 2018 | 127.7 | 10.5 | 120.5 | 4.6 | 376.7 | 11.4 | 641.8 | 8.7 | 14099.0 | 6.8 |
| 1-(2-Furanyl)-1,2-Ethanediol | 2015 | 774.2 | 4.2 | 594.5 | 13.7 | 957.6 | 1.9 | 5938.3 | 8.8 | 12514.4 | 2.6 |
| | 2016 | 653.4 | 3.5 | 278.4 | 1.5 | 2282.7 | 7.5 | 1420.8 | 6.9 | 14995.6 | 10.9 |
| | 2017 | 864.2 | 3.1 | 295.1 | 2.8 | 1166.0 | 3.1 | 1858.9 | 6.2 | 15521.4 | 0.2 |
| | 2018 | 528.1 | 7.2 | 375.5 | 5.1 | 1829.7 | 8.6 | 2827.5 | 7.1 | 22502.6 | 10.8 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Dihydro-4-Hydroxy-2(3H)-Furanone | 2015 | 302.9 | 8.0 | 468.5 | 10.8 | 563.4 | 6.0 | 2839.7 | 7.6 | 13815.3 | 4.1 |
| | 2016 | 372.5 | 1.4 | 615.7 | 7.4 | 1479.0 | 8.6 | 2716.2 | 8.5 | 19296.8 | 4.3 |
| | 2017 | 160.4 | 3.3 | 314.6 | 7.2 | 1077.3 | 6.5 | 2724.5 | 4.9 | 23371.3 | 0.8 |
| | 2018 | 317.7 | 11.1 | 300.5 | 0.5 | 1287.5 | 8.7 | 2551.9 | 5.0 | 29163.2 | 13.9 |
| | **TOTAL (Nº)** | **126** | | **136** | | **136** | | **136** | | **147** | |

**Table S25. Mean, minimum and maximum peak area values of identified VOCs in samples from SCH processing stages during 2015-2018 production years.**

| **Volatile Organic Compounds** | **Relative Peak Areas (x $10^3$)** | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **S1** | | | **S2** | | | **S3** | | | **S4** | | | **S5** | | |
| | **Mean** | **Min** | **Max** | **Mean** | **Min** | **Max** | **Mean** | **Min** | **Max** | **Mean** | **Min** | **Max** | **Mean** | **Min** | **Max** |
| Pentane | 36.3 | 13.8 | 62.3 | 15.1 | 6.6 | 29.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 44.9 | 19.0 | 60.5 |
| Hexane | 19.7 | 4.3 | 51.6 | 26.7 | 9.2 | 54.8 | 92.1 | 46.3 | 198.9 | 128.3 | 66.8 | 196.0 | 121.8 | 77.8 | 167.5 |
| Ethyl Ether | 5.3 | 2.5 | 10.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1,4-Pentadiene | 14.8 | 1.9 | 28.8 | 4.1 | 3.0 | 5.3 | 5.4 | 4.2 | 6.9 | 6.4 | 3.0 | 9.1 | 0.0 | 0.0 | 0.0 |
| Methanethiol | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 23.3 | 12.0 | 38.3 | 38.9 | 18.4 | 52.8 | 284.6 | 163.4 | 448.0 |
| Ethanal | 30.5 | 6.7 | 61.6 | 52.8 | 19.4 | 71.2 | 376.6 | 220.5 | 471.5 | 652.4 | 480.8 | 790.9 | 8481.3 | 3942.1 | 12257.1 |
| Dimethyl Sulfide | 812.9 | 233.1 | 1899.9 | 8968.1 | 7881.9 | 9680.8 | 158.4 | 78.3 | 236.3 | 34.6 | 8.4 | 96.4 | 1528.6 | 894.2 | 2272.4 |
| Propanal | 21.7 | 14.6 | 28.2 | 26.4 | 15.3 | 38.3 | 86.2 | 72.2 | 99.1 | 85.6 | 34.5 | 129.1 | 733.2 | 293.4 | 1390.6 |
| Furan | 0.0 | 0.0 | 0.0 | 120.3 | 89.4 | 140.0 | 520.6 | 351.9 | 687.3 | 92.0 | 39.1 | 208.2 | 3253.2 | 593.1 | 6029.2 |
| 2-Methyl-Propanal | 74.2 | 17.0 | 180.7 | 123.1 | 13.9 | 180.4 | 2076.7 | 1479.8 | 2518.7 | 960.0 | 424.2 | 1549.0 | 14353.6 | 6454.5 | 21889.5 |
| Ethyl Formate | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2679.3 | 0.0 | 7155.3 |
| 2-Propenal | 14.2 | 2.0 | 34.5 | 11.8 | 5.4 | 20.2 | 51.3 | 23.4 | 94.3 | 40.5 | 27.8 | 59.7 | 409.1 | 310.2 | 572.5 |
| 2-Methyl-Furan | 19.2 | 6.6 | 27.8 | 51.3 | 15.0 | 99.7 | 1507.8 | 1319.5 | 1886.2 | 650.3 | 151.1 | 1514.8 | 3093.5 | 708.2 | 6988.8 |
| Ethyl Acetate | 161.0 | 51.2 | 410.7 | 121.0 | 27.5 | 216.2 | 5.1 | 2.0 | 7.4 | 16.8 | 15.5 | 18.5 | 10414.5 | 280.0 | 25389.2 |
| 2-Butanone | 0.0 | 0.0 | 0.0 | 14.8 | 11.2 | 17.1 | 53.6 | 36.3 | 66.5 | 35.1 | 22.7 | 44.9 | 686.1 | 217.2 | 1133.4 |
| 2-Methyl-Butanal | 130.7 | 39.3 | 319.1 | 183.0 | 132.6 | 279.9 | 7119.3 | 5826.5 | 8792.8 | 1845.2 | 880.8 | 2894.0 | 25093.1 | 12966.1 | 37630.2 |
| 3-Methyl-Butanal | 151.6 | 34.7 | 289.4 | 309.5 | 210.4 | 505.0 | 10681.8 | 9778.3 | 12036.5 | 2180.7 | 1437.3 | 3576.7 | 23881.8 | 7073.4 | 41914.2 |
| Ethanol | 1475.1 | 733.4 | 3305.8 | 943.2 | 535.3 | 1488.6 | 485.0 | 185.5 | 991.0 | 861.2 | 677.3 | 1271.0 | 131937.0 | 107855.0 | 159606.9 |
| Benzene | 16.5 | 6.1 | 26.9 | 7.9 | 2.1 | 11.8 | 12.5 | 8.8 | 18.8 | 17.8 | 11.6 | 34.7 | 110.0 | 53.8 | 200.4 |
| 3-Buten-2-one | 0.0 | 0.0 | 0.0 | 30.2 | 15.0 | 49.6 | 54.9 | 44.3 | 63.8 | 83.0 | 25.3 | 218.5 | 2843.3 | 341.5 | 5111.2 |
| 2-Ethyl-Furan | 0.0 | 0.0 | 0.0 | 164.1 | 63.6 | 362.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,5-Dimethyl-Furan | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 223.8 | 197.4 | 250.7 | 35.3 | 4.9 | 61.7 | 2194.6 | 880.9 | 3919.7 |
| Ethyl Ester Propanoic Acid | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 580.3 | 0.0 | 1881.4 |
| 3-Pentanone | 123.3 | 29.8 | 203.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Pentanal | 0.0 | 0.0 | 0.0 | 226.5 | 152.3 | 286.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2,3-Butanedione | 0.0 | 0.0 | 0.0 | 191.4 | 4.8 | 560.9 | 1362.0 | 405.0 | 2051.6 | 2328.9 | 32.1 | 3962.0 | 21750.0 | 1397.2 | 49665.1 |
| 1-Penten-3-one | 65.8 | 6.5 | 190.7 | 14.5 | 3.6 | 25.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1-Propanol | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 55.0 | 0.0 | 92.1 |
| 2-Ethyl-5-Methyl-Furan | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 9.2 | 4.5 | 16.3 | 6.0 | 3.6 | 8.7 | 369.0 | 240.6 | 544.9 |
| Toluene | 69.0 | 18.1 | 146.3 | 184.5 | 60.5 | 331.5 | 54.6 | 38.4 | 70.5 | 29.8 | 16.5 | 49.2 | 19731.1 | 651.6 | 53948.0 |
| 2-Methyl-3-Buten-2-ol | 90.5 | 15.6 | 191.5 | 27.1 | 2.3 | 43.2 | 55.5 | 37.0 | 75.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Nonomethyl Succinate | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 426.6 | 0.0 | 1202.6 |
| 2,3-Pentanedione | 62.4 | 11.5 | 209.6 | 118.7 | 14.2 | 283.6 | 1273.1 | 418.3 | 1951.0 | 1110.3 | 33.8 | 1736.8 | 6006.6 | 886.0 | 17911.1 |
| Dimethyl Disulfide | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 168.0 | 0.0 | 322.5 |
| 2-Ethenyl-Furan | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 141.8 | 96.2 | 168.6 | 36.0 | 12.0 | 101.2 | 146.0 | 27.9 | 263.5 |
| Hexanal | 186.3 | 31.0 | 455.6 | 261.4 | 137.5 | 503.5 | 17.1 | 6.6 | 26.6 | 10.8 | 5.4 | 21.0 | 0.0 | 0.0 | 0.0 |
| 2-Methyl-1-Propanol | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 5315.7 | 0.0 | 19137.9 |
| Methyl 2-Ethylpentanoate | 108.0 | 25.4 | 320.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 5-Butyl-Dihydro-2(3H)-Furanone | 0.0 | 0.0 | 0.0 | 537.2 | 254.7 | 1245.5 | 108.5 | 92.1 | 119.5 | 6.9 | 4.2 | 14.5 | 1302.1 | 506.1 | 1942.4 |
| m-Cresol | 4.7 | 3.9 | 6.0 | 12.2 | 6.5 | 17.1 | 166.8 | 94.7 | 226.8 | 83.3 | 3.8 | 206.6 | 1607.3 | 269.3 | 3490.7 |
| 1-Butanol | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 398.4 | 34.9 | 1044.9 |
| 5-Propyl-Dihydro-2(3H)-Furanone | 0.0 | 0.0 | 0.0 | 288.4 | 129.8 | 643.3 | 49.4 | 38.2 | 59.5 | 6.4 | 2.9 | 12.4 | 716.9 | 274.4 | 1047.0 |
| 3-Methyl-Pyridazine | 0.0 | 0.0 | 0.0 | 34.5 | 9.7 | 60.0 | 281.8 | 70.9 | 422.2 | 373.1 | 10.9 | 741.4 | 4726.1 | 2183.3 | 8754.7 |
| 1-Penten-3-ol | 204.3 | 89.6 | 282.2 | 26.1 | 3.1 | 57.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2-Heptanone | 436.3 | 5.7 | 1558.9 | 70.4 | 16.7 | 110.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Heptanal | 0.0 | 0.0 | 0.0 | 53.9 | 7.2 | 119.7 | 9.0 | 2.3 | 16.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| m-Menthane | 0.0 | 0.0 | 0.0 | 17.2 | 3.4 | 33.6 | 7.1 | 3.3 | 14.4 | 8.5 | 4.5 | 16.1 | 28.7 | 7.1 | 63.7 |
| 1,3-Diazine | 0.0 | 0.0 | 0.0 | 26.6 | 3.6 | 49.1 | 14.5 | 3.4 | 44.3 | 22.3 | 8.7 | 46.0 | 141.4 | 27.2 | 325.7 |
| 2-Methyl-1-Butanol | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 10274.0 | 0.0 | 21874.3 |
| 2-Propyl-Furan | 59.8 | 8.0 | 142.4 | 90.3 | 7.0 | 185.6 | 37.4 | 22.2 | 46.6 | 107.5 | 11.5 | 191.1 | 10251.8 | 7982.1 | 11826.9 |
| 3-Methyl-1-Butanol | 186.6 | 32.2 | 300.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2-Pentyl-Furan | 133.1 | 17.4 | 263.2 | 139.9 | 14.3 | 240.0 | 31.3 | 20.5 | 45.0 | 9.4 | 3.8 | 21.1 | 38.8 | 12.0 | 110.9 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3-Octanone | 75.4 | 32.7 | 117.1 | 13.8 | 2.9 | 28.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1-Pentanol | 74.0 | 46.1 | 142.0 | 49.0 | 34.3 | 67.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2-Methyl-Pyrazine | 223.0 | 3.7 | 864.4 | 108.0 | 2.0 | 203.1 | 460.3 | 274.7 | 566.1 | 176.7 | 39.6 | 270.7 | 1156.4 | 454.2 | 2077.3 |
| 2-Methyl-Dihydro-2(3H)-Furanone | 16.1 | 3.8 | 26.6 | 56.8 | 1.5 | 152.1 | 1250.2 | 1015.8 | 1645.6 | 496.4 | 153.8 | 817.3 | 17001.2 | 11415.6 | 21675.5 |
| p-Cymene | 53.6 | 2.9 | 195.4 | 2.8 | 0.6 | 5.7 | 10.4 | 2.9 | 16.3 | 3.8 | 0.4 | 7.3 | 62.3 | 20.7 | 120.3 |
| Mesitylene | 395.8 | 8.2 | 1532.1 | 18.2 | 2.0 | 25.9 | 24.1 | 19.6 | 31.2 | 12.5 | 8.9 | 17.2 | 866.3 | 3.5 | 3436.8 |
| 3,5-Xylenol | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 45.7 | 39.9 | 61.1 | 11.7 | 2.9 | 22.1 | 223.1 | 97.3 | 350.1 |
| 3-Hydroxy-2-Butanone | 79.2 | 15.8 | 116.5 | 105.0 | 24.6 | 155.5 | 164.3 | 121.0 | 209.5 | 252.6 | 77.8 | 360.6 | 3023.0 | 1477.8 | 5088.3 |
| Vinylene Carbonate | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 801.0 | 330.7 | 1079.4 | 1694.9 | 717.3 | 2090.4 | 16593.2 | 9172.5 | 21659.4 |
| 2,6-Xylenol | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 406.6 | 350.5 | 504.5 | 55.5 | 21.9 | 116.3 | 1000.6 | 480.3 | 1624.2 |
| Octanal | 0.0 | 0.0 | 0.0 | 30.1 | 19.2 | 40.1 | 54.4 | 48.6 | 61.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1-Hydroxy-2-Propanone | 1463.8 | 804.1 | 2960.0 | 1500.4 | 1274.6 | 1722.8 | 2100.1 | 1659.9 | 2414.8 | 4757.8 | 3062.3 | 6784.9 | 17501.9 | 6411.6 | 28531.5 |
| cis-2-Heptanal | 442.1 | 12.7 | 1707.7 | 14.5 | 7.3 | 22.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2,5-Dimethyl-Pyrazine | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 267.5 | 78.5 | 464.0 | 18.3 | 10.8 | 23.5 | 605.7 | 41.8 | 1178.3 |
| cis-2-Pentenol | 119.2 | 39.1 | 205.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2,6-Dimethyl-Pyrazine | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 358.3 | 183.9 | 484.3 | 89.0 | 62.4 | 152.6 | 1281.7 | 1075.6 | 1374.8 |
| 2-Heptanol | 473.3 | 12.2 | 1452.9 | 22.2 | 8.3 | 34.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2-Pentene | 205.3 | 7.8 | 590.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2-Cyclopenten-1-one | 95.7 | 48.4 | 118.0 | 109.3 | 53.5 | 197.2 | 212.2 | 181.9 | 240.0 | 274.6 | 224.5 | 334.2 | 2532.6 | 1387.8 | 3582.4 |
| 1-Hexanol | 477.0 | 91.3 | 747.3 | 67.6 | 49.7 | 93.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2-Methyl-2-Cyclopenten-1-one | 11.3 | 5.3 | 22.1 | 15.9 | 8.7 | 26.8 | 124.2 | 115.8 | 133.5 | 138.2 | 115.8 | 183.8 | 1236.0 | 485.5 | 1830.1 |
| 5-Methyl-2-Furanmethanethiol | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3159.9 | 27.9 | 8526.8 |
| 1-Hydroxy-2-Butanone | 129.2 | 29.1 | 314.3 | 105.9 | 37.1 | 169.0 | 397.1 | 257.6 | 497.1 | 777.9 | 635.9 | 976.6 | 5534.9 | 656.2 | 9836.8 |
| 2-Ethyl-6-Methyl-Pyrazine | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 43.2 | 26.3 | 55.8 | 9.3 | 4.1 | 11.5 | 148.5 | 130.3 | 181.4 |
| Nonanal | 12.8 | 8.4 | 18.6 | 65.4 | 43.2 | 104.2 | 74.8 | 53.2 | 94.3 | 131.7 | 70.3 | 220.8 | 1269.4 | 508.3 | 2511.5 |
| 1-Ethyl-1-Methyl-Cyclopentane | 33.6 | 5.2 | 86.1 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | 82.5 | 9.9 | 240.9 | 56.6 | 27.6 | 92.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2-Octanol | 117.9 | 3.0 | 383.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2-Cyclohexen-1-one | 11.3 | 6.6 | 19.2 | 6.8 | 2.9 | 10.0 | 38.2 | 22.5 | 54.0 | 48.0 | 6.4 | 70.1 | 355.6 | 31.8 | 746.9 |
| trans-2-Octenal | 103.4 | 2.9 | 340.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 5-Methyl-2(3H)-Furanone | 0.0 | 0.0 | 0.0 | 123.8 | 36.3 | 177.0 | 572.1 | 308.8 | 706.7 | 1271.9 | 1163.4 | 1356.4 | 8187.9 | 5683.0 | 10002.6 |
| 1,3-Dihydro-4-Methyl-2H-Imidazol-2-one | 28.9 | 17.6 | 39.8 | 46.5 | 18.1 | 76.3 | 272.6 | 102.9 | 358.1 | 551.7 | 475.4 | 597.6 | 4107.0 | 1816.1 | 6696.1 |
| 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 81.2 | 64.8 | 108.3 | 8.6 | 3.0 | 18.6 | 435.3 | 192.8 | 694.6 |
| 1-Octen-3-ol | 351.9 | 151.6 | 460.6 | 85.9 | 46.3 | 129.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1-Heptanol | 30.1 | 7.3 | 43.6 | 9.8 | 6.0 | 13.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Furfural | 7946.3 | 5340.1 | 9343.6 | 8746.3 | 6632.6 | 10268.8 | 15953.2 | 14841.3 | 17582.7 | 17902.0 | 17116.0 | 18300.5 | 29664.8 | 24513.0 | 34806.3 |
| Ethanoic Acid | 5881.4 | 2514.7 | 8609.0 | 6732.4 | 2973.5 | 8815.0 | 15081.9 | 11058.8 | 19983.3 | 22335.7 | 18791.3 | 31012.7 | 132229.6 | 66429.6 | 194203.0 |
| 2-Nonen-4-one | 0.0 | 0.0 | 0.0 | 29.6 | 18.8 | 42.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1,2,3,4-Tetrahydro-1,6,8-Trimethyl-Naphthalene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 70.1 | 53.9 | 96.9 | 23.8 | 9.6 | 47.1 | 747.4 | 447.6 | 1265.3 |
| 2-Ethyl-1-Hexanol | 34.6 | 21.5 | 50.1 | 42.0 | 32.8 | 51.1 | 72.4 | 56.5 | 88.7 | 85.9 | 42.3 | 109.0 | 1505.7 | 392.4 | 2997.0 |
| trans,trans-2,4-Heptadienal | 0.0 | 0.0 | 0.0 | 33.5 | 20.0 | 48.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 3-Methyl-Furfural | 239.7 | 83.5 | 439.1 | 390.0 | 145.6 | 690.2 | 2098.0 | 1342.7 | 2852.6 | 2535.7 | 1820.7 | 3975.3 | 523.5 | 275.2 | 848.6 |
| Furfuryl Formate | 80.3 | 58.1 | 97.4 | 135.0 | 118.0 | 167.3 | 186.4 | 159.0 | 246.2 | 372.9 | 282.6 | 429.5 | 3292.9 | 1820.2 | 4359.7 |
| 1-(2-Furanyl)-Ethanone | 773.6 | 409.6 | 1064.0 | 1118.0 | 533.6 | 1531.5 | 4838.1 | 3309.3 | 6772.3 | 5121.5 | 4075.8 | 5929.1 | 13847.7 | 10890.1 | 15542.0 |
| Decanal | 18.1 | 9.3 | 25.5 | 26.7 | 5.3 | 58.8 | 43.2 | 10.1 | 91.8 | 54.7 | 6.3 | 107.1 | 1726.8 | 250.3 | 3199.5 |
| Benzaldehyde | 139.2 | 90.3 | 264.5 | 179.5 | 114.9 | 248.5 | 217.5 | 183.5 | 238.0 | 161.8 | 124.7 | 206.3 | 1071.4 | 611.7 | 1623.6 |
| Furfuryl Acetate | 21.5 | 11.4 | 27.2 | 26.3 | 12.5 | 39.2 | 74.5 | 28.5 | 92.2 | 209.8 | 156.3 | 243.4 | 2208.4 | 1123.8 | 3456.7 |
| Propanoic Acid | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 76.9 | 7.6 | 192.3 | 661.3 | 485.4 | 773.1 | 2532.7 | 299.8 | 6815.4 |
| 1-Octanol | 56.4 | 28.0 | 71.6 | 29.0 | 17.8 | 34.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Dimethyl Sulfoxide | 6.6 | 5.6 | 8.9 | 211.6 | 6.7 | 365.1 | 40.3 | 24.5 | 65.5 | 37.0 | 8.0 | 65.7 | 414.7 | 267.6 | 514.9 |
| 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 65.2 | 52.4 | 79.8 | 11.7 | 4.5 | 23.8 | 319.2 | 118.3 | 571.3 |
| 5-Methyl-Furfural | 1646.8 | 875.8 | 2072.4 | 2114.2 | 1429.0 | 3172.0 | 3305.4 | 1864.1 | 4953.3 | 5330.3 | 2230.6 | 7971.7 | 18953.0 | 17003.7 | 22090.1 |
| 4-Cyclopentene-1,3-dione | 356.3 | 111.9 | 517.0 | 477.2 | 152.9 | 699.4 | 3039.9 | 1416.1 | 4026.4 | 6553.9 | 4404.3 | 8184.9 | 18193.7 | 13308.5 | 21389.0 |
| 2-Methyl-Benzofuran | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 884.2 | 654.3 | 1154.6 | 118.3 | 74.9 | 193.1 | 7348.1 | 2345.0 | 9803.4 |
| 1-(5-Methyl-2-Furanyl)-Ethanone | 47.5 | 39.6 | 53.7 | 51.9 | 35.5 | 77.2 | 109.0 | 72.5 | 133.9 | 151.1 | 120.5 | 177.1 | 2057.2 | 1012.7 | 2693.8 |
| trans-2-Octenol | 23.3 | 4.3 | 70.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Diethylene Glycol Ethyl Ether | 124.1 | 77.0 | 181.7 | 151.5 | 2.6 | 257.9 | 366.8 | 318.9 | 397.6 | 439.7 | 414.3 | 498.9 | 3571.2 | 1868.5 | 5243.0 |
| 3-Methyl-Dihydro-2(3H)-Furanone | 38.0 | 15.5 | 55.3 | 32.3 | 9.6 | 50.3 | 148.8 | 67.9 | 198.5 | 207.5 | 139.9 | 251.3 | 1486.8 | 863.8 | 1932.1 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 81.5 | 31.7 | 130.8 |
| Benzeneacetaldehyde | 62.9 | 6.2 | 190.8 | 100.4 | 20.6 | 168.0 | 742.0 | 403.4 | 1095.6 | 754.6 | 200.1 | 1028.7 | 8658.6 | 3591.8 | 12558.9 |
| 3,5-Dimethyl-Dihydro-2-Furanone | 59.5 | 28.7 | 100.2 | 48.4 | 4.3 | 74.7 | 97.3 | 85.2 | 108.0 | 133.8 | 88.3 | 229.6 | 1522.5 | 540.0 | 3382.9 |
| 3-Methyl-Benzaldehyde | 59.0 | 5.9 | 213.4 | 40.2 | 2.4 | 82.8 | 687.4 | 38.5 | 1108.7 | 745.9 | 51.9 | 1036.0 | 0.0 | 0.0 | 0.0 |
| 2-Propenoic Acid | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 836.6 | 348.5 | 1273.2 | 1086.4 | 541.9 | 1486.6 | 8601.3 | 3090.4 | 13197.2 |
| Acetophenone | 27.5 | 5.0 | 78.3 | 62.8 | 17.1 | 147.0 | 25.2 | 16.0 | 34.4 | 37.8 | 32.9 | 42.9 | 396.3 | 184.2 | 786.4 |
| 2-Furanmethanol | 3303.3 | 2271.0 | 4746.7 | 2952.1 | 1447.7 | 4241.9 | 7670.3 | 3947.7 | 12212.7 | 14535.3 | 7715.6 | 18003.1 | 29016.4 | 18617.5 | 52489.4 |
| 3-Furanmethanol | 1520.4 | 1196.3 | 1835.1 | 1520.2 | 1264.3 | 1814.9 | 3889.1 | 1973.8 | 4921.9 | 15578.1 | 9522.2 | 19884.2 | 30349.9 | 16348.3 | 64212.9 |
| 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 59.1 | 41.4 | 81.3 | 21.9 | 3.8 | 60.6 | 389.5 | 271.4 | 529.9 |
| 2-(2-Furanylmethyl)-5-Methyl-Furan | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 33.0 | 24.3 | 38.8 | 39.2 | 11.7 | 52.5 | 634.3 | 353.0 | 995.9 |
| 3-Methyl-2(5H)-Furanone | 39.9 | 23.6 | 66.5 | 29.4 | 9.4 | 47.0 | 90.3 | 81.6 | 101.6 | 116.9 | 107.0 | 123.8 | 805.7 | 579.3 | 985.7 |
| 5-Methyl-2-Furanmethanol | 39.1 | 2.0 | 65.6 | 42.1 | 9.2 | 84.0 | 375.8 | 303.8 | 470.4 | 522.3 | 456.2 | 648.6 | 3533.3 | 1929.1 | 5391.7 |
| Phenylmethyl Acetate | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 223.2 | 0.0 | 366.5 |
| Naphthalene | 31.8 | 21.3 | 48.8 | 43.1 | 11.6 | 121.8 | 30.0 | 29.7 | 30.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2(5H)-Furanone | 668.9 | 256.6 | 1190.9 | 722.2 | 311.9 | 964.6 | 2551.9 | 1179.3 | 3285.7 | 5056.4 | 4014.6 | 5773.8 | 22826.6 | 7999.2 | 37096.8 |
| 2,2'-Methylenebis[5-Methyl-Furan | 0.0 | 0.0 | 0.0 | 5.1 | 2.6 | 7.5 | 87.5 | 71.2 | 114.5 | 30.5 | 24.7 | 37.9 | 884.6 | 377.1 | 1462.2 |
| 1,2-Cyclopentanedione | 289.5 | 97.1 | 370.4 | 617.3 | 170.1 | 949.4 | 4169.0 | 2263.9 | 4881.9 | 7560.9 | 6971.0 | 8094.2 | 31006.2 | 24006.4 | 39417.0 |
| Diethylene Glycol Monobutyl Ether | 26.2 | 2.6 | 71.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2-Cyclohexenol | 309.0 | 93.3 | 403.6 | 342.6 | 126.6 | 510.7 | 930.1 | 471.0 | 1133.3 | 1838.8 | 1642.0 | 2139.5 | 12528.0 | 7666.5 | 16990.4 |
| 2-Phenylethyl Acetate | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2984.0 | 364.5 | 6220.2 |
| 3-Methyl-1,2-Cyclopentanedione | 302.7 | 84.4 | 501.5 | 291.0 | 117.9 | 421.1 | 1049.6 | 619.3 | 1254.6 | 1936.5 | 1813.8 | 2212.6 | 15370.7 | 9727.3 | 21664.8 |
| β-Damascenone | 0.0 | 0.0 | 0.0 | 67.3 | 47.8 | 101.5 | 67.3 | 56.4 | 88.7 | 321.2 | 10.4 | 784.5 | 3856.0 | 292.9 | 10703.7 |
| 2-Methyl-Propanoic Acid | 64.1 | 11.9 | 117.9 | 71.7 | 5.1 | 125.8 | 438.9 | 198.7 | 569.7 | 899.1 | 655.7 | 1196.2 | 7489.7 | 3305.0 | 12086.5 |
| 4-(1-Methylpropyl)-Phenol | 0.0 | 0.0 | 0.0 | 13.7 | 9.6 | 17.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2,4,6-Trihydroxypyrimidine | 966.7 | 194.2 | 1515.8 | 1253.7 | 1039.8 | 1719.0 | 2816.4 | 1222.0 | 4108.4 | 8143.5 | 5641.7 | 10220.5 | 24238.0 | 17663.8 | 27315.9 |
| Mequinol | 23.9 | 15.9 | 38.1 | 23.8 | 13.5 | 37.2 | 154.3 | 124.5 | 171.9 | 149.6 | 120.1 | 186.7 | 1441.5 | 931.4 | 2222.2 |
| 2,2-Diethyl-3-Methyl-Oxazolidine | 255.4 | 168.3 | 373.1 | 340.2 | 208.2 | 408.4 | 488.8 | 239.6 | 609.3 | 1104.0 | 898.9 | 1372.6 | 8616.2 | 3790.2 | 13662.4 |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Oxypurinol | 474.0 | 233.5 | 758.5 | 414.0 | 272.0 | 526.2 | 682.6 | 294.7 | 842.2 | 1550.7 | 986.7 | 1943.1 | 10375.1 | 7792.4 | 12480.4 |
| Benzenemethanol | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 36.1 | 27.8 | 41.8 | 593.9 | 261.2 | 805.1 |
| 4-Methyl-2(5H)-Furanone | 161.5 | 124.4 | 256.8 | 139.4 | 118.9 | 186.0 | 292.8 | 210.6 | 325.0 | 442.4 | 426.5 | 452.0 | 4135.8 | 2280.4 | 6962.8 |
| 3-Ethyl-2-Hydroxy-2-Cyclopenten-1-one | 26.6 | 3.3 | 47.2 | 28.3 | 2.4 | 45.7 | 161.6 | 100.5 | 194.0 | 271.2 | 213.9 | 322.3 | 2637.0 | 1543.9 | 3729.0 |
| Benzeneethanol | 73.0 | 10.2 | 202.2 | 59.7 | 30.8 | 92.7 | 31.1 | 17.9 | 51.2 | 19.8 | 19.0 | 20.6 | 289.0 | 178.5 | 464.1 |
| 1,4-Butanediol | 52.6 | 13.6 | 81.1 | 44.3 | 3.0 | 65.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Acrylamide | 0.0 | 0.0 | 0.0 | 131.5 | 115.4 | 143.3 | 290.6 | 126.9 | 400.7 | 682.8 | 536.4 | 798.3 | 5492.3 | 2951.1 | 6777.6 |
| Erythritol | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 10864.2 | 4625.2 | 17525.1 |
| 2,3-Dimethyl-3-Pyrazolin-5-one | 21.9 | 17.5 | 29.6 | 27.8 | 22.1 | 33.9 | 90.7 | 55.3 | 107.9 | 165.3 | 157.6 | 177.4 | 1383.8 | 838.8 | 1934.6 |
| Furfural Acetone | 79.3 | 65.9 | 97.4 | 76.3 | 65.4 | 89.3 | 88.0 | 62.9 | 102.2 | 171.3 | 116.7 | 213.1 | 1368.7 | 782.5 | 2071.1 |
| Cyclotene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 548.9 | 383.5 | 638.5 | 5345.3 | 3217.2 | 7902.0 |
| 2-Methyl-1,4-Benzenediol | 66.3 | 54.7 | 77.7 | 43.5 | 17.4 | 54.1 | 188.6 | 118.0 | 254.2 | 361.9 | 308.7 | 462.0 | 3124.0 | 1131.4 | 6209.2 |
| Maltol | 637.4 | 487.1 | 866.1 | 871.5 | 632.9 | 1127.1 | 1295.6 | 774.0 | 1576.3 | 2616.1 | 2446.3 | 2844.9 | 16546.2 | 12514.7 | 20498.4 |
| 2-Acetylpyrrole | 22.1 | 10.6 | 40.8 | 32.1 | 19.1 | 42.7 | 1556.2 | 1239.5 | 1969.3 | 1371.5 | 1104.9 | 1658.0 | 11322.0 | 7404.8 | 14430.4 |
| 2,5-Furandicarboxaldehyde | 1306.2 | 884.9 | 1824.8 | 1665.8 | 1361.4 | 2231.3 | 1953.3 | 1409.5 | 2306.5 | 2726.5 | 1716.8 | 3391.1 | 25356.6 | 16453.0 | 33001.5 |
| 2H-Pyran-2,6(3H)-Dione | 3.4 | 1.1 | 6.7 | 14.7 | 5.0 | 35.6 | 583.0 | 87.8 | 772.5 | 1587.7 | 1180.5 | 1935.2 | 12895.9 | 6873.8 | 16447.7 |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | 492.9 | 265.2 | 624.1 | 1308.9 | 387.5 | 1833.6 | 2712.3 | 1125.8 | 4403.7 | 8007.5 | 5546.3 | 11155.4 | 31232.7 | 17626.4 | 57419.4 |
| Phenol | 120.4 | 101.7 | 145.0 | 117.1 | 93.9 | 146.1 | 303.3 | 199.3 | 371.7 | 444.3 | 274.2 | 527.7 | 5384.3 | 2987.2 | 8204.7 |
| 1H-Pyrrole-2-Carboxaldehyde | 0.0 | 0.0 | 0.0 | 44.9 | 17.1 | 60.9 | 139.1 | 123.2 | 169.4 | 175.7 | 117.4 | 202.5 | 3344.1 | 835.0 | 5897.6 |
| Phloroglucinol | 0.0 | 0.0 | 0.0 | 112.7 | 11.8 | 214.9 | 631.0 | 171.9 | 898.2 | 1512.2 | 1179.2 | 1814.0 | 12265.7 | 5238.3 | 16640.6 |
| Furaneol | 337.1 | 149.2 | 552.9 | 428.5 | 171.8 | 619.8 | 2417.2 | 929.6 | 3731.6 | 6199.8 | 3697.5 | 7750.0 | 15660.7 | 13267.4 | 18232.8 |
| Octanoic Acid | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 330.0 | 203.2 | 403.5 |
| 5-Acetyl-Dihydro-2(3H)-Furanone (Solerone) | 623.5 | 237.1 | 873.1 | 692.3 | 206.8 | 985.9 | 2302.5 | 1063.0 | 3089.9 | 4891.1 | 3598.1 | 6381.1 | 14045.2 | 11865.3 | 17076.3 |
| 2-Furanpropionic Acid | 53.1 | 35.6 | 64.7 | 92.6 | 56.2 | 127.1 | 386.2 | 117.9 | 562.2 | 1051.4 | 635.6 | 1329.2 | 8916.7 | 4640.8 | 11266.7 |
| 1,3-Dihydroxy-2-Propanone | 15961.3 | 13268.3 | 17624.6 | 20545.0 | 17036.2 | 24784.6 | 43595.8 | 30861.4 | 55866.8 | 116211.3 | 93703.1 | 127263.4 | 381433.2 | 325658.0 | 432011.6 |
| Tetrahydro-5-Methyl-2-Furanmethanol | 2774.8 | 2499.9 | 3215.6 | 2284.6 | 1925.4 | 2727.5 | 3818.5 | 3137.4 | 4774.1 | 4443.1 | 2533.1 | 5406.5 | 9946.1 | 1093.5 | 16415.9 |
| 4,5-Dimethyl Vinylene Carbonate | 104.5 | 12.1 | 228.9 | 229.7 | 42.1 | 356.0 | 1023.1 | 551.7 | 1487.2 | 1963.5 | 1809.9 | 2265.0 | 12259.4 | 6807.3 | 16353.7 |
| 2-Hydroxy-Dihydro-2(3H)-Furanone | 7777.1 | 2994.5 | 10996.3 | 6532.7 | 1787.8 | 8715.0 | 13531.0 | 11553.6 | 14379.4 | 16576.5 | 15092.2 | 19027.7 | 16009.4 | 5312.8 | 30587.2 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Ethyl-Phenol | 61.3 | 0.0 | 126.8 | 29.4 | 20.7 | 36.7 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 5-Acetoxymethyl-2-Furfural A | 2100.4 | 1195.7 | 3245.2 | 2378.5 | 1393.6 | 3102.3 | 2994.4 | 2020.7 | 4680.0 | 6897.7 | 4627.7 | 8624.5 | 13896.3 | 9644.0 | 17759.4 |
| 5-Acetoxymethyl-2-Furfural B | 1597.3 | 1091.9 | 2203.5 | 1752.8 | 1316.6 | 2131.9 | 2578.5 | 2378.1 | 3098.5 | 5834.2 | 4508.0 | 6700.1 | 18284.9 | 15313.4 | 21514.3 |
| 2-Methoxy-4-Vinyl-Phenol | 59.5 | 39.3 | 83.2 | 188.0 | 133.6 | 268.6 | 839.6 | 564.1 | 1148.8 | 475.0 | 282.1 | 581.0 | 3556.1 | 1441.2 | 6340.0 |
| 3-Methyl-2,4(3H,5H)-Furandione | 71.6 | 36.8 | 106.2 | 96.6 | 51.4 | 137.1 | 529.1 | 251.9 | 686.6 | 897.2 | 315.8 | 1249.5 | 7784.2 | 5296.3 | 10253.6 |
| 3-Hydroxy-2,3-Dihydro-Maltol | 220.5 | 56.3 | 293.9 | 329.0 | 77.2 | 575.3 | 1179.0 | 512.5 | 1558.5 | 3473.9 | 2868.8 | 4156.8 | 11653.0 | 9991.1 | 13316.2 |
| Decanoic Acid | 50.5 | 7.2 | 133.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 125.2 | 45.2 | 175.4 | 779.3 | 211.6 | 1697.1 |
| 5-Hydroxy-Maltol | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 1833.2 | 709.9 | 2500.5 | 4754.5 | 3068.4 | 5793.5 | 28988.8 | 20736.5 | 38102.8 |
| 2,3-Dihydro-Benzofuran | 71.8 | 39.6 | 104.9 | 375.0 | 185.9 | 509.9 | 562.2 | 405.8 | 734.5 | 507.6 | 291.4 | 612.0 | 2898.7 | 1486.6 | 5430.7 |
| 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | 222.1 | 180.4 | 287.6 | 286.6 | 114.2 | 437.6 | 501.8 | 409.9 | 585.9 | 652.2 | 320.8 | 877.1 | 6237.8 | 4620.5 | 8321.9 |
| 4-Pyridinol | 105.1 | 60.5 | 157.1 | 193.2 | 160.9 | 240.7 | 631.2 | 394.6 | 713.3 | 1174.2 | 880.2 | 1350.9 | 10326.4 | 6563.0 | 13378.4 |
| 4-Amino-Phenol | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 204.3 | 117.6 | 460.6 | 744.7 | 373.5 | 887.3 | 6638.3 | 3681.8 | 10392.8 |
| Benzoic Acid | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 22.9 | 15.4 | 37.5 | 558.1 | 241.1 | 887.7 | 2282.5 | 1495.7 | 2990.6 |
| Dimethylhydrazone 3-Pentanone | 149.8 | 33.6 | 215.7 | 221.1 | 7.7 | 420.5 | 379.8 | 173.2 | 687.1 | 2630.1 | 2113.2 | 3409.1 | 12664.0 | 5269.3 | 22368.8 |
| Undecanoic Acid | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 731.1 | 161.6 | 1775.2 |
| 5-(Hydroxymethyl)-Dihydro-2(3H)-Furanone | 1196.0 | 940.6 | 1313.6 | 1190.0 | 932.8 | 1411.4 | 4964.1 | 1854.7 | 6758.3 | 10180.3 | 9091.5 | 11615.3 | 42329.6 | 20401.6 | 75799.6 |
| Benzophenone | 22.6 | 9.3 | 51.2 | 49.2 | 11.4 | 132.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Dodecanoic Acid | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 64.4 | 46.6 | 85.5 | 2123.6 | 1125.4 | 3671.4 |
| 5-(Hydroxymethyl)-2-Furfural | 2204.6 | 1800.5 | 2600.4 | 23735.9 | 15739.2 | 28637.3 | 37632.3 | 29204.2 | 44507.0 | 86354.6 | 51156.7 | 101861.5 | 175037.3 | 164599.0 | 198276.1 |
| 3-Methoxy-1,2-Benzenediol | 130.8 | 36.3 | 202.3 | 133.6 | 40.9 | 206.0 | 310.9 | 140.5 | 392.4 | 895.2 | 641.8 | 1177.6 | 7764.0 | 3640.6 | 14099.0 |
| 1-(2-Furanyl)-1,2-Ethanediol | 705.0 | 528.1 | 864.2 | 385.9 | 278.4 | 594.5 | 1559.0 | 957.6 | 2282.7 | 3011.4 | 1420.8 | 5938.3 | 16383.5 | 12514.4 | 22502.6 |
| 4-Hydroxy-Dihydro-2(3H)-Furanone | 288.4 | 160.4 | 372.5 | 424.8 | 300.5 | 615.7 | 1101.8 | 563.4 | 1479.0 | 2708.1 | 2551.9 | 2839.7 | 21411.6 | 13815.3 | 29163.2 |

**Table S26. VOCs identified in samples from SCH processing stages during 2015-2018 production years previously identified in others SC-based products.**

| Volatile Organic Compounds | Sugarcane-Based Products | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **SCH** 1 | **Juice** 2–7 | **Sugar** 6,8–11 | **Treacle** 12 | **Molasses** 13–15 | **Syrup** 1,6,16–18 | **Rum** 19–25 | **Infusion** 26 | **Alcoholic Fermented Beverage** 27,28 |
| Pentane | | | | | | | | | |
| Hexane | | | | | | | | | |
| Ethyl Ether | | | | | | | | | |
| 1,4-Pentadiene | | | | | | | | | |
| Methanethiol | | | | | | | | | |
| Ethanal | X | | X | | | X | X | | |
| Dimethyl Sulfide | X | X | X | X | | X | | | |
| Propanal | | | | | | X | X | | |
| Furan | X | | | | | X | | | |
| 2-Methyl-Propanal | X | | X | X | | X | | | |
| Ethyl Formate | | | | | | | | | |
| 2-Propenal | | | | | | | | | |
| 2-Methyl-Furan | X | X | | | | X | | | |
| Ethyl Acetate | X | X | | | | X | X | | |
| 2-Butanone | X | | | X | | X | | | |
| 2-Methyl-Butanal | X | | X | X | X | X | X | | |
| 3-Methyl-Butanal | X | X | X | X | X | X | X | | |
| Ethanol | X | X | X | X | | X | X | | |
| Benzene | | | | | | | | | |
| 3-Buten-2-one | | | | | | | | | |
| 2-Ethyl-Furan | | | | | | | | | |
| 2,5-Dimethyl-Furan | X | | | | | X | | | |
| Ethyl Propanoate | X | | | | | X | | | |
| 3-Pentanone | | | | | | | | | |
| Pentanal | | X | | | | X | X | | |
| 2,3-Butanedione | X | X | X | | X | X | X | | |
| 1-Penten-3-one | | X | | | | | | | |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 1-Propanol | | | | | | X | X | | | |
| 2-Ethyl-5-Methyl-Furan | X | | | | | X | | | | |
| Toluene | | | | | | | | | | |
| 2-Methyl-3-Buten-2-ol | X | | | X | | X | | | | |
| Nonomethyl Succinate | | | | | | | | | | |
| 2,3-Pentanedione | X | | | | | X | | | | |
| Dimethyl Disulfide | | | | | | X | | | | |
| 2-Ethenyl-Furan | | | | | | | | | | |
| Hexanal | X | X | X | | | X | X | | | |
| 2-Methyl-1-Propanol | X | X | | X | X | X | X | | | X |
| Methyl 2-Ethylpentanoate | | | | | | | | | | |
| 5-Butyl-Dihydro-2(3H)-Furanone (γ-Octalactone) | X | | | | | X | | | | |
| m-Cresol | | | | | X | | X | | | |
| 1-Butanol | X | | | | | X | X | | | |
| 5-Propyl-Dihydro-2(3H)-Furanone (γ-Heptalactone) | | | | | | | | | | |
| 3-Methyl-Pyridazine | | | | | | X | | | | |
| 1-Penten-3-ol | | | | | | | | | | |
| 2-Heptanone | | X | | | | | | | | |
| Heptanal | X | X | | | | X | X | | | |
| m-Menthane | | | | | | | | | | |
| 1,3-Diazine | | | | | | | | | | |
| 2-Methyl-1-Butanol | X | | | X | X | X | X | | | X |
| 2-Propyl-Furan | | | | | | | | | | |
| 3-Methyl-1-Butanol | X | X | | X | X | X | X | | | X |
| 2-Pentyl-Furan | | X | | | | | | | | |
| 3-Octanone | | | | | | | | | | |
| 1-Pentanol | | X | X | | | | | | | |
| 2-Methyl-Pyrazine | | X | X | | | X | | X | | |
| 2-Methyl-Dihydro-2(3H)-Furanone | X | | X | | | X | | | | |
| p-Cymene | X | X | X | | | X | | | | |
| Mesitylene | | | | | | | | | | |
| 3,5-Xylenol | | | | | | | | | | |
| 3-Hydroxy-2-Butanone | | X | X | X | X | X | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Vinylene Carbonate | | | | | | | | |
| 2,6-Xylenol | | | | | | | | |
| Octanal | X | X | | | | X | | |
| 1-Hydroxy-2-Propanone | X | X | X | X | | X | | |
| cis-2-Heptanal | X | | | | | X | | |
| 2,5-Dimethyl-Pyrazine | | X | X | | X | X | | X |
| cis-2-Pentenol | | X | | | | | | |
| 2,6-Dimethyl-Pyrazine | X | X | X | | | X | | |
| 2-Heptanol | | X | | | | | X | |
| 2-Pentene | | X | | | | | | |
| 2-Cyclopenten-1-one | | | | | | | X | |
| 1-Hexanol | X | X | | | | | X | |
| 2-Methyl-2-Cyclopenten-1-one | | | | | | X | | |
| 5-Methyl-2-Furanmethanethiol | X | | | | | X | | |
| 1-Hydroxy-2-Butanone | | | | | | | | |
| 2-Ethyl-6-Methyl-Pyrazine | X | | X | | | X | | |
| Nonanal | X | X | X | | | X | X | |
| 1-Ethyl-1-Methyl-Cyclopentane | | | | | | | | |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | | | | | | | | |
| 2-Octanol | | X | | | | | X | |
| 2-Cyclohexen-1-one | | | | | | | | |
| trans-2-Octenal | | X | | | | | | |
| 5-Methyl-2(3H)-Furanone (β-Angelica Lactone) | | | | | | | | |
| 1,3-Dihydro-4-Methyl-2H-Imidazol-2-one | | | | | | | | |
| 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | X | | | | | X | | |
| 1-Octen-3-ol | | X | | | | | X | |
| 1-Heptanol | | | | | | | X | |
| Furfural | X | X | X | X | | X | X | X |
| Ethanoic Acid | X | X | X | X | X | X | X | |
| 2-Nonen-4-one | | | | | | | | |
| 1,2,3,4-Tetrahydro-1,6,8-Trimethyl-Naphthalene | | | | | | | | |
| 2-Ethyl-1-Hexanol | | X | X | | | | | |
| trans,trans-2,4-Heptadienal | | X | | | | | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 3-Methyl-Furfural | | | | | | | | | |
| Furfuryl Formate | | | | | | | | | |
| 1-(2-Furanyl)-Ethanone | X | | X | | X | X | | | |
| Decanal | X | | | | | X | X | | |
| Benzaldehyde | X | X | X | | | X | | | |
| Furfuryl Acetate | X | | | | | X | | | |
| Propanoic Acid | | | X | X | | | X | X | |
| 1-Octanol | | X | X | | | X | X | | X |
| Dimethyl Sulfoxide | | X | X | | | X | | | |
| 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | | | | | | X | | | |
| 5-Methyl-Furfural | X | X | | X | X | X | | | |
| 4-Cyclopentene-1,3-dione | | | | | | | | | |
| 2-Methyl-Benzofuran | X | | | | | X | | | |
| 1-(5-Methyl-2-Furanyl)-Ethanone | | | | | X | | | | |
| trans-2-Octenol | | X | | | | | | | |
| Diethylene Glycol Ethyl Ether | | | | | | | | | |
| 3-Methyl-Dihydro-2(3H)-Furanone | | | X | | | | | | |
| 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | | | | | | | | | |
| Benzeneacetaldehyde | X | X | | | | X | | | |
| 3,5-Dimethyl-Dihydro-2-Furanone | | | | | | | | | |
| 3-Methyl-Benzaldehyde | | | | | | | | | |
| 2-Propenoic Acid | | | X | | | | | | |
| Acetophenone | | | | | | | | | |
| 2-Furanmethanol | X | X | X | X | X | X | | X | |
| 3-Furanmethanol | | | | | | | | | |
| 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | | | | | | | | | |
| 2-(2-Furanylmethyl)-5-Methyl-Furan | | | | | | | | | |
| 3-Methyl-2(5H)-Furanone | | | | | | | | | |
| 5-Methyl-2-Furanmethanol | X | | X | | | X | | | |
| Phenylmethyl Acetate | X | | | | | X | | | |
| Naphthalene | | | | | | | | | |
| 2(5H)-Furanone | | X | X | | | | | | |
| 2,2'-Methylenebis[5-Methyl-Furan | X | | | | | X | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 1,2-Cyclopentanedione | | | | | | | | |
| Diethylene Glycol Monobutyl Ether | | | | | | | | |
| 2-Cyclohexenol | | | | | | | | |
| 2-Phenylethyl Acetate | X | | | | X | X | | |
| 3-Methyl-1,2-Cyclopentanedione | | | X | | | | | |
| β-Damascenone | | | | X | | X | | |
| 2-Methyl-Propanoic Acid | | | X | | | X | X | X |
| 4-(1-Methylpropyl)-Phenol | | | | | | | | |
| 2,4,6-Trihydroxypyrimidine | | | | | | | | |
| Mequinol | X | X | X | X | X | X | | |
| 2,2-Diethyl-3-Methyl-Oxazolidine | | | | | | | | |
| Oxypurinol | | | | | | | | |
| Benzenemethanol | X | X | X | X | X | | | |
| 4-Methyl-2(5H)-Furanone | | | | | | | | |
| 3-Ethyl-2-Hydroxy-2-Cyclopenten-1-one | | | | | | | | |
| Benzeneethanol | X | X | | X | X | X | | |
| 1,4-Butanediol | | | | | | | | X |
| Acrylamide | | | | X | | | | |
| Erythritol | | | | | | | | |
| 2,3-Dimethyl-3-Pyrazolin-5-one | | | | | | | | |
| Furfural Acetone | | | | | | | | |
| Cyclotene | | | | X | | | | |
| 2-Methyl-1,4-Benzenediol | | | | | | | | |
| Maltol | | | | | | | | |
| 2-Acetylpyrrole | X | | X | X | X | | | |
| 2,5-Furandicarboxaldehyde | | X | | | | | | |
| 2H-Pyran-2,6(3H)-Dione | | | | | | | | |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | | | | | | | | |
| Phenol | X | X | | | X | | | |
| 1H-Pyrrole-2-Carboxaldehyde | | | | | | | | |
| Phloroglucinol | | | | | | | | |
| Furaneol | | | X | X | | X | | |
| Octanoic Acid | | | X | | | X | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 5-Acetyl-Dihydro-2(3H)-Furanone (Solerone) | | | | | X | | | | |
| 2-Furanpropionic Acid | | | | | | | | | |
| 1,3-Dihydroxy-2-Propanone | | | | | | | | | |
| Tetrahydro-5-Methyl-2-Furanmethanol | | | | | | | X | | |
| 4,5-Dimethyl Vinylene Carbonate | | | | | | | | | |
| 2-Hydroxy-Dihydro-2(3H)-Furanone | | | | | | | | | |
| 2-Ethyl-Phenol | | | | | X | | X | | |
| 5-Acetoxymethyl-2-Furfural A | | | | | | | | | |
| 5-Acetoxymethyl-2-Furfural B | | | | | | | | | |
| 2-Methoxy-4-Vinyl-Phenol | | X | X | | X | | X | | |
| 3-Methyl-2,4(3H,5H)-Furandione | | | | | | | | | |
| 3-Hydroxy-2,3-Dihydro-Maltol | | X | X | | | | | | |
| Decanoic Acid | | | | | X | | X | | |
| 5-Hydroxy-Maltol | | | | | | | | | |
| 2,3-Dihydro-Benzofuran | | | | | X | | | | |
| 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | | | | | X | | | | |
| 4-Pyridinol | | | | | | | | | |
| 4-Amino-Phenol | | | | | | | | | |
| Benzoic Acid | | | X | | X | | | | |
| Dimethylhydrazone 3-Pentanone | | | | | | | | | |
| Undecanoic Acid | | | | | | | | | |
| 5-(Hydroxymethyl)-Dihydro-2(3H)-Furanone | | | X | | | | | | |
| Benzophenone | | | X | | | X | | | |
| Dodecanoic Acid | | | X | | | | X | | |
| 5-(Hydroxymethyl)-2-Furfural | X | X | X | X | X | X | X | | |
| 3-Methoxy-1,2-Benzenediol | | | | | | | | | |
| 1-(2-Furanyl)-1,2-Ethanediol | | | | | | | | | |
| 4-Hydroxy-Dihydro-2(3H)-Furanone | | X | | | X | | | | |
| **TOTAL (Nº)** | **54** | **51** | **45** | **18** | **31** | **66** | **41** | **6** | **6** |

**Table S27. Summary of number of volatile organic compounds identified, relative peak areas and total relative peak areas (%) values of main chemical classes identified in samples from SCH processing stages during 2015-2018 production years.**

| Main Chemical Class | Abbreviation | Year | Sugarcane Honey Stages | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | S1 | | | S2 | | | S3 | | | S4 | | | S5 | |
| | | | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) |
| Alcohol | ALC | 2015 | 16 | 1927.5 | 2.32 | 12 | 1324.1 | 1.10 | 4 | 794.9 | 0.43 | 3 | 3518.7 | 0.68 | 8 | 125395.5 | 9.28 |
| | | 2016 | 16 | 5623.2 | 6.85 | 12 | 1815.1 | 1.32 | 4 | 1391.0 | 0.48 | 3 | 2578.0 | 0.54 | 8 | 177045.8 | 10.35 |
| | | 2017 | 16 | 3700.9 | 6.05 | 12 | 2107.4 | 2.43 | 4 | 1727.4 | 0.72 | 3 | 2439.3 | 0.71 | 8 | 193986.4 | 9.20 |
| | | 2018 | 16 | 5051.9 | 6.61 | 12 | 1509.2 | 1.42 | 4 | 2258.8 | 0.85 | 3 | 2607.5 | 0.55 | 5 | 195083.9 | 8.39 |
| Aldehyde | ALD | 2015 | 11 | 240.3 | 0.29 | 14 | 1366.5 | 1.13 | 11 | 18007.2 | 9.74 | 9 | 9211.7 | 1.77 | 8 | 31888.3 | 2.36 |
| | | 2016 | 11 | 253.1 | 0.31 | 14 | 1602.8 | 1.16 | 11 | 22712.9 | 7.89 | 9 | 4948.1 | 1.04 | 8 | 57728.9 | 3.37 |
| | | 2017 | 11 | 1347.8 | 2.20 | 14 | 1562.8 | 1.80 | 11 | 18469.6 | 7.69 | 9 | 3560.6 | 1.04 | 8 | 93029.6 | 4.41 |
| | | 2018 | 11 | 2901.4 | 3.79 | 14 | 1142.0 | 1.07 | 11 | 23172.1 | 8.71 | 9 | 6125.7 | 1.30 | 8 | 121146.1 | 5.21 |
| Benzene | BNZ | 2015 | 11 | 633.7 | 0.76 | 11 | 1213.5 | 1.01 | 11 | 1388.6 | 0.75 | 12 | 4510.8 | 0.87 | 13 | 19716.1 | 1.46 |
| | | 2016 | 11 | 609.8 | 0.74 | 11 | 931.8 | 0.68 | 11 | 3195.8 | 1.11 | 12 | 4135.0 | 0.87 | 13 | 49834.5 | 2.91 |
| | | 2017 | 11 | 652.4 | 1.07 | 11 | 670.7 | 0.77 | 11 | 2112.4 | 0.88 | 12 | 1981.0 | 0.58 | 13 | 82986.7 | 3.94 |
| | | 2018 | 11 | 2354.9 | 3.08 | 11 | 702.0 | 0.66 | 11 | 2569.8 | 0.97 | 12 | 3898.3 | 0.83 | 12 | 39840.2 | 1.71 |
| Benzofuran | BZF | 2015 | 1 | 39.6 | 0.05 | 1 | 448.7 | 0.37 | 2 | 1375.2 | 0.74 | 2 | 805.1 | 0.15 | 2 | 3831.6 | 0.28 |
| | | 2016 | 1 | 104.9 | 0.13 | 1 | 509.9 | 0.37 | 2 | 1708.8 | 0.59 | 2 | 630.6 | 0.13 | 2 | 9944.9 | 0.58 |
| | | 2017 | 1 | 47.2 | 0.08 | 1 | 185.9 | 0.21 | 2 | 1641.5 | 0.68 | 2 | 366.3 | 0.11 | 2 | 12790.7 | 0.61 |
| | | 2018 | 1 | 95.6 | 0.12 | 1 | 355.5 | 0.33 | 2 | 1060.1 | 0.40 | 2 | 701.4 | 0.15 | 2 | 14420.0 | 0.62 |
| Carboxylic Acid | CAC | 2015 | 3 | 8423.8 | 10.12 | 2 | 8574.9 | 7.11 | 4 | 11836.7 | 6.40 | 6 | 23499.8 | 4.52 | 8 | 80140.2 | 5.93 |
| | | 2016 | 3 | 8814.2 | 10.74 | 2 | 8940.8 | 6.49 | 4 | 17649.4 | 6.13 | 6 | 21919.9 | 4.61 | 8 | 105433.3 | 6.16 |
| | | 2017 | 3 | 2533.8 | 4.14 | 2 | 2978.6 | 3.43 | 4 | 21093.8 | 8.79 | 6 | 21853.1 | 6.41 | 8 | 211106.3 | 10.01 |
| | | 2018 | 3 | 4212.4 | 5.51 | 2 | 6721.7 | 6.31 | 4 | 15157.4 | 5.70 | 6 | 33415.9 | 7.11 | 8 | 222589.7 | 9.57 |
| Ester | EST | 2015 | 3 | 479.9 | 0.58 | 2 | 228.0 | 0.19 | 3 | 889.2 | 0.48 | 3 | 4351.5 | 0.84 | 6 | 22868.8 | 1.69 |
| | | 2016 | 3 | 227.3 | 0.28 | 2 | 572.2 | 0.42 | 3 | 2253.0 | 0.78 | 3 | 3753.9 | 0.79 | 6 | 57830.9 | 3.38 |
| | | 2017 | 3 | 383.3 | 0.63 | 2 | 219.3 | 0.25 | 3 | 1950.3 | 0.81 | 3 | 2678.4 | 0.79 | 6 | 53139.5 | 2.52 |
| | | 2018 | 3 | 403.5 | 0.53 | 2 | 383.3 | 0.36 | 3 | 2224.2 | 0.84 | 3 | 3917.1 | 0.83 | 3 | 37973.7 | 1.63 |
| Ether | ETH | 2015 | 3 | 159.3 | 0.19 | 1 | 257.9 | 0.21 | 1 | 318.9 | 0.17 | 1 | 421.9 | 0.08 | 1 | 2017.9 | 0.15 |
| | | 2016 | 3 | 97.8 | 0.12 | 1 | 205.0 | 0.15 | 1 | 397.0 | 0.14 | 1 | 423.8 | 0.09 | 1 | 1868.5 | 0.11 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 2017 | 3 | 159.0 | 0.26 | 1 | 2.6 | 0.00 | 1 | 397.6 | 0.17 | 1 | 414.3 | 0.12 | 1 | 5243.0 | 0.25 |
| | | 2018 | 3 | 206.2 | 0.27 | 1 | 140.4 | 0.13 | 1 | 353.8 | 0.13 | 1 | 498.9 | 0.11 | 1 | 5155.3 | 0.22 |
| Furan | FUR | 2015 | 34 | 44125.3 | 53.03 | 40 | 66127.2 | 54.81 | 43 | 94767.4 | 51.25 | 43 | 272695.3 | 52.47 | 44 | 525330.3 | 38.88 |
| | | 2016 | 34 | 41876.7 | 51.02 | 40 | 76755.3 | 55.74 | 43 | 143237.3 | 49.73 | 43 | 252156.8 | 53.03 | 44 | 631849.8 | 36.92 |
| | | 2017 | 34 | 30341.8 | 49.60 | 40 | 45759.0 | 52.71 | 43 | 127703.1 | 53.20 | 43 | 164804.7 | 48.31 | 44 | 615820.9 | 29.21 |
| | | 2018 | 34 | 37342.6 | 48.84 | 40 | 62123.1 | 58.30 | 43 | 133578.4 | 50.19 | 43 | 234161.1 | 49.83 | 44 | 759486.8 | 32.66 |
| Hydrocarbon | HYD | 2015 | 5 | 47.0 | 0.06 | 3 | 88.6 | 0.07 | 2 | 53.2 | 0.03 | 2 | 205.0 | 0.04 | 2 | 96.8 | 0.01 |
| | | 2016 | 5 | 51.9 | 0.06 | 3 | 32.4 | 0.02 | 2 | 71.8 | 0.02 | 2 | 138.5 | 0.03 | 2 | 195.0 | 0.01 |
| | | 2017 | 5 | 383.5 | 0.63 | 3 | 38.9 | 0.04 | 2 | 203.5 | 0.08 | 2 | 125.6 | 0.04 | 2 | 147.2 | 0.01 |
| | | 2018 | 5 | 756.6 | 0.99 | 3 | 23.6 | 0.02 | 2 | 61.3 | 0.02 | 2 | 69.8 | 0.01 | 2 | 228.0 | 0.01 |
| Indene | IND | 2015 | 0 | 0.0 | 0.00 | 0 | 0.0 | 0.00 | 1 | 64.0 | 0.03 | 1 | 60.6 | 0.01 | 2 | 319.2 | 0.02 |
| | | 2016 | 0 | 0.0 | 0.00 | 0 | 0.0 | 0.00 | 1 | 49.7 | 0.02 | 1 | 14.4 | 0.00 | 2 | 353.3 | 0.02 |
| | | 2017 | 0 | 0.0 | 0.00 | 0 | 0.0 | 0.00 | 1 | 41.4 | 0.02 | 1 | 8.6 | 0.00 | 2 | 599.9 | 0.03 |
| | | 2018 | 0 | 0.0 | 0.00 | 0 | 0.0 | 0.00 | 1 | 81.3 | 0.03 | 1 | 3.8 | 0.00 | 2 | 611.6 | 0.03 |
| Ketone | KET | 2015 | 18 | 22787.6 | 27.38 | 19 | 26897.3 | 22.29 | 15 | 44460.3 | 24.05 | 16 | 158718.8 | 30.54 | 16 | 399621.1 | 29.58 |
| | | 2016 | 18 | 20368.7 | 24.82 | 19 | 29623.9 | 21.51 | 15 | 73547.7 | 25.54 | 16 | 145021.2 | 30.50 | 16 | 432673.9 | 25.28 |
| | | 2017 | 18 | 17609.4 | 28.79 | 19 | 19577.0 | 22.55 | 15 | 47116.2 | 19.63 | 16 | 116120.0 | 34.04 | 16 | 587460.4 | 27.87 |
| | | 2018 | 18 | 17194.8 | 22.49 | 19 | 21044.2 | 19.75 | 15 | 66057.2 | 24.82 | 16 | 151697.5 | 32.28 | 16 | 642068.5 | 27.61 |
| Naphthalene | NPH | 2015 | 1 | 48.8 | 0.06 | 1 | 121.8 | 0.10 | 4 | 241.5 | 0.13 | 3 | 89.6 | 0.02 | 3 | 809.7 | 0.06 |
| | | 2016 | 1 | 35.8 | 0.04 | 1 | 14.6 | 0.01 | 4 | 201.7 | 0.07 | 3 | 30.3 | 0.01 | 3 | 1571.0 | 0.09 |
| | | 2017 | 1 | 21.3 | 0.03 | 1 | 24.2 | 0.03 | 4 | 228.2 | 0.10 | 3 | 29.7 | 0.01 | 3 | 2531.2 | 0.12 |
| | | 2018 | 1 | 21.5 | 0.03 | 1 | 11.6 | 0.01 | 4 | 314.7 | 0.12 | 3 | 27.0 | 0.01 | 3 | 1095.5 | 0.05 |
| Nitrogen | NIT | 2015 | 9 | 2734.5 | 3.29 | 13 | 2761.2 | 2.29 | 16 | 5656.7 | 3.06 | 16 | 21745.3 | 4.18 | 16 | 62281.5 | 4.61 |
| | | 2016 | 9 | 2334.8 | 2.84 | 13 | 3806.8 | 2.76 | 16 | 11686.5 | 4.06 | 16 | 20801.9 | 4.37 | 16 | 86139.9 | 5.03 |
| | | 2017 | 9 | 1417.1 | 2.32 | 13 | 2439.7 | 2.81 | 16 | 8238.4 | 3.43 | 16 | 13744.2 | 4.03 | 16 | 123169.9 | 5.84 |
| | | 2018 | 9 | 2501.5 | 3.27 | 13 | 2488.4 | 2.34 | 16 | 9511.9 | 3.57 | 16 | 16661.8 | 3.55 | 16 | 128123.7 | 5.51 |
| Phenol | PHE | 2015 | 5 | 213.6 | 0.26 | 7 | 509.1 | 0.42 | 8 | 2139.7 | 1.16 | 8 | 4219.2 | 0.81 | 8 | 15126.8 | 1.12 |
| | | 2016 | 5 | 275.6 | 0.34 | 7 | 732.4 | 0.53 | 8 | 3323.3 | 1.15 | 8 | 3862.3 | 0.81 | 8 | 29236.6 | 1.71 |
| | | 2017 | 5 | 332.8 | 0.54 | 7 | 296.8 | 0.34 | 8 | 2839.7 | 1.18 | 8 | 2274.8 | 0.67 | 8 | 34839.3 | 1.65 |
| | | 2018 | 5 | 257.3 | 0.34 | 7 | 449.5 | 0.42 | 8 | 2703.6 | 1.02 | 8 | 3549.3 | 0.76 | 8 | 49265.3 | 2.12 |
| Pyran | PYR | 2015 | 4 | 1074.6 | 1.29 | 4 | 1545.2 | 1.28 | 5 | 2494.1 | 1.35 | 5 | 14644.0 | 2.82 | 5 | 56802.8 | 4.20 |
| | | 2016 | 4 | 1146.0 | 1.40 | 4 | 2175.7 | 1.58 | 5 | 6384.1 | 2.22 | 5 | 14953.8 | 3.15 | 5 | 65920.6 | 3.85 |
| | | 2017 | 4 | 1124.3 | 1.84 | 4 | 1097.9 | 1.26 | 5 | 6017.3 | 2.51 | 5 | 10719.7 | 3.14 | 5 | 87171.8 | 4.14 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 2018 | 4 | 988.6 | 1.29 | 4 | 1188.6 | 1.12 | 5 | 6675.1 | 2.51 | 5 | 12020.1 | 2.56 | 5 | 95391.3 | 4.10 |
| Sulfur | SUL | 2015 | 2 | 258.4 | 0.31 | 2 | 9024.6 | 7.48 | 3 | 287.6 | 0.16 | 3 | 207.4 | 0.04 | 4 | 1585.0 | 0.12 |
| | | 2016 | 2 | 238.7 | 0.29 | 2 | 9842.1 | 7.15 | 3 | 141.1 | 0.05 | 3 | 80.3 | 0.02 | 4 | 2304.8 | 0.13 |
| | | 2017 | 2 | 875.2 | 1.43 | 2 | 9687.5 | 11.16 | 3 | 184.5 | 0.08 | 3 | 34.8 | 0.01 | 4 | 3538.1 | 0.17 |
| | | 2018 | 2 | 1905.9 | 2.49 | 2 | 8164.5 | 7.66 | 3 | 274.9 | 0.10 | 3 | 119.3 | 0.03 | 4 | 2155.4 | 0.09 |
| Terpene / Terpenoid | TER | 2015 | 2 | 21.9 | 0.03 | 4 | 166.6 | 0.14 | 3 | 119.4 | 0.06 | 3 | 807.9 | 0.16 | 3 | 3357.2 | 0.25 |
| | | 2016 | 2 | 15.6 | 0.02 | 4 | 133.6 | 0.10 | 3 | 71.2 | 0.02 | 3 | 29.4 | 0.01 | 3 | 1264.2 | 0.07 |
| | | 2017 | 2 | 244.9 | 0.40 | 4 | 170.7 | 0.20 | 3 | 81.3 | 0.03 | 3 | 16.3 | 0.00 | 3 | 340.9 | 0.02 |
| | | 2018 | 2 | 262.0 | 0.34 | 4 | 104.3 | 0.10 | 3 | 66.9 | 0.03 | 3 | 480.6 | 0.10 | 3 | 10825.9 | 0.47 |

[1]Number of volatile organic compounds identified.
[2]Relative Peak Areas values.
[3]Total Relative Peak Areas percentage values.

**Table S28. One-way ANOVA test results based on the relative peak areas of the identified VOCs in samples from SCH processing stages during 2015-2018 production years.**

| Volatile Organic Compounds | One-way ANOVA Test | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Between All Stages | | Between S1-S2 | | Between S2-S3 | | Between S3-S4 | | Between S4-S5 | |
| | F[1] | P[2] | F[1] | P[2] | F[1] | P[2] | F[1] | P[2] | F[1] | P[2] |
| Pentane | 28.63 | 7.05E-13 | 8.63 | 7.61E-03 | 31.69 | 1.20E-05 | | | 89.47 | 3.29E-09 |
| Hexane | 18.27 | 1.34E-09 | 0.79 | 3.84E-01 | 11.14 | 2.98E-03 | 2.37 | 1.38E-01 | 0.13 | 7.18E-01 |
| Ethyl Ether | 29.17 | 5.01E-13 | 29.17 | 2.00E-05 | | | | | | |
| 1,4-Pentadiene | 15.88 | 1.07E-08 | 13.27 | 1.44E-03 | 10.31 | 4.02E-03 | 1.77 | 1.97E-01 | 89.95 | 3.13E-09 |
| Methanethiol | 64.30 | ≤ 1.00E-17 | | | 65.63 | 4.79E-08 | 10.41 | 3.89E-03 | 53.03 | 2.71E-07 |
| Ethanal | 81.12 | ≤ 1.00E-17 | 6.79 | 1.61E-02 | 118.85 | 2.45E-10 | 35.75 | 5.00E-06 | 73.61 | 1.81E-08 |
| Dimethyl Sulfide | 562.68 | ≤ 1.00E-17 | 646.03 | ≤ 1.00E-17 | 1272.68 | ≤ 1.00E-17 | 27.84 | 2.70E-05 | 96.12 | 1.73E-09 |
| Propanal | 28.79 | 6.35E-13 | 1.89 | 1.83E-01 | 173.66 | 6.45E-12 | 0.01 | 9.58E-01 | 26.02 | 4.10E-05 |
| Furan | 24.64 | 1.02E-11 | 332.67 | 9.10E-15 | 90.14 | 3.08E-09 | 85.02 | 5.17E-09 | 25.70 | 4.40E-05 |
| 2-Methyl-Propanal | 56.97 | ≤ 1.00E-17 | 3.10 | 9.22E-02 | 232.16 | 3.58E-13 | 39.60 | 2.00E-06 | 55.00 | 2.03E-07 |
| Ethyl Formate | 10.36 | 2.52E-06 | | | | | | | 10.36 | 3.96E-03 |
| 2-Propenal | 139.12 | ≤ 1.00E-17 | 0.33 | 5.69E-01 | 20.49 | 1.67E-04 | 1.36 | 2.57E-01 | 142.26 | 4.47E-11 |
| 2-Methyl-Furan | 15.30 | 1.81E-08 | 10.98 | 3.16E-03 | 422.24 | 7.77E-15 | 24.37 | 6.10E-05 | 11.17 | 2.96E-03 |
| Ethyl Acetate | 11.96 | 4.64E-07 | 0.64 | 4.33E-01 | 24.07 | 6.60E-05 | 226.07 | 4.68E-13 | 12.09 | 2.14E-03 |
| 2-Butanone | 32.27 | 7.57E-14 | 381.17 | 2.22E-15 | 118.07 | 2.61E-10 | 18.13 | 3.21E-04 | 31.26 | 1.30E-05 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 2-Methyl-Butanal | 64.35 | ≤ 1.00E-17 | 1.89 | 1.83E-01 | 316.63 | 1.51E-14 | 134.79 | 7.48E-11 | 63.28 | 6.48E-08 |
| 3-Methyl-Butanal | 28.84 | 6.16E-13 | 9.85 | 4.78E-03 | 880.87 | ≤ 1.00E-17 | 392.05 | 1.67E-15 | 26.53 | 3.70E-05 |
| Ethanol | 409.24 | ≤ 1.00E-17 | 2.48 | 1.30E-01 | 10.33 | 4.00E-03 | 9.84 | 4.79E-03 | 410.94 | 9.99E-16 |
| Benzene | 31.75 | 1.03E-13 | 9.80 | 4.87E-03 | 7.23 | 1.34E-02 | 2.86 | 1.05E-01 | 29.71 | 1.80E-05 |
| 3-Buten-2-one | 17.07 | 3.73E-09 | 57.14 | 1.49E-07 | 28.34 | 2.40E-05 | 1.39 | 2.51E-01 | 16.56 | 5.09E-04 |
| 2-Ethyl-Furan | 20.84 | 1.69E-10 | 20.84 | 1.52E-04 | 20.84 | 1.52E-04 | | | | |
| 2,5-Dimethyl-Furan | 41.15 | 6.66E-16 | | | 779.32 | ≤ 1.00E-17 | 348.29 | 5.66E-15 | 41.92 | 2.00E-06 |
| Ethyl Propanoate | 6.41 | 2.61E-04 | | | | | | | 6.41 | 1.90E-02 |
| 3-Pentanone | 27.90 | 1.13E-12 | 27.90 | 2.70E-05 | | | | | | |
| Pentanal | 213.44 | ≤ 1.00E-17 | 213.44 | 8.34E-13 | 213.44 | 8.34E-13 | | | | |
| 2,3-Butanedione | 11.14 | 1.09E-06 | 8.41 | 8.30E-03 | 27.65 | 2.80E-05 | 3.39 | 7.91E-02 | 9.64 | 5.17E-03 |
| 1-Penten-3-one | 8.10 | 3.31E-05 | 5.25 | 3.20E-02 | 38.06 | 3.00E-06 | | | | |
| 1-Propanol | 22.64 | 4.29E-11 | | | | | | | 22.64 | 9.50E-05 |
| 2-Ethyl-5-Methyl-Furan | 113.06 | ≤ 1.00E-17 | | | 39.05 | 3.00E-06 | 4.06 | 5.63E-02 | 111.86 | 4.31E-10 |
| Toluene | 9.54 | 6.25E-06 | 8.12 | 9.32E-03 | 11.77 | 2.39E-03 | 22.15 | 1.08E-04 | 9.59 | 5.26E-03 |
| 2-Methyl-3-Buten-2-ol | 17.40 | 2.79E-09 | 9.83 | 4.81E-03 | 18.26 | 3.09E-04 | 134.38 | 7.70E-11 | | |
| Nonomethyl Succinate | 8.41 | 2.28E-05 | | | | | | | 8.41 | 8.30E-03 |
| 2,3-Pentanedione | 6.83 | 1.55E-04 | 1.82 | 1.91E-01 | 35.21 | 6.00E-06 | 0.34 | 5.67E-01 | 5.44 | 2.92E-02 |
| Dimethyl Disulfide | 14.60 | 3.45E-08 | | | | | | | 14.60 | 9.32E-04 |
| 2-Ethenyl-Furan | 29.99 | 2.99E-13 | | | 281.94 | 4.97E-14 | 55.61 | 1.86E-07 | 14.48 | 9.68E-04 |
| Hexanal | 15.21 | 1.97E-08 | 1.18 | 2.89E-01 | 30.59 | 1.50E-05 | 3.62 | 7.03E-02 | 31.66 | 1.20E-05 |
| 2-Methyl-1-Propanol | 4.77 | 2.24E-03 | | | | | | | 4.77 | 3.99E-02 |
| Methyl 2-Ethylpentanoate | 8.40 | 2.32E-05 | 8.40 | 8.35E-03 | | | | | | |
| 5-Butyl-Dihydro-2(3H)-Furanone (γ-Octalactone) | 35.71 | 1.08E-14 | 18.60 | 2.81E-04 | 11.83 | 2.34E-03 | 597.94 | ≤ 1.00E-17 | 60.81 | 9.00E-08 |
| m-Cresol | 14.13 | 5.37E-08 | 38.10 | 3.00E-06 | 111.63 | 4.40E-10 | 9.50 | 5.44E-03 | 13.73 | 1.24E-03 |
| 1-Butanol | 10.91 | 1.40E-06 | | | | | | | 10.91 | 3.24E-03 |
| 5-Propyl-Dihydro-2(3H)-Furanone (γ-Heptalactone) | 34.13 | 2.59E-14 | 20.88 | 1.50E-04 | 14.30 | 1.03E-03 | 172.34 | 6.95E-12 | 51.94 | 3.19E-07 |
| 3-Methyl-Pyridazine | 35.55 | 1.17E-14 | 26.40 | 3.80E-05 | 38.37 | 3.00E-06 | 0.87 | 3.60E-01 | 32.38 | 1.00E-05 |
| 1-Penten-3-ol | 68.30 | ≤ 1.00E-17 | 54.56 | 2.16E-07 | 18.38 | 3.00E-04 | | | | |
| 2-Heptanone | 4.68 | 2.53E-03 | 3.48 | 7.54E-02 | 45.02 | 1.00E-06 | | | | |
| Heptanal | 17.44 | 2.71E-09 | 18.80 | 2.66E-04 | 12.82 | 1.67E-03 | 28.89 | 2.10E-05 | | |
| m-Menthane | 9.61 | 5.78E-06 | 17.17 | 4.25E-04 | 5.40 | 2.98E-02 | 0.59 | 4.50E-01 | 9.18 | 6.16E-03 |
| 1,3-Diazine | 12.38 | 3.00E-07 | 21.96 | 1.13E-04 | 2.46 | 1.31E-01 | 1.34 | 2.60E-01 | 11.30 | 2.82E-03 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 2-Methyl-1-Butanol | 15.83 | 1.11E-08 | | | | | | | 15.83 | 6.35E-04 |
| 2-Propyl-Furan | 10.18 | 3.06E-06 | 1.04 | 3.18E-01 | 4.44 | 4.67E-02 | 10.02 | 4.48E-03 | 9.71 | 5.04E-03 |
| 3-Methyl-1-Butanol | 39.62 | 1.33E-15 | 39.62 | 2.00E-06 | | | | | | |
| 2-Pentyl-Furan | 10.04 | 3.58E-06 | 0.03 | 8.71E-01 | 18.67 | 2.76E-04 | 32.37 | 1.00E-05 | 5.31 | 3.10E-02 |
| 3-Octanone | 51.93 | ≤ 1.00E-17 | 36.79 | 4.00E-06 | 18.10 | 3.24E-04 | | | | |
| 1-Pentanol | 37.90 | 3.33E-15 | 3.89 | 6.12E-02 | 147.57 | 3.14E-11 | | | | |
| 2-Methyl-Pyrazine | 19.72 | 4.07E-10 | 1.02 | 3.24E-01 | 72.81 | 1.99E-08 | 41.02 | 2.00E-06 | 29.43 | 1.90E-05 |
| 2-Methyl-Dihydro-2(3H)-Furanone | 183.31 | ≤ 1.00E-17 | 4.84 | 3.86E-02 | 257.11 | 1.27E-13 | 53.27 | 2.62E-07 | 182.25 | 4.01E-12 |
| p-Cymene | 5.69 | 6.60E-04 | 4.21 | 5.23E-02 | 23.66 | 7.30E-05 | 15.83 | 6.35E-04 | 28.27 | 2.50E-05 |
| Mesitylene | 2.90 | 2.99E-02 | 3.64 | 6.97E-02 | 3.43 | 7.74E-02 | 46.14 | 1.00E-06 | 3.60 | 7.11E-02 |
| 3,5-Xylenol | 46.69 | ≤ 1.00E-17 | | | 235.28 | 3.13E-13 | 73.12 | 1.92E-08 | 46.45 | 1.00E-06 |
| 3-Hydroxy-2-Butanone | 46.99 | ≤ 1.00E-17 | 1.84 | 1.89E-01 | 10.20 | 4.19E-03 | 6.66 | 1.71E-02 | 43.70 | 1.00E-06 |
| Vinylene Carbonate | 114.33 | ≤ 1.00E-17 | | | 77.74 | 1.13E-08 | 20.75 | 1.55E-04 | 98.93 | 1.33E-09 |
| 2,6-Xylenol | 46.49 | ≤ 1.00E-17 | | | 438.49 | 5.55E-16 | 246.89 | 1.92E-13 | 45.66 | 1.00E-06 |
| Octanal | 343.03 | ≤ 1.00E-17 | 150.65 | 2.57E-11 | 66.60 | 4.24E-08 | 1030.05 | ≤ 1.00E-17 | | |
| 1-Hydroxy-2-Propanone | 33.95 | 2.86E-14 | 0.02 | 8.95E-01 | 27.08 | 3.20E-05 | 28.19 | 2.50E-05 | 23.70 | 7.20E-05 |
| cis-2-Heptanal | 3.96 | 6.79E-03 | 3.76 | 6.54E-02 | 76.47 | 1.31E-08 | 32.25 | 1.00E-05 | 14.14 | 1.08E-03 |
| 2,5-Dimethyl-Pyrazine | 13.28 | 1.22E-07 | | | 37.22 | 4.00E-06 | | | | |
| cis-2-Pentenol | 43.96 | 1.11E-16 | 43.96 | 1.00E-06 | | | | | | |
| 2,6-Dimethyl-Pyrazine | 523.62 | ≤ 1.00E-17 | | | 107.37 | 6.30E-10 | 54.81 | 2.08E-07 | 876.01 | ≤ 1.00E-17 |
| 2-Heptanol | 7.03 | 1.20E-04 | 6.53 | 1.81E-02 | 40.09 | 2.00E-06 | | | | |
| 2-Pentene | 8.37 | 2.39E-05 | 8.37 | 8.43E-03 | | | | | | |
| 2-Cyclopenten-1-one | 59.32 | ≤ 1.00E-17 | 0.46 | 5.04E-01 | 27.85 | 2.70E-05 | 15.24 | 7.63E-04 | 54.31 | 2.24E-07 |
| 1-Hexanol | 40.45 | 8.88E-16 | 31.39 | 1.20E-05 | 159.60 | 1.47E-11 | | | | |
| 2-Methyl-2-Cyclopenten-1-one | 57.16 | ≤ 1.00E-17 | 2.32 | 1.42E-01 | 991.44 | ≤ 1.00E-17 | 0.62 | 4.40E-01 | 50.72 | 3.85E-07 |
| 5-Methyl-2-Furanmethanethiol | 10.49 | 2.19E-06 | | | | | | | 10.49 | 3.77E-03 |
| 1-Hydroxy-2-Butanone | 22.75 | 3.98E-11 | 0.40 | 5.34E-01 | 81.13 | 7.81E-09 | 50.49 | 3.99E-07 | 18.94 | 2.55E-04 |
| 2-Ethyl-6-Methyl-Pyrazine | 369.28 | ≤ 1.00E-17 | | | 173.87 | 6.37E-12 | 98.95 | 1.33E-09 | 448.59 | 4.44E-16 |
| Nonanal | 25.03 | 7.78E-12 | 52.88 | 2.77E-07 | 1.21 | 2.83E-01 | 10.30 | 4.05E-03 | 22.45 | 9.90E-05 |
| 1-Ethyl-1-Methyl-Cyclopentane | 11.66 | 6.33E-07 | 11.66 | 2.49E-03 | | | | | | |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | 8.74 | 1.56E-05 | 0.76 | 3.91E-01 | 46.94 | 1.00E-06 | | | | |
| 2-Octanol | 6.27 | 3.13E-04 | 6.27 | 2.02E-02 | | | | | | |
| 2-Cyclohexen-1-one | 11.93 | 4.79E-07 | 7.21 | 1.35E-02 | 76.93 | 1.24E-08 | 1.37 | 2.55E-01 | 10.26 | 4.10E-03 |

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|---|---|---|---|---|---|---|---|---|---|---|
| trans-2-Octenal | 6.07 | 4.06E-04 | 6.07 | 2.21E-02 | | | | | | |
| 5-Methyl-2(3H)-Furanone (β-Angelica Lactone) | 251.27 | ≤ 1.00E-17 | 52.43 | 2.97E-07 | 72.83 | 1.99E-08 | 139.53 | 5.38E-11 | 201.07 | 1.51E-12 |
| 1,3-Dihydro-4-Methyl-2H-Imidazol-2-one | 54.41 | ≤ 1.00E-17 | 5.90 | 2.38E-02 | 52.06 | 3.13E-07 | 62.04 | 7.63E-08 | 45.13 | 1.00E-06 |
| 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | 57.32 | ≤ 1.00E-17 | | | 244.94 | 2.08E-13 | 174.39 | 6.19E-12 | 59.72 | 1.04E-07 |
| 1-Octen-3-ol | 88.44 | ≤ 1.00E-17 | 88.44 | 3.65E-09 | | | | | | |
| 1-Heptanol | 46.76 | ≤ 1.00E-17 | 22.63 | 9.50E-05 | 100.11 | 1.20E-09 | | | | |
| Furfural | 137.75 | ≤ 1.00E-17 | 1.61 | 2.18E-01 | 188.43 | 2.89E-12 | 22.17 | 1.07E-04 | 60.71 | 9.12E-08 |
| Ethanoic Acid | 42.63 | 3.33E-16 | 0.63 | 4.35E-01 | 44.47 | 1.00E-06 | 15.42 | 7.20E-04 | 35.59 | 5.00E-06 |
| 2-Nonen-4-one | 121.21 | ≤ 1.00E-17 | 121.21 | 2.04E-10 | 121.21 | 2.04E-10 | | | | |
| 1,2,3,4-Tetrahydro-1,6,8-Trimethyl-Naphthalene | 56.27 | ≤ 1.00E-17 | | | 190.60 | 2.58E-12 | 48.63 | 1.00E-06 | 55.93 | 1.77E-07 |
| 2-Ethyl-1-Hexanol | 23.17 | 2.93E-11 | 2.83 | 1.07E-01 | 39.35 | 3.00E-06 | 2.10 | 1.61E-01 | 22.29 | 1.04E-04 |
| trans,trans-2,4-Heptadienal | 79.12 | ≤ 1.00E-17 | 79.12 | 9.72E-09 | 79.12 | 9.72E-09 | | | | |
| 3-Methyl-Furfural | 49.17 | ≤ 1.00E-17 | 3.05 | 9.49E-02 | 72.54 | 1.01E-08 | 1.81 | 1.92E-01 | 53.81 | 2.42E-07 |
| Furfuryl Formate | 101.39 | ≤ 1.00E-17 | 51.18 | 3.58E-07 | 16.44 | 5.28E-04 | 75.37 | 1.48E-08 | 89.60 | 3.25E-09 |
| 1-(2-Furanyl)-Ethanone | 225.90 | ≤ 1.00E-17 | 6.31 | 1.98E-02 | 78.75 | 2.05E-08 | 0.37 | 5.51E-01 | 175.40 | 5.85E-12 |
| Decanal | 25.28 | 6.53E-12 | 1.79 | 1.94E-01 | 1.98 | 1.73E-01 | 0.61 | 4.44E-01 | 24.73 | 5.60E-05 |
| Benzaldehyde | 43.70 | 2.22E-16 | 2.03 | 1.68E-01 | 3.90 | 6.10E-02 | 21.10 | 1.42E-04 | 46.89 | 1.00E-06 |
| Furfuryl Acetate | 71.03 | ≤ 1.00E-17 | 1.91 | 1.81E-01 | 30.69 | 1.40E-05 | 89.51 | 3.28E-09 | 62.49 | 7.20E-08 |
| Propanoic Acid | 9.58 | 5.96E-06 | | | 12.27 | 2.01E-03 | 47.46 | 1.00E-06 | 6.40 | 1.91E-02 |
| 1-Octanol | 102.61 | ≤ 1.00E-17 | 24.04 | 6.70E-05 | 189.28 | 2.76E-12 | | | | |
| Dimethyl Sulfoxide | 58.00 | ≤ 1.00E-17 | 24.95 | 5.30E-05 | 17.19 | 4.22E-04 | 0.14 | 7.16E-01 | 166.78 | 9.58E-12 |
| 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | 29.22 | 4.84E-13 | | | 477.41 | 2.22E-16 | 200.63 | 1.55E-12 | 29.60 | 1.80E-05 |
| 5-Methyl-Furfural | 248.78 | ≤ 1.00E-17 | 3.60 | 7.11E-02 | 7.96 | 9.94E-03 | 7.65 | 1.13E-02 | 218.08 | 6.72E-13 |
| 4-Cyclopentene-1,3-dione | 200.16 | ≤ 1.00E-17 | 2.41 | 1.35E-01 | 58.52 | 1.23E-07 | 39.90 | 2.00E-06 | 107.70 | 6.12E-10 |
| 2-Methyl-Benzofuran | 64.00 | ≤ 1.00E-17 | | | 184.44 | 3.56E-12 | 132.45 | 8.84E-11 | 65.87 | 4.64E-08 |
| 1-(5-Methyl-2-Furanyl)-Ethanone | 104.87 | ≤ 1.00E-17 | 0.72 | 4.04E-01 | 38.41 | 3.00E-06 | 15.82 | 6.38E-04 | 98.45 | 1.39E-09 |
| trans-2-Octenol | 8.00 | 3.69E-05 | 8.00 | 9.77E-03 | | | | | | |
| Diethylene Glycol Ethyl Ether | 43.10 | 2.22E-16 | 0.73 | 4.03E-01 | 47.33 | 1.00E-06 | 22.63 | 9.50E-05 | 38.64 | 3.00E-06 |
| 3-Methyl-Dihydro-2(3H)-Furanone | 121.00 | ≤ 1.00E-17 | 0.83 | 3.73E-01 | 51.91 | 3.21E-07 | 8.34 | 8.55E-03 | 104.30 | 8.22E-10 |
| 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | 58.83 | ≤ 1.00E-17 | | | | | | | 58.83 | 1.18E-07 |
| Benzeneacetaldehyde | 67.37 | ≤ 1.00E-17 | 1.76 | 1.98E-01 | 69.05 | 3.13E-08 | 0.01 | 9.20E-01 | 61.82 | 7.86E-08 |
| 3,5-Dimethyl-Dihydro-2-Furanone | 17.25 | 3.18E-09 | 0.90 | 3.54E-01 | 30.57 | 1.50E-05 | 4.22 | 5.20E-02 | 16.07 | 5.90E-04 |
| 3-Methyl-Benzaldehyde | 19.48 | 4.94E-10 | 0.44 | 5.15E-01 | 18.59 | 2.82E-04 | 0.76 | 3.94E-01 | 37.36 | 4.00E-06 |

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|---|---|---|---|---|---|---|---|---|---|---|
| 2-Propenoic Acid | 42.78 | 3.33E-16 | | | 105.40 | 7.46E-10 | 1.08 | 3.11E-01 | 36.33 | 5.00E-06 |
| Acetophenone | 24.19 | 1.40E-11 | 3.95 | 5.94E-02 | 5.91 | 2.36E-02 | 25.27 | 4.90E-05 | 25.57 | 4.60E-05 |
| 2-Furanmethanol | 29.10 | 5.23E-13 | 0.65 | 4.27E-01 | 18.83 | 2.63E-04 | 17.89 | 3.44E-04 | 11.05 | 3.08E-03 |
| 3-Furanmethanol | 20.94 | 1.56E-10 | 0.00 | 9.99E-01 | 40.69 | 2.00E-06 | 83.09 | 6.34E-09 | 5.87 | 2.41E-02 |
| 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | 110.35 | ≤ 1.00E-17 | | | 148.56 | 2.95E-11 | 19.54 | 2.16E-04 | 109.13 | 5.42E-10 |
| 2-(2-Furanylmethyl)-5-Methyl-Furan | 66.32 | ≤ 1.00E-17 | | | 335.60 | 8.33E-15 | 1.36 | 2.56E-01 | 61.62 | 8.08E-08 |
| 3-Methyl-2(5H)-Furanone | 177.33 | ≤ 1.00E-17 | 2.62 | 1.20E-01 | 148.98 | 2.87E-11 | 38.78 | 3.00E-06 | 155.77 | 1.86E-11 |
| 5-Methyl-2-Furanmethanol | 63.28 | ≤ 1.00E-17 | 0.07 | 7.91E-01 | 208.41 | 1.06E-12 | 20.93 | 1.48E-04 | 52.16 | 3.09E-07 |
| Phenylmethyl Acetate | 28.50 | 7.67E-13 | | | | | | | 28.50 | 2.30E-05 |
| Naphthalene | 9.93 | 4.04E-06 | 0.68 | 4.17E-01 | 0.97 | 3.36E-01 | 1643.14 | ≤ 1.00E-17 | | |
| 2(5H)-Furanone | 41.61 | 5.55E-16 | 0.14 | 7.12E-01 | 45.55 | 1.00E-06 | 49.79 | 4.44E-07 | 30.15 | 1.60E-05 |
| 2,2'-Methylenebis[5-Methyl-Furan | 48.21 | ≤ 1.00E-17 | 51.36 | 3.49E-07 | 238.48 | 2.73E-13 | 105.67 | 7.29E-10 | 47.93 | 1.00E-06 |
| 1,2-Cyclopentanedione | 220.79 | ≤ 1.00E-17 | 11.99 | 2.21E-03 | 97.39 | 1.53E-09 | 76.45 | 1.31E-08 | 153.53 | 2.14E-11 |
| Diethylene Glycol Monobutyl Ether | 10.12 | 3.27E-06 | 10.12 | 4.32E-03 | | | | | | |
| 2-Cyclohexenol | 95.32 | ≤ 1.00E-17 | 0.35 | 5.62E-01 | 39.26 | 3.00E-06 | 69.97 | 2.80E-08 | 79.38 | 9.44E-09 |
| 2-Phenylethyl Acetate | 22.23 | 5.85E-11 | | | | | | | 22.23 | 1.05E-04 |
| 3-Methyl-1,2-Cyclopentanedione | 91.69 | ≤ 1.00E-17 | 0.04 | 8.37E-01 | 74.19 | 1.70E-08 | 74.83 | 1.58E-08 | 78.45 | 1.05E-08 |
| β-Damascenone | 9.10 | 1.02E-05 | 106.93 | 6.54E-10 | 0.01 | 1.00E+00 | 6.58 | 1.77E-02 | 8.08 | 9.47E-03 |
| 2-Methyl-Propanoic Acid | 54.48 | ≤ 1.00E-17 | 0.19 | 6.71E-01 | 62.96 | 6.76E-08 | 37.41 | 4.00E-06 | 46.24 | 1.00E-06 |
| 4-(1-Methylpropyl)-Phenol | 187.99 | ≤ 1.00E-17 | 187.99 | 2.95E-12 | 187.99 | 2.95E-12 | | | | |
| 2,4,6-Trihydroxypyrimidine | 230.84 | ≤ 1.00E-17 | 2.64 | 1.18E-01 | 20.07 | 1.87E-04 | 63.07 | 6.66E-08 | 133.88 | 7.98E-11 |
| Mequinol | 74.89 | ≤ 1.00E-17 | 0.00 | 9.95E-01 | 354.91 | 4.66E-15 | 0.21 | 6.52E-01 | 67.61 | 3.73E-08 |
| 2,2-Diethyl-3-Methyl-Oxazolidine | 55.70 | ≤ 1.00E-17 | 6.24 | 2.05E-02 | 8.17 | 9.15E-03 | 56.26 | 1.69E-07 | 48.01 | 1.00E-06 |
| Oxypurinol | 204.15 | ≤ 1.00E-17 | 0.77 | 3.91E-01 | 12.45 | 1.89E-03 | 40.56 | 2.00E-06 | 174.38 | 6.19E-12 |
| Benzenemethanol | 85.65 | ≤ 1.00E-17 | | | | | 439.33 | 4.44E-16 | 77.64 | 1.15E-08 |
| 4-Methyl-2(5H)-Furanone | 51.48 | ≤ 1.00E-17 | 1.30 | 2.66E-01 | 74.66 | 1.61E-08 | 72.19 | 2.14E-08 | 46.59 | 1.00E-06 |
| 3-Ethyl-2-Hydroxy-2-Cyclopenten-1-one | 90.88 | ≤ 1.00E-17 | 0.05 | 8.19E-01 | 107.77 | 6.08E-10 | 41.59 | 2.00E-06 | 79.96 | 8.86E-09 |
| Benzeneethanol | 32.92 | 5.18E-14 | 0.30 | 5.91E-01 | 11.75 | 2.40E-03 | 7.53 | 1.19E-02 | 57.69 | 1.38E-07 |
| 1,4-Butanediol | 31.25 | 1.39E-13 | 0.60 | 4.47E-01 | 34.16 | 7.00E-06 | | | | |
| Acrylamide | 126.86 | ≤ 1.00E-17 | 897.91 | ≤ 1.00E-17 | 25.57 | 4.60E-05 | 74.23 | 1.69E-08 | 107.06 | 6.47E-10 |
| Erythritol | 53.80 | ≤ 1.00E-17 | | | | | | | 53.80 | 2.42E-07 |
| 2,3-Dimethyl-3-Pyrazolin-5-one | 100.65 | ≤ 1.00E-17 | 8.21 | 8.99E-03 | 84.75 | 5.32E-09 | 89.33 | 3.34E-09 | 86.83 | 4.29E-09 |
| Furfural Acetone | 72.60 | ≤ 1.00E-17 | 0.35 | 5.58E-01 | 4.34 | 4.92E-02 | 45.11 | 1.00E-06 | 64.89 | 5.27E-08 |

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|---|---|---|---|---|---|---|---|---|---|---|
| Cyclotene | 103.42 | ≤ 1.00E-17 | | | | | 282.50 | 4.87E-14 | 86.81 | 4.30E-09 |
| 2-Methyl-1,4-Benzenediol | 26.69 | 2.51E-12 | 17.75 | 3.59E-04 | 83.40 | 6.13E-09 | 46.21 | 1.00E-06 | 23.06 | 8.50E-05 |
| Maltol | 261.99 | ≤ 1.00E-17 | 10.80 | 3.37E-03 | 15.02 | 8.17E-04 | 118.88 | 2.45E-10 | 221.02 | 5.88E-13 |
| 2-Acetylpyrrole | 129.05 | ≤ 1.00E-17 | 4.60 | 4.33E-02 | 359.27 | 4.11E-15 | 3.42 | 7.80E-02 | 112.45 | 4.11E-10 |
| 2,5-Furandicarboxaldehyde | 119.52 | ≤ 1.00E-17 | 5.02 | 3.54E-02 | 3.50 | 7.49E-02 | 10.52 | 3.73E-03 | 112.00 | 4.26E-10 |
| 2H-Pyran-2,6(3H)-Dione | 121.86 | ≤ 1.00E-17 | 8.98 | 6.64E-03 | 42.79 | 1.00E-06 | 59.99 | 1.01E-07 | 101.42 | 1.06E-09 |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | 35.91 | 9.66E-15 | 22.75 | 9.20E-05 | 12.20 | 2.06E-03 | 44.12 | 1.00E-06 | 23.43 | 7.80E-05 |
| Phenol | 75.14 | ≤ 1.00E-17 | 0.17 | 6.80E-01 | 81.84 | 7.23E-09 | 14.69 | 9.05E-04 | 69.30 | 3.03E-08 |
| 1H-Pyrrole-2-Carboxaldehyde | 18.93 | 7.78E-10 | 73.40 | 1.86E-08 | 146.52 | 3.36E-11 | 9.34 | 5.79E-03 | 17.90 | 3.43E-04 |
| Phloroglucinol | 79.23 | ≤ 1.00E-17 | 25.71 | 4.40E-05 | 35.35 | 6.00E-06 | 54.36 | 2.23E-07 | 66.34 | 4.38E-08 |
| Furaneol | 315.94 | ≤ 1.00E-17 | 1.62 | 2.17E-01 | 40.31 | 2.00E-06 | 43.95 | 1.00E-06 | 162.67 | 1.22E-11 |
| Octanoic Acid | 183.47 | ≤ 1.00E-17 | | | | | | | 183.47 | 3.75E-12 |
| 5-Acetyl-Dihydro-2(3H)-Furanone (Solerone) | 224.75 | ≤ 1.00E-17 | 0.36 | 5.55E-01 | 40.38 | 2.00E-06 | 40.49 | 2.00E-06 | 133.20 | 8.37E-11 |
| 2-Furanpropionic Acid | 119.32 | ≤ 1.00E-17 | 15.61 | 6.80E-04 | 32.28 | 1.00E-05 | 42.76 | 1.00E-06 | 101.00 | 1.10E-09 |
| 1,3-Dihydroxy-2-Propanone | 549.57 | ≤ 1.00E-17 | 14.97 | 8.30E-04 | 46.34 | 1.00E-06 | 177.03 | 5.34E-12 | 345.01 | 6.22E-15 |
| Tetrahydro-5-Methyl-2-Furanmethanol | 15.09 | 2.20E-08 | 13.36 | 1.39E-03 | 52.65 | 2.87E-07 | 2.48 | 1.30E-01 | 9.81 | 4.85E-03 |
| 4,5-Dimethyl Vinylene Carbonate | 84.46 | ≤ 1.00E-17 | 6.79 | 1.61E-02 | 50.37 | 4.06E-07 | 57.03 | 1.52E-07 | 67.68 | 3.70E-08 |
| 2-Hydroxy-Dihydro-2(3H)-Furanone | 8.46 | 2.16E-05 | 1.02 | 3.23E-01 | 56.99 | 1.52E-07 | 20.51 | 1.66E-04 | 0.03 | 8.67E-01 |
| 2-Ethyl-Phenol | 15.44 | 1.59E-08 | 4.22 | 5.21E-02 | 247.38 | 1.89E-13 | | | | |
| 5-Acetoxymethyl-2-Furfural A | 83.56 | ≤ 1.00E-17 | 0.85 | 3.67E-01 | 2.81 | 1.08E-01 | 41.57 | 2.00E-06 | 37.41 | 4.00E-06 |
| 5-Acetoxymethyl-2-Furfural B | 395.90 | ≤ 1.00E-17 | 1.01 | 3.27E-01 | 37.14 | 4.00E-06 | 110.68 | 4.76E-10 | 259.23 | 1.17E-13 |
| 2-Methoxy-4-Vinyl-Phenol | 34.83 | 1.74E-14 | 60.97 | 8.80E-08 | 90.40 | 3.00E-09 | 22.50 | 9.80E-05 | 32.08 | 1.10E-05 |
| 3-Methyl-2,4(3H,5H)-Furandione | 128.42 | ≤ 1.00E-17 | 3.78 | 6.48E-02 | 68.40 | 3.38E-08 | 9.68 | 5.10E-03 | 111.22 | 4.55E-10 |
| 3-Hydroxy-2,3-Dihydro-Maltol | 318.36 | ≤ 1.00E-17 | 3.02 | 9.63E-02 | 37.67 | 4.00E-06 | 114.40 | 3.50E-10 | 194.76 | 2.08E-12 |
| Decanoic Acid | 18.38 | 1.22E-09 | 11.56 | 2.57E-03 | | | 69.49 | 2.96E-08 | 14.30 | 1.03E-03 |
| 5-Hydroxy-Maltol | 136.53 | ≤ 1.00E-17 | | | 77.69 | 1.14E-08 | 54.19 | 2.28E-07 | 105.43 | 7.45E-10 |
| 2,3-Dihydro-Benzofuran | 27.95 | 1.09E-12 | 61.32 | 8.40E-08 | 11.85 | 2.32E-03 | 0.95 | 3.41E-01 | 24.80 | 5.50E-05 |
| 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | 146.81 | ≤ 1.00E-17 | 2.94 | 1.00E-01 | 25.35 | 4.80E-05 | 4.70 | 4.12E-02 | 135.71 | 7.01E-11 |
| 4-Pyridinol | 135.63 | ≤ 1.00E-17 | 34.28 | 7.00E-06 | 97.65 | 1.50E-09 | 56.41 | 1.66E-07 | 117.53 | 2.72E-10 |
| 4-Amino-Phenol | 61.31 | ≤ 1.00E-17 | | | 20.49 | 1.67E-04 | 45.27 | 1.00E-06 | 51.55 | 3.39E-07 |
| Benzoic Acid | 103.43 | ≤ 1.00E-17 | | | 71.00 | 2.47E-08 | 47.78 | 1.00E-06 | 63.40 | 6.39E-08 |
| Dimethylhydrazone 3-Pentanone | 34.81 | 1.77E-14 | 1.88 | 1.84E-01 | 4.31 | 4.99E-02 | 173.05 | 6.68E-12 | 24.20 | 6.40E-05 |
| Undecanoic Acid | 14.02 | 6.02E-08 | | | | | | | 14.02 | 1.13E-03 |

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|---|---|---|---|---|---|---|---|---|---|---|
| 5-(Hydroxymethyl)-Dihydro-2(3H)-Furanone | 37.06 | 5.22E-15 | 0.01 | 9.42E-01 | 43.02 | 1.00E-06 | 62.42 | 7.26E-08 | 25.61 | 4.50E-05 |
| Benzophenone | 9.95 | 3.94E-06 | 2.96 | 9.92E-02 | 11.35 | 2.76E-03 | | | | |
| Dodecanoic Acid | 46.16 | 1.11E-16 | | | | | 202.98 | 1.38E-12 | 44.03 | 1.00E-06 |
| 5-(Hydroxymethyl)-2-Furfural | 338.26 | ≤ 1.00E-17 | 210.80 | 9.45E-13 | 37.98 | 3.00E-06 | 56.22 | 1.70E-07 | 121.06 | 2.06E-10 |
| 3-Methoxy-1,2-Benzenediol | 38.68 | 2.22E-15 | 0.01 | 9.17E-01 | 23.74 | 7.20E-05 | 73.54 | 1.83E-08 | 33.10 | 9.00E-06 |
| 1-(2-Furanyl)-1,2-Ethanediol | 134.76 | ≤ 1.00E-17 | 33.25 | 8.00E-06 | 49.70 | 4.50E-07 | 6.71 | 1.67E-02 | 106.97 | 6.52E-10 |
| 4-Hydroxy-Dihydro-2(3H)-Furanone | 132.15 | ≤ 1.00E-17 | 8.61 | 7.68E-03 | 36.03 | 5.00E-06 | 182.69 | 3.92E-12 | 111.62 | 4.40E-10 |

**Table S29. Information summary of PCA and PLS based on the RPA of the identified VOCs in samples from SCH processing stages during 2015-2018 production years.**

| Analysis | Component | $R^2X$ | Eigenvalues | $R^2Y$ | $Q^2$ | Significance | Iterations |
|---|---|---|---|---|---|---|---|
| PCA | 1 | 0.5709 | 118.18 | n.a. | 0.546 | S | 5 |
| | 2 | 0.0869 | 17.99 | n.a. | 0.070 | S | 11 |
| | 3 | 0.0721 | 14.92 | n.a. | 0.080 | S | 21 |
| | 4 | 0.0508 | 10.52 | n.a. | 0.134 | S | 10 |
| | 5 | 0.0415 | 8.59 | n.a. | 0.145 | S | 17 |
| | 6 | 0.0286 | 5.93 | n.a. | -0.095 | S | 31 |
| | 7 | 0.0280 | 5.80 | n.a. | 0.078 | S | 14 |
| | 8 | 0.0242 | 5.00 | n.a. | 0.117 | S | 9 |
| | 9 | 0.0144 | 2.98 | n.a. | -0.020 | S | 13 |
| | 10 | 0.0132 | 2.74 | n.a. | -0.063 | S | 30 |
| | 11 | 0.0125 | 2.59 | n.a. | -0.027 | S | 47 |
| | 12 | 0.0110 | 2.28 | n.a. | 0.102 | S | 17 |
| | 13 | 0.0077 | 1.59 | n.a. | -0.100 | S | 17 |
| | 14 | 0.0069 | 1.43 | n.a. | -0.100 | UNKNOWN | 21 |
| PLS | 1 | 0.6160 | 118.27 | 0.052 | -0.003 | S | 4 |
| | 2 | 0.0932 | 17.90 | 0.053 | 0.012 | S | 10 |
| | 3 | 0.0724 | 13.90 | 0.053 | 0.011 | S | 26 |
| | 4 | 0.0552 | 10.60 | 0.053 | 0.025 | S | 7 |
| | 5 | 0.0393 | 7.55 | 0.053 | 0.017 | S | 16 |
| | 6 | 0.0262 | 5.03 | 0.053 | 0.004 | S | 50 |
| | 7 | 0.0257 | 4.92 | 0.053 | 0.028 | S | 31 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 8 | 0.0217 | 4.17 | 0.052 | 0.039 | S | 22 |
| 9 | 0.0155 | 2.97 | 0.053 | 0.035 | S | 6 |
| 10 | 0.0089 | 1.70 | 0.052 | 0.036 | S | 35 |
| 11 | 0.0082 | 1.57 | 0.052 | 0.050 | S | 24 |
| 12 | 0.0065 | 1.25 | 0.052 | 0.099 | S | 9 |
| 13 | 0.0029 | 0.56 | 0.052 | 0.046 | S | 7 |
| 14 | 0.0021 | 0.41 | 0.051 | 0.077 | S | 7 |
| 15 | 0.0015 | 0.28 | 0.051 | 0.118 | S | 17 |
| 16 | 0.0009 | 0.17 | 0.052 | 0.119 | S | 10 |
| 17 | 0.0005 | 0.10 | 0.052 | 0.063 | S | 31 |
| 18 | 0.0010 | 0.09 | 0.050 | 0.211 | S | 5 |
| 19 | 0.0010 | 0.06 | 0.050 | 0.782 | S | 4 |
| 20 | 0.0009 | 0.16 | 0.002 | -0.001 | S | 7 |

**Table S30. Loading results and variable importance in projection scores of variables from PCA and PLS based on the RPA of the identified VOCs in samples from SCH processing stages during 2015-2018 production years.**

| ID Number | Volatile Organic Compounds | Abbreviations | PCA | | | | | PLS | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | VIP[1] | | | | | VIP[1] | |
| | | | 1 | 2 | 3 | Importance | Power (x 100) | 1 | 2 | 3 | Importance | Power (x 100) |
| 1 | Pentane | PTANE | -0.528 | -0.800 | 0.023 | 78 | 99.70 | -0.049 | -0.189 | 0.006 | 79 | 6.23 |
| 2 | Hexane | HXANE | -0.495 | 0.363 | 0.032 | 182 | 97.37 | -0.045 | 0.089 | 0.010 | 1 | 19.03 |
| 3 | Ethyl Ether | EETHR | 0.274 | -0.471 | 0.054 | 119 | 99.53 | 0.025 | -0.117 | 0.014 | 13 | 12.15 |
| 4 | 1,4-Pentadiene | PT14DIENE | 0.496 | -0.636 | 0.121 | 177 | 98.15 | 0.046 | -0.148 | 0.032 | 20 | 11.49 |
| 5 | Methanethiol | METHIOL | -0.947 | -0.032 | 0.052 | 140 | 99.32 | -0.087 | -0.008 | 0.014 | 126 | 4.19 |
| 6 | Ethanal | ETAL | -0.984 | -0.090 | 0.044 | 60 | 99.74 | -0.090 | -0.021 | 0.012 | 178 | 2.67 |
| 7 | Dimethyl Sulfide | DMSULFI | 0.165 | -0.057 | 0.027 | 59 | 99.74 | 0.015 | -0.013 | 0.006 | 40 | 8.59 |
| 8 | Propanal | PPAL | -0.906 | -0.053 | 0.226 | 84 | 99.69 | -0.083 | -0.013 | 0.061 | 116 | 4.69 |
| 9 | Furan | FUR | -0.911 | -0.082 | 0.105 | 19 | 99.90 | -0.084 | -0.019 | 0.029 | 115 | 4.69 |
| 10 | 2-Methyl-Propanal | MPPAL | -0.978 | -0.056 | 0.157 | 92 | 99.66 | -0.090 | -0.013 | 0.043 | 152 | 3.19 |
| 11 | Ethyl Formate | EESTFA | -0.596 | -0.129 | -0.745 | 1 | 99.98 | -0.055 | -0.029 | -0.200 | 92 | 5.42 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 12 | 2-Propenal | PPENAL | -0.881 | -0.057 | -0.343 | 133 | 99.41 | -0.081 | -0.013 | -0.092 | 78 | 6.26 |
| 13 | 2-Methyl-Furan | M2FUR | -0.806 | 0.107 | 0.435 | 172 | 98.37 | -0.074 | 0.025 | 0.118 | 23 | 10.59 |
| 14 | Ethyl Acetate | EESTAA | -0.639 | -0.143 | -0.716 | 22 | 99.89 | -0.059 | -0.032 | -0.192 | 96 | 5.30 |
| 15 | 2-Butanone | BT2ONE | -0.915 | -0.067 | 0.247 | 111 | 99.55 | -0.084 | -0.016 | 0.067 | 137 | 3.81 |
| 16 | 2-Methyl-Butanal | M2BTAL | -0.964 | 0.003 | 0.157 | 129 | 99.45 | -0.089 | 0.001 | 0.043 | 117 | 4.66 |
| 17 | 3-Methyl-Butanal | M3BTAL | -0.891 | 0.051 | 0.299 | 117 | 99.54 | -0.082 | 0.012 | 0.081 | 114 | 4.85 |
| 18 | Ethanol | ETOL | -0.976 | -0.115 | -0.015 | 91 | 99.66 | -0.090 | -0.028 | -0.004 | 154 | 3.16 |
| 19 | Benzene | BNZ | -0.903 | -0.136 | 0.251 | 139 | 99.32 | -0.083 | -0.033 | 0.068 | 63 | 6.79 |
| 20 | 3-Buten-2-one | BT3ONE | -0.880 | -0.110 | 0.336 | 15 | 99.92 | -0.081 | -0.027 | 0.091 | 118 | 4.59 |
| 21 | 2-Ethyl-Furan | E2FUR | 0.235 | 0.019 | 0.041 | 150 | 99.14 | 0.022 | 0.005 | 0.010 | 12 | 12.18 |
| 22 | 2,5-Dimethyl-Furan | DM25FUR | -0.862 | -0.104 | -0.398 | 62 | 99.74 | -0.079 | -0.024 | -0.106 | 125 | 4.19 |
| 23 | Ethyl Propanoate | EESTPA | -0.500 | -0.116 | -0.749 | 4 | 99.96 | -0.046 | -0.026 | -0.201 | 82 | 6.05 |
| 24 | 3-Pentanone | PT3ONE | 0.266 | -0.374 | 0.029 | 137 | 99.39 | 0.024 | -0.096 | 0.008 | 22 | 10.92 |
| 25 | Pentanal | PTNAL | 0.289 | 0.052 | 0.041 | 174 | 98.34 | 0.027 | 0.013 | 0.009 | 36 | 9.07 |
| 26 | 2,3-Butanedione | BT23DONE | -0.826 | -0.055 | 0.526 | 95 | 99.64 | -0.076 | -0.014 | 0.142 | 104 | 5.05 |
| 27 | 1-Penten-3-one | PT1E3ONE | 0.273 | -0.775 | 0.095 | 141 | 99.31 | 0.025 | -0.181 | 0.025 | 39 | 8.68 |
| 28 | 1-Propanol | P1POL | -0.653 | -0.057 | -0.399 | 89 | 99.68 | -0.060 | -0.014 | -0.107 | 60 | 6.95 |
| 29 | 2-Ethyl-5-Methyl-Furan | E2M5FUR | -0.916 | -0.116 | -0.323 | 162 | 98.79 | -0.084 | -0.027 | -0.086 | 134 | 3.84 |
| 30 | Toluene | TOLNE | -0.672 | -0.135 | -0.350 | 134 | 99.41 | -0.062 | -0.031 | -0.093 | 74 | 6.48 |
| 31 | 2-Methyl-3-Buten-2-ol | M3BT2OL | 0.434 | -0.652 | 0.105 | 168 | 98.56 | 0.040 | -0.152 | 0.028 | 17 | 11.87 |
| 32 | Nonomethyl Succinate | METESTBA | -0.661 | -0.139 | -0.370 | 101 | 99.61 | -0.061 | -0.032 | -0.099 | 70 | 6.67 |
| 33 | 2,3-Pentanedione | PTDONE | -0.702 | 0.036 | 0.645 | 138 | 99.33 | -0.064 | 0.007 | 0.173 | 53 | 7.44 |
| 34 | Dimethyl Disulfide | DMDSFD | -0.699 | -0.146 | -0.630 | 8 | 99.94 | -0.064 | -0.033 | -0.169 | 97 | 5.24 |
| 35 | 2-Ethenyl-Furan | ENYL2FUR | -0.676 | 0.231 | 0.090 | 184 | 96.79 | -0.062 | 0.056 | 0.026 | 10 | 13.71 |
| 36 | Hexanal | HXAL | 0.405 | -0.558 | 0.096 | 153 | 99.02 | 0.037 | -0.129 | 0.024 | 31 | 9.32 |
| 37 | 2-Methyl-1-Propanol | M2PP1OL | -0.458 | -0.116 | -0.733 | 106 | 99.59 | -0.042 | -0.026 | -0.197 | 76 | 6.39 |
| 38 | Methyl 2-Ethylpentanoate | EMESTPTA | 0.227 | -0.755 | 0.092 | 41 | 99.82 | 0.021 | -0.176 | 0.024 | 50 | 7.81 |
| 39 | 5-Butyl-Dihydro-2(3H)-Furanone (γ-Octalactone) | BDH2FURONE | -0.794 | -0.108 | -0.234 | 85 | 99.68 | -0.073 | -0.025 | -0.063 | 66 | 6.75 |
| 40 | m-Cresol | MCREOL | -0.858 | -0.065 | 0.479 | 17 | 99.91 | -0.079 | -0.016 | 0.129 | 123 | 4.35 |
| 41 | 1-Butanol | BT1OL | -0.642 | -0.142 | -0.664 | 48 | 99.79 | -0.059 | -0.032 | -0.178 | 88 | 5.56 |
| 42 | 5-Propyl-Dihydro-2(3H)-Furanone (γ-Heptalactone) | PDH2FURONE | -0.780 | -0.115 | -0.319 | 58 | 99.75 | -0.072 | -0.026 | -0.086 | 73 | 6.51 |
| 43 | 3-Methyl-Pyridazine | M3PYRDZNE | -0.940 | -0.062 | 0.303 | 94 | 99.64 | -0.086 | -0.015 | 0.082 | 140 | 3.73 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 44 | 1-Penten-3-ol | PT1E3OL | 0.363 | -0.898 | 0.071 | 123 | 99.52 | 0.033 | -0.213 | 0.018 | 80 | 6.18 |
| 45 | 2-Heptanone | HPT2ONE | 0.205 | -0.594 | -0.001 | 26 | 99.87 | 0.019 | -0.139 | -0.001 | 37 | 8.99 |
| 46 | Heptanal | HPTAL | 0.255 | 0.066 | 0.047 | 179 | 97.87 | 0.023 | 0.017 | 0.011 | 9 | 13.73 |
| 47 | m-Menthane | MMTHANE | -0.663 | 0.063 | 0.444 | 181 | 97.41 | -0.061 | 0.015 | 0.119 | 16 | 11.92 |
| 48 | 1,3-Diazine | D13ZINE | -0.689 | -0.042 | -0.407 | 176 | 98.30 | -0.063 | -0.008 | -0.109 | 44 | 8.42 |
| 49 | 2-Methyl-1-Butanol | M2BT1OL | -0.679 | -0.136 | -0.700 | 116 | 99.54 | -0.063 | -0.031 | -0.187 | 109 | 4.96 |
| 50 | 2-Propyl-Furan | PP2FUR | -0.736 | -0.085 | 0.188 | 81 | 99.70 | -0.068 | -0.021 | 0.051 | 71 | 6.57 |
| 51 | 3-Methyl-1-Butanol | M3BT1OL | 0.297 | -0.755 | 0.048 | 47 | 99.79 | 0.027 | -0.180 | 0.012 | 26 | 9.84 |
| 52 | 2-Pentyl-Furan | PT2FUR | 0.340 | -0.643 | 0.047 | 185 | 96.38 | 0.031 | -0.150 | 0.011 | 11 | 12.67 |
| 53 | 3-Octanone | OCT3ONE | 0.366 | -0.755 | 0.074 | 105 | 99.60 | 0.034 | -0.181 | 0.019 | 29 | 9.59 |
| 54 | 1-Pentanol | PT1OL | 0.449 | -0.762 | 0.107 | 124 | 99.51 | 0.041 | -0.180 | 0.027 | 69 | 6.68 |
| 55 | 2-Methyl-Pyrazine | MPYZNE | -0.713 | -0.116 | -0.347 | 166 | 98.68 | -0.066 | -0.026 | -0.093 | 41 | 8.59 |
| 56 | 2-Methyl-Dihydro-2(3H)-Furanone | MDH2FURONE | -0.986 | -0.090 | -0.064 | 88 | 99.68 | -0.091 | -0.021 | -0.017 | 167 | 2.85 |
| 57 | p-Cymene | PCYMNE | -0.294 | -0.512 | -0.259 | 72 | 99.72 | -0.027 | -0.120 | -0.069 | 38 | 8.96 |
| 58 | Mesitylene | MESTLNE | -0.300 | -0.319 | -0.676 | 164 | 98.69 | -0.028 | -0.073 | -0.181 | 57 | 7.15 |
| 59 | 3,5-Xylenol | XYL35NOL | -0.962 | -0.036 | 0.200 | 145 | 99.23 | -0.088 | -0.009 | 0.054 | 98 | 5.21 |
| 60 | 3-Hydroxy-2-Butanone | HXY3BT2ONE | -0.962 | -0.080 | 0.238 | 74 | 99.72 | -0.088 | -0.020 | 0.064 | 150 | 3.23 |
| 61 | Vinylene Carbonate | CVYLESTCA | -0.993 | -0.073 | 0.006 | 136 | 99.39 | -0.091 | -0.017 | 0.002 | 163 | 2.96 |
| 62 | 2,6-Xylenol | XYL26NOL | -0.916 | 0.044 | 0.241 | 155 | 98.98 | -0.084 | 0.011 | 0.065 | 84 | 5.75 |
| 63 | Octanal | OCTAL | 0.324 | 0.423 | 0.048 | 163 | 98.77 | 0.030 | 0.102 | 0.013 | 14 | 11.94 |
| 64 | 1-Hydroxy-2-Propanone | HXY1PP2ONE | -0.939 | -0.033 | 0.078 | 156 | 98.95 | -0.086 | -0.008 | 0.022 | 47 | 8.00 |
| 65 | cis-2-Heptanal | CH2PTAL | 0.169 | -0.552 | -0.010 | 3 | 99.96 | 0.016 | -0.129 | -0.003 | 35 | 9.10 |
| 66 | 2,5-Dimethyl-Pyrazine | DM25PYZNE | -0.723 | 0.015 | 0.035 | 183 | 97.29 | -0.066 | 0.004 | 0.010 | 8 | 13.90 |
| 67 | cis-2-Pentenol | CPT1E2OL | 0.303 | -0.847 | 0.043 | 44 | 99.81 | 0.028 | -0.201 | 0.011 | 77 | 6.38 |
| 68 | 2,6-Dimethyl-Pyrazine | DM26PYZNE | -0.925 | 0.046 | -0.086 | 135 | 99.39 | -0.085 | 0.011 | -0.023 | 62 | 6.84 |
| 69 | 2-Heptanol | HPT2OL | 0.215 | -0.701 | 0.014 | 9 | 99.94 | 0.020 | -0.164 | 0.003 | 45 | 8.20 |
| 70 | 2-Pentene | PT2ENE | 0.217 | -0.734 | 0.018 | 52 | 99.77 | 0.020 | -0.172 | 0.005 | 48 | 7.92 |
| 71 | 2-Cyclopenten-1-one | CY2PT1EONE | -0.963 | -0.064 | 0.192 | 40 | 99.82 | -0.089 | -0.016 | 0.052 | 157 | 3.09 |
| 72 | 1-Hexanol | HX1OL | 0.345 | -0.845 | 0.052 | 55 | 99.76 | 0.032 | -0.200 | 0.013 | 54 | 7.43 |
| 73 | 2-Methyl-2-Cyclopenten-1-one | M2CY2PT1EONE | -0.983 | -0.065 | 0.110 | 66 | 99.74 | -0.090 | -0.016 | 0.030 | 145 | 3.51 |
| 74 | 5-Methyl-2-Furanmethanethiol | M2FURTHOL | -0.583 | -0.121 | -0.753 | 12 | 99.93 | -0.054 | -0.027 | -0.202 | 89 | 5.46 |
| 75 | 1-Hydroxy-2-Butanone | H1BT2ONE | -0.881 | -0.028 | 0.420 | 28 | 99.86 | -0.081 | -0.008 | 0.113 | 127 | 4.14 |
| 76 | 2-Ethyl-6-Methyl-Pyrazine | E6MPYZNE | -0.940 | 0.031 | -0.116 | 100 | 99.61 | -0.086 | 0.007 | -0.031 | 90 | 5.44 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 77 | Nonanal | NONAL | -0.910 | -0.060 | 0.383 | 128 | 99.47 | -0.084 | -0.015 | 0.103 | 106 | 5.03 |
| 78 | 1-Ethyl-1-Methyl-Cyclopentane | E1M1CYPTANE | 0.248 | -0.829 | 0.085 | 7 | 99.94 | 0.023 | -0.194 | 0.022 | 56 | 7.25 |
| 79 | 3-Ethyl-2-Methyl-1,3-Hexadiene | E3M2HX13DENE | 0.339 | -0.735 | 0.105 | 46 | 99.80 | 0.031 | -0.171 | 0.027 | 51 | 7.73 |
| 80 | 2-Octanol | OCT2OL | 0.196 | -0.661 | 0.006 | 132 | 99.42 | 0.018 | -0.155 | 0.001 | 42 | 8.55 |
| 81 | 2-Cyclohexen-1-one | C2HEXONE | -0.707 | -0.101 | -0.535 | 82 | 99.69 | -0.065 | -0.022 | -0.143 | 64 | 6.77 |
| 82 | trans-2-Octenal | TOCT2EAL | 0.207 | -0.737 | 0.090 | 16 | 99.92 | 0.019 | -0.171 | 0.023 | 46 | 8.19 |
| 83 | 5-Methyl-2(3H)-Furanone (β-Angelica Lactone) | M5FURONE | -0.989 | -0.035 | -0.097 | 118 | 99.53 | -0.091 | -0.008 | -0.026 | 165 | 2.86 |
| 84 | 1,3-Dihydro-4-Methyl-2H-Imidazol-2-one | M4IMDZONE | -0.970 | -0.056 | 0.149 | 27 | 99.86 | -0.089 | -0.014 | 0.040 | 142 | 3.61 |
| 85 | 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | T116TNP | -0.929 | -0.076 | -0.216 | 69 | 99.73 | -0.085 | -0.017 | -0.057 | 112 | 4.88 |
| 86 | 1-Octen-3-ol | OCT3E1OL | -0.929 | -0.076 | -0.216 | 70 | 99.73 | -0.085 | -0.017 | -0.057 | 113 | 4.88 |
| 87 | 1-Heptanol | HPT1OL | 0.405 | -0.869 | 0.081 | 35 | 99.83 | 0.037 | -0.206 | 0.021 | 59 | 6.98 |
| 88 | Furfural | FURAL | -0.926 | 0.262 | 0.029 | 170 | 98.53 | -0.085 | 0.062 | 0.009 | 91 | 5.43 |
| 89 | Ethanoic Acid | ETNOIC | -0.959 | -0.040 | 0.206 | 114 | 99.55 | -0.088 | -0.010 | 0.056 | 111 | 4.92 |
| 90 | 2-Nonen-4-one | NON2ONE | 0.278 | 0.078 | 0.026 | 147 | 99.21 | 0.026 | 0.019 | 0.006 | 19 | 11.74 |
| 91 | 1,2,3,4-Tetrahydro-1,6,8-Trimethyl-Naphthalene | T168TNP | -0.921 | -0.090 | -0.169 | 161 | 98.82 | -0.085 | -0.021 | -0.045 | 130 | 4.04 |
| 92 | 2-Ethyl-1-Hexanol | E2HX1OL | -0.839 | -0.130 | -0.308 | 75 | 99.71 | -0.077 | -0.030 | -0.082 | 100 | 5.13 |
| 93 | trans,trans-2,4-Heptadienal | TTHPT24DAL | 0.275 | 0.057 | 0.032 | 187 | 91.76 | 0.025 | 0.014 | 0.007 | 4 | 15.12 |
| 94 | 3-Methyl-Furfural | M3FURAL | 0.115 | 0.657 | 0.096 | 175 | 98.30 | 0.011 | 0.158 | 0.027 | 5 | 15.08 |
| 95 | Furfuryl Formate | FURYLFMTE | -0.970 | -0.082 | -0.065 | 31 | 99.86 | -0.089 | -0.019 | -0.017 | 156 | 3.14 |
| 96 | 1-(2-Furanyl)-Ethanone | FURYLONE | -0.950 | 0.163 | -0.101 | 178 | 98.14 | -0.087 | 0.039 | -0.026 | 32 | 9.22 |
| 97 | Decanal | DECAL | -0.928 | -0.120 | 0.280 | 103 | 99.60 | -0.085 | -0.029 | 0.076 | 131 | 3.90 |
| 98 | Benzaldehyde | BENZAL | -0.950 | -0.102 | 0.246 | 115 | 99.54 | -0.087 | -0.025 | 0.066 | 124 | 4.27 |
| 99 | Furfuryl Acetate | FURYLACTE | -0.970 | -0.081 | 0.097 | 76 | 99.71 | -0.089 | -0.020 | 0.026 | 161 | 3.02 |
| 100 | Propanoic Acid | PPANOIC | -0.522 | -0.018 | -0.691 | 108 | 99.56 | -0.048 | -0.003 | -0.185 | 52 | 7.48 |
| 101 | 1-Octanol | OCT1OL | 0.466 | -0.814 | 0.080 | 73 | 99.72 | 0.043 | -0.194 | 0.020 | 61 | 6.88 |
| 102 | Dimethyl Sulfoxide | DMSULFO | -0.717 | 0.006 | -0.303 | 157 | 98.94 | -0.066 | 0.001 | -0.082 | 24 | 10.36 |
| 103 | 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | T158TNP | -0.816 | -0.063 | -0.439 | 146 | 99.23 | -0.075 | -0.014 | -0.117 | 95 | 5.31 |
| 104 | 5-Methyl-Furfural | M5FURAL | -0.969 | 0.042 | -0.041 | 127 | 99.48 | -0.089 | 0.009 | -0.011 | 83 | 5.78 |
| 105 | 4-Cyclopentene-1,3-dione | CPT4E13DONE | -0.973 | 0.094 | -0.036 | 38 | 99.82 | -0.089 | 0.022 | -0.009 | 128 | 4.09 |
| 106 | 2-Methyl-Benzofuran | M2BNZFUR | -0.970 | -0.101 | -0.071 | 110 | 99.56 | -0.089 | -0.024 | -0.018 | 143 | 3.58 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 107 | 1-(5-Methyl-2-Furanyl)-Ethanone | M5FURYLONE | -0.985 | -0.104 | -0.035 | 93 | 99.66 | -0.091 | -0.025 | -0.009 | 184 | 2.62 |
| 108 | trans-2-Octenol | TOCTE2OL | 0.224 | -0.749 | 0.092 | 10 | 99.93 | 0.021 | -0.175 | 0.024 | 49 | 7.84 |
| 109 | Diethylene Glycol Ethyl Ether | DENGOLEETHR | -0.953 | -0.066 | 0.211 | 130 | 99.45 | -0.088 | -0.016 | 0.057 | 146 | 3.50 |
| 110 | 3-Methyl-Dihydro-2(3H)-Furanone | M3DHFURONE | -0.980 | -0.050 | -0.062 | 99 | 99.62 | -0.090 | -0.012 | -0.016 | 122 | 4.43 |
| 111 | 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | DHT1146MIDNE | -0.949 | -0.147 | -0.123 | 6 | 99.95 | -0.087 | -0.035 | -0.033 | 149 | 3.32 |
| 112 | Benzeneacetaldehyde | BENZACETAL | -0.985 | -0.079 | 0.060 | 34 | 99.84 | -0.091 | -0.019 | 0.017 | 164 | 2.94 |
| 113 | 3,5-Dimethyl-Dihydro-2-Furanone | DM35DHFURONE | -0.832 | -0.096 | 0.078 | 20 | 99.89 | -0.076 | -0.023 | 0.021 | 87 | 5.62 |
| 114 | 3-Methyl-Benzaldehyde | M3BENZAL | 0.212 | 0.493 | 0.047 | 165 | 98.68 | 0.020 | 0.119 | 0.014 | 2 | 18.97 |
| 115 | 2-Propenoic Acid | PPE2NOIC | -0.912 | -0.051 | -0.135 | 68 | 99.73 | -0.084 | -0.012 | -0.036 | 121 | 4.45 |
| 116 | Acetophenone | ACETPHONE | -0.877 | -0.070 | 0.330 | 96 | 99.63 | -0.081 | -0.018 | 0.089 | 108 | 4.98 |
| 117 | 2-Furanmethanol | FUR2OL | -0.866 | 0.140 | 0.322 | 109 | 99.56 | -0.080 | 0.033 | 0.087 | 67 | 6.73 |
| 118 | 3-Furanmethanol | FUR3OL | -0.795 | 0.119 | 0.438 | 86 | 99.68 | -0.073 | 0.027 | 0.118 | 81 | 6.10 |
| 119 | 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | DHT1156MIDNE | -0.978 | -0.034 | 0.118 | 125 | 99.50 | -0.090 | -0.009 | 0.032 | 93 | 5.42 |
| 120 | 2-(2-Furanylmethyl)-5-Methyl-Furan | FURYLMFUR | -0.951 | -0.076 | 0.067 | 98 | 99.62 | -0.087 | -0.018 | 0.018 | 147 | 3.42 |
| 121 | 3-Methyl-2(5H)-Furanone | M3FURONE | -0.993 | -0.049 | 0.013 | 43 | 99.81 | -0.091 | -0.012 | 0.004 | 173 | 2.74 |
| 122 | 5-Methyl-2-Furanmethanol | M5FUR2OL | -0.983 | -0.032 | 0.176 | 42 | 99.81 | -0.090 | -0.008 | 0.048 | 183 | 2.62 |
| 123 | Phenylmethyl Acetate | PMESTAA | -0.642 | -0.057 | -0.582 | 107 | 99.57 | -0.059 | -0.014 | -0.156 | 65 | 6.77 |
| 124 | Naphthalene | NPHNE | 0.420 | -0.094 | 0.080 | 160 | 98.87 | 0.039 | -0.024 | 0.021 | 3 | 15.25 |
| 125 | 2(5H)-Furanone | FURONE | -0.908 | 0.014 | 0.156 | 33 | 99.85 | -0.084 | 0.002 | 0.042 | 119 | 4.56 |
| 126 | 2,2'-Methylenebis[5-Methyl-Furan | MNEB5MFUR | -0.953 | -0.093 | 0.011 | 87 | 99.68 | -0.088 | -0.022 | 0.004 | 141 | 3.62 |
| 127 | 1,2-Cyclopentanedione | CPT12DONE | -0.979 | 0.045 | 0.059 | 63 | 99.74 | -0.090 | 0.010 | 0.016 | 132 | 3.89 |
| 128 | Diethylene Glycol Monobutyl Ether | DETNGOLBTHR | 0.209 | -0.264 | 0.019 | 149 | 99.14 | 0.019 | -0.069 | 0.005 | 7 | 14.04 |
| 129 | 2-Cyclohexenol | CHEX2E1OL | -0.990 | -0.051 | 0.096 | 21 | 99.89 | -0.091 | -0.012 | 0.026 | 182 | 2.63 |
| 130 | 2-Phenylethyl Acetate | PEESTAA | -0.673 | -0.108 | -0.708 | 83 | 99.69 | -0.062 | -0.025 | -0.190 | 107 | 5.02 |
| 131 | 3-Methyl-1,2-Cyclopentanedione | M3CPT12DONE | -0.988 | -0.055 | 0.124 | 23 | 99.88 | -0.091 | -0.014 | 0.034 | 181 | 2.63 |
| 132 | β-Damascenone | DAMSNONE | -0.688 | -0.011 | 0.559 | 79 | 99.70 | -0.063 | -0.005 | 0.150 | 68 | 6.73 |
| 133 | 2-Methyl-Propanoic Acid | M2PPOICA | -0.975 | -0.064 | 0.163 | 30 | 99.86 | -0.090 | -0.015 | 0.044 | 171 | 2.78 |
| 134 | 4-(1-Methylpropyl)-Phenol | MPPYLPHEOL | 0.286 | 0.062 | 0.034 | 171 | 98.38 | 0.026 | 0.015 | 0.008 | 27 | 9.82 |
| 135 | 2,4,6-Trihydroxypyrimidine | THDXYPYMNE | -0.964 | 0.050 | -0.150 | 113 | 99.55 | -0.089 | 0.012 | -0.040 | 101 | 5.11 |
| 136 | Mequinol | MEQNOL | -0.977 | -0.046 | 0.189 | 37 | 99.82 | -0.090 | -0.011 | 0.051 | 169 | 2.80 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 137 | 2,2-Diethyl-3-Methyl-Oxazolidine | DEMOXZDNE | -0.975 | -0.075 | 0.160 | 54 | 99.76 | -0.090 | -0.018 | 0.043 | 158 | 3.08 |
| 138 | Oxypurinol | OXYPUROL | -0.989 | -0.068 | -0.003 | 51 | 99.78 | -0.091 | -0.017 | -0.001 | 159 | 3.05 |
| 139 | Benzenemethanol | BENZMTOL | -0.794 | -0.055 | -0.444 | 97 | 99.63 | -0.073 | -0.013 | -0.119 | 85 | 5.74 |
| 140 | 4-Methyl-2(5H)-Furanone | M4FUR2ONE | -0.960 | -0.073 | 0.229 | 57 | 99.75 | -0.088 | -0.018 | 0.062 | 155 | 3.15 |
| 141 | 3-Ethyl-2-Hydroxy-2-Cyclopenten-1-one | E3H2C2PT1ONE | -0.990 | -0.066 | 0.102 | 102 | 99.60 | -0.091 | -0.016 | 0.028 | 186 | 2.49 |
| 142 | Benzeneethanol | BENZETOL | -0.761 | -0.209 | -0.490 | 144 | 99.29 | -0.070 | -0.050 | -0.131 | 55 | 7.36 |
| 143 | 1,4-Butanediol | BT14DIOL | 0.422 | -0.362 | 0.040 | 148 | 99.19 | 0.039 | -0.091 | 0.010 | 21 | 11.24 |
| 144 | Acrylamide | ACRYLMDE | -0.991 | -0.065 | -0.067 | 36 | 99.83 | -0.091 | -0.015 | -0.017 | 185 | 2.61 |
| 145 | Erythritol | ERYTOL | -0.968 | -0.126 | 0.187 | 2 | 99.96 | -0.089 | -0.030 | 0.051 | 172 | 2.75 |
| 146 | 2,3-Dimethyl-3-Pyrazolin-5-one | DM23PYZLONE | -0.990 | -0.062 | 0.087 | 131 | 99.44 | -0.091 | -0.015 | 0.024 | 175 | 2.70 |
| 147 | Furfural Acetone | FURALTONE | -0.980 | -0.090 | 0.158 | 14 | 99.92 | -0.090 | -0.022 | 0.043 | 180 | 2.63 |
| 148 | Cyclotene | CYTENE | -0.983 | -0.080 | 0.096 | 18 | 99.90 | -0.090 | -0.020 | 0.026 | 176 | 2.69 |
| 149 | 2-Methyl-1,4-Benzenediol | M2BNZ14DIOL | -0.918 | -0.065 | 0.343 | 13 | 99.93 | -0.084 | -0.016 | 0.092 | 144 | 3.52 |
| 150 | Maltol | MALTOL | -0.990 | -0.053 | -0.016 | 39 | 99.82 | -0.091 | -0.013 | -0.004 | 170 | 2.79 |
| 151 | 2-Acetylpyrrole | ACTLPYROLE | -0.993 | -0.026 | 0.029 | 61 | 99.74 | -0.091 | -0.006 | 0.008 | 151 | 3.19 |
| 152 | 2,5-Furandicarboxaldehyde | FUR25DIAL | -0.990 | -0.090 | 0.058 | 32 | 99.85 | -0.091 | -0.022 | 0.016 | 179 | 2.64 |
| 153 | 2H-Pyran-2,6(3H)-Dione | PYR26DIONE | -0.985 | -0.069 | -0.067 | 80 | 99.70 | -0.091 | -0.016 | -0.017 | 133 | 3.85 |
| 154 | 1-(2-Furanyl)-2-Hydroxy-Ethanone | H2FURYLONE | -0.806 | 0.000 | -0.410 | 120 | 99.53 | -0.074 | 0.001 | -0.110 | 72 | 6.54 |
| 155 | Phenol | PHEOL | -0.980 | -0.085 | 0.135 | 122 | 99.52 | -0.090 | -0.021 | 0.037 | 177 | 2.69 |
| 156 | 1H-Pyrrole-2-Carboxaldehyde | PYRLE2AL | -0.887 | -0.088 | 0.356 | 65 | 99.74 | -0.081 | -0.022 | 0.096 | 129 | 4.08 |
| 157 | Phloroglucinol | PHLOGLNOL | -0.978 | -0.071 | -0.043 | 5 | 99.95 | -0.090 | -0.017 | -0.011 | 162 | 3.02 |
| 158 | Furaneol | FUREOL | -0.895 | 0.145 | -0.093 | 112 | 99.55 | -0.082 | 0.034 | -0.024 | 75 | 6.44 |
| 159 | Octanoic Acid | OCTOIC | -0.908 | -0.074 | 0.038 | 53 | 99.77 | -0.084 | -0.019 | 0.010 | 105 | 5.04 |
| 160 | 5-Acetyl-Dihydro-2(3H)-Furanone (Solerone) | ACYLDHFURONE | -0.965 | 0.082 | -0.045 | 126 | 99.49 | -0.089 | 0.019 | -0.011 | 94 | 5.37 |
| 161 | 2-Furanpropionic Acid | FURPPIONIC | -0.988 | -0.076 | -0.065 | 11 | 99.93 | -0.091 | -0.018 | -0.017 | 174 | 2.73 |
| 162 | 1,3-Dihydroxy-2-Propanone | DHYPPAONE | -0.975 | 0.038 | -0.055 | 45 | 99.80 | -0.090 | 0.009 | -0.014 | 148 | 3.39 |
| 163 | Tetrahydro-5-Methyl-2-Furanmethanol | TEHYMFUROL | -0.606 | 0.031 | -0.496 | 180 | 97.84 | -0.056 | 0.008 | -0.133 | 15 | 11.94 |
| 164 | 4,5-Dimethyl Vinylene Carbonate | DM45CVYLESTCA | -0.960 | -0.016 | 0.137 | 158 | 98.90 | -0.088 | -0.004 | 0.037 | 136 | 3.83 |
| 165 | 2-Hydroxy-Dihydro-2(3H)-Furanone | HY2DHFURONE | -0.162 | 0.446 | -0.494 | 169 | 98.55 | -0.015 | 0.105 | -0.132 | 25 | 10.30 |
| 166 | 2-Ethyl-Phenol | E2PHEOL | 0.363 | -0.701 | 0.091 | 25 | 99.88 | 0.033 | -0.166 | 0.024 | 28 | 9.68 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 167 | 5-Acetoxymethyl-2-Furfural A | ACTYMFURALA | -0.914 | 0.076 | 0.079 | 186 | 96.26 | -0.084 | 0.018 | 0.022 | 18 | 11.81 |
| 168 | 5-Acetoxymethyl-2-Furfural B | ACTYMFURALB | -0.969 | 0.007 | -0.127 | 121 | 99.52 | -0.089 | 0.002 | -0.033 | 102 | 5.10 |
| 169 | 2-Methoxy-4-Vinyl-Phenol | MXY2VYL4PHEOL | -0.938 | 0.001 | 0.246 | 143 | 99.30 | -0.086 | 0.000 | 0.066 | 86 | 5.70 |
| 170 | 3-Methyl-2,4(3H,5H)-Furandione | M3FURDIONE | -0.992 | -0.053 | 0.066 | 67 | 99.74 | -0.091 | -0.013 | 0.018 | 160 | 3.04 |
| 171 | 3-Hydroxy-2,3-Dihydro-Maltol | HX3DH23MALTOL | -0.969 | 0.049 | -0.033 | 159 | 98.89 | -0.089 | 0.011 | -0.008 | 103 | 5.07 |
| 172 | Decanoic Acid | DECOIC | -0.579 | 0.038 | -0.010 | 77 | 99.70 | -0.053 | 0.006 | -0.003 | 30 | 9.47 |
| 173 | 5-Hydroxy-Maltol | HX5MALTOL | -0.985 | -0.020 | 0.093 | 29 | 99.86 | -0.091 | -0.005 | 0.025 | 168 | 2.84 |
| 174 | 2,3-Dihydro-Benzofuran | DHBNZFUR | -0.918 | 0.015 | 0.369 | 104 | 99.60 | -0.084 | 0.003 | 0.099 | 99 | 5.17 |
| 175 | 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | GLUPYROSE | -0.974 | -0.066 | 0.008 | 142 | 99.30 | -0.090 | -0.016 | 0.002 | 138 | 3.78 |
| 176 | 4-Pyridinol | PYRDINOL | -0.995 | -0.065 | 0.035 | 64 | 99.74 | -0.091 | -0.016 | 0.010 | 187 | 2.36 |
| 177 | 4-Amino-Phenol | AMIPHEOL | -0.975 | -0.065 | 0.197 | 90 | 99.67 | -0.090 | -0.016 | 0.053 | 153 | 3.16 |
| 178 | Benzoic Acid | BNZOIC | -0.961 | -0.008 | 0.090 | 167 | 98.65 | -0.088 | -0.002 | 0.025 | 34 | 9.17 |
| 179 | Dimethylhydrazone 3-Pentanone | DMHDZPTONE | -0.912 | -0.037 | 0.137 | 56 | 99.75 | -0.084 | -0.009 | 0.037 | 120 | 4.52 |
| 180 | Undecanoic Acid | UNDECOIC | -0.518 | 0.012 | -0.167 | 49 | 99.79 | -0.048 | 0.001 | -0.045 | 33 | 9.18 |
| 181 | 5-(Hydroxymethyl)-Dihydro-2(3H)-Furanone | HM5FURONE | -0.883 | 0.024 | 0.202 | 50 | 99.78 | -0.081 | 0.005 | 0.055 | 110 | 4.95 |
| 182 | Benzophenone | BENZPONE | 0.295 | -0.133 | 0.059 | 173 | 98.34 | 0.027 | -0.034 | 0.015 | 6 | 14.67 |
| 183 | Dodecanoic Acid | DODECOIC | -0.931 | -0.117 | 0.037 | 151 | 99.03 | -0.086 | -0.028 | 0.010 | 135 | 3.84 |
| 184 | 5-(Hydroxymethyl)-2-Furfural | HM5FURAL | -0.894 | 0.209 | -0.199 | 154 | 98.99 | -0.082 | 0.050 | -0.053 | 43 | 8.53 |
| 185 | 3-Methoxy-1,2-Benzenediol | M3BNZDIOL | -0.945 | -0.066 | 0.281 | 24 | 99.88 | -0.087 | -0.017 | 0.076 | 139 | 3.73 |
| 186 | 1-(2-Furanyl)-1,2-Ethanediol | FURYLETDIOL | -0.977 | -0.029 | 0.059 | 152 | 99.02 | -0.090 | -0.008 | 0.016 | 58 | 7.09 |
| 187 | 4-Hydroxy-Dihydro-2(3H)-Furanone | DHYHYFURONE | -0.992 | -0.061 | 0.054 | 71 | 99.72 | -0.091 | -0.015 | 0.015 | 166 | 2.85 |

[1]VIP - Variable Importance in Projection scores.

**Table S31. Loading results of samples and variables from PCA and PLS based on the RPA of the identified VOCs in samples from SCH processing stages during 2015-2018 production years.**

| ID Code | Stages | PCA | | | PLS | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 1 | 2 | 3 |
| S1-15 | Stage 1 - 2015 | 0.14 | -0.06 | 0.02 | n.a. | n.a. | n.a. |
| S1-16 | Stage 1 - 2016 | 0.15 | -0.19 | 0.01 | n.a. | n.a. | n.a. |
| S1-17 | Stage 1 - 2017 | 0.18 | -0.64 | 0.09 | n.a. | n.a. | n.a. |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| S1-18 | Stage 1 - 2018 | 0.16 | -0.54 | -0.01 | n.a. | n.a. | n.a. |
| S2-15 | Stage 2 - 2015 | 0.14 | 0.00 | 0.04 | n.a. | n.a. | n.a. |
| S2-16 | Stage 2 - 2016 | 0.13 | 0.06 | 0.00 | n.a. | n.a. | n.a. |
| S2-17 | Stage 2 - 2017 | 0.14 | 0.00 | 0.03 | n.a. | n.a. | n.a. |
| S2-18 | Stage 2 - 2018 | 0.14 | 0.06 | 0.00 | n.a. | n.a. | n.a. |
| S3-15 | Stage 3 - 2015 | 0.09 | 0.15 | 0.01 | n.a. | n.a. | n.a. |
| S3-16 | Stage 3 - 2016 | 0.07 | 0.20 | 0.02 | n.a. | n.a. | n.a. |
| S3-17 | Stage 3 - 2017 | 0.08 | 0.19 | 0.02 | n.a. | n.a. | n.a. |
| S3-18 | Stage 3 - 2018 | 0.08 | 0.18 | 0.01 | n.a. | n.a. | n.a. |
| S4-15 | Stage 4 - 2015 | 0.04 | 0.21 | 0.03 | n.a. | n.a. | n.a. |
| S4-16 | Stage 4 - 2016 | 0.06 | 0.20 | 0.02 | n.a. | n.a. | n.a. |
| S4-17 | Stage 4 - 2017 | 0.08 | 0.17 | 0.00 | n.a. | n.a. | n.a. |
| S4-18 | Stage 4 - 2018 | 0.06 | 0.19 | 0.00 | n.a. | n.a. | n.a. |
| S5-15 | Stage 5 - 2015 | -0.21 | 0.08 | -0.15 | n.a. | n.a. | n.a. |
| S5-16 | Stage 5 - 2016 | -0.40 | -0.10 | -0.72 | n.a. | n.a. | n.a. |
| S5-17 | Stage 5 - 2017 | -0.54 | -0.11 | -0.10 | n.a. | n.a. | n.a. |
| S5-18 | Stage 5 - 2018 | -0.59 | -0.05 | 0.69 | n.a. | n.a. | n.a. |
| C-S1 | Centroid - Stage 1 | n.a. | n.a. | n.a. | 0.031 | -0.187 | 0.016 |
| C-S2 | Centroid - Stage 2 | n.a. | n.a. | n.a. | 0.027 | 0.015 | 0.008 |
| C-S3 | Centroid - Stage 3 | n.a. | n.a. | n.a. | 0.016 | 0.094 | 0.010 |
| C-S4 | Centroid - Stage 4 | n.a. | n.a. | n.a. | 0.012 | 0.102 | 0.008 |
| C-S5 | Centroid - Stage 5 | n.a. | n.a. | n.a. | -0.087 | -0.025 | -0.042 |

**Table S32. Results of variables from LDA after matrix reduction method to 20 % of original dimension according with higher on the VIP scores values from the PLS analysis based on the RPA of the identified VOCs in samples from SCH processing stages during 2015-2018 production years**.

| Volatile Organic Compounds | Abbreviations | PLS | | LDA | |
|---|---|---|---|---|---|
| | | VIP[1] | | | |
| | | Importance | Power (x 100) | W[2] | F[3] |

| | | | | | |
|---|---|---|---|---|---|
| Hexane | HXANE | 1 | 19.03 | 1.44E-78 | 2.37E+78 |
| 3-Methyl-Benzaldehyde | M3BENZAL | 2 | 18.97 | 2.20E-77 | 1.55E+77 |
| Naphthalene | NPHNE | 3 | 15.25 | 1.29E-85 | 3.48E+85 |
| trans,trans-2,4-Heptadienal | TTHPT24DAL | 4 | 15.12 | 7.09E-77 | 4.79E+76 |
| 3-Methyl-Furfural | M3FURAL | 5 | 15.08 | 8.60E-86 | 5.23E+85 |
| Benzophenone | BENZPONE | 6 | 14.67 | 3.10E-76 | 1.10E+76 |
| Diethylene Glycol Monobutyl Ether | DETNGOLBTHR | 7 | 14.04 | Removed from analysis. | |
| 2,5-Dimethyl-Pyrazine | DM25PYZNE | 8 | 13.90 | 2.70E-79 | 1.26E+79 |
| Heptanal | HPTAL | 9 | 13.73 | 7.94E-79 | 4.28E+78 |
| 2-Ethenyl-Furan | ENYL2FUR | 10 | 13.71 | 8.23E-86 | 5.47E+85 |
| 2-Pentyl-Furan | PT2FUR | 11 | 12.67 | 1.03E-75 | 3.29E+75 |
| 2-Ethyl-Furan | E2FUR | 12 | 12.18 | 1.05E-67 | 2.53E+67 |
| Ethyl Ether | EETHR | 13 | 12.15 | 6.04E-84 | 7.46E+83 |
| Octanal | OCTAL | 14 | 11.94 | 2.60E-75 | 1.31E+75 |
| Tetrahydro-5-Methyl-2-Furanmethanol | TEHYMFUROL | 15 | 11.94 | 6.06E-79 | 5.61E+78 |
| m-Menthane | MMTHANE | 16 | 11.92 | 6.71E-86 | 6.71E+85 |
| 2-Methyl-3-Buten-2-ol | M3BT2OL | 17 | 11.87 | 2.77E-85 | 1.62E+85 |
| 5-Acetoxymethyl-2-Furfural A | ACTYMFURALA | 18 | 11.81 | 6.63E-86 | 6.79E+85 |
| 2-Nonen-4-one | NON2ONE | 19 | 11.74 | 1.24E-83 | 3.61E+83 |
| 1,4-Pentadiene | PT14DIENE | 20 | 11.49 | 1.07E-85 | 4.21E+85 |
| 1,4-Butanediol | BT14DIOL | 21 | 11.24 | 8.14E-77 | 4.18E+76 |
| 3-Pentanone | PT3ONE | 22 | 10.92 | 2.39E-77 | 1.42E+77 |
| 2-Methyl-Furan | M2FUR | 23 | 10.59 | 4.38E-86 | 1.03E+86 |
| Dimethyl Sulfoxide | DMSULFO | 24 | 10.36 | 3.34E-79 | 1.02E+79 |
| 2-Hydroxy-Dihydro-2(3H)-Furanone | HY2DHFURONE | 25 | 10.30 | 2.25E-78 | 1.51E+78 |
| 3-Methyl-1-Butanol | M3BT1OL | 26 | 9.84 | 1.91E-75 | 1.78E+75 |
| 4-(1-Methylpropyl)-Phenol | MPPYLPHEOL | 27 | 9.82 | 1.03E-82 | 4.35E+82 |
| 2-Ethyl-Phenol | E2PHEOL | 28 | 9.68 | 3.40E-75 | 1.00E+75 |
| 3-Octanone | OCT3ONE | 29 | 9.59 | 1.93E-78 | 1.76E+78 |
| Decanoic Acid | DECOIC | 30 | 9.47 | 4.37E-86 | 1.03E+86 |
| Hexanal | HXAL | 31 | 9.32 | Removed from analysis. | |
| 1-(2-Furanyl)-Ethanone | FURYLONE | 32 | 9.22 | 1.00E-77 | 3.40E+77 |
| Undecanoic Acid | UNDECOIC | 33 | 9.18 | 1.73E-79 | 1.97E+79 |

| | | | | | |
|---|---|---|---|---|---|
| Benzoic Acid | BNZOIC | 34 | 9.17 | 2.84E-78 | 1.20E+78 |
| cis-2-Heptanal | CH2PTAL | 35 | 9.10 | 4.29E-85 | 1.05E+85 |
| Pentanal | PTNAL | 36 | 9.07 | Removed from analysis. | |
| 2-Heptanone | HPT2ONE | 37 | 8.99 | 6.28E-78 | 5.41E+77 |

[1]VIP - Variable Importance in Projection scores.

**Table S33. CDF Coefficients and Highest Probability Classification results of samples from LDA after matrix reduction method obtained from One-way ANOVA test based on the RPA of identified VOCs in samples from SCH processing stages during 2015-2018 production years.**

| ID Replicate Code | ID Stage Code | LDA | | | | | | | | | PLS | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | CDF[1] | | | CDF[1] Class Means | | | Highest Probability Classification | | | Score Value | | | Loading Value | | |
| | | 1 | 2 | 3 | 1 | 2 | 3 | First | Second | Third | 1 | 2 | 3 | 1 | 2 | 3 |
| S1-15A | S1 | 705.0 | 202.8 | -122.4 | 705.0 | 201.4 | -125.9 | S1 | S3 | S4 | 3.51 | 1.44 | -1.34 | 0.058 | 0.172 | -0.305 |
| S1-15B | | 705.2 | 200.2 | -128.9 | | | | S1 | S3 | S4 | 3.43 | 1.44 | -1.33 | | | |
| S1-15C | | 705.1 | 201.5 | -125.6 | | | | S1 | S3 | S4 | 3.47 | 1.44 | -1.33 | | | |
| S1-16A | | 704.3 | 200.0 | -125.6 | | | | S1 | S3 | S4 | 3.51 | 1.44 | -1.33 | | | |
| S1-16B | | 705.0 | 202.4 | -126.4 | | | | S1 | S3 | S4 | 3.49 | 1.45 | -1.32 | | | |
| S1-16C | | 704.7 | 201.2 | -126.0 | | | | S1 | S3 | S4 | 3.50 | 1.45 | -1.33 | | | |
| S1-17A | | 700.6 | 200.1 | -124.6 | | | | S1 | S3 | S4 | 3.61 | 1.33 | -1.37 | | | |
| S1-17B | | 709.5 | 202.8 | -127.4 | | | | S1 | S3 | S4 | 3.61 | 1.32 | -1.38 | | | |
| S1-17C | | 705.1 | 201.4 | -126.0 | | | | S1 | S3 | S4 | 3.61 | 1.32 | -1.37 | | | |
| S1-18A | | 706.9 | 202.2 | -123.2 | | | | S1 | S3 | S4 | 3.53 | 1.19 | -1.35 | | | |
| S1-18B | | 703.6 | 200.6 | -128.7 | | | | S1 | S3 | S4 | 3.61 | 1.23 | -1.36 | | | |
| S1-18C | | 705.2 | 201.4 | -126.0 | | | | S1 | S3 | S4 | 3.57 | 1.21 | -1.36 | | | |
| S2-15A | S2 | 740.6 | 314.9 | 59.1 | 741.3 | 315.1 | 60.3 | S2 | S3 | S4 | 3.87 | -3.64 | -0.43 | 0.064 | -0.465 | -0.037 |
| S2-15B | | 741.6 | 315.2 | 61.5 | | | | S2 | S3 | S4 | 3.84 | -3.72 | -0.47 | | | |
| S2-15C | | 741.1 | 315.1 | 60.3 | | | | S2 | S3 | S4 | 3.85 | -3.68 | -0.45 | | | |
| S2-16A | | 741.0 | 315.9 | 58.6 | | | | S2 | S3 | S4 | 3.75 | -3.89 | 0.01 | | | |
| S2-16B | | 741.3 | 314.2 | 62.2 | | | | S2 | S3 | S4 | 3.79 | -4.27 | 0.18 | | | |
| S2-16C | | 741.2 | 315.1 | 60.4 | | | | S2 | S3 | S4 | 3.77 | -4.08 | 0.10 | | | |
| S2-17A | | 743.3 | 310.8 | 61.1 | | | | S2 | S3 | S4 | 3.96 | -3.03 | -0.29 | | | |

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|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| S2-17B | | 739.5 | 319.2 | 59.9 | | | | S2 | S3 | S4 | 3.95 | -3.04 | -0.18 | | | | |
| S2-17C | | 741.4 | 315.0 | 60.5 | | | | S2 | S3 | S4 | 3.96 | -3.03 | -0.23 | | | | |
| S2-18A | | 741.9 | 314.7 | 60.2 | | | | S2 | S3 | S4 | 3.96 | -3.54 | 0.04 | | | | |
| S2-18B | | 741.4 | 315.7 | 60.1 | | | | S2 | S3 | S4 | 4.01 | -4.10 | -0.16 | | | | |
| S2-18C | | 741.6 | 315.2 | 60.1 | | | | S2 | S3 | S4 | 3.99 | -3.82 | -0.06 | | | | |
| S3-15A | | 489.2 | -51.7 | 89.4 | | | | S3 | S2 | S4 | 2.64 | 1.17 | 2.54 | | | | |
| S3-15B | | 489.0 | -53.1 | 91.3 | | | | S3 | S2 | S4 | 2.65 | 1.15 | 2.72 | | | | |
| S3-15C | | 489.1 | -52.4 | 90.4 | | | | S3 | S2 | S4 | 2.65 | 1.16 | 2.63 | | | | |
| S3-16A | | 489.3 | -51.3 | 91.2 | | | | S3 | S2 | S4 | 1.88 | 1.14 | 3.03 | | | | |
| S3-16B | | 488.9 | -53.4 | 89.7 | | | | S3 | S2 | S4 | 1.71 | 1.12 | 3.11 | | | | |
| S3-16C | S3 | 489.1 | -52.3 | 90.5 | 489.1 | -52.3 | 90.4 | S3 | S2 | S4 | 1.79 | 1.13 | 3.07 | 0.036 | 0.146 | 0.623 | |
| S3-17A | | 489.1 | -52.7 | 90.8 | | | | S3 | S2 | S4 | 2.44 | 1.12 | 2.77 | | | | |
| S3-17B | | 489.2 | -52.0 | 90.1 | | | | S3 | S2 | S4 | 2.23 | 1.19 | 2.54 | | | | |
| S3-17C | | 489.2 | -52.4 | 90.5 | | | | S3 | S2 | S4 | 2.33 | 1.15 | 2.66 | | | | |
| S3-18A | | 489.2 | -51.9 | 90.1 | | | | S3 | S2 | S4 | 2.13 | 1.12 | 2.80 | | | | |
| S3-18B | | 488.9 | -52.3 | 90.7 | | | | S3 | S2 | S4 | 2.01 | 1.17 | 2.54 | | | | |
| S3-18C | | 489.1 | -52.1 | 90.4 | | | | S3 | S2 | S4 | 2.07 | 1.14 | 2.67 | | | | |
| S4-15A | | 381.2 | -528.1 | -21.2 | | | | S4 | S3 | S2 | 0.18 | 1.58 | -1.22 | | | | |
| S4-15B | | 380.9 | -528.6 | -21.6 | | | | S4 | S3 | S2 | 0.72 | 1.56 | -1.21 | | | | |
| S4-15C | | 381.0 | -528.3 | -21.4 | | | | S4 | S3 | S2 | 0.45 | 1.57 | -1.22 | | | | |
| S4-16A | | 380.9 | -528.3 | -21.3 | | | | S4 | S3 | S2 | 0.97 | 1.59 | -1.23 | | | | |
| S4-16B | | 381.2 | -528.2 | -21.5 | | | | S4 | S3 | S2 | 0.67 | 1.60 | -1.20 | | | | |
| S4-16C | S4 | 381.0 | -528.3 | -21.4 | 381.0 | -528.3 | -21.4 | S4 | S3 | S2 | 0.82 | 1.60 | -1.22 | 0.016 | 0.203 | -0.270 | |
| S4-17A | | 381.4 | -527.2 | -21.4 | | | | S4 | S3 | S2 | 1.65 | 1.61 | -1.15 | | | | |
| S4-17B | | 380.7 | -529.3 | -21.3 | | | | S4 | S3 | S2 | 1.49 | 1.61 | -1.14 | | | | |
| S4-17C | | 381.1 | -528.2 | -21.4 | | | | S4 | S3 | S2 | 1.57 | 1.61 | -1.15 | | | | |
| S4-18A | | 380.8 | -528.3 | -21.7 | | | | S4 | S3 | S2 | 1.21 | 1.59 | -1.20 | | | | |
| S4-18B | | 381.2 | -528.6 | -21.1 | | | | S4 | S3 | S2 | 0.91 | 1.60 | -1.20 | | | | |
| S4-18C | | 381.0 | -528.5 | -21.4 | | | | S4 | S3 | S2 | 1.06 | 1.59 | -1.20 | | | | |
| S5-15A | | -2316.3 | 64.3 | -3.3 | | | | S5 | S3 | S4 | -7.43 | 0.00 | -0.03 | | | | |
| S5-15B | S5 | -2316.6 | 64.1 | -3.6 | -2316.5 | 64.2 | -3.4 | S5 | S3 | S4 | -8.25 | -0.02 | -0.04 | -0.174 | -0.056 | -0.012 | |
| S5-15C | | -2316.5 | 64.2 | -3.4 | | | | S5 | S3 | S4 | -7.84 | -0.01 | -0.04 | | | | |
| S5-16A | | -2316.4 | 64.2 | -3.4 | | | | S5 | S3 | S4 | -10.44 | -0.35 | -0.07 | | | | |

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|---|---|---|---|---|---|---|---|---|---|
| S5-16B | -2316.5 | 64.2 | -3.5 | S5 | S3 | S4 | -8.73 | -0.23 | -0.17 |
| S5-16C | -2316.5 | 64.2 | -3.4 | S5 | S3 | S4 | -9.59 | -0.29 | -0.12 |
| S5-17A | -2316.4 | 64.2 | -3.5 | S5 | S3 | S4 | -11.55 | -0.71 | 0.03 |
| S5-17B | -2316.5 | 64.2 | -3.4 | S5 | S3 | S4 | -12.12 | -0.71 | 0.09 |
| S5-17C | -2316.5 | 64.2 | -3.4 | S5 | S3 | S4 | -11.84 | -0.71 | 0.06 |
| S5-18A | -2316.5 | 64.1 | -3.5 | S5 | S3 | S4 | -11.87 | -0.65 | -0.19 |
| S5-18B | -2316.5 | 64.3 | -3.4 | S5 | S3 | S4 | -14.52 | -0.85 | -0.02 |
| S5-18C | -2316.5 | 64.2 | -3.5 | S5 | S3 | S4 | -13.20 | -0.75 | -0.11 |

[1]CDF - Canonical Discriminant Function Coefficients.

**Table S34. Information summary of PLS based only on the RPA of the 35 most predictive VOCs identified in samples from SCH processing stages during 2015-2018 production years.**

| Analysis | Component | $R^2X$ | Eigenvalues | $R^2Y$ | $Q^2$ | Significance | Iterations |
|---|---|---|---|---|---|---|---|
| PLS | 1 | 0.7686 | 30.743 | 0.0525 | 0.0339 | S | 4 |
| | 2 | 0.0991 | 3.965 | 0.0526 | 0.0187 | S | 9 |
| | 3 | 0.0558 | 2.230 | 0.0526 | 0.0232 | S | 3 |
| | 4 | 0.0409 | 1.636 | 0.0526 | 0.0280 | S | 4 |
| | 5 | 0.0105 | 0.421 | 0.0516 | 0.0288 | S | 12 |
| | 6 | 0.0094 | 0.374 | 0.0523 | 0.0367 | S | 14 |
| | 7 | 0.0063 | 0.251 | 0.0521 | 0.0733 | S | 10 |
| | 8 | 0.0026 | 0.103 | 0.0514 | 0.0204 | S | 11 |
| | 9 | 0.0018 | 0.070 | 0.0498 | 0.0458 | S | 17 |
| | 10 | 0.0012 | 0.048 | 0.0504 | 0.0531 | S | 10 |
| | 11 | 0.0008 | 0.030 | 0.0466 | 0.0089 | S | 10 |
| | 12 | 0.0006 | 0.024 | 0.0442 | 0.0339 | S | 11 |
| | 13 | 0.0003 | 0.013 | 0.0481 | 0.0260 | S | 29 |
| | 14 | 0.0003 | 0.011 | 0.0457 | 0.0337 | S | 32 |
| | 15 | 0.0003 | 0.010 | 0.0391 | 0.0400 | S | 23 |
| | 16 | 0.0004 | 0.011 | 0.0285 | -0.0687 | NS | 22 |

**Table S35. 1 ID replicate number, ID replicate code, ID sample code, ID group code, processing year, processing type, geographic origin and regional certification of SC-based syrups samples.**

| ID Replicate Number | ID Replicate Code | ID Sample Code | ID Group Code | Processing Year | Processing Type | Geographic Origin | Regional Certification |
|---|---|---|---|---|---|---|---|
| 1 | FRS07A | | | | | | |
| 2 | FRS07B | FRS07 | CERT | 2007 | Industrial | Madeira Island, Portugal, Atlantic Region | Certified |
| 3 | FRS07C | | | | | | |
| 4 | FRS13A | | | | | | |
| 5 | FRS13B | FRS13 | CERT | 2013 | Industrial | Madeira Island, Portugal, Atlantic Region | Certified |
| 6 | FRS13C | | | | | | |
| 7 | FRS14A | | | | | | |
| 8 | FRS14B | FRS14 | CERT | 2014 | Industrial | Madeira Island, Portugal, Atlantic Region | Certified |
| 9 | FRS14C | | | | | | |
| 10 | FRS15A | | | | | | |
| 11 | FRS15B | FRS15 | CERT | 2015 | Industrial | Madeira Island, Portugal, Atlantic Region | Certified |
| 12 | FRS15C | | | | | | |
| 13 | FRS16A | | | | | | |
| 14 | FRS16B | FRS16 | CERT | 2016 | Industrial | Madeira Island, Portugal, Atlantic Region | Certified |
| 15 | FRS16C | | | | | | |
| 16 | FRS17A | | | | | | |
| 17 | FRS17B | FRS17 | CERT | 2017 | Industrial | Madeira Island, Portugal, Atlantic Region | Certified |
| 18 | FRS17C | | | | | | |
| 19 | FRS18A | | | | | | |
| 20 | FRS18B | FRS18 | CERT | 2018 | Industrial | Madeira Island, Portugal, Atlantic Region | Certified |
| 21 | FRS18C | | | | | | |
| 22 | ECAL14A | | | | | | |
| 23 | ECAL14B | ECAL14 | NCERT | 2014 | Industrial | Madeira Island, Portugal, Atlantic Region | Non-Certified |
| 24 | ECAL14C | | | | | | |
| 25 | ENCAL14A | | | | | | |
| 26 | ENCAL14B | ENCAL14 | NCERT | 2014 | Industrial | Madeira Island, Portugal, Atlantic Region | Non-Certified |
| 27 | ENCAL14C | | | | | | |
| 28 | GLA14A | ECAL16 | NCERT | 2014 | Home-made | | Non-Certified |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 29 | GLA14B | | | | | Madeira Island, Portugal, Atlantic Region | |
| 30 | GLA14C | | | | | | |
| 31 | ESP16A | | | | | | |
| 32 | ESP16B | ESP16 | MED | 2016 | Industrial | Spain, Mediterranean Region | Not Applicable |
| 33 | ESP16C | | | | | | |
| 34 | EGP17A | | | | | | |
| 35 | EGP17B | EGP17 | MED | 2017 | Industrial | Spain, Mediterranean Region | Not Applicable |
| 36 | EGP17C | | | | | | |
| 37 | EGPA16A | | | | | | |
| 38 | EGPA16B | EGPA16 | MED | 2016 | Industrial | Spain, Mediterranean Region | Not Applicable |
| 39 | EGPA16C | | | | | | |
| 40 | EGPB16A | | | | | | |
| 41 | EGPB16B | EGPB16 | MED | 2016 | Industrial | Spain, Mediterranean Region | Not Applicable |
| 42 | EGPB16C | | | | | | |
| 43 | EGPC16A | | | | | | |
| 44 | EGPC16B | EGPC16 | MED | 2016 | Industrial | Egypt, Mediterranean Region | Not Applicable |
| 45 | EGPC16C | | | | | | |
| 46 | MCBR14A | | | | | | |
| 47 | MCBR14B | MCBR14 | STH | 2014 | Industrial | Brazil, Southern Hemisphere Region | Not Applicable |
| 48 | MCBR14C | | | | | | |
| 49 | MDBR14A | | | | | | |
| 50 | MDBR14B | MDBR14 | STH | 2014 | Industrial | Brazil, Southern Hemisphere Region | Not Applicable |
| 51 | MDBR14C | | | | | | |
| 52 | AUS17A | | | | | | |
| 53 | AUS17B | AUS17 | STH | 2017 | Industrial | Australia, Southern Hemisphere Region | Not Applicable |
| 54 | AUS17C | | | | | | |

**Table S36. ID number, retention time, main ions (m/z), target ion, match percent, IUPAC name, NIST database, abbreviation, CAS number, molecular formula and main chemical class of identified VOCs in SC-based syrups samples.**

| ID Number | RT (min) | m/z | Target Ion | Match Percent (%) | IUPAC Name | NIST Database Name | Abbreviations | CAS Number | Molecular Formula | Main Chemical Class |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 4.253 | 43; 42; 41 | 43 | 86 | pentane | Pentane | PTANE | 109-66-0 | C5H12 | Hydrocarbon |
| 2 | 4.518 | 57; 41; 56 | 57 | 84 | hexane | Hexane | HXANE | 110-54-3 | C6H14 | Hydrocarbon |
| 3 | 4.586 | 67; 68; 53 | 67 | 90 | penta-1,4-diene | 1,4-Pentadiene | PT14DIENE | 591-93-5 | C5H8 | Hydrocarbon |
| 4 | 4.709 | 47; 48; 45 | 47 | 87 | methanethiol | Methanethiol | METHIOL | 74-93-1 | CH4S | Sulfur |
| 5 | 4.903 | 44; 43; 42 | 44 | 88 | acetaldehyde | Ethanal | ETAL | 75-07-0 | C2H4O | Aldehyde |
| 6 | 5.282 | 47; 62; 45 | 47 | 97 | methylsulfanylmethane | Dimethyl Sulfide | DMSULFI | 75-18-3 | C2H6S | Sulfur |
| 7 | 5.713 | 58; 57; 59 | 58 | 79 | propanal | Propanal | PPAL | 123-38-6 | C3H6O | Aldehyde |
| 8 | 5.830 | 68; 39; 40 | 68 | 91 | furan | Furan | FUR | 110-00-9 | C4H4O | Furan |
| 9 | 6.041 | 43; 41; 72 | 72 | 86 | 2-methylpropanal | 2-Methyl-Propanal | MPPAL | 78-84-2 | C4H8O | Aldehyde |
| 10 | 6.255 | 31; 45; 74 | 31 | 80 | ethyl formate | Ethyl Formate | EESTFA | 109-94-4 | C3H6O2 | Ester |
| 11 | 6.632 | 56; 55; 37 | 56 | 78 | prop-2-enal | 2-Propenal | PPENAL | 107-02-8 | C3H4O | Aldehyde |
| 12 | 7.199 | 82; 53; 81 | 82 | 94 | 2-methylfuran | 2-Methyl-Furan | M2FUR | 534-22-5 | C5H6O | Furan |
| 13 | 7.591 | 43; 61; 70 | 43 | 90 | ethyl acetate | Ethyl Acetate | EESTAA | 141-78-6 | C4H8O2 | Ester |
| 14 | 7.906 | 43; 72; 57 | 72 | 78 | butan-2-one | 2-Butanone | BT2ONE | 78-93-3 | C4H8O | Ketone |
| 15 | 8.338 | 57; 41; 58 | 57 | 86 | 2-methylbutanal | 2-Methyl-Butanal | M2BTAL | 96-17-3 | C5H10O | Aldehyde |
| 16 | 8.494 | 44; 41, 43 | 41 | 93 | 3-methylbutanal | 3-Methyl-Butanal | M3BTAL | 590-86-3 | C5H10O | Aldehyde |
| 17 | 8.946 | 31; 45; 46 | 31 | 78 | ethanol | Ethanol | ETOL | 64-17-5 | C2H6O | Alcohol |
| 18 | 9.379 | 78; 77; 52 | 78 | 83 | Benzene | Benzene | BNZ | 71-43-2 | C6H6 | Benzene |
| 19 | 9.569 | 55; 43; 70 | 55 | 80 | but-3-en-2-one | 3-Buten-2-one | BT3ONE | 78-94-4 | C4H6O | Ketone |
| 20 | 10.058 | 96; 95; 43 | 96 | 94 | 2,5-dimethylfuran | 2,5-Dimethyl-Furan | DM25FUR | 625-86-5 | C6H8O | Furan |
| 21 | 10.190 | 57; 75; 102 | 57 | 82 | ethyl propanoate | Ethyl Propanoate | EESTPA | 105-37-3 | C5H10O2 | Ester |
| 22 | 11.412 | 43; 86; 41 | 86 | 80 | butane-2,3-dione | 2,3-Butanedione | BT23DONE | 431-03-8 | C4H6O2 | Ketone |
| 23 | 12.557 | 43; 56; 73 | 56 | 82 | 2-methylpropyl acetate | 2-Methylpropyl Acetate | MP2ESTAA | 110-19-0 | C6H12O2 | Ester |
| 24 | 14.801 | 31; 59; 42 | 31 | 80 | propan-1-ol | 1-Propanol | P1POL | 71-23-8 | C3H8O | Alcohol |
| 25 | 14.903 | 95; 110; 43 | 95 | 86 | 2-ethyl-5-methylfuran | 2-Ethyl-5-Methyl-Furan | E2M5FUR | 1703-52-2 | C7H10O | Furan |
| 26 | 15.111 | 91; 92; 65 | 91 | 94 | toluene | Toluene | TOLNE | 108-88-3 | C7H8 | Benzene |
| 27 | 15.268 | 43; 71; 88 | 88 | 84 | ethyl butanoate | Ethyl Butanoate | EESTBA | 105-54-4 | C6H12O2 | Ester |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 28 | 15.327 | 71; 43; 59 | 71 | 78 | 2-methylbut-3-en-2-ol | 2-Methyl-3-Buten-2-ol | M3BT2OL | 115-18-4 | C5H10O | Alcohol |
| 29 | 16.166 | 101; 55; 73 | 101 | 82 | nonomethyl succinate | Nonomethyl Succinate | METESTBA | 3878-55-5 | C5H8O4 | Ester |
| 30 | 17.382 | 43; 57; 100 | 57 | 83 | pentane-2,3-dione | 2,3-Pentanedione | PTDONE | 600-14-6 | C5H8O2 | Ketone |
| 31 | 18.081 | 94; 45; 79 | 94 | 90 | (methyldisulfanyl)methane | Dimethyl Disulfide | DMDSFD | 624-92-0 | C2H6S2 | Sulfur |
| 32 | 18.284 | 94; 65; 39 | 94 | 78 | 2-ethenylfuran | 2-Ethenyl-Furan | ENYL2FUR | 1487-18-9 | C6H6O | Furan |
| 33 | 18.723 | 81; 99; 55 | 81 | 83 | 2,5-diethyloxolane | 2,5-Diethyltetrahydro-Furan | DE25TTHYFUR | 41239-48-9 | C8H16O | Furan |
| 34 | 18.905 | 44; 56; 43 | 44 | 94 | hexanal | Hexanal | HXAL | 66-25-1 | C6H12O | Aldehyde |
| 35 | 21.231 | 43; 42; 41 | 43 | 90 | 2-methylpropan-1-ol | 2-Methyl-1-Propanol | M2PP1OL | 78-83-1 | C4H10O | Alcohol |
| 36 | 25.551 | 85; 41; 56 | 85 | 80 | 5-butyloxolan-2-one | 5-Butyl-Dihydro-2(3H)-Furanone | BDH2FURONE | 104-50-7 | C8H14O2 | Furan |
| 37 | 27.262 | 108; 107; 77 | 108 | 80 | 3-methylphenol | m-Cresol | MCREOL | 108-39-4 | C7H8O | Phenol |
| 38 | 27.966 | 56; 31; 41 | 56 | 80 | butan-1-ol | 1-Butanol | BT1OL | 71-36-3 | C4H10O | Alcohol |
| 39 | 28.085 | 85; 56; 41 | 85 | 82 | 5-propyloxolan-2-one | 5-Propyl-Dihydro-2(3H)-Furanone | PDH2FURONE | 105-21-5 | C7H12O2 | Furan |
| 40 | 29.054 | 94; 39; 65 | 94 | 87 | 3-methylpyridazine | 3-Methyl-Pyridazine | M3PYRDZNE | 1632-76-4 | C5H6N2 | Nitrogen |
| 41 | 29.851 | 43; 58; 71 | 58 | 91 | heptan-2-one | 2-Heptanone | HPT2ONE | 110-43-0 | C7H14O | Ketone |
| 42 | 32.080 | 95; 138; 67 | 95 | 85 | 1-methyl-3-propan-2-ylcyclohexane | m-Menthane | MMTHANE | 16580-24-8 | C10H20 | Terpenoid |
| 43 | 32.436 | 80; 53; 52 | 80 | 80 | pyrimidine | 1,3-Diazine | D13ZINE | 289-95-2 | C4H4N2 | Nitrogen |
| 44 | 32.630 | 57; 41; 56 | 57 | 83 | 2-methylbutan-1-ol | 2-Methyl-1-Butanol | M2BT1OL | 137-32-6 | C5H12O | Alcohol |
| 45 | 33.174 | 82; 53; 81 | 82 | 90 | 2-propylfuran | 2-Propyl-Furan | PP2FUR | 4229-91-8 | C7H10O | Furan |
| 46 | 34.163 | 88; 43; 99 | 88 | 83 | ethyl hexanoate | Ethyl Hexanoate | EESTHA | 123-66-0 | C8H16O2 | Ester |
| 47 | 34.394 | 81; 82; 138 | 81 | 94 | 2-pentylfuran | 2-Pentyl-Furan | PT2FUR | 3777-69-3 | C9H14O | Furan |
| 48 | 36.565 | 94; 67; 53 | 94 | 81 | 2-methylpyrazine | 2-Methyl-Pyrazine | MPYZNE | 109-08-0 | C5H6N | Nitrogen |
| 49 | 37.622 | 43; 72; 100 | 72 | 91 | 2-methyloxolan-3-one | 2-Methyl-Dihydro-2(3H)-Furanone | MDH2FURONE | 3188-00-9 | C5H8O2 | Furan |
| 50 | 37.261 | 119; 134; 91 | 119 | 84 | 1-methyl-4-propan-2-ylbenzene | p-Cymene | PCYMNE | 99-87-6 | C10H14 | Terpenoid |
| 51 | 37.369 | 105; 120; 77 | 105 | 95 | 1,3,5-trimethylbenzene | Mesitylene | MESTLNE | 108-67-8 | C9H12 | Benzene |
| 52 | 38.007 | 122; 107; 121 | 122 | 80 | 3,5-dimethylphenol | 3,5-Xylenol | XYL35NOL | 108-68-9 | C8H10O | Phenol |
| 53 | 38.238 | 45; 43; 88 | 45 | 90 | 3-hydroxybutan-2-one | 3-Hydroxy-2-Butanone | HXY3BT2ONE | 513-86-0 | C4H8O2 | Ketone (Alcohol) |
| 54 | 38.261 | 86; 42; 58 | 86 | 82 | 1,3-dioxol-2-one | Vinylene Carbonate | VYLESTCA | 96-49-1 | C3H4O3 | Ester (Ketone) |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 55 | 38.738 | 122; 107; 121 | 122 | 82 | 2,6-dimethylphenol | 2,6-Xylenol | XYL26NOL | 576-26-1 | C8H10O | Phenol |
| 56 | 39.324 | 43; 31; 74 | 43 | 90 | 1-hydroxypropan-2-one | 1-Hydroxy-2-Propanone | HXY1PP2ONE | 116-09-6 | C3H6O2 | Ketone (Alcohol) |
| 57 | 40.500 | 108; 42; 40 | 108 | 80 | 2,5-dimethylpyrazine | 2,5-Dimethyl-Pyrazine | DM25PYZNE | 123-32-0 | C6H8N2 | Nitrogen |
| 58 | 40.910 | 108; 42; 40 | 108 | 90 | 2,6-dimethylpyrazine | 2,6-Dimethyl-Pyrazine | DM26PYZNE | 108-50-9 | C6H8N2 | Nitrogen |
| 59 | 42.422 | 82; 39; 54 | 82 | 91 | cyclopent-2-en-1-one | 2-Cyclopenten-1-one | CY2PT1EONE | 930-30-3 | C5H6O | Ketone |
| 60 | 41.788 | 159; 174; 144 | 159 | 82 | 1,2,3,4-tetramethyl-5-prop-1-en-2-ylbenzene | 1,2,3,4-Tetramethyl-4-(1-methylethenyl)-Benzene | TM4MEYL1BNZ | 61142-76-5 | C13H20 | Benzene |
| 61 | 43.239 | 67; 96; 53 | 67 | 83 | 2-methylcyclopent-2-en-1-one | 2-Methyl-2-Cyclopenten-1-one | M2CY2PT1EONE | 1120-73-6 | C6H8O | Ketone |
| 62 | 43.444 | 95; 43; 96 | 95 | 80 | (5-methylfuran-2-yl)methanethiol | 5-Methyl-2-Furanmethanethiol | M2FURTHOL | 59303-05-8 | C6H8OS | Furan (Sulfur) |
| 63 | 43.682 | 57; 88; 56 | 57 | 79 | 1-hydroxybutan-2-one | 1-Hydroxy-2-Butanone | H1BT2ONE | 5077-67-8 | C4H8O2 | Ketone (Alcohol) |
| 64 | 44.389 | 121; 122; 39 | 121 | 80 | 2-ethyl-6-methylpyrazine | 2-Ethyl-6-Methyl-Pyrazine | E6MPYZNE | 13925-03-6 | C7H10N2 | Nitrogen |
| 65 | 44.691 | 121; 122; 39 | 121 | 77 | 2-ethyl-5-methylpyrazine | 2-Ethyl-5-Methyl-Pyrazine | E5MPYZNE | 13360-64-0 | C7H10N2 | Nitrogen |
| 66 | 45.234 | 57; 41; 43 | 57 | 93 | nonanal | Nonanal | NONAL | 124-19-6 | C9H18O | Aldehyde |
| 67 | 45.745 | 42; 122; 81 | 122 | 78 | 2,3,5-trimethylpyrazine | Trimethyl-Pyrazine | TMPYZNE | 14667-55-1 | C7H10N2 | Nitrogen |
| 68 | 45.956 | 67; 95; 124 | 67 | 81 | (3E)-3-ethyl-2-methylhexa-1,3-diene | 3-Ethyl-2-Methyl-1,3-Hexadiene | E3M2HX13DENE | 61142-36-7 | C9H16 | Terpene |
| 69 | 46.726 | 68; 96; 40 | 68 | 82 | cyclohex-2-en-1-one | 2-Cyclohexen-1-one | C2HEXONE | 930-68-7 | C6H8O | Ketone |
| 70 | 46.901 | 55; 43; 98 | 55 | 87 | 2-methyl-2H-furan-5-one | 5-Methyl-2(3H)-Furanone | M5FURONE | 591-12-8 | C5H6O2 | Furan |
| 71 | 47.214 | 98; 42; 69 | 98 | 84 | 4-methyl-1,3-dihydroimidazol-2-one | 1,3-Dihydro-4-Methyl-2H-Imidazol-2-one | M4IMDZONE | 214-751-9 | C4H6N2O | Nitrogen (Ketone) |
| 72 | 47.569 | 88; 101; 57 | 88 | 89 | ethyl octanoate | Ethyl Octanoate | EESTOA | 106-32-1 | C10H20O2 | Ester |
| 73 | 47.861 | 159; 174; 131 | 159 | 94 | 1,2,3,4-tetrahydro-1,1,6-trimethylnaphthalene | 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | T116TNP | 475-03-6 | C13H18 | Naphthalene |
| 74 | 48.559 | 96; 95; 39 | 96 | 96 | 2-furanaldehyde | Furfural | FURAL | 98-01-1 | C5H4O2 | Furan (Aldehyde) |
| 75 | 49.502 | 43; 45; 60 | 43 | 90 | Acetic Acid | Ethanoic Acid | ETNOIC | 64-19-7 | C2H4O2 | Carboxylic Acid |
| 76 | 49.783 | 159; 174; 131 | 159 | 96 | 1,2,3,4-tetrahydro-1,6,8-trimethylnaphthalene | 1,2,3,4-Tetrahydro-1,6,8-Trimethyl-Naphthalene | T168TNP | 30316-36-0 | C13H18 | Naphthalene |
| 77 | 50.004 | 57; 41; 55 | 57 | 82 | 2-ethylhexan-1-ol | 2-Ethyl-1-Hexanol | E2HX1OL | 104-76-7 | C8H18O | Alcohol |
| 78 | 50.131 | 110; 109; 53 | 110 | 92 | 3-methyl-2-furanaldehyde | 3-Methyl-Furfural | M3FURAL | 33342-48-2 | C6H6O2 | Furan (Aldehyde) |
| 79 | 50.259 | 81; 53; 126 | 81 | 82 | furan-2-ylmethyl formate | Furfuryl Formate | FURYLFMTE | 13493-97-5 | C6H6O3 | Furan (Ester) |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 80 | 50.655 | 57; 43; 55 | 57 | 93 | decanal | Decanal | DECAL | 112-31-2 | C10H2O | Aldehyde |
| 81 | 50.895 | 95; 110; 39 | 95 | 91 | 1-(furan-2-yl)ethanone | 1-(2-Furanyl)-Ethanone | FURYLONE | 1192-62-7 | C6H6O2 | Furan (Ketone) |
| 82 | 51.329 | 106; 105; 77 | 106 | 95 | benzaldehyde | Benzaldehyde | BENZAL | 100-52-7 | C7H6O | Benzene (Aldehyde) |
| 83 | 51.771 | 81; 98; 52 | 81 | 95 | furan-2-ylmethyl acetate | Furfuryl Acetate | FURYLACTE | 623-17-6 | C7H8O3 | Furan (Ester) |
| 84 | 52.336 | 74; 45; 73 | 74 | 90 | propanoic acid | Propanoic Acid | PPANOIC | 79-09-4 | C3H6O2 | Carboxylic Acid |
| 85 | 53.078 | 63; 78; 45 | 63 | 91 | methylsulfinylmethane | Dimethyl Sulfoxide | DMSULFO | 67-68-5 | C2H6OS | Sulfur |
| 86 | 53.245 | 159; 174; 131 | 159 | 94 | 1,2,3,4-tetrahydro-1,5,8-trimethylnaphthalene | 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | T158TNP | 21693-51-6 | C13H18 | Naphthalene |
| 87 | 53.657 | 110; 109; 53 | 110 | 94 | 5-methyl-2-furanaldehyde | 5-Methyl-Furfural | M5FURAL | 620-02-0 | C6H6O2 | Furan (Aldehyde) |
| 88 | 54.207 | 96; 42; 68 | 96 | 91 | cyclopent-4-ene-1,3-dione | 4-Cyclopentene-1,3-dione | CPT4E13DONE | 930-60-9 | C5H4O2 | Ketone |
| 89 | 54.861 | 131; 132; 103 | 131 | 97 | 2-methyl-1-benzofuran | 2-Methyl-Benzofuran | M2BNZFUR | 4265-25-2 | C9H8O | Benzofuran |
| 90 | 55.678 | 109; 124; 81 | 109 | 80 | 1-(5-methylfuran-2-yl)ethanone | 1-(5-Methyl-2-Furanyl)-Ethanone | M5FURYLONE | 1193-79-9 | C7H8O2 | Furan (Ketone) |
| 91 | 55.835 | 45; 59; 72 | 45 | 90 | 2-(2-ethoxyethoxy)ethanol | Diethylene Glycol Ethyl Ether | DENGOLEETHR | 111-90-0 | C6H14O3 | Ether (Alcohol) |
| 92 | 56.251 | 42; 41; 56 | 42 | 82 | 3-methyloxolan-3-one | 3-Methyl-Dihydro-2(3H)-Furanone | M3DHFURONE | 1679-47-6 | C5H8O2 | Furan (Lactone) |
| 93 | 56.693 | 159; 174; 128 | 159 | 86 | 3,3,5,7-tetramethyl-1,2-dihydroindene | 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | DHT1146MIDNE | 941-60-6 | C13H18 | Indene |
| 94 | 57.065 | 91; 92; 120 | 91 | 90 | 2-phenylacetaldehyde | Benzeneacetaldehyde | BENZACETAL | 122-78-1 | C8H8O | Benzene (Aldehyde) |
| 95 | 57.117 | 69; 41; 112 | 91 | 87 | 2,4-dimethyl-2H-furan-5-one | 3,5-Dimethyl-Dihydro-2-Furanone | DM35DHFURONE | 5584-69-0 | C6H8O2 | Furan (Lactone) |
| 96 | 57.323 | 72; 55; 45 | 72 | 78 | prop-2-enoic acid | 2-Propenoic Acid | PPE2NOIC | 79-10-7 | C3H4O2 | Carboxylic Acid |
| 97 | 57.337 | 88; 101; 73 | 88 | 89 | ethyl decanoate | Ethyl Decanoate | EESTDA | 110-38-3 | C12H24O2 | Ester |
| 98 | 57.354 | 105; 77; 51 | 105 | 87 | 1-phenylethanone | Acetophenone | ACETPHONE | 98-86-2 | C8H8O | Benzene (Ketone) |
| 99 | 57.744 | 98; 41; 81 | 98 | 98 | furan-2-ylmethanol | 2-Furanmethanol | FUR2OL | 98-00-0 | C5H6O2 | Furan (Alcohol) |
| 100 | 57.981 | 98; 41; 97 | 97 | 93 | furan-3-ylmethanol | 3-Furanmethanol | FUR3OL | 4412-91-3 | C5H6O2 | Furan (Alcohol) |
| 101 | 58.675 | 159; 128; 144 | 159 | 86 | 3,3,5,6-tetramethyl-1,2-dihydroindene | 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | DHT1156MIDNE | 942-43-8 | C13H18 | Indene |
| 102 | 58.897 | 162; 91; 43 | 162 | 91 | 2-(2-furylmethyl)-5-methylfuran | 2-(2-Furanylmethyl)-5-Methyl-Furan | FURYLMFUR | 13678-51-8 | C10H10O2 | Furan |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 103 | 60.229 | 41; 69; 98 | 41 | 83 | 4-methyl-2H-furan-5-one | 3-Methyl-2(5H)-Furanone | M3FURONE | 22122-36-7 | C5H6O2 | Furan (Lactone) |
| 104 | 60.456 | 95; 112; 43 | 95 | 93 | (5-methylfuran-2-yl)methanol | 5-Methyl-2-Furanmethanol | M5FUR2OL | 3857-25-8 | C6H8O2 | Furan (Alcohol) |
| 105 | 60.947 | 108; 91; 90 | 108 | 75 | benzyl acetate | Benzyl Acetate | PMESTAA | 140-11-4 | C9H10O2 | Benzene (Ester) |
| 106 | 61.749 | 55; 84; 54 | 55 | 80 | 2H-furan-5-one | 2(5H)-Furanone | FURONE | 497-23-4 | C4H4O2 | Furan (Lactone) |
| 107 | 62.073 | 176; 43; 161 | 176 | 96 | 2-methyl-5-[(5-methylfuran-2-yl)methyl]furan | 2,2'-Methylenebis[5-Methyl-Furan | MNEB5MFUR | 13679-43-1 | C10H10O2 | Furan |
| 108 | 62.421 | 98; 55; 42 | 98 | 90 | cyclopentane-1,2-dione | 1,2-Cyclopentanedione | CPT12DONE | 3008-40-0 | C5H6O2 | Ketone |
| 109 | 63.971 | 70; 39; 41 | 70 | 84 | cyclohex-2-en-1-ol | 2-Cyclohexenol | CHEX2E1OL | 822-67-3 | C6H10O | Alcohol |
| 110 | 64.539 | 104; 43; 91 | 104 | 84 | 2-phenylethyl acetate | 2-Phenylethyl Acetate | PEESTAA | 103-45-7 | C10H12O2 | Benzene (Ester) |
| 111 | 64.803 | 112; 69; 41 | 112 | 93 | 3-methylcyclopentane-1,2-dione | 3-Methyl-1,2-Cyclopentanedione | M3CPT12DONE | 765-70-8 | C6H8O2 | Ketone |
| 112 | 64.824 | 73; 88; 41 | 73 | 89 | 2-ethylhexanoic acid | 2-Ethyl-Hexanoic Acid | E2HXNOIC | 149-57-5 | C8H16O2 | Carboxylic Acid |
| 113 | 64.922 | 69; 121; 41 | 69 | 96 | 1-(2,6,6-trimethylcyclohexa-1,3-dien-1-yl)but-2-en-1-one | β-Damascenone | DAMSNONE | 23726-93-4 | C13H18O | Terpenoid (Ketone) |
| 114 | 65.265 | 88; 101; 73 | 88 | 80 | ethyl undecanoate | Ethyl Undecanoate | EESTUNDA | 627-90-7 | C13H26O2 | Ester |
| 115 | 65.660 | 43; 41; 73 | 43 | 79 | 2-methylpropanoic acid | 2-Methyl-Propanoic Acid | M2PPOICA | 79-31-2 | C4H8O2 | Carboxylic Acid |
| 116 | 65.986 | 128; 57; 85 | 128 | 77 | 1,3-diazinane-2,4,6-trione | 2,4,6-Trihydroxypyrimidine | THDXYPYMNE | 67-52-7 | C4H4N2O3 | Nitrogen |
| 117 | 66.118 | 109; 124, 81 | 109 | 90 | 4-methoxyphenol | Mequinol | MEQNOL | 150-76-5 | C7H8O2 | Phenol (Ether) |
| 118 | 66.384 | 114; 58; 57 | 114 | 84 | 2,2-diethyl-3-methyl-1,3-oxazolidine | 2,2-Diethyl-3-Methyl-Oxazolidine | DEMOXZDNE | | C8H17NO | Nitrogen |
| 119 | 66.461 | 109; 152, 52 | 109 | 82 | 1,7-dihydropyrazolo[3,4-d]pyrimidine-4,6-dione | Oxypurinol | OXYPUROL | 2465-59-0 | C5H4N4O2 | Nitrogen |
| 120 | 66.688 | 79; 108; 77 | 79 | 92 | phenylmethanol | Benzenemethanol | BENZMTOL | 100-51-6 | C7H8O | Benzene (Alcohol) |
| 121 | 67.106 | 69; 41; 39 | 69 | 87 | 3-methyl-2H-furan-5-one | 4-Methyl-2(5H)-Furanone | M4FUR2ONE | 6124-79-4 | C5H6O2 | Furan (Lactone) |
| 122 | 67.293 | 126; 55; 83 | 126 | 95 | 3-ethyl-2-hydroxycyclopent-2-en-1-one | 3-Ethyl-2-Hydroxy-2-Cyclopenten-1-one | E3H2C2PT1ONE | 21835-01-8 | C7H10O2 | Ketone (Alcohol) |
| 123 | 68.036 | 91; 92; 122 | 91 | 78 | 2-phenylethanol | Benzeneethanol | BENZETOL | 60-12-8 | C8H10O | Benzene (Alcohol) |
| 124 | 68.580 | 44; 71; 55 | 44 | 80 | prop-2-enamide | Acrylamide | ACRYLMDE | 79-06-1 | C3H5NO | Nitrogen |
| 125 | 68.698 | 61; 44; 43 | 61 | 79 | (2S,3R)-butane-1,2,3,4-tetrol | Erythritol | ERYTOL | 149-32-6 | C4H10O4 | Alcohol (Polyol) |

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|---|---|---|---|---|---|---|---|---|---|---|
| 126 | 68.890 | 112; 111; 39 | 112 | 80 | 2,3-dimethyl-1H-pyrazol-5-one | 2,3-Dimethyl-3-Pyrazolin-5-one | DM23PYZLONE | 3201-28-3 | C5H8N2O | Nitrogen |
| 127 | 69.323 | 136; 121; 65 | 136 | 87 | (E)-4-(furan-2-yl)but-3-en-2-one | Furfural Acetone | FURALTONE | 623-15-4 | C8H8O2 | Furan (Ketone) |
| 128 | 69.469 | 112; 69; 55 | 112 | 85 | 2-hydroxy-3-methylcyclopent-2-en-1-one | Cyclotene | CYTENE | 80-71-7 | C6H8O2 | Ketone (Alcohol) |
| 129 | 69.557 | 124; 95; 107 | 124 | 80 | 2-methylbenzene-1,4-diol | 2-Methyl-1,4-Benzenediol | M2BNZ14DIOL | 95-71-6 | C7H8O2 | Benzene (Alcohol) |
| 130 | 69.706 | 73; 60; 41 | 73 | 77 | heptanoic Acid | Heptanoic Acid | HPTOIC | 111-14-8 | C7H14O2 | Carboxylic Acid |
| 131 | 69.883 | 126; 71; 43 | 126 | 95 | 3-hydroxy-2-methylpyran-4-one | Maltol | MALTOL | 118-71-8 | C6H6O3 | Pyran |
| 132 | 70.149 | 94; 109; 66 | 94 | 95 | 1-(1H-pyrrol-2-yl)ethanone | 2-Acetylpyrrole | ACTLPYROLE | 1072-83-9 | C6H7NO | Nitrogen (Pyrrole) |
| 133 | 70.504 | 124; 123; 95 | 124 | 91 | furan-2,5-dicarbaldehyde | 2,5-Furandicarboxaldehyde | FUR25DIAL | 823-82-5 | C6H4O3 | Furan (Aldehyde) |
| 134 | 70.953 | 112; 55; 84 | 112 | 80 | 3H-pyran-2,6-dione | 2H-Pyran-2,6(3H)-Dione | PYR26DIONE | 5926-95-4 | C5H4O3 | Pyran |
| 135 | 71.427 | 95; 126; 67 | 95 | 84 | 1,3-bis(furan-2-yl)-1,3-dihydroxypropan-2-one | 1-(2-Furanyl)-2-Hydroxy-Ethanone | H2FURYLONE | 17678-19-2 | C6H6O3 | Furan (Ketone) |
| 136 | 71.638 | 94; 66; 65 | 94 | 89 | phenol | Phenol | PHEOL | 108-95-2 | C6H6O | Phenol |
| 137 | 72.019 | 95; 94; 66 | 95 | 84 | 1H-pyrrole-2-carbaldehyde | 1H-Pyrrole-2-Carboxaldehyde | PYRLE2AL | 1003-29-8 | C5H5NO | Nitrogen (Pyrrole) |
| 138 | 72.070 | 126; 69; 85 | 126 | 79 | benzene-1,3,5-triol | Phloroglucinol | PHLOGLNOL | 108-73-6 | C6H6O3 | Phenol |
| 139 | 72.219 | 43; 57; 128 | 43 | 91 | 4-hydroxy-2,5-dimethylfuran-3-one | Furaneol | FUREOL | 3658-77-3 | C6H8O3 | Furan (Ketone) |
| 140 | 72.823 | 60; 73; 43 | 60 | 84 | octanoic acid | Octanoic Acid | OCTOIC | 124-07-2 | C8H16O2 | Carboxylic Acid |
| 141 | 73.300 | 85; 43; 57 | 85 | 78 | 5-acetyloxolan-2-one | 5-Acetyl-Dihydro-2(3H)-Furanone | ACYLDHFURONE | 29393-32-6 | C6H8O3 | Furan (Lactone) |
| 142 | 73.838 | 81; 140; 53 | 81 | 80 | 3-(furan-2-yl)propanoic acid | 2-Furanpropionic Acid | FURPPIONIC | 935-13-7 | C7H8O3 | Furan (Acid) |
| 143 | 74.038 | 31; 43; 42, 60 | 31 | 83 | 1,3-dihydroxypropan-2-one | 1,3-Dihydroxy-2-Propanone | DHYPPAONE | 96-26-4 | C3H6O3 | Ketone (Alcohol) |
| 144 | 74.258 | 85; 43; 41 | 85 | 82 | [(2S,5R)-5-methyloxolan-2-yl]methanol | Tetrahydro-5-Methyl-2-Furanmethanol | TEHYMFUROL | 6126-49-4 | C6H12O2 | Furan (Alcohol) |
| 145 | 74.965 | 43; 55; 114 | 55 | 79 | 4,5-dimethyl-1,3-dioxol-2-one | 4,5-Dimethyl Vinylene Carbonate | DM45VYLESTCA | 37830-90-3 | C5H6O3 | Ester (Ketone) |
| 146 | 76.832 | 57; 58; 44 | 57 | 83 | 3-hydroxyoxolan-2-one | 2-Hydroxy-Dihydro-2(3H)-Furanone | HY2DHFURONE | 19444-84-9 | C4H6O3 | Furan (Lactone) |
| 147 | 77.493 | 126; 43; 79 | 126 | 87 | (5-formylfuran-2-yl)methyl acetate | 5-Acetoxymethyl-2-Furfural A | ACTYMFURALA | 10551-58-3 | C8H8O4 | Furan (Aldehyde / Ether) |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 148 | 77.713 | 126; 43; 79 | 126 | 90 | (5-formylfuran-2-yl)methyl acetate | 5-Acetoxymethyl-2-Furfural B | ACTYMFURALB | 10551-58-3 | C8H8O4 | Furan (Aldehyde / Ether) |
| 149 | 77.842 | 135; 150; 77 | 135 | 86 | 4-ethenyl-2-methoxyphenol | 2-Methoxy-4-Vinyl-Phenol | MXY2VYL4PHEOL | 7786-61-0 | C9H10O2 | Phenol (Ether) |
| 150 | 78.094 | 56; 114; 42 | 56 | 82 | 3-methyloxolane-2,4-dione | 3-Methyl-2,4(3H,5H)-Furandione | M3FURDIONE | 616-02-4 | C5H4O3 | Furan (Lactone) |
| 151 | 79.890 | 43; 42; 144 | 43 | 94 | 3,5-dihydroxy-6-methyl-2,3-dihydropyran-4-one | 3-Hydroxy-2,3-Dihydro-Maltol | HX3DH23MALTOL | 28564-83-2 | C6H8O4 | Pyran (Alcohol / Ether) |
| 152 | 80.260 | 60; 73; 41 | 60 | 91 | decanoic acid | Decanoic Acid | DECOIC | 334-48-5 | C10H20O2 | Carboxylic Acid |
| 153 | 80.469 | 142; 43; 68 | 142 | 83 | 3,5-dihydroxy-2-methylpyran-4-one | 5-Hydroxy-Maltol | HX5MALTOL | 1073-96-7 | C6H6O4 | Pyran (Ether) |
| 154 | 83.557 | 120; 91; 119 | 120 | 82 | 2,3-dihydro-1-benzofuran | 2,3-Dihydro-Benzofuran | DHBNZFUR | 496-16-2 | C8H8O | Benzofuran |
| 155 | 83.819 | 69; 57; 41 | 69 | 97 | (1R,3R,6R,7R,9R)-2,5,8-Trioxatricyclo[4.2.1.0~3,7~]nonan-9-ol | 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | GLUPYROSE | 4451-31-4 | C6H8O4 | Pyran (Derivative) |
| 156 | 84.222 | 95; 39; 68 | 95 | 90 | 1H-pyridin-4-one | 4-Pyridinol | PYRDINOL | 626-64-2 | C5H5NO | Nitrogen |
| 157 | 84.511 | 109; 80; 53 | 109 | 80 | 4-aminophenol | 4-Amino-Phenol | AMIPHEOL | 123-30-8 | C6H7NO | Phenol (Amine) |
| 158 | 85.024 | 105; 122; 77 | 105 | 95 | benzoic acid | Benzoic Acid | BNZOIC | 65-85-0 | C7H6O2 | Benzene (Acid) |
| 159 | 85.202 | 55; 84; 128 | 55 | 78 | N-methyl-N-(pentan-3-ylideneamino)methanamine | Dimethylhydrazone 3-Pentanone | DMHDZPTONE | 16795-73-6 | C7H16N2 | Nitrogen (Amine) |
| 160 | 85.552 | 60; 73; 43 | 60 | 82 | undecanoic acid | Undecanoic Acid | UNDECOIC | 112-37-8 | C11H22O2 | Carboxylic Acid |
| 161 | 86.034 | 85; 86; 57 | 85 | 91 | 5-(hydroxymethyl)oxolan-2-one | 5-(Hydroxymethyl)-Dihydro-2(3H)-Furanone | HM5FURONE | 10374-51-3 | C5H8O3 | Furan (Lactone) |
| 162 | 86.481 | 60; 73; 43 | 60 | 82 | dodecanoic acid | Dodecanoic Acid | DODECOIC | 143-07-7 | C12H24O2 | Carboxylic Acid |
| 163 | 86.680 | 97; 126; 41 | 97 | 98 | 5-(hydroxymethyl)furan-2-carbaldehyde | 5-(Hydroxymethyl)-2-Furfural | HM5FURAL | 67-47-0 | C6H6O3 | Furan (Aldehyde) |
| 164 | 87.210 | 140; 125; 97 | 140 | 80 | 3-methoxybenzene-1,2-diol | 3-Methoxy-1,2-Benzenediol | M3BNZDIOL | 934-00-9 | C7H8O3 | Benzene (Alcohol / Ether) |
| 165 | 89.065 | 97; 41; 128 | 97 | 84 | 1-(furan-2-yl)ethane-1,2-diol | 1-(2-Furanyl)-1,2-Ethanediol | FURYLETDIOL | 19377-75-4 | C6H8O3 | Furan (Alcohol) |
| 166 | 89.906 | 44; 74; 102 | 44 | 82 | 4-hydroxyoxolan-2-one | 4-Hydroxy-Dihydro-2(3H)-Furanone | DHYHYFURONE | 5469-16-9 | C4H6O | Furan (Lactone) |

**Table S37A. Mean and relative standard deviation values of identified VOCs in SC-based syrups samples.**

| Volatile Organic Compound | Relative Peak Areas (x $10^2$) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CERT | | | | | | | | | | | | | |
| | FRS07 | | FRS13 | | FRS14 | | FRS15 | | FRS16 | | FRS17 | | FRS18 | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| Pentane | 98.7 | 1.3 | 28.9 | 11.0 | 21.0 | 0.8 | 19.0 | 11.8 | 52.2 | 1.8 | 47.9 | 6.2 | 60.5 | 4.4 |
| Hexane | 259.4 | 2.2 | 105.1 | 9.9 | 61.8 | 2.3 | 77.8 | 1.6 | 142.7 | 2.6 | 99.3 | 5.7 | 167.5 | 1.9 |
| 1,4-Pentadiene | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Methanethiol | 1022.5 | 6.5 | 134.3 | 12.0 | 123.2 | 2.8 | 208.9 | 11.3 | 163.4 | 2.9 | 448.0 | 7.4 | 318.0 | 3.3 |
| Ethanal | 13128.8 | 6.6 | 1904.3 | 10.5 | 3153.9 | 7.1 | 3942.1 | 1.7 | 8786.9 | 3.9 | 8939.0 | 9.4 | 12257.1 | 9.3 |
| Dimethyl Sulfide | 7542.8 | 8.6 | 643.3 | 10.5 | 1135.7 | 2.1 | 894.2 | 5.3 | 1378.0 | 7.3 | 2272.4 | 8.0 | 1569.8 | 6.2 |
| Propanal | 412.8 | 2.4 | 334.8 | 11.7 | 424.8 | 8.2 | 293.4 | 11.0 | 753.7 | 4.3 | 495.0 | 12.5 | 1390.6 | 11.5 |
| Furan | 1810.2 | 2.7 | 1160.9 | 6.5 | 530.8 | 1.0 | 593.1 | 1.0 | 2149.9 | 12.7 | 6029.2 | 0.2 | 4240.4 | 7.2 |
| 2-Methyl-Propanal | 34308.8 | 11.7 | 8319.7 | 2.3 | 8395.9 | 5.3 | 6454.5 | 3.5 | 11410.9 | 5.8 | 17659.5 | 7.9 | 21889.5 | 8.7 |
| Ethyl Formate | 2461.8 | 17.7 | 1922.9 | 2.3 | 757.1 | 14.2 | 894.4 | 5.3 | 7155.3 | 5.1 | 2667.3 | 2.1 | 0.0 | |
| 2-Propenal | 234.5 | 2.1 | 245.3 | 12.8 | 149.8 | 3.1 | 400.3 | 0.3 | 572.5 | 1.0 | 310.2 | 6.9 | 353.4 | 13.2 |
| 2-Methyl-Furan | 5413.8 | 8.0 | 1691.1 | 1.3 | 701.9 | 11.0 | 708.2 | 9.7 | 2031.0 | 11.0 | 2646.0 | 10.7 | 6988.8 | 6.3 |
| Ethyl Acetate | 7851.5 | 10.5 | 7412.5 | 1.4 | 5835.8 | 0.3 | 2801.0 | 5.8 | 25389.2 | 1.8 | 13187.9 | 7.0 | 280.0 | 4.6 |
| 2-Butanone | 4215.0 | 9.4 | 231.7 | 13.3 | 540.0 | 9.1 | 404.9 | 3.7 | 217.2 | 12.9 | 1133.4 | 7.4 | 988.7 | 1.6 |
| 2-Methyl-Butanal | 33453.8 | 15.1 | 21469.2 | 0.5 | 15687.0 | 0.7 | 12966.1 | 3.7 | 19612.8 | 1.2 | 30163.3 | 8.7 | 37630.2 | 9.5 |
| 3-Methyl-Butanal | 26013.0 | 6.9 | 12150.8 | 2.8 | 7858.3 | 8.9 | 7073.4 | 9.5 | 14668.8 | 5.7 | 31870.8 | 4.7 | 41914.2 | 13.0 |
| Ethanol | 202215.3 | 7.3 | 121001.6 | 1.0 | 99323.0 | 0.3 | 107855.0 | 4.4 | 115261.9 | 3.6 | 145024.3 | 1.6 | 159606.9 | 2.9 |
| Benzene | 161.1 | 5.5 | 73.5 | 0.7 | 18.0 | 5.4 | 53.8 | 1.5 | 101.2 | 9.1 | 84.4 | 5.9 | 200.4 | 4.3 |
| 3-Buten-2-one | 570.3 | 17.3 | 894.1 | 8.3 | 267.5 | 1.5 | 341.5 | 3.4 | 872.8 | 5.1 | 5111.2 | 3.4 | 5047.9 | 5.4 |
| 2,5-Dimethyl-Furan | 515.4 | 6.3 | 907.0 | 2.6 | 824.3 | 10.6 | 880.9 | 6.2 | 3919.7 | 9.0 | 2021.6 | 6.6 | 1956.1 | 4.6 |
| Ethyl Propanoate | 594.9 | 12.1 | 361.7 | 1.9 | 28.0 | 11.4 | 132.7 | 11.3 | 1881.4 | 4.4 | 307.1 | 8.6 | 0.0 | |
| 2,3-Butanedione | 31364.2 | 6.8 | 16140.5 | 2.6 | 1754.9 | 3.4 | 2814.3 | 7.2 | 1397.2 | 13.2 | 33123.4 | 11.0 | 49665.1 | 11.3 |
| 2-Methylpropyl Acetate | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 1-Propanol | 17.5 | 7.8 | 55.0 | 13.7 | 54.5 | 1.9 | 89.0 | 2.2 | 38.8 | 13.4 | 92.1 | 7.1 | 0.0 | |
| 2-Ethyl-5-Methyl-Furan | 45.8 | 7.6 | 89.6 | 7.6 | 28.0 | 12.1 | 240.6 | 10.8 | 544.9 | 9.3 | 350.0 | 11.4 | 340.4 | 0.4 |
| Toluene | 2074.3 | 11.4 | 5078.0 | 8.1 | 4285.8 | 10.8 | 4721.7 | 9.8 | 19603.0 | 8.9 | 53948.0 | 9.8 | 651.6 | 2.2 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ethyl Butanoate | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2-Methyl-3-Buten-2-ol | 2976.6 | 7.4 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Nonomethyl Succinate | 3520.9 | 7.4 | 332.6 | 9.3 | 45.6 | 14.0 | 30.5 | 16.3 | 477.6 | 11.6 | 1202.6 | 5.2 | 0.0 | |
| 2,3-Pentanedione | 4322.8 | 13.0 | 4040.4 | 1.0 | 5621.8 | 13.2 | 2025.1 | 11.2 | 886.0 | 6.1 | 3204.1 | 12.5 | 17911.1 | 2.4 |
| Dimethyl Disulfide | 0.0 | | 37.5 | 13.6 | 250.0 | 13.9 | 46.6 | 0.8 | 322.5 | 1.0 | 302.9 | 1.5 | 0.0 | |
| 2-Ethenyl-Furan | 267.2 | 8.6 | 48.3 | 7.9 | 141.6 | 9.0 | 27.9 | 9.2 | 106.8 | 4.6 | 263.5 | 5.5 | 185.8 | 1.6 |
| 2,5-Diethyltetrahydro-Furan | 1238.2 | 15.7 | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Hexanal | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2-Methyl-1-Propanol | 83.9 | 7.0 | 2613.3 | 0.2 | 1033.2 | 10.7 | 23.1 | 13.4 | 19137.9 | 10.8 | 2101.6 | 1.1 | 0.0 | |
| 5-Butyl-Dihydro-2(3H)-Furanone | 9084.9 | 11.1 | 1375.7 | 4.4 | 975.3 | 1.0 | 506.1 | 1.7 | 1645.1 | 1.4 | 1942.4 | 6.1 | 1114.9 | 9.6 |
| m-Cresol | 2042.9 | 4.7 | 169.2 | 12.8 | 238.8 | 14.6 | 269.3 | 4.1 | 368.4 | 15.0 | 2300.9 | 5.2 | 3490.7 | 8.4 |
| 1-Butanol | 125.1 | 8.8 | 18.5 | 9.5 | 40.6 | 12.3 | 34.9 | 1.0 | 1044.9 | 5.3 | 408.2 | 14.4 | 105.6 | 4.6 |
| 5-Propyl-Dihydro-2(3H)-Furanone | 2635.8 | 5.8 | 642.2 | 10.6 | 300.4 | 9.9 | 274.4 | 0.8 | 1009.7 | 1.5 | 1047.0 | 7.3 | 536.6 | 5.0 |
| 3-Methyl-Pyridazine | 3329.2 | 5.0 | 1590.5 | 4.1 | 2096.3 | 0.8 | 2183.3 | 13.2 | 3201.6 | 8.1 | 4764.7 | 11.2 | 8754.7 | 4.1 |
| 2-Heptanone | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| m-Menthane | 139.5 | 11.6 | 3.5 | 11.3 | 9.0 | 14.4 | 7.1 | 9.7 | 16.9 | 2.2 | 27.3 | 16.0 | 63.7 | 10.2 |
| 1,3-Diazine | 171.6 | 7.7 | 23.2 | 13.5 | 22.1 | 6.1 | 27.2 | 11.1 | 325.7 | 12.0 | 62.5 | 12.3 | 150.1 | 2.9 |
| 2-Methyl-1-Butanol | 1953.7 | 11.5 | 8135.5 | 4.9 | 5740.1 | 6.8 | 4709.4 | 1.8 | 21874.3 | 8.6 | 14512.1 | 11.9 | 0.0 | |
| 2-Propyl-Furan | 1425.1 | 6.4 | 397.5 | 2.0 | 552.3 | 16.2 | 83.9 | 8.0 | 2172.7 | 9.4 | 105.7 | 11.8 | 3291.2 | 11.8 |
| Ethyl Hexanoate | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2-Pentyl-Furan | 12.9 | 6.6 | 2.6 | 10.8 | 3.7 | 8.9 | 110.9 | 5.8 | 13.0 | 5.8 | 19.4 | 1.9 | 12.0 | 10.3 |
| 2-Methyl-Pyrazine | 1015.8 | 7.6 | 213.5 | 12.0 | 1265.2 | 15.5 | 1014.2 | 6.9 | 1080.1 | 3.1 | 2077.3 | 10.6 | 454.2 | 2.2 |
| 2-Methyl-Dihydro-2(3H)-Furanone | 34004.1 | 1.5 | 17299.6 | 1.8 | 13953.8 | 13.9 | 11415.6 | 8.6 | 15831.7 | 7.7 | 21675.5 | 7.5 | 19081.9 | 11.8 |
| p-Cymene | 39.2 | 2.5 | 49.7 | 10.1 | 57.7 | 2.3 | 49.6 | 10.4 | 120.3 | 0.5 | 20.7 | 5.8 | 58.5 | 7.3 |
| Mesitylene | 22.6 | 1.9 | 6.4 | 2.1 | 3.2 | 13.9 | 3.5 | 9.4 | 3436.8 | 11.6 | 14.9 | 9.7 | 10.2 | 5.3 |
| 3,5-Xylenol | 148.7 | 6.8 | 49.1 | 11.6 | 81.3 | 6.8 | 97.3 | 8.5 | 158.9 | 5.7 | 286.1 | 9.3 | 350.1 | 13.2 |
| 3-Hydroxy-2-Butanone | 4692.4 | 4.1 | 1264.0 | 1.1 | 1671.9 | 8.8 | 1477.8 | 7.2 | 2171.8 | 13.4 | 3354.1 | 8.4 | 5088.3 | 6.7 |
| Vinylene Carbonate | 25513.2 | 6.7 | 4045.3 | 1.3 | 7828.1 | 12.9 | 9172.5 | 9.7 | 16120.0 | 4.0 | 19420.9 | 12.7 | 21659.4 | 10.7 |
| 2,6-Xylenol | 137.0 | 13.8 | 217.9 | 7.2 | 265.8 | 13.9 | 480.3 | 4.2 | 648.1 | 3.0 | 1249.9 | 8.2 | 1624.2 | 3.4 |
| 1-Hydroxy-2-Propanone | 14507.6 | 11.3 | 5406.5 | 0.9 | 10358.2 | 0.4 | 6411.6 | 1.6 | 13091.7 | 5.4 | 28531.5 | 7.0 | 21972.9 | 10.8 |
| 2,5-Dimethyl-Pyrazine | 64.0 | 12.1 | 45.8 | 15.1 | 1523.4 | 0.4 | 41.8 | 12.8 | 1053.3 | 4.8 | 149.4 | 2.2 | 1178.3 | 13.8 |
| 2,6-Dimethyl-Pyrazine | 3332.6 | 3.5 | 1301.8 | 12.5 | 1474.2 | 4.0 | 1374.8 | 1.1 | 1075.6 | 5.0 | 1368.4 | 5.3 | 1308.0 | 2.8 |
| 2-Cyclopenten-1-one | 5688.4 | 4.8 | 1141.1 | 3.1 | 1669.0 | 10.2 | 1692.7 | 1.4 | 1387.8 | 1.8 | 3467.5 | 0.5 | 3582.4 | 12.3 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1,2,3,4-Tetramethyl-4-(1-methylethenyl)-Benzene | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2-Methyl-2-Cyclopenten-1-one | 2219.1 | 1.8 | 332.6 | 2.9 | 624.1 | 2.7 | 485.5 | 2.9 | 1094.2 | 11.9 | 1534.2 | 7.8 | 1830.1 | 5.4 |
| 5-Methyl-2-Furanmethanethiol | 695.8 | 14.2 | 3004.1 | 10.5 | 1084.2 | 6.4 | 1428.4 | 1.3 | 8526.8 | 0.9 | 2656.3 | 5.7 | 27.9 | 9.2 |
| 1-Hydroxy-2-Butanone | 7661.4 | 12.3 | 1482.4 | 3.8 | 2305.3 | 4.1 | 3674.1 | 1.9 | 656.2 | 4.7 | 7972.4 | 1.6 | 9836.8 | 10.8 |
| 2-Ethyl-6-Methyl-Pyrazine | 386.2 | 12.1 | 128.0 | 8.9 | 177.9 | 2.6 | 138.2 | 2.5 | 130.3 | 11.7 | 181.4 | 6.5 | 144.0 | 6.9 |
| 2-Ethyl-5-Methyl-Pyrazine | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Nonanal | 984.8 | 13.5 | 637.1 | 1.0 | 643.0 | 10.8 | 508.3 | 7.2 | 681.2 | 5.2 | 1376.7 | 15.2 | 2511.5 | 5.6 |
| Trimethyl-Pyrazine | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2-Cyclohexen-1-one | 41.6 | 13.4 | 15.0 | 13.4 | 10.0 | 14.5 | 56.4 | 6.1 | 587.2 | 3.1 | 746.9 | 6.2 | 31.8 | 13.7 |
| 5-Methyl-2(3H)-Furanone | 12211.5 | 6.5 | 3164.5 | 9.5 | 5377.5 | 10.8 | 5683.0 | 3.9 | 8085.5 | 2.0 | 10002.6 | 1.5 | 8980.7 | 5.3 |
| 1,3-Dihydro-4-Methyl-2H-Imidazol-2-one | 4383.4 | 0.3 | 1450.9 | 7.8 | 1885.4 | 1.0 | 1816.1 | 7.9 | 3910.9 | 1.8 | 4005.1 | 1.2 | 6696.1 | 9.9 |
| Ethyl Octanoate | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | 16.2 | 5.3 | 267.2 | 6.6 | 246.3 | 14.9 | 192.8 | 2.0 | 483.1 | 2.7 | 694.6 | 4.7 | 370.7 | 8.4 |
| Furfural | 40114.7 | 3.1 | 25043.5 | 2.4 | 26413.9 | 1.6 | 24513.0 | 6.4 | 26387.8 | 10.5 | 32952.1 | 2.7 | 34806.3 | 14.1 |
| Ethanoic Acid | 622455.5 | 2.2 | 317668.4 | 3.2 | 349871.7 | 2.9 | 66429.6 | 5.0 | 76709.6 | 9.1 | 191576.4 | 0.8 | 194203.0 | 2.0 |
| 1,2,3,4-Tetrahydro-1,6,8-Trimethyl-Naphthalene | 830.2 | 4.8 | 555.3 | 2.4 | 794.6 | 4.9 | 447.6 | 1.0 | 670.1 | 2.8 | 1265.3 | 15.7 | 606.5 | 5.1 |
| 2-Ethyl-1-Hexanol | 783.3 | 7.0 | 593.1 | 5.6 | 552.3 | 4.6 | 392.4 | 12.2 | 1777.5 | 0.0 | 2997.0 | 4.4 | 855.9 | 8.7 |
| 3-Methyl-Furfural | 569.9 | 4.2 | 168.2 | 0.2 | 230.6 | 14.0 | 275.2 | 5.0 | 514.6 | 4.3 | 455.5 | 10.0 | 848.6 | 7.2 |
| Furfuryl Formate | 1604.2 | 9.3 | 869.2 | 13.0 | 1344.4 | 14.4 | 1820.2 | 10.4 | 3999.8 | 8.9 | 2991.8 | 0.5 | 4359.7 | 11.4 |
| Decanal | 1724.8 | 7.3 | 922.2 | 1.1 | 78.0 | 4.5 | 250.3 | 0.8 | 1242.0 | 8.6 | 2215.3 | 13.5 | 3199.5 | 10.7 |
| 1-(2-Furanyl)-Ethanone | 15678.7 | 3.8 | 10543.7 | 2.3 | 11113.3 | 8.1 | 10890.1 | 3.1 | 14842.7 | 4.5 | 14116.0 | 5.9 | 15542.0 | 13.8 |
| Benzaldehyde | 1868.9 | 2.8 | 895.8 | 5.2 | 562.4 | 17.7 | 611.7 | 7.8 | 675.0 | 1.2 | 1375.2 | 5.9 | 1623.6 | 1.8 |
| Furfuryl Acetate | 2230.8 | 4.5 | 592.7 | 12.7 | 938.8 | 16.7 | 1123.8 | 6.1 | 2237.2 | 8.4 | 2016.1 | 5.0 | 3456.7 | 1.1 |
| Propanoic Acid | 734.6 | 4.6 | 226.4 | 3.3 | 220.6 | 6.2 | 2314.0 | 6.0 | 6815.4 | 7.8 | 299.8 | 5.8 | 701.6 | 13.0 |
| Dimethyl Sulfoxide | 659.5 | 16.5 | 49.1 | 12.5 | 306.0 | 9.7 | 435.3 | 3.3 | 441.0 | 4.4 | 514.9 | 8.1 | 267.6 | 12.3 |
| 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | 444.0 | 3.5 | 215.7 | 13.5 | 293.5 | 8.8 | 169.3 | 1.5 | 417.8 | 11.7 | 571.3 | 10.9 | 118.3 | 4.3 |
| 5-Methyl-Furfural | 21904.3 | 10.5 | 12916.4 | 9.7 | 14819.6 | 1.1 | 17003.7 | 4.2 | 17848.8 | 5.6 | 18869.5 | 2.1 | 22090.1 | 11.1 |
| 4-Cyclopentene-1,3-dione | 20612.7 | 13.7 | 12474.9 | 10.2 | 15726.9 | 2.6 | 13308.5 | 8.6 | 17196.2 | 6.4 | 20881.1 | 2.1 | 21389.0 | 8.8 |
| 2-Methyl-Benzofuran | 13073.7 | 14.1 | 4250.3 | 8.3 | 2762.1 | 5.9 | 2345.0 | 6.0 | 8254.9 | 1.6 | 9803.4 | 6.9 | 8989.3 | 0.6 |
| 1-(5-Methyl-2-Furanyl)-Ethanone | 3859.6 | 13.6 | 558.6 | 10.6 | 662.8 | 8.1 | 1012.7 | 5.4 | 2278.6 | 3.5 | 2243.6 | 8.0 | 2693.8 | 5.3 |
| Diethylene Glycol Ethyl Ether | 3325.1 | 0.3 | 1713.8 | 3.6 | 1815.2 | 5.9 | 2017.9 | 5.4 | 1868.5 | 11.4 | 5243.0 | 10.1 | 5155.3 | 13.4 |
| 3-Methyl-Dihydro-2(3H)-Furanone | 1730.1 | 10.1 | 765.8 | 13.5 | 869.4 | 14.4 | 863.8 | 7.4 | 1738.1 | 2.1 | 1413.1 | 8.4 | 1932.1 | 7.7 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | 48.6 | 13.4 | 44.2 | 10.6 | 62.5 | 2.6 | 31.7 | 7.2 | 81.9 | 4.4 | 130.8 | 4.4 | 81.7 | 7.6 |
| Benzeneacetaldehyde | 17699.7 | 8.2 | 776.3 | 6.4 | 972.7 | 5.3 | 3591.8 | 4.3 | 8725.4 | 5.7 | 9758.5 | 6.4 | 12558.9 | 11.9 |
| 3,5-Dimethyl-Dihydro-2-Furanone | 1745.3 | 12.9 | 512.9 | 17.0 | 662.5 | 2.1 | 614.7 | 10.6 | 540.0 | 3.0 | 3382.9 | 1.0 | 1552.4 | 8.3 |
| 2-Propenoic Acid | 2598.8 | 7.4 | 45.3 | 11.4 | 3912.6 | 13.2 | 3090.4 | 8.7 | 13197.2 | 2.3 | 6314.2 | 1.4 | 11803.3 | 8.6 |
| Ethyl Decanoate | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Acetophenone | 577.9 | 0.2 | 121.0 | 8.4 | 123.7 | 12.7 | 184.2 | 12.3 | 313.8 | 12.7 | 300.7 | 3.0 | 786.4 | 12.5 |
| 2-Furanmethanol | 28914.3 | 9.8 | 21515.7 | 0.3 | 24661.9 | 3.0 | 18617.5 | 2.7 | 21685.3 | 7.5 | 23273.4 | 11.9 | 52489.4 | 8.4 |
| 3-Furanmethanol | 49757.8 | 1.0 | 27453.7 | 11.7 | 35307.1 | 13.4 | 22481.4 | 7.7 | 16348.3 | 6.7 | 18357.0 | 11.2 | 64212.9 | 7.2 |
| 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | 274.2 | 11.5 | 91.9 | 9.9 | 223.7 | 11.2 | 287.5 | 1.9 | 271.4 | 11.2 | 469.1 | 4.3 | 529.9 | 7.7 |
| 2-(2-Furanylmethyl)-5-Methyl-Furan | 872.0 | 14.8 | 129.6 | 13.9 | 184.9 | 15.9 | 353.0 | 1.7 | 708.5 | 2.5 | 479.6 | 10.0 | 995.9 | 12.7 |
| 3-Methyl-2(5H)-Furanone | 594.7 | 13.9 | 265.6 | 7.1 | 595.2 | 10.6 | 579.3 | 3.8 | 681.4 | 9.7 | 976.3 | 4.6 | 985.7 | 3.5 |
| 5-Methyl-2-Furanmethanol | 3490.5 | 10.2 | 1341.8 | 7.3 | 2427.7 | 18.6 | 1929.1 | 6.4 | 2637.3 | 11.0 | 4174.9 | 0.4 | 5391.7 | 12.7 |
| Benzyl Acetate | 268.3 | 8.1 | 219.5 | 6.9 | 44.5 | 1.7 | 366.5 | 7.7 | 289.6 | 10.6 | 236.9 | 15.0 | 0.0 | |
| 2(5H)-Furanone | 32145.9 | 12.9 | 14215.7 | 0.6 | 14375.6 | 12.8 | 19058.4 | 5.4 | 7999.2 | 4.7 | 37096.8 | 2.6 | 27152.0 | 3.0 |
| 2,2'-Methylenebis[5-Methyl-Furan | 728.7 | 11.2 | 333.1 | 12.1 | 505.7 | 14.5 | 377.1 | 2.2 | 681.3 | 7.6 | 1462.2 | 8.4 | 1018.0 | 10.4 |
| 1,2-Cyclopentanedione | 39093.3 | 3.2 | 16481.8 | 12.7 | 23452.4 | 4.2 | 26782.4 | 0.9 | 24006.4 | 5.9 | 33818.8 | 4.7 | 39417.0 | 8.6 |
| 2-Cyclohexenol | 17588.4 | 6.9 | 5266.8 | 3.7 | 6902.3 | 4.9 | 7666.5 | 5.0 | 9665.4 | 2.5 | 15789.5 | 3.1 | 16990.4 | 4.8 |
| 2-Phenylethyl Acetate | 597.1 | 13.8 | 1309.2 | 16.8 | 512.0 | 11.1 | 2664.2 | 6.6 | 6220.2 | 1.5 | 2687.3 | 12.4 | 364.5 | 4.9 |
| 3-Methyl-1,2-Cyclopentanedione | 24451.5 | 11.2 | 6196.1 | 0.5 | 7471.7 | 9.8 | 9727.3 | 4.3 | 11541.9 | 7.6 | 18549.0 | 0.9 | 21664.8 | 11.6 |
| 2-Ethyl-Hexanoic Acid | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| β-Damascenone | 10111.1 | 8.0 | 339.6 | 2.4 | 201.6 | 3.2 | 3300.4 | 9.6 | 1127.0 | 5.7 | 292.9 | 4.0 | 10703.7 | 5.0 |
| Ethyl Undecanoate | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2-Methyl-Propanoic Acid | 9201.1 | 16.0 | 2211.9 | 1.7 | 2846.1 | 4.9 | 3305.0 | 7.8 | 6630.5 | 9.8 | 7936.8 | 6.8 | 12086.5 | 10.5 |
| 2,4,6-Trihydroxypyrimidine | 31204.5 | 10.5 | 16976.0 | 3.4 | 18202.4 | 6.5 | 17663.8 | 8.2 | 27315.9 | 11.7 | 25867.3 | 3.7 | 26105.2 | 7.7 |
| Mequinol | 3005.5 | 12.2 | 556.4 | 3.1 | 756.6 | 3.2 | 931.4 | 3.3 | 1039.0 | 3.1 | 1573.3 | 3.2 | 2222.2 | 9.7 |
| 2,2-Diethyl-3-Methyl-Oxazolidine | 6418.8 | 8.6 | 2199.8 | 11.0 | 2857.8 | 17.2 | 3790.2 | 1.9 | 7490.0 | 11.4 | 9522.3 | 4.3 | 13662.4 | 2.5 |
| Oxypurinol | 13727.5 | 12.7 | 4555.7 | 3.7 | 4692.5 | 6.5 | 7792.4 | 12.8 | 8884.9 | 6.7 | 12480.4 | 4.6 | 12342.7 | 8.5 |
| Benzenemethanol | 9833.6 | 11.0 | 1495.9 | 10.8 | 301.1 | 6.0 | 805.1 | 10.2 | 704.4 | 10.5 | 604.8 | 0.1 | 261.2 | 9.7 |
| 4-Methyl-2(5H)-Furanone | 5819.4 | 7.7 | 1480.4 | 5.2 | 2186.2 | 5.7 | 2280.4 | 11.8 | 3179.6 | 9.7 | 4120.6 | 7.5 | 6962.8 | 10.5 |
| 3-Ethyl-2-Hydroxy-2-Cyclopenten-1-one | 6395.2 | 14.3 | 936.9 | 8.4 | 1288.2 | 5.9 | 1543.9 | 9.2 | 2151.0 | 12.2 | 3124.1 | 9.3 | 3729.0 | 10.2 |
| Benzeneethanol | 58.8 | 9.4 | 287.9 | 2.3 | 72.7 | 13.6 | 194.6 | 5.4 | 464.1 | 12.7 | 318.8 | 5.0 | 178.5 | 4.3 |
| Acrylamide | 5432.4 | 11.3 | 1208.8 | 5.0 | 2462.7 | 9.7 | 2951.1 | 8.9 | 6052.4 | 5.0 | 6188.3 | 6.0 | 6777.6 | 10.7 |
| Erythritol | 13181.9 | 8.0 | 3805.6 | 5.8 | 4221.0 | 6.5 | 4625.2 | 11.4 | 8245.1 | 5.2 | 13061.5 | 1.1 | 17525.1 | 7.7 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,3-Dimethyl-3-Pyrazolin-5-one | 2201.5 | 4.6 | 519.9 | 3.5 | 725.2 | 13.1 | 838.8 | 5.9 | 1175.7 | 6.9 | 1585.9 | 12.1 | 1934.6 | 12.1 |
| Furfural Acetone | 1677.6 | 13.2 | 504.4 | 9.8 | 683.7 | 6.7 | 782.5 | 10.6 | 1097.1 | 10.8 | 1524.1 | 0.8 | 2071.1 | 7.9 |
| Cyclotene | 4710.4 | 12.4 | 1578.7 | 10.1 | 2362.1 | 17.5 | 3217.2 | 5.3 | 4823.6 | 8.3 | 5438.5 | 5.0 | 7902.0 | 4.7 |
| 2-Methyl-1,4-Benzenediol | 9547.5 | 6.0 | 907.8 | 4.6 | 1155.0 | 11.6 | 1131.4 | 4.6 | 2171.6 | 11.0 | 2983.8 | 3.5 | 6209.2 | 5.4 |
| Heptanoic Acid | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Maltol | 23760.6 | 7.6 | 8143.1 | 13.2 | 10318.0 | 5.4 | 12514.7 | 6.2 | 15762.4 | 7.3 | 17409.2 | 5.4 | 20498.4 | 10.8 |
| 2-Acetylpyrrole | 28102.8 | 10.5 | 7518.7 | 6.9 | 8496.4 | 2.7 | 7404.8 | 5.7 | 9360.2 | 7.7 | 14430.4 | 5.7 | 14092.6 | 9.3 |
| 2,5-Furandicarboxaldehyde | 44213.2 | 8.7 | 13933.4 | 6.3 | 12905.7 | 14.9 | 16453.0 | 3.7 | 20916.9 | 14.1 | 31055.1 | 1.6 | 33001.5 | 6.5 |
| 2H-Pyran-2,6(3H)-Dione | 13931.4 | 7.1 | 2037.0 | 6.7 | 3432.3 | 18.1 | 6873.8 | 11.2 | 14810.2 | 5.9 | 13451.8 | 6.9 | 16447.7 | 6.4 |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | 28012.7 | 11.6 | 12311.1 | 4.3 | 20375.4 | 8.8 | 20822.3 | 12.7 | 57419.4 | 0.3 | 17626.4 | 1.2 | 29062.9 | 6.3 |
| Phenol | 11182.0 | 14.6 | 1877.7 | 4.5 | 2431.7 | 9.6 | 2987.2 | 8.8 | 4626.4 | 8.3 | 5719.0 | 12.4 | 8204.7 | 11.4 |
| 1H-Pyrrole-2-Carboxaldehyde | 5622.0 | 10.5 | 637.0 | 5.9 | 872.0 | 4.2 | 911.5 | 3.4 | 835.0 | 11.1 | 5732.3 | 9.3 | 5897.6 | 4.1 |
| Phloroglucinol | 13128.8 | 5.7 | 2680.8 | 9.8 | 4080.1 | 13.0 | 5238.3 | 12.2 | 14692.0 | 6.2 | 12492.0 | 0.3 | 16640.6 | 7.7 |
| Furaneol | 17628.1 | 0.4 | 14166.2 | 2.1 | 15189.2 | 0.8 | 18232.8 | 7.9 | 13267.4 | 1.5 | 15414.6 | 0.6 | 15728.2 | 3.8 |
| Octanoic Acid | 189.7 | 10.0 | 261.9 | 8.2 | 344.2 | 17.5 | 403.5 | 3.0 | 203.2 | 14.5 | 330.1 | 7.0 | 383.4 | 8.7 |
| 5-Acetyl-Dihydro-2(3H)-Furanone | 17646.6 | 1.3 | 11472.5 | 0.5 | 12424.4 | 0.1 | 11865.3 | 5.9 | 11931.0 | 7.9 | 17076.3 | 7.3 | 15308.2 | 7.6 |
| 2-Furanpropionic Acid | 10673.2 | 10.1 | 2355.8 | 6.6 | 3286.1 | 11.3 | 4640.8 | 5.7 | 10089.4 | 8.5 | 9669.9 | 1.3 | 11266.7 | 6.0 |
| 1,3-Dihydroxy-2-Propanone | 456536.2 | 4.1 | 285396.7 | 2.8 | 355341.2 | 6.1 | 325658.0 | 3.0 | 350592.8 | 3.7 | 417470.4 | 1.4 | 432011.6 | 0.0 |
| Tetrahydro-5-Methyl-2-Furanmethanol | 148.2 | 4.4 | 12061.3 | 6.8 | 56.7 | 2.9 | 13027.6 | 3.1 | 9247.3 | 1.3 | 16415.9 | 2.4 | 588.9 | 13.2 |
| 4,5-Dimethyl Vinylene Carbonate | 19934.1 | 5.9 | 6180.3 | 9.3 | 8154.2 | 13.7 | 9842.0 | 5.9 | 6807.3 | 2.1 | 16353.7 | 2.5 | 16034.3 | 10.2 |
| 2-Hydroxy-Dihydro-2(3H)-Furanone | 4070.6 | 8.5 | 31046.0 | 2.2 | 35819.7 | 0.7 | 30587.2 | 1.2 | 22563.2 | 3.5 | 5312.8 | 1.4 | 5574.3 | 9.1 |
| 5-Acetoxymethyl-2-Furfural A | 13502.8 | 7.5 | 11357.1 | 6.0 | 12593.0 | 7.0 | 12051.8 | 10.6 | 9644.0 | 2.8 | 17759.4 | 6.7 | 16129.7 | 11.1 |
| 5-Acetoxymethyl-2-Furfural B | 19318.5 | 3.7 | 12399.1 | 1.5 | 13399.5 | 3.7 | 15313.4 | 5.4 | 17830.9 | 5.1 | 21514.3 | 2.0 | 18481.1 | 9.1 |
| 2-Methoxy-4-Vinyl-Phenol | 4120.0 | 8.6 | 817.6 | 10.5 | 1235.9 | 5.1 | 1441.2 | 1.6 | 3060.6 | 13.6 | 3382.6 | 12.2 | 6340.0 | 9.2 |
| 3-Methyl-2,4(3H,5H)-Furandione | 10561.0 | 9.7 | 3018.8 | 3.1 | 4239.9 | 8.6 | 5296.3 | 3.7 | 6246.8 | 9.6 | 9340.2 | 6.1 | 10253.6 | 10.0 |
| 3-Hydroxy-2,3-Dihydro-Maltol | 11035.1 | 7.4 | 7496.4 | 11.0 | 9867.8 | 8.4 | 10080.8 | 9.0 | 9991.1 | 8.6 | 13316.2 | 13.9 | 13223.8 | 0.8 |
| Decanoic Acid | 3604.8 | 0.7 | 959.2 | 5.3 | 884.3 | 7.9 | 1697.1 | 3.0 | 408.7 | 12.0 | 211.6 | 9.6 | 799.9 | 1.9 |
| 5-Hydroxy-Maltol | 46789.7 | 13.0 | 10577.0 | 10.9 | 15988.5 | 14.0 | 22443.4 | 3.7 | 20736.5 | 8.9 | 34672.7 | 4.3 | 38102.8 | 9.9 |
| 2,3-Dihydro-Benzofuran | 3548.8 | 11.3 | 852.6 | 3.7 | 1228.6 | 3.3 | 1486.6 | 1.8 | 1690.0 | 2.3 | 2987.3 | 6.2 | 5430.7 | 9.4 |
| 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | 8562.3 | 3.9 | 2663.7 | 3.9 | 2815.7 | 0.8 | 4890.1 | 3.8 | 4620.5 | 9.6 | 8321.9 | 4.2 | 7118.6 | 6.5 |
| 4-Pyridinol | 16057.9 | 6.9 | 3758.5 | 0.4 | 5495.9 | 12.7 | 6563.0 | 3.9 | 8979.0 | 4.2 | 12385.3 | 8.3 | 13378.4 | 8.4 |
| 4-Amino-Phenol | 11355.1 | 7.5 | 2040.5 | 2.2 | 3431.0 | 7.8 | 3681.8 | 4.6 | 4643.1 | 0.4 | 7835.5 | 6.7 | 10392.8 | 11.8 |
| Benzoic Acid | 14984.6 | 6.5 | 44.6 | 7.1 | 15.6 | 5.1 | 1746.9 | 3.7 | 1495.7 | 5.6 | 2990.6 | 2.7 | 2896.9 | 2.6 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Dimethylhydrazone 3-Pentanone | 14574.4 | 6.0 | 5343.2 | 9.5 | 7146.6 | 3.9 | 7770.4 | 5.0 | 5269.3 | 0.2 | 22368.8 | 0.3 | 15247.3 | 12.2 |
| Undecanoic Acid | 10566.7 | 6.6 | 79.7 | 9.7 | 228.5 | 5.5 | 1775.2 | 3.1 | 161.6 | 4.5 | 766.0 | 1.6 | 221.6 | 13.9 |
| 5-(Hydroxymethyl)-Dihydro-2(3H)-Furanone | 34037.4 | 12.5 | 27394.2 | 5.2 | 30405.2 | 6.3 | 31683.7 | 8.0 | 41433.5 | 3.5 | 20401.6 | 4.4 | 75799.6 | 11.3 |
| Dodecanoic Acid | 3489.1 | 10.2 | 74.7 | 7.9 | 194.0 | 4.4 | 1125.4 | 3.8 | 1307.2 | 6.3 | 3671.4 | 5.8 | 2390.5 | 13.6 |
| 5-(Hydroxymethyl)-2-Furfural | 159244.2 | 5.2 | 178092.7 | 0.4 | 207323.6 | 4.9 | 164599.0 | 4.5 | 198276.1 | 10.3 | 165006.0 | 1.3 | 172268.3 | 5.2 |
| 3-Methoxy-1,2-Benzenediol | 6999.2 | 4.2 | 2006.7 | 6.8 | 2443.1 | 14.8 | 3640.6 | 1.4 | 5633.7 | 9.9 | 7682.9 | 3.9 | 14099.0 | 6.8 |
| 1-(2-Furanyl)-1,2-Ethanediol | 42992.2 | 1.4 | 14002.0 | 10.1 | 11221.4 | 8.4 | 12514.4 | 2.6 | 14995.6 | 10.9 | 15521.4 | 0.2 | 22502.6 | 10.8 |
| 4-Hydroxy-Dihydro-2(3H)-Furanone | 27068.9 | 10.8 | 6722.6 | 6.9 | 9676.9 | 13.5 | 13815.3 | 4.1 | 19296.8 | 4.3 | 23371.3 | 0.8 | 29163.2 | 13.9 |

**Table 37B. Mean and relative standard deviation values of identified VOCs in SC-based syrups samples.**

| Volatile Organic Compound | Relative Peak Areas (x $10^3$) | | | | | |
|---|---|---|---|---|---|---|
| | NCERT | | | | | |
| | ECAL14 | | ENCAL14 | | GLA14 | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| Pentane | 42.5 | 4.6 | 41.7 | 6.5 | 122.3 | 12.6 |
| Hexane | 112.2 | 5.2 | 69.7 | 0.5 | 235.8 | 3.0 |
| 1,4-Pentadiene | 0.0 | | 2.6 | 8.5 | 0.0 | |
| Methanethiol | 494.9 | 3.9 | 177.0 | 2.4 | 161.3 | 5.9 |
| Ethanal | 4952.9 | 12.1 | 48.2 | 0.2 | 10061.5 | 3.0 |
| Dimethyl Sulfide | 2901.7 | 9.6 | 7643.0 | 10.1 | 558.4 | 8.5 |
| Propanal | 827.2 | 5.1 | 315.0 | 6.8 | 1421.5 | 6.5 |
| Furan | 1982.9 | 0.9 | 2777.0 | 8.9 | 2118.5 | 4.8 |
| 2-Methyl-Propanal | 12951.6 | 5.0 | 6195.3 | 0.7 | 9333.3 | 2.4 |
| Ethyl Formate | 3245.0 | 6.9 | 0.0 | | 2067.2 | 5.7 |
| 2-Propenal | 519.3 | 8.2 | 27.8 | 6.6 | 350.3 | 5.3 |
| 2-Methyl-Furan | 2158.4 | 3.4 | 166.1 | 0.2 | 2450.4 | 1.6 |
| Ethyl Acetate | 10340.2 | 3.3 | 8.5 | 14.9 | 20056.1 | 6.9 |
| 2-Butanone | 382.6 | 8.5 | 70.3 | 8.9 | 545.4 | 9.0 |
| 2-Methyl-Butanal | 23157.1 | 1.3 | 8960.3 | 0.4 | 14780.3 | 3.4 |
| 3-Methyl-Butanal | 28252.9 | 1.3 | 1592.0 | 7.7 | 8899.9 | 2.2 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Ethanol | 59701.7 | 5.1 | 47501.2 | 8.0 | 3150.3 | 5.7 |
| Benzene | 118.8 | 3.9 | 3.7 | 6.7 | 35.5 | 11.6 |
| 3-Buten-2-one | 1046.7 | 4.7 | 46.2 | 10.5 | 3489.1 | 0.5 |
| 2,5-Dimethyl-Furan | 1296.2 | 4.3 | 88.4 | 5.6 | 2696.3 | 9.4 |
| Ethyl Propanoate | 0.0 | | 0.0 | | 10327.3 | 1.0 |
| 2,3-Butanedione | 11909.1 | 9.6 | 212.0 | 7.4 | 20966.1 | 0.9 |
| 2-Methylpropyl Acetate | 58.4 | 5.6 | 0.0 | | 1987.0 | 7.1 |
| 1-Propanol | 1677.6 | 9.7 | 0.0 | | 10237.8 | 2.5 |
| 2-Ethyl-5-Methyl-Furan | 14.8 | 8.0 | 0.0 | | 703.9 | 6.1 |
| Toluene | 3899.0 | 10.5 | 1258.9 | 9.0 | 5073.9 | 0.4 |
| Ethyl Butanoate | 0.0 | | 0.0 | | 1270.8 | 6.5 |
| 2-Methyl-3-Buten-2-ol | 840.5 | 9.0 | 18.8 | 0.1 | 0.0 | |
| Nonomethyl Succinate | 324.2 | 1.2 | 24.0 | 8.9 | 0.0 | |
| 2,3-Pentanedione | 5060.6 | 7.7 | 125.7 | 3.8 | 9459.5 | 6.0 |
| Dimethyl Disulfide | 2179.6 | 4.9 | 0.0 | | 0.0 | |
| 2-Ethenyl-Furan | 219.2 | 2.3 | 27.7 | 1.1 | 35.3 | 12.1 |
| 2,5-Diethyltetrahydro-Furan | 210.2 | 10.2 | 0.0 | | 0.0 | |
| Hexanal | 0.0 | | 13.3 | 2.9 | 0.0 | |
| 2-Methyl-1-Propanol | 18.9 | 3.9 | 7.6 | 4.1 | 41073.2 | 2.9 |
| 5-Butyl-Dihydro-2(3H)-Furanone | 1079.8 | 11.1 | 33.4 | 12.2 | 15.0 | 4.4 |
| m-Cresol | 132.2 | 7.3 | 19.4 | 3.4 | 986.8 | 1.5 |
| 1-Butanol | 68.4 | 12.7 | 0.0 | | 1059.2 | 2.9 |
| 5-Propyl-Dihydro-2(3H)-Furanone | 728.4 | 5.7 | 9.8 | 3.5 | 14.4 | 8.0 |
| 3-Methyl-Pyridazine | 776.7 | 9.3 | 11.8 | 2.6 | 2473.6 | 3.2 |
| 2-Heptanone | 8.6 | 1.9 | 0.0 | | 0.0 | |
| m-Menthane | 0.0 | | 0.0 | | 0.0 | |
| 1,3-Diazine | 364.4 | 6.3 | 1.6 | 2.5 | 988.6 | 4.9 |
| 2-Methyl-1-Butanol | 5493.2 | 9.8 | 976.9 | 9.1 | 19225.4 | 1.0 |
| 2-Propyl-Furan | 55.7 | 12.9 | 7.3 | 7.0 | 528.1 | 7.2 |
| Ethyl Hexanoate | 0.0 | | 0.0 | | 295.7 | 15.2 |
| 2-Pentyl-Furan | 0.0 | | 10.8 | 8.1 | 0.0 | |
| 2-Methyl-Pyrazine | 1828.5 | 6.9 | 36.1 | 5.7 | 799.4 | 1.3 |
| 2-Methyl-Dihydro-2(3H)-Furanone | 17829.4 | 5.2 | 69.7 | 14.3 | 2505.0 | 5.3 |

| | | | | | | |
|---|---|---|---|---|---|---|
| p-Cymene | 53.9 | 3.4 | 0.0 | | 212.6 | 8.6 |
| Mesitylene | 3.8 | 1.7 | 0.0 | | 116.7 | 3.3 |
| 3,5-Xylenol | 0.0 | | 0.0 | | 88.4 | 1.3 |
| 3-Hydroxy-2-Butanone | 715.2 | 2.8 | 368.0 | 12.7 | 1920.1 | 2.2 |
| Vinylene Carbonate | 4192.5 | 9.8 | 83.3 | 4.5 | 12628.8 | 4.7 |
| 2,6-Xylenol | 186.0 | 9.2 | 4.8 | 4.8 | 269.9 | 7.2 |
| 1-Hydroxy-2-Propanone | 8601.1 | 13.8 | 3732.0 | 1.7 | 20944.0 | 2.3 |
| 2,5-Dimethyl-Pyrazine | 108.5 | 4.9 | 94.8 | 4.8 | 127.6 | 4.2 |
| 2,6-Dimethyl-Pyrazine | 1440.2 | 4.9 | 29.4 | 9.0 | 997.5 | 4.2 |
| 2-Cyclopenten-1-one | 391.5 | 1.9 | 17.1 | 3.2 | 1074.8 | 5.6 |
| 1,2,3,4-Tetramethyl-4-(1-methylethenyl)-Benzene | 0.0 | | 0.0 | | 0.0 | |
| 2-Methyl-2-Cyclopenten-1-one | 168.8 | 2.6 | 21.9 | 16.7 | 419.5 | 3.9 |
| 5-Methyl-2-Furanmethanethiol | 2029.3 | 1.3 | 11.5 | 3.6 | 13381.6 | 3.2 |
| 1-Hydroxy-2-Butanone | 1318.8 | 14.3 | 102.7 | 3.7 | 4740.7 | 2.0 |
| 2-Ethyl-6-Methyl-Pyrazine | 144.0 | 9.7 | 14.1 | 2.1 | 31.9 | 8.5 |
| 2-Ethyl-5-Methyl-Pyrazine | 0.0 | | 0.0 | | 0.0 | |
| Nonanal | 2078.7 | 5.6 | 202.0 | 7.4 | 472.8 | 0.4 |
| Trimethyl-Pyrazine | 0.0 | | 0.0 | | 0.0 | |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | 0.0 | | 0.0 | | 0.0 | |
| 2-Cyclohexen-1-one | 24.0 | 4.4 | 98.9 | 10.9 | 84.5 | 12.0 |
| 5-Methyl-2(3H)-Furanone | 1670.7 | 4.8 | 157.5 | 0.3 | 4396.5 | 3.3 |
| 1,3-Dihydro-4-Methyl-2H-Imidazol-2-one | 861.2 | 0.5 | 79.9 | 9.4 | 2433.8 | 0.5 |
| Ethyl Octanoate | 0.0 | | 0.0 | | 1247.6 | 4.7 |
| 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | 111.7 | 4.8 | 3.4 | 8.4 | 70.1 | 3.6 |
| Furfural | 24065.2 | 7.8 | 26526.1 | 8.4 | 39888.4 | 7.6 |
| Ethanoic Acid | 351640.1 | 0.1 | 235969.8 | 9.2 | 436448.0 | 0.7 |
| 1,2,3,4-Tetrahydro-1,6,8-Trimethyl-Naphthalene | 214.9 | 6.7 | 4.9 | 1.2 | 357.8 | 3.4 |
| 2-Ethyl-1-Hexanol | 543.4 | 5.0 | 67.7 | 6.1 | 11461.3 | 2.6 |
| 3-Methyl-Furfural | 4521.9 | 6.4 | 1949.6 | 0.9 | 232.6 | 5.9 |
| Furfuryl Formate | 344.6 | 10.6 | 54.9 | 0.6 | 1513.1 | 1.2 |
| Decanal | 150.9 | 0.9 | 82.7 | 7.8 | 447.3 | 11.5 |
| 1-(2-Furanyl)-Ethanone | 10443.6 | 9.5 | 42.1 | 4.0 | 15861.4 | 5.5 |
| Benzaldehyde | 402.0 | 11.8 | 6.1 | 13.1 | 1237.3 | 1.5 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Furfuryl Acetate | 211.6 | 10.9 | 105.7 | 1.5 | 946.5 | 1.6 |
| Propanoic Acid | 905.5 | 9.3 | 0.0 | | 6991.8 | 1.5 |
| Dimethyl Sulfoxide | 89.7 | 6.6 | 49.9 | 11.1 | 313.5 | 11.9 |
| 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | 101.1 | 9.0 | 5.3 | 6.5 | 299.5 | 1.9 |
| 5-Methyl-Furfural | 5231.7 | 10.3 | 371.9 | 3.4 | 18746.7 | 1.9 |
| 4-Cyclopentene-1,3-dione | 4418.4 | 6.4 | 253.9 | 4.6 | 11639.3 | 11.8 |
| 2-Methyl-Benzofuran | 3396.0 | 6.1 | 22.4 | 12.9 | 2444.4 | 7.3 |
| 1-(5-Methyl-2-Furanyl)-Ethanone | 267.2 | 2.9 | 110.8 | 6.6 | 970.2 | 0.9 |
| Diethylene Glycol Ethyl Ether | 1027.6 | 14.2 | 24.3 | 7.5 | 2046.1 | 6.9 |
| 3-Methyl-Dihydro-2(3H)-Furanone | 438.6 | 12.0 | 135.6 | 5.8 | 1905.2 | 2.6 |
| 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | 0.0 | | 0.0 | | 0.0 | |
| Benzeneacetaldehyde | 211.6 | 8.4 | 105.4 | 12.7 | 5725.5 | 2.6 |
| 3,5-Dimethyl-Dihydro-2-Furanone | 467.1 | 15.0 | 15782.3 | 11.6 | 1210.6 | 2.1 |
| 2-Propenoic Acid | 1392.2 | 4.8 | 876.8 | 5.8 | 7719.3 | 4.3 |
| Ethyl Decanoate | 0.0 | | 0.0 | | 2251.8 | 3.3 |
| Acetophenone | 0.0 | | 0.0 | | 0.0 | |
| 2-Furanmethanol | 22314.2 | 1.7 | 26043.7 | 0.3 | 28262.0 | 4.2 |
| 3-Furanmethanol | 36432.8 | 9.1 | 35767.9 | 7.5 | 29598.2 | 0.4 |
| 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | 0.0 | | 6.5 | 15.1 | 298.0 | 0.3 |
| 2-(2-Furanylmethyl)-5-Methyl-Furan | 0.0 | | 14.6 | 4.1 | 20.1 | 6.7 |
| 3-Methyl-2(5H)-Furanone | 341.1 | 4.9 | 107.5 | 6.2 | 729.4 | 2.6 |
| 5-Methyl-2-Furanmethanol | 1525.8 | 4.2 | 156.8 | 1.4 | 1766.7 | 0.0 |
| Benzyl Acetate | 14.4 | 4.6 | 26.1 | 3.6 | 2030.0 | 2.1 |
| 2(5H)-Furanone | 4672.0 | 11.5 | 8830.0 | 0.9 | 18121.2 | 1.3 |
| 2,2'-Methylenebis[5-Methyl-Furan | 164.8 | 3.9 | 8.1 | 4.8 | 335.5 | 10.3 |
| 1,2-Cyclopentanedione | 13747.0 | 11.4 | 636.5 | 8.3 | 23467.2 | 10.7 |
| 2-Cyclohexenol | 2332.9 | 15.6 | 173.5 | 6.7 | 6820.4 | 7.8 |
| 2-Phenylethyl Acetate | 728.0 | 3.7 | 12.1 | 1.3 | 8907.3 | 3.6 |
| 3-Methyl-1,2-Cyclopentanedione | 3671.9 | 11.0 | 123.4 | 2.0 | 9352.2 | 6.2 |
| 2-Ethyl-Hexanoic Acid | 0.0 | | 0.0 | | 0.0 | |
| β-Damascenone | 1788.6 | 4.8 | 420.2 | 6.1 | 335.3 | 6.1 |
| Ethyl Undecanoate | 0.0 | | 0.0 | | 4396.7 | 4.3 |
| 2-Methyl-Propanoic Acid | 2987.5 | 8.4 | 200.4 | 8.4 | 7779.0 | 1.6 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 2,4,6-Trihydroxypyrimidine | 115.1 | 8.1 | 110.2 | 4.6 | 183.7 | 13.9 |
| Mequinol | 568.3 | 4.2 | 87.9 | 6.4 | 1098.4 | 0.5 |
| 2,2-Diethyl-3-Methyl-Oxazolidine | 1488.0 | 9.0 | 14.6 | 4.7 | 7218.6 | 1.3 |
| Oxypurinol | 2013.4 | 10.8 | 86.6 | 0.6 | 5598.4 | 9.5 |
| Benzenemethanol | 97.7 | 8.0 | 712.9 | 5.4 | 6035.1 | 5.0 |
| 4-Methyl-2(5H)-Furanone | 345.8 | 6.1 | 180.4 | 4.6 | 1516.3 | 9.4 |
| 3-Ethyl-2-Hydroxy-2-Cyclopenten-1-one | 57.2 | 8.1 | 147.9 | 2.0 | 58.7 | 9.5 |
| Benzeneethanol | 21.0 | 11.7 | 234.3 | 8.5 | 3935.6 | 1.3 |
| Acrylamide | 318.3 | 5.1 | 158.8 | 5.7 | 4892.5 | 1.6 |
| Erythritol | 4033.2 | 11.3 | 162.3 | 3.6 | 11590.7 | 2.5 |
| 2,3-Dimethyl-3-Pyrazolin-5-one | 430.1 | 3.8 | 228.8 | 0.5 | 918.4 | 5.1 |
| Furfural Acetone | 275.0 | 3.3 | 25.7 | 8.8 | 680.4 | 3.0 |
| Cyclotene | 918.1 | 1.8 | 34.9 | 4.2 | 2451.7 | 0.7 |
| 2-Methyl-1,4-Benzenediol | 607.3 | 4.7 | 51.6 | 4.8 | 2668.6 | 6.9 |
| Heptanoic Acid | 0.0 | | 0.0 | | 0.0 | |
| Maltol | 4193.9 | 6.7 | 452.2 | 0.4 | 18265.0 | 6.2 |
| 2-Acetylpyrrole | 12048.1 | 11.9 | 162.2 | 1.0 | 6616.0 | 6.6 |
| 2,5-Furandicarboxaldehyde | 2000.1 | 10.7 | 207.5 | 8.0 | 10560.1 | 8.4 |
| 2H-Pyran-2,6(3H)-Dione | 3697.3 | 14.9 | 408.8 | 10.6 | 8833.4 | 0.6 |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | 8757.6 | 12.3 | 322.7 | 16.5 | 22009.4 | 0.1 |
| Phenol | 1355.1 | 11.5 | 249.8 | 7.0 | 3044.0 | 7.3 |
| 1H-Pyrrole-2-Carboxaldehyde | 465.0 | 5.0 | 271.3 | 2.9 | 764.6 | 1.5 |
| Phloroglucinol | 3482.9 | 5.4 | 197.4 | 6.4 | 11418.1 | 6.6 |
| Furaneol | 12225.3 | 5.2 | 210.8 | 10.9 | 17418.6 | 2.3 |
| Octanoic Acid | 0.0 | | 0.0 | | 0.0 | |
| 5-Acetyl-Dihydro-2(3H)-Furanone | 10035.2 | 2.9 | 4429.2 | 10.3 | 13329.8 | 1.0 |
| 2-Furanpropionic Acid | 1702.5 | 3.8 | 254.4 | 7.9 | 3792.1 | 9.9 |
| 1,3-Dihydroxy-2-Propanone | 485174.0 | 3.9 | 388898.4 | 5.5 | 591962.9 | 2.8 |
| Tetrahydro-5-Methyl-2-Furanmethanol | 22011.4 | 0.6 | 23174.0 | 0.2 | 25808.6 | 6.7 |
| 4,5-Dimethyl Vinylene Carbonate | 10237.0 | 4.3 | 849.0 | 9.7 | 20933.8 | 4.7 |
| 2-Hydroxy-Dihydro-2(3H)-Furanone | 28684.2 | 1.6 | 1801.7 | 4.2 | 31450.3 | 15.9 |
| 5-Acetoxymethyl-2-Furfural A | 3533.0 | 12.4 | 460.0 | 0.8 | 16472.2 | 3.0 |
| 5-Acetoxymethyl-2-Furfural B | 6645.3 | 10.9 | 161.8 | 4.0 | 14550.9 | 9.3 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 2-Methoxy-4-Vinyl-Phenol | 473.5 | 9.6 | 32.5 | 6.9 | 2040.3 | 8.3 |
| 3-Methyl-2,4(3H,5H)-Furandione | 1946.3 | 0.4 | 108.9 | 8.7 | 4473.0 | 2.7 |
| 3-Hydroxy-2,3-Dihydro-Maltol | 9598.6 | 4.6 | 379.0 | 9.4 | 17345.5 | 6.1 |
| Decanoic Acid | 1076.2 | 11.3 | 0.0 | | 1723.3 | 9.2 |
| 5-Hydroxy-Maltol | 10933.8 | 6.9 | 293.4 | 11.8 | 15669.2 | 2.4 |
| 2,3-Dihydro-Benzofuran | 677.8 | 3.1 | 15.5 | 1.8 | 2176.2 | 6.0 |
| 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | 2210.5 | 12.9 | 224.5 | 15.1 | 5059.1 | 10.8 |
| 4-Pyridinol | 209.9 | 5.6 | 167.5 | 7.9 | 764.5 | 2.0 |
| 4-Amino-Phenol | 1906.5 | 8.1 | 329.2 | 2.5 | 5969.6 | 10.8 |
| Benzoic Acid | 412.8 | 2.9 | 83.8 | 1.8 | 4420.2 | 8.2 |
| Dimethylhydrazone 3-Pentanone | 7288.3 | 6.8 | 355.5 | 0.2 | 21524.1 | 7.6 |
| Undecanoic Acid | 0.0 | | 750.8 | 2.7 | 0.0 | |
| 5-(Hydroxymethyl)-Dihydro-2(3H)-Furanone | 27257.6 | 1.4 | 349.1 | 1.2 | 34394.5 | 7.4 |
| Dodecanoic Acid | 1030.8 | 8.8 | 0.0 | | 1051.1 | 9.1 |
| 5-(Hydroxymethyl)-2-Furfural | 140874.2 | 7.0 | 149808.3 | 4.0 | 132041.3 | 6.7 |
| 3-Methoxy-1,2-Benzenediol | 111.4 | 4.7 | 167.7 | 5.6 | 586.3 | 0.2 |
| 1-(2-Furanyl)-1,2-Ethanediol | 22317.1 | 10.3 | 28897.8 | 7.0 | 45811.6 | 10.0 |
| 4-Hydroxy-Dihydro-2(3H)-Furanone | 7639.0 | 0.0 | 323.0 | 8.8 | 19828.1 | 4.9 |

**Table 37C. Mean and relative standard deviation values of identified VOCs in SC-based syrups samples.**

| Volatile Organic Compound | Relative Peak Areas (x $10^3$) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | MED | | | | | | | | | |
| | ESP16 | | EGP17 | | EGPA16 | | EGPB16 | | EGPC16 | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| Pentane | 85.8 | 1.7 | 257.6 | 11.5 | 326.1 | 7.6 | 256.5 | 6.0 | 353.1 | 9.7 |
| Hexane | 293.5 | 9.6 | 410.6 | 5.5 | 470.4 | 2.7 | 63.2 | 0.8 | 161.9 | 4.5 |
| 1,4-Pentadiene | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Methanethiol | 122.6 | 13.7 | 758.4 | 12.2 | 991.6 | 15.0 | 289.7 | 4.5 | 15.4 | 2.7 |
| Ethanal | 2100.1 | 4.5 | 6375.9 | 9.8 | 6589.4 | 14.4 | 2052.6 | 1.1 | 1209.7 | 2.8 |
| Dimethyl Sulfide | 31.0 | 2.5 | 14592.5 | 0.5 | 16372.3 | 4.1 | 13183.5 | 3.8 | 10944.4 | 3.1 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Propanal | 693.9 | 1.9 | 985.5 | 8.8 | 1310.8 | 4.2 | 345.4 | 8.6 | 263.6 | 2.3 |
| Furan | 892.0 | 1.6 | 2921.2 | 6.1 | 3175.7 | 2.4 | 1756.8 | 1.0 | 604.9 | 8.3 |
| 2-Methyl-Propanal | 4577.4 | 4.4 | 8903.1 | 0.7 | 11437.7 | 3.8 | 8057.4 | 6.8 | 7306.5 | 3.0 |
| Ethyl Formate | 0.0 | | 0.0 | | 0.0 | | 797.2 | 2.3 | 0.0 | |
| 2-Propenal | 375.1 | 2.8 | 543.1 | 4.2 | 773.1 | 1.3 | 115.1 | 2.2 | 39.4 | 3.5 |
| 2-Methyl-Furan | 1863.5 | 2.9 | 1991.1 | 5.5 | 5079.6 | 2.8 | 752.6 | 1.8 | 453.1 | 6.2 |
| Ethyl Acetate | 807.2 | 5.7 | 9272.9 | 4.4 | 368.7 | 3.6 | 643.5 | 5.4 | 78.1 | 9.7 |
| 2-Butanone | 212.2 | 11.7 | 516.6 | 3.3 | 718.2 | 0.8 | 291.4 | 13.7 | 236.9 | 7.9 |
| 2-Methyl-Butanal | 6177.6 | 8.6 | 11354.7 | 4.3 | 13906.9 | 3.0 | 11606.8 | 7.2 | 8844.6 | 3.3 |
| 3-Methyl-Butanal | 3173.7 | 0.6 | 10858.7 | 4.0 | 27573.6 | 3.2 | 10669.6 | 9.7 | 4376.8 | 3.5 |
| Ethanol | 47770.4 | 5.9 | 104713.6 | 0.9 | 53733.8 | 5.3 | 37606.6 | 3.4 | 11995.2 | 1.6 |
| Benzene | 46.3 | 4.1 | 133.2 | 2.1 | 62.7 | 4.5 | 48.7 | 8.7 | 47.0 | 4.7 |
| 3-Buten-2-one | 931.3 | 6.5 | 2533.4 | 5.6 | 1003.1 | 11.5 | 278.6 | 12.5 | 44.6 | 3.2 |
| 2,5-Dimethyl-Furan | 829.2 | 12.9 | 1637.8 | 0.2 | 1041.0 | 1.0 | 826.6 | 7.7 | 144.5 | 5.6 |
| Ethyl Propanoate | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2,3-Butanedione | 8645.1 | 9.0 | 16239.7 | 10.6 | 15944.2 | 2.2 | 4665.0 | 10.4 | 1349.8 | 0.2 |
| 2-Methylpropyl Acetate | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 1-Propanol | 0.0 | | 0.0 | | 0.0 | | 649.4 | 9.7 | 0.0 | |
| 2-Ethyl-5-Methyl-Furan | 82.2 | 5.4 | 464.6 | 9.8 | 153.4 | 2.6 | 175.3 | 2.0 | 7.8 | 9.4 |
| Toluene | 19.7 | 0.2 | 1126.6 | 4.9 | 6926.8 | 1.1 | 1548.1 | 3.4 | 292.2 | 2.3 |
| Ethyl Butanoate | 0.0 | | 144.3 | 0.7 | 7.5 | 10.4 | 0.0 | | 0.0 | |
| 2-Methyl-3-Buten-2-ol | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Nonomethyl Succinate | 0.0 | | 3151.5 | 1.9 | 44.0 | 12.8 | 909.5 | 6.2 | 58.8 | 2.3 |
| 2,3-Pentanedione | 3718.4 | 1.2 | 8015.3 | 3.5 | 7548.8 | 3.3 | 497.5 | 10.2 | 282.8 | 2.3 |
| Dimethyl Disulfide | 55.3 | 1.7 | 161.3 | 2.3 | 365.7 | 7.4 | 476.0 | 1.7 | 38.8 | 11.0 |
| 2-Ethenyl-Furan | 57.5 | 5.1 | 454.0 | 2.3 | 629.7 | 2.4 | 104.6 | 8.7 | 34.8 | 6.1 |
| 2,5-Diethyltetrahydro-Furan | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Hexanal | 0.0 | | 417.7 | 0.1 | 612.9 | 10.7 | 27.7 | 8.2 | 50.2 | 12.7 |
| 2-Methyl-1-Propanol | 31.0 | 12.8 | 140.1 | 6.4 | 41.2 | 6.9 | 71.1 | 4.0 | 14.2 | 3.0 |
| 5-Butyl-Dihydro-2(3H)-Furanone | 88.1 | 3.3 | 95.3 | 4.3 | 98.1 | 5.0 | 7.0 | 6.5 | 10.8 | 2.3 |
| m-Cresol | 72.9 | 10.2 | 382.2 | 0.8 | 172.9 | 6.7 | 5.4 | 5.7 | 4.7 | 3.8 |
| 1-Butanol | 18.1 | 4.9 | 0.0 | | 0.0 | | 0.0 | | 18.0 | 5.7 |
| 5-Propyl-Dihydro-2(3H)-Furanone | 11.2 | 6.2 | 131.2 | 1.4 | 671.5 | 3.0 | 15.8 | 2.1 | 10.4 | 1.6 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 3-Methyl-Pyridazine | 66.2 | 7.7 | 535.5 | 1.8 | 1044.8 | 7.7 | 24.4 | 4.7 | 2.7 | 3.7 |
| 2-Heptanone | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| m-Menthane | 0.0 | | 430.5 | 1.9 | 114.8 | 3.8 | 51.2 | 2.9 | 3.7 | 0.7 |
| 1,3-Diazine | 20.3 | 0.8 | 1092.3 | 1.4 | 1773.1 | 2.2 | 30.1 | 16.3 | 11.4 | 3.5 |
| 2-Methyl-1-Butanol | 539.1 | 2.1 | 0.0 | | 0.0 | | 4223.2 | 11.6 | 18.3 | 3.3 |
| 2-Propyl-Furan | 15.2 | 4.3 | 72.3 | 1.2 | 296.4 | 3.1 | 31.2 | 10.1 | 8.1 | 5.8 |
| Ethyl Hexanoate | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2-Pentyl-Furan | 6.5 | 6.9 | 50.3 | 4.6 | 40.8 | 8.4 | 29.9 | 5.9 | 16.5 | 3.7 |
| 2-Methyl-Pyrazine | 0.0 | | 1562.7 | 2.6 | 1021.2 | 10.2 | 311.1 | 5.2 | 10.2 | 7.1 |
| 2-Methyl-Dihydro-2(3H)-Furanone | 4119.1 | 5.3 | 2887.6 | 2.7 | 5045.5 | 9.2 | 3174.6 | 2.0 | 1562.8 | 4.8 |
| p-Cymene | 5.7 | 3.2 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Mesitylene | 3.3 | 9.8 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 3,5-Xylenol | 10.7 | 2.7 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 3-Hydroxy-2-Butanone | 877.6 | 0.4 | 2151.9 | 1.3 | 1096.0 | 3.1 | 175.9 | 5.8 | 74.0 | 10.6 |
| Vinylene Carbonate | 5097.1 | 12.9 | 7713.3 | 5.4 | 7058.4 | 12.1 | 1616.0 | 1.5 | 895.7 | 13.9 |
| 2,6-Xylenol | 257.1 | 7.3 | 15.5 | 2.5 | 163.2 | 3.9 | 14.6 | 0.8 | 4.7 | 12.9 |
| 1-Hydroxy-2-Propanone | 1597.1 | 4.2 | 15435.8 | 1.9 | 11458.2 | 2.5 | 6837.4 | 1.8 | 2665.1 | 2.2 |
| 2,5-Dimethyl-Pyrazine | 5.6 | 14.4 | 283.2 | 3.5 | 279.0 | 11.8 | 10.1 | 5.0 | 13.3 | 4.8 |
| 2,6-Dimethyl-Pyrazine | 20.8 | 8.6 | 746.4 | 5.7 | 970.8 | 6.0 | 76.0 | 6.3 | 158.7 | 5.7 |
| 2-Cyclopenten-1-one | 134.8 | 4.4 | 102.2 | 9.5 | 562.7 | 2.8 | 243.3 | 9.4 | 111.8 | 2.7 |
| 1,2,3,4-Tetramethyl-4-(1-methylethenyl)-Benzene | 46.6 | 4.9 | 0.0 | | 0.0 | | 8.9 | 3.8 | 0.0 | |
| 2-Methyl-2-Cyclopenten-1-one | 284.0 | 0.2 | 282.1 | 3.7 | 403.7 | 8.9 | 28.1 | 6.4 | 17.7 | 6.0 |
| 5-Methyl-2-Furanmethanethiol | 230.6 | 3.8 | 2616.0 | 9.2 | 46.0 | 14.1 | 256.4 | 5.0 | 5.9 | 0.3 |
| 1-Hydroxy-2-Butanone | 491.1 | 2.0 | 875.1 | 1.1 | 498.9 | 10.3 | 4493.7 | 2.7 | 1818.9 | 3.2 |
| 2-Ethyl-6-Methyl-Pyrazine | 8.7 | 1.8 | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2-Ethyl-5-Methyl-Pyrazine | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Nonanal | 386.4 | 12.9 | 832.3 | 10.0 | 979.5 | 0.9 | 772.5 | 1.8 | 250.1 | 8.6 |
| Trimethyl-Pyrazine | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | 0.0 | | 0.0 | | 0.0 | | 21.4 | 11.3 | 0.0 | |
| 2-Cyclohexen-1-one | 304.8 | 5.2 | 22.4 | 4.4 | 450.6 | 2.3 | 21.1 | 6.9 | 13.9 | 4.1 |
| 5-Methyl-2(3H)-Furanone | 1383.9 | 5.9 | 2997.1 | 10.0 | 1720.9 | 2.4 | 1401.9 | 4.4 | 346.3 | 3.2 |
| 1,3-Dihydro-4-Methyl-2H-Imidazol-2-one | 744.5 | 4.5 | 1906.7 | 6.2 | 1821.9 | 5.3 | 350.7 | 11.7 | 453.0 | 7.1 |
| Ethyl Octanoate | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | 1344.5 | 1.4 | 1472.8 | 9.6 | 567.4 | 10.9 | 1486.2 | 2.9 | 9.5 | 8.2 |
| Furfural | 28145.9 | 9.6 | 34757.9 | 6.0 | 47378.6 | 8.3 | 36404.9 | 1.6 | 30413.7 | 2.1 |
| Ethanoic Acid | 204531.3 | 8.2 | 525881.1 | 3.0 | 663791.3 | 11.5 | 265425.9 | 9.8 | 199330.3 | 9.5 |
| 1,2,3,4-Tetrahydro-1,6,8-Trimethyl-Naphthalene | 862.1 | 1.0 | 1009.5 | 0.8 | 353.3 | 15.7 | 806.7 | 0.8 | 40.2 | 8.0 |
| 2-Ethyl-1-Hexanol | 451.8 | 3.3 | 786.3 | 5.0 | 327.4 | 6.2 | 300.8 | 1.9 | 297.1 | 1.6 |
| 3-Methyl-Furfural | 127.8 | 0.7 | 175.5 | 0.7 | 161.1 | 3.6 | 56.2 | 12.2 | 29.0 | 10.8 |
| Furfuryl Formate | 352.6 | 2.4 | 1135.2 | 3.4 | 980.7 | 0.4 | 734.3 | 2.1 | 300.7 | 5.5 |
| Decanal | 169.1 | 2.1 | 105.9 | 5.7 | 72.1 | 2.5 | 94.9 | 8.4 | 48.1 | 4.6 |
| 1-(2-Furanyl)-Ethanone | 4662.3 | 3.5 | 15360.0 | 2.6 | 12957.8 | 3.1 | 12403.3 | 3.1 | 5226.3 | 4.5 |
| Benzaldehyde | 435.4 | 2.4 | 355.7 | 13.9 | 288.3 | 16.1 | 90.9 | 6.9 | 64.0 | 8.8 |
| Furfuryl Acetate | 161.9 | 15.8 | 557.3 | 0.5 | 458.8 | 16.7 | 459.8 | 2.7 | 25.6 | 4.2 |
| Propanoic Acid | 1074.2 | 3.7 | 1837.2 | 1.0 | 1021.4 | 4.5 | 4673.1 | 4.4 | 4153.1 | 2.2 |
| Dimethyl Sulfoxide | 17.9 | 11.5 | 1654.7 | 10.8 | 1739.2 | 5.4 | 420.3 | 10.3 | 50.4 | 11.1 |
| 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | 258.5 | 3.5 | 0.0 | | 0.0 | | 438.5 | 2.8 | 0.0 | |
| 5-Methyl-Furfural | 6144.0 | 14.9 | 21002.4 | 3.5 | 16615.1 | 1.0 | 15673.5 | 2.9 | 10488.3 | 3.4 |
| 4-Cyclopentene-1,3-dione | 4236.2 | 5.6 | 6329.9 | 7.0 | 2903.8 | 14.8 | 4060.6 | 9.0 | 4194.6 | 5.9 |
| 2-Methyl-Benzofuran | 716.8 | 8.3 | 303.3 | 7.8 | 44.2 | 7.9 | 628.2 | 5.9 | 14.8 | 4.0 |
| 1-(5-Methyl-2-Furanyl)-Ethanone | 388.0 | 5.3 | 1008.7 | 4.7 | 853.4 | 9.9 | 910.0 | 6.3 | 477.6 | 7.1 |
| Diethylene Glycol Ethyl Ether | 650.2 | 2.5 | 2312.5 | 12.3 | 3373.0 | 4.9 | 3420.0 | 6.9 | 1168.5 | 4.3 |
| 3-Methyl-Dihydro-2(3H)-Furanone | 295.4 | 1.4 | 428.4 | 8.9 | 1144.2 | 10.5 | 393.5 | 13.1 | 1454.3 | 2.5 |
| 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | 175.8 | 5.7 | 0.0 | | 0.0 | | 132.6 | 1.7 | 6.2 | 12.6 |
| Benzeneacetaldehyde | 18.1 | 4.8 | 1667.0 | 6.8 | 2877.6 | 9.2 | 1090.0 | 9.9 | 239.3 | 14.5 |
| 3,5-Dimethyl-Dihydro-2-Furanone | 359.6 | 6.4 | 940.5 | 10.2 | 936.1 | 10.1 | 890.8 | 1.7 | 901.1 | 3.3 |
| 2-Propenoic Acid | 56.0 | 10.9 | 570.0 | 5.4 | 10367.4 | 10.4 | 331.0 | 9.1 | 1014.8 | 7.8 |
| Ethyl Decanoate | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| Acetophenone | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2-Furanmethanol | 19541.0 | 1.2 | 30165.7 | 10.0 | 24400.6 | 3.4 | 24535.3 | 1.0 | 21311.4 | 5.7 |
| 3-Furanmethanol | 15671.3 | 1.2 | 22768.3 | 0.5 | 25676.2 | 3.2 | 17544.2 | 1.5 | 11589.6 | 3.8 |
| 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | 479.3 | 7.2 | 1137.1 | 4.1 | 272.8 | 10.3 | 744.3 | 2.4 | 62.4 | 6.6 |
| 2-(2-Furanylmethyl)-5-Methyl-Furan | 0.0 | | 0.0 | | 0.0 | | 12.7 | 8.1 | 0.0 | |
| 3-Methyl-2(5H)-Furanone | 103.2 | 5.2 | 836.5 | 5.2 | 848.2 | 1.0 | 192.6 | 6.6 | 147.3 | 2.7 |
| 5-Methyl-2-Furanmethanol | 787.7 | 8.1 | 2193.5 | 7.6 | 0.0 | | 727.6 | 8.9 | 404.8 | 2.6 |
| Benzyl Acetate | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 2(5H)-Furanone | 4156.5 | 11.6 | 12488.8 | 5.9 | 7932.5 | 4.5 | 4913.4 | 2.2 | 3494.8 | 9.4 |
| 2,2'-Methylenebis[5-Methyl-Furan | 49.5 | 0.1 | 124.6 | 6.5 | 85.3 | 3.1 | 86.4 | 14.5 | 6.6 | 10.5 |
| 1,2-Cyclopentanedione | 18344.3 | 4.1 | 22941.3 | 13.5 | 24973.7 | 4.5 | 18434.2 | 1.8 | 16030.2 | 5.5 |
| 2-Cyclohexenol | 704.8 | 0.6 | 5050.5 | 6.3 | 4231.7 | 6.7 | 3208.6 | 8.6 | 1076.5 | 3.3 |
| 2-Phenylethyl Acetate | 109.0 | 5.1 | 12084.7 | 4.0 | 33.9 | 10.7 | 1504.0 | 1.4 | 6.1 | 3.6 |
| 3-Methyl-1,2-Cyclopentanedione | 3391.4 | 2.1 | 7922.6 | 3.1 | 6026.4 | 3.7 | 3696.0 | 11.0 | 2952.7 | 9.4 |
| 2-Ethyl-Hexanoic Acid | 0.0 | | 1171.3 | 0.0 | 1670.2 | 12.7 | 2260.1 | 9.0 | 502.2 | 6.9 |
| β-Damascenone | 478.2 | 3.5 | 983.0 | 2.1 | 456.9 | 6.1 | 391.3 | 2.3 | 21.7 | 7.7 |
| Ethyl Undecanoate | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 2-Methyl-Propanoic Acid | 676.0 | 1.1 | 5280.0 | 8.8 | 5265.2 | 8.9 | 1107.0 | 1.1 | 111.6 | 0.7 |
| 2,4,6-Trihydroxypyrimidine | 164.2 | 10.9 | 377.1 | 8.3 | 396.7 | 4.1 | 111.6 | 9.5 | 91.4 | 1.7 |
| Mequinol | 744.8 | 3.0 | 1490.0 | 1.8 | 152.6 | 8.6 | 377.9 | 2.3 | 117.5 | 6.1 |
| 2,2-Diethyl-3-Methyl-Oxazolidine | 908.3 | 3.2 | 6727.0 | 2.0 | 5941.0 | 4.4 | 317.1 | 6.0 | 1502.5 | 7.2 |
| Oxypurinol | 499.4 | 4.4 | 5320.4 | 10.7 | 4183.2 | 5.7 | 3530.7 | 9.5 | 2274.8 | 14.4 |
| Benzenemethanol | 21.9 | 13.8 | 84.0 | 2.2 | 97.4 | 10.4 | 43.1 | 9.6 | 67.9 | 7.0 |
| 4-Methyl-2(5H)-Furanone | 428.4 | 10.0 | 968.8 | 6.4 | 1466.7 | 4.0 | 1025.2 | 3.4 | 529.3 | 14.3 |
| 3-Ethyl-2-Hydroxy-2-Cyclopenten-1-one | 19.0 | 5.6 | 98.8 | 4.7 | 966.2 | 7.9 | 958.3 | 5.4 | 669.3 | 6.6 |
| Benzeneethanol | 867.2 | 1.4 | 1760.5 | 3.0 | 213.9 | 4.0 | 122.3 | 4.2 | 110.2 | 9.1 |
| Acrylamide | 22.0 | 6.8 | 4884.7 | 2.8 | 1039.9 | 2.1 | 163.4 | 1.4 | 496.7 | 7.9 |
| Erythritol | 1691.9 | 3.3 | 3848.6 | 3.7 | 7592.8 | 0.4 | 310.8 | 1.8 | 841.8 | 5.3 |
| 2,3-Dimethyl-3-Pyrazolin-5-one | 0.0 | | 605.2 | 6.9 | 596.9 | 6.1 | 195.9 | 4.5 | 23.9 | 12.9 |
| Furfural Acetone | 220.6 | 6.6 | 264.0 | 11.8 | 317.1 | 1.7 | 325.3 | 2.2 | 152.9 | 2.1 |
| Cyclotene | 368.6 | 0.7 | 2140.8 | 8.8 | 1375.6 | 6.0 | 222.2 | 5.1 | 206.9 | 6.4 |
| 2-Methyl-1,4-Benzenediol | 201.9 | 5.8 | 912.0 | 6.3 | 1676.9 | 2.5 | 360.4 | 10.7 | 451.4 | 5.4 |
| Heptanoic Acid | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 118.9 | 8.9 |
| Maltol | 2927.0 | 9.4 | 9132.6 | 1.6 | 9095.6 | 0.3 | 8504.1 | 11.0 | 5157.7 | 9.6 |
| 2-Acetylpyrrole | 2100.4 | 5.8 | 3804.0 | 8.1 | 3154.5 | 11.5 | 2493.3 | 7.5 | 699.1 | 6.2 |
| 2,5-Furandicarboxaldehyde | 2058.9 | 8.5 | 7971.6 | 1.2 | 10350.8 | 1.4 | 7332.6 | 5.8 | 3450.5 | 14.0 |
| 2H-Pyran-2,6(3H)-Dione | 2561.5 | 7.3 | 7322.9 | 4.9 | 6084.3 | 5.7 | 4069.1 | 6.6 | 3737.3 | 3.7 |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | 7511.3 | 9.9 | 28156.8 | 10.3 | 21112.8 | 3.2 | 8488.0 | 7.6 | 6400.2 | 2.0 |
| Phenol | 2100.0 | 7.3 | 4499.7 | 6.3 | 2457.0 | 8.1 | 3237.9 | 13.7 | 1658.8 | 11.1 |
| 1H-Pyrrole-2-Carboxaldehyde | 369.0 | 9.2 | 1012.2 | 2.7 | 1899.6 | 3.1 | 429.6 | 11.1 | 275.4 | 2.3 |
| Phloroglucinol | 1682.2 | 5.4 | 7709.9 | 10.4 | 6758.4 | 11.5 | 1843.9 | 2.9 | 201.2 | 4.9 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Furaneol | 10011.8 | 6.9 | 14041.5 | 7.4 | 14676.6 | 1.4 | 10283.5 | 3.7 | 9742.6 | 8.3 |
| Octanoic Acid | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 5-Acetyl-Dihydro-2(3H)-Furanone | 8964.3 | 6.8 | 12269.9 | 7.1 | 12879.9 | 13.8 | 7160.2 | 3.1 | 6083.8 | 9.7 |
| 2-Furanpropionic Acid | 2146.9 | 9.7 | 4652.1 | 4.9 | 4047.3 | 3.9 | 2263.1 | 3.5 | 1877.3 | 6.6 |
| 1,3-Dihydroxy-2-Propanone | 471324.1 | 1.0 | 585026.4 | 1.2 | 882133.4 | 9.8 | 516521.2 | 10.8 | 413356.1 | 5.7 |
| Tetrahydro-5-Methyl-2-Furanmethanol | 16541.6 | 1.9 | 24267.4 | 2.3 | 27213.4 | 7.3 | 22737.9 | 0.4 | 14263.5 | 3.6 |
| 4,5-Dimethyl Vinylene Carbonate | 4719.2 | 0.1 | 17222.0 | 7.8 | 15798.9 | 1.7 | 1529.8 | 13.5 | 4095.9 | 2.3 |
| 2-Hydroxy-Dihydro-2(3H)-Furanone | 29797.0 | 5.7 | 33121.2 | 4.6 | 28324.7 | 7.0 | 28439.7 | 4.8 | 20712.5 | 7.3 |
| 5-Acetoxymethyl-2-Furfural A | 3560.9 | 7.8 | 14316.1 | 5.9 | 14914.9 | 4.2 | 7232.0 | 6.4 | 4774.4 | 6.4 |
| 5-Acetoxymethyl-2-Furfural B | 5073.6 | 7.6 | 14739.2 | 2.5 | 15041.5 | 6.0 | 8248.8 | 5.0 | 5347.4 | 3.8 |
| 2-Methoxy-4-Vinyl-Phenol | 455.4 | 4.9 | 1360.7 | 5.7 | 1262.1 | 6.7 | 590.6 | 0.9 | 169.7 | 7.0 |
| 3-Methyl-2,4(3H,5H)-Furandione | 1624.7 | 1.5 | 2817.9 | 7.2 | 2723.2 | 0.8 | 1514.2 | 6.3 | 1344.5 | 2.0 |
| 3-Hydroxy-2,3-Dihydro-Maltol | 8759.9 | 3.0 | 13181.7 | 14.5 | 5983.6 | 0.7 | 25737.7 | 2.8 | 19949.5 | 13.1 |
| Decanoic Acid | 607.5 | 3.8 | 1436.8 | 8.5 | 1303.6 | 7.0 | 0.0 | | 0.0 | |
| 5-Hydroxy-Maltol | 7607.8 | 11.9 | 14293.3 | 6.2 | 27699.0 | 8.1 | 9341.8 | 1.0 | 2268.1 | 10.2 |
| 2,3-Dihydro-Benzofuran | 675.6 | 6.0 | 1714.6 | 9.2 | 1933.1 | 5.5 | 837.0 | 2.9 | 599.6 | 4.9 |
| 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | 3672.3 | 9.4 | 4346.6 | 8.3 | 6253.6 | 8.1 | 3581.6 | 4.0 | 1960.6 | 1.3 |
| 4-Pyridinol | 419.3 | 6.9 | 926.0 | 3.6 | 662.8 | 12.6 | 388.8 | 2.9 | 143.7 | 4.0 |
| 4-Amino-Phenol | 122.9 | 8.1 | 7602.0 | 7.3 | 6263.4 | 2.8 | 844.7 | 3.6 | 596.1 | 3.6 |
| Benzoic Acid | 435.2 | 1.1 | 1196.7 | 1.8 | 1773.2 | 3.9 | 128.6 | 5.4 | 253.7 | 12.6 |
| Dimethylhydrazone 3-Pentanone | 5390.8 | 4.9 | 18281.5 | 6.4 | 17348.6 | 9.5 | 4562.2 | 4.2 | 3431.6 | 11.6 |
| Undecanoic Acid | 0.0 | | 2459.5 | 3.6 | 1318.0 | 4.7 | 230.9 | 2.3 | 220.9 | 11.6 |
| 5-(Hydroxymethyl)-Dihydro-2(3H)-Furanone | 26678.3 | 13.4 | 33530.5 | 8.4 | 32799.5 | 9.7 | 24323.9 | 10.2 | 17277.8 | 5.3 |
| Dodecanoic Acid | 0.0 | | 0.0 | | 0.0 | | 0.0 | | 0.0 | |
| 5-(Hydroxymethyl)-2-Furfural | 104330.5 | 3.7 | 178324.6 | 6.0 | 228281.1 | 2.1 | 188304.0 | 0.5 | 161590.9 | 5.2 |
| 3-Methoxy-1,2-Benzenediol | 56.1 | 3.4 | 603.2 | 11.5 | 734.9 | 10.1 | 507.0 | 6.0 | 85.9 | 14.2 |
| 1-(2-Furanyl)-1,2-Ethanediol | 21390.0 | 7.2 | 75845.7 | 14.2 | 67596.9 | 11.9 | 483.7 | 12.4 | 19537.8 | 6.0 |
| 4-Hydroxy-Dihydro-2(3H)-Furanone | 30763.5 | 5.0 | 17737.7 | 9.7 | 15722.5 | 11.0 | 35188.3 | 8.4 | 4367.2 | 3.3 |

**Table S37D. Mean and relative standard deviation values of identified VOCs in SC-based syrups samples.**

| Volatile Organic Compound | Relative Peak Areas (x $10^3$) | | | | | |
|---|---|---|---|---|---|---|
| | STH | | | | | |
| | MCBR14 | | MDBR14 | | AUS17 | |
| | Mean | RSD (%) | Mean | RSD (%) | Mean | RSD (%) |
| Pentane | 286.5 | 7.7 | 539.5 | 2.4 | 277.5 | 5.6 |
| Hexane | 47.5 | 11.2 | 281.7 | 0.7 | 312.7 | 12.4 |
| 1,4-Pentadiene | 39.5 | 7.8 | 115.9 | 4.2 | 44.4 | 1.7 |
| Methanethiol | 124.4 | 5.7 | 691.5 | 1.8 | 361.8 | 5.7 |
| Ethanal | 1897.7 | 3.4 | 6446.1 | 0.8 | 4042.1 | 8.8 |
| Dimethyl Sulfide | 293.9 | 7.9 | 28601.0 | 2.1 | 11883.7 | 0.9 |
| Propanal | 420.1 | 2.9 | 2615.0 | 7.0 | 248.4 | 9.9 |
| Furan | 3045.0 | 9.5 | 2846.8 | 8.0 | 6643.8 | 12.7 |
| 2-Methyl-Propanal | 7352.8 | 6.6 | 3278.2 | 7.0 | 8446.6 | 2.9 |
| Ethyl Formate | 1308.1 | 4.4 | 0.0 | | 0.0 | |
| 2-Propenal | 277.3 | 5.4 | 1413.5 | 1.6 | 406.4 | 5.2 |
| 2-Methyl-Furan | 1572.6 | 2.9 | 5821.4 | 3.3 | 11228.2 | 2.9 |
| Ethyl Acetate | 731.4 | 2.8 | 54.9 | 6.2 | 92.5 | 6.1 |
| 2-Butanone | 351.2 | 10.3 | 1282.1 | 1.4 | 961.2 | 7.2 |
| 2-Methyl-Butanal | 9301.9 | 10.8 | 10566.0 | 0.3 | 11345.9 | 4.5 |
| 3-Methyl-Butanal | 4848.3 | 6.5 | 6680.9 | 4.9 | 4338.9 | 4.8 |
| Ethanol | 37076.6 | 5.0 | 15898.0 | 4.1 | 66393.5 | 7.7 |
| Benzene | 51.8 | 5.1 | 379.6 | 1.8 | 32.9 | 8.4 |
| 3-Buten-2-one | 893.9 | 9.3 | 4776.0 | 2.5 | 328.9 | 13.5 |
| 2,5-Dimethyl-Furan | 2850.0 | 6.5 | 1794.1 | 4.7 | 3066.5 | 1.5 |
| Ethyl Propanoate | 0.0 | | 0.0 | | 0.0 | |
| 2,3-Butanedione | 10220.2 | 6.1 | 31495.0 | 2.9 | 7161.8 | 8.3 |
| 2-Methylpropyl Acetate | 0.0 | | 0.0 | | 0.0 | |
| 1-Propanol | 0.0 | | 0.0 | | 0.0 | |
| 2-Ethyl-5-Methyl-Furan | 418.7 | 3.7 | 413.2 | 4.6 | 363.3 | 13.5 |
| Toluene | 793.3 | 11.4 | 2311.5 | 7.3 | 8.2 | 2.8 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Ethyl Butanoate | 0.0 | | 0.0 | | 0.0 | |
| 2-Methyl-3-Buten-2-ol | 427.9 | 8.4 | 1880.3 | 5.1 | 0.0 | |
| Nonomethyl Succinate | 846.3 | 5.4 | 0.0 | | 0.0 | |
| 2,3-Pentanedione | 3405.7 | 5.1 | 15461.8 | 4.9 | 1843.2 | 4.8 |
| Dimethyl Disulfide | 0.0 | | 0.0 | | 1860.0 | 7.7 |
| 2-Ethenyl-Furan | 50.0 | 12.9 | 520.2 | 0.4 | 0.0 | |
| 2,5-Diethyltetrahydro-Furan | 62.5 | 11.9 | 0.0 | | 402.3 | 11.0 |
| Hexanal | 0.0 | | 8030.0 | 3.4 | 0.0 | |
| 2-Methyl-1-Propanol | 145.7 | 6.4 | 61.1 | 2.4 | 39.1 | 10.3 |
| 5-Butyl-Dihydro-2(3H)-Furanone | 1125.9 | 4.4 | 22209.1 | 2.7 | 1823.3 | 4.7 |
| m-Cresol | 8.8 | 2.9 | 26.8 | 0.7 | 4.2 | 7.5 |
| 1-Butanol | 0.0 | | 0.0 | | 0.0 | |
| 5-Propyl-Dihydro-2(3H)-Furanone | 47.9 | 4.6 | 18187.8 | 7.3 | 424.2 | 12.4 |
| 3-Methyl-Pyridazine | 132.8 | 5.4 | 549.0 | 3.2 | 317.4 | 7.7 |
| 2-Heptanone | 0.0 | | 0.0 | | 0.0 | |
| m-Menthane | 0.0 | | 17.7 | 6.4 | 0.0 | |
| 1,3-Diazine | 3.4 | 4.3 | 78.9 | 4.1 | 283.9 | 8.7 |
| 2-Methyl-1-Butanol | 74.0 | 0.6 | 299.4 | 1.6 | 224.1 | 3.7 |
| 2-Propyl-Furan | 22.8 | 12.5 | 14.0 | 2.8 | 8.6 | 9.2 |
| Ethyl Hexanoate | 0.0 | | 0.0 | | 0.0 | |
| 2-Pentyl-Furan | 17.5 | 4.2 | 618.1 | 4.6 | 19.2 | 5.4 |
| 2-Methyl-Pyrazine | 0.0 | | 18.6 | 2.0 | 2648.4 | 5.0 |
| 2-Methyl-Dihydro-2(3H)-Furanone | 13256.6 | 8.7 | 4917.5 | 6.2 | 11510.2 | 7.0 |
| p-Cymene | 3.3 | 9.4 | 0.0 | | 8.7 | 13.0 |
| Mesitylene | 5.4 | 12.1 | 0.0 | | 4.8 | 10.1 |
| 3,5-Xylenol | 172.6 | 4.7 | 0.0 | | 0.0 | |
| 3-Hydroxy-2-Butanone | 224.2 | 10.2 | 4437.5 | 9.2 | 264.5 | 7.0 |
| Vinylene Carbonate | 4188.6 | 3.3 | 11592.4 | 0.9 | 2263.5 | 6.5 |
| 2,6-Xylenol | 753.1 | 11.6 | 22.1 | 4.6 | 4.2 | 4.3 |
| 1-Hydroxy-2-Propanone | 27593.0 | 7.2 | 34460.5 | 8.8 | 2254.8 | 5.4 |
| 2,5-Dimethyl-Pyrazine | 95.9 | 8.7 | 14.2 | 1.3 | 2183.0 | 6.1 |
| 2,6-Dimethyl-Pyrazine | 96.5 | 3.6 | 108.8 | 7.3 | 2052.0 | 3.8 |
| 2-Cyclopenten-1-one | 948.1 | 2.9 | 12436.6 | 5.8 | 286.3 | 13.2 |

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|---|---|---|---|---|---|---|
| 1,2,3,4-Tetramethyl-4-(1-methylethenyl)-Benzene | 0.0 | | 981.3 | 0.1 | 0.0 | |
| 2-Methyl-2-Cyclopenten-1-one | 136.4 | 6.6 | 1472.2 | 4.5 | 100.5 | 4.7 |
| 5-Methyl-2-Furanmethanethiol | 691.8 | 8.1 | 21.5 | 2.2 | 6.1 | 10.5 |
| 1-Hydroxy-2-Butanone | 4780.2 | 5.3 | 13379.9 | 6.4 | 407.8 | 8.7 |
| 2-Ethyl-6-Methyl-Pyrazine | 5.0 | 4.1 | 0.0 | | 965.4 | 2.1 |
| 2-Ethyl-5-Methyl-Pyrazine | 0.0 | | 0.0 | | 411.2 | 4.6 |
| Nonanal | 719.0 | 3.9 | 465.4 | 2.4 | 57.0 | 6.2 |
| Trimethyl-Pyrazine | 0.0 | | 0.0 | | 349.3 | 3.5 |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | 0.0 | | 878.3 | 1.6 | 0.0 | |
| 2-Cyclohexen-1-one | 17.3 | 9.0 | 9266.3 | 1.0 | 6.3 | 8.6 |
| 5-Methyl-2(3H)-Furanone | 1350.1 | 4.6 | 4675.6 | 2.9 | 1065.0 | 10.8 |
| 1,3-Dihydro-4-Methyl-2H-Imidazol-2-one | 1133.2 | 10.6 | 5605.2 | 2.2 | 580.6 | 6.8 |
| Ethyl Octanoate | 0.0 | | 0.0 | | 0.0 | |
| 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | 453.6 | 3.8 | 7118.8 | 4.0 | 65.6 | 6.8 |
| Furfural | 32710.8 | 10.8 | 29394.4 | 6.9 | 28442.4 | 9.5 |
| Ethanoic Acid | 331784.7 | 1.1 | 458847.3 | 0.7 | 258647.0 | 6.3 |
| 1,2,3,4-Tetrahydro-1,6,8-Trimethyl-Naphthalene | 2291.4 | 9.3 | 5266.4 | 0.3 | 207.0 | 12.1 |
| 2-Ethyl-1-Hexanol | 780.9 | 7.3 | 1378.2 | 5.4 | 528.5 | 8.4 |
| 3-Methyl-Furfural | 132.4 | 12.0 | 351.1 | 1.2 | 42.3 | 1.2 |
| Furfuryl Formate | 656.1 | 8.4 | 657.3 | 1.5 | 253.3 | 7.8 |
| Decanal | 98.4 | 7.0 | 136.0 | 1.8 | 129.9 | 9.5 |
| 1-(2-Furanyl)-Ethanone | 8719.1 | 11.3 | 13854.3 | 2.4 | 1157.4 | 7.3 |
| Benzaldehyde | 19.2 | 9.3 | 11608.6 | 3.7 | 34.5 | 10.5 |
| Furfuryl Acetate | 533.8 | 4.4 | 778.7 | 3.5 | 295.2 | 3.8 |
| Propanoic Acid | 4814.3 | 7.2 | 10580.2 | 2.3 | 53.1 | 1.9 |
| Dimethyl Sulfoxide | 77.5 | 9.1 | 1709.4 | 2.0 | 114.7 | 8.7 |
| 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | 102.5 | 9.8 | 1546.0 | 1.4 | 0.0 | |
| 5-Methyl-Furfural | 10730.2 | 10.0 | 7039.8 | 9.9 | 6260.5 | 7.0 |
| 4-Cyclopentene-1,3-dione | 7077.1 | 5.2 | 13667.6 | 5.4 | 1381.5 | 3.4 |
| 2-Methyl-Benzofuran | 187.9 | 4.4 | 610.9 | 0.3 | 89.4 | 9.3 |
| 1-(5-Methyl-2-Furanyl)-Ethanone | 420.3 | 12.6 | 968.9 | 3.5 | 550.4 | 6.3 |
| Diethylene Glycol Ethyl Ether | 3573.1 | 10.0 | 264.1 | 9.2 | 410.6 | 10.7 |
| 3-Methyl-Dihydro-2(3H)-Furanone | 1240.4 | 6.4 | 4245.1 | 1.1 | 470.8 | 7.9 |

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|---|---|---|---|---|---|---|
| 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | 643.2 | 6.9 | 1438.7 | 6.0 | 27.4 | 5.2 |
| Benzeneacetaldehyde | 207.9 | 13.1 | 902.7 | 3.5 | 216.9 | 4.0 |
| 3,5-Dimethyl-Dihydro-2-Furanone | 1106.4 | 11.2 | 3943.8 | 1.5 | 1103.7 | 7.6 |
| 2-Propenoic Acid | 4715.6 | 9.6 | 8655.5 | 6.1 | 67.2 | 9.9 |
| Ethyl Decanoate | 0.0 | | 0.0 | | 0.0 | |
| Acetophenone | 0.0 | | 516.3 | 1.2 | 0.0 | |
| 2-Furanmethanol | 40480.6 | 8.3 | 20947.7 | 3.2 | 19671.2 | 3.9 |
| 3-Furanmethanol | 41382.7 | 9.9 | 20633.1 | 0.6 | 12577.1 | 7.5 |
| 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | 2190.9 | 4.7 | 5077.2 | 2.6 | 145.0 | 7.1 |
| 2-(2-Furanylmethyl)-5-Methyl-Furan | 8.5 | 5.4 | 4.2 | 5.1 | 0.0 | |
| 3-Methyl-2(5H)-Furanone | 368.3 | 9.3 | 2167.0 | 2.2 | 155.9 | 5.2 |
| 5-Methyl-2-Furanmethanol | 1066.8 | 6.5 | 3940.1 | 2.7 | 1573.3 | 9.8 |
| Benzyl Acetate | 4.4 | 3.5 | 0.0 | | 0.0 | |
| 2(5H)-Furanone | 7639.9 | 12.0 | 27146.8 | 2.2 | 2958.0 | 6.8 |
| 2,2'-Methylenebis[5-Methyl-Furan | 353.2 | 6.8 | 42.5 | 4.1 | 26.8 | 11.3 |
| 1,2-Cyclopentanedione | 32232.0 | 2.8 | 27157.7 | 8.4 | 11403.5 | 4.7 |
| 2-Cyclohexenol | 3243.0 | 3.0 | 4990.1 | 2.9 | 2575.8 | 11.4 |
| 2-Phenylethyl Acetate | 0.0 | | 0.0 | | 22.8 | 2.6 |
| 3-Methyl-1,2-Cyclopentanedione | 5183.4 | 10.2 | 24172.1 | 4.0 | 3155.1 | 8.4 |
| 2-Ethyl-Hexanoic Acid | 0.0 | | 1114.6 | 0.2 | 0.0 | |
| β-Damascenone | 966.1 | 5.8 | 1997.2 | 2.0 | 1365.1 | 10.4 |
| Ethyl Undecanoate | 1151.6 | 2.2 | 0.0 | | 0.0 | |
| 2-Methyl-Propanoic Acid | 2824.1 | 12.4 | 26647.2 | 2.8 | 662.9 | 3.3 |
| 2,4,6-Trihydroxypyrimidine | 153.7 | 3.1 | 789.7 | 2.0 | 208.9 | 6.9 |
| Mequinol | 132.2 | 9.0 | 274.1 | 1.7 | 1272.9 | 0.4 |
| 2,2-Diethyl-3-Methyl-Oxazolidine | 2313.4 | 7.9 | 1732.9 | 1.3 | 81.6 | 10.7 |
| Oxypurinol | 3634.0 | 10.6 | 2952.8 | 9.9 | 791.4 | 6.9 |
| Benzenemethanol | 73.9 | 13.5 | 236.9 | 1.6 | 28.0 | 5.5 |
| 4-Methyl-2(5H)-Furanone | 607.9 | 3.8 | 4930.2 | 6.6 | 1099.4 | 4.5 |
| 3-Ethyl-2-Hydroxy-2-Cyclopenten-1-one | 692.8 | 4.9 | 6840.8 | 0.9 | 252.5 | 11.9 |
| Benzeneethanol | 602.9 | 3.0 | 315.8 | 0.6 | 66.0 | 9.0 |
| Acrylamide | 54.9 | 1.1 | 437.1 | 4.5 | 364.5 | 16.9 |
| Erythritol | 2087.8 | 3.0 | 34108.0 | 0.7 | 178.0 | 3.6 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 2,3-Dimethyl-3-Pyrazolin-5-one | 0.0 | | 1329.4 | 4.3 | 29.4 | 15.2 |
| Furfural Acetone | 278.8 | 11.4 | 670.7 | 1.3 | 186.9 | 4.4 |
| Cyclotene | 881.6 | 5.4 | 3771.7 | 8.6 | 40.5 | 3.6 |
| 2-Methyl-1,4-Benzenediol | 738.3 | 8.8 | 576.5 | 5.2 | 305.6 | 8.3 |
| Heptanoic Acid | 0.0 | | 1995.1 | 5.1 | 0.0 | |
| Maltol | 6016.3 | 3.9 | 4303.6 | 8.1 | 1559.3 | 1.7 |
| 2-Acetylpyrrole | 2384.6 | 6.5 | 618.1 | 5.7 | 1289.9 | 8.3 |
| 2,5-Furandicarboxaldehyde | 3215.6 | 11.4 | 2408.0 | 3.1 | 2015.9 | 7.2 |
| 2H-Pyran-2,6(3H)-Dione | 7078.0 | 4.3 | 1870.8 | 5.3 | 66.9 | 8.7 |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | 7788.8 | 8.1 | 10007.4 | 4.8 | 2681.3 | 9.6 |
| Phenol | 3347.2 | 12.6 | 9421.8 | 3.7 | 2690.1 | 6.8 |
| 1H-Pyrrole-2-Carboxaldehyde | 169.3 | 11.4 | 8401.2 | 3.5 | 667.4 | 9.0 |
| Phloroglucinol | 1176.9 | 4.0 | 3703.4 | 11.3 | 136.6 | 10.1 |
| Furaneol | 13922.3 | 6.6 | 20922.6 | 4.9 | 7929.2 | 14.2 |
| Octanoic Acid | 0.0 | | 5041.2 | 7.3 | 0.0 | |
| 5-Acetyl-Dihydro-2(3H)-Furanone | 11221.8 | 12.1 | 17729.2 | 5.3 | 6473.0 | 12.1 |
| 2-Furanpropionic Acid | 2306.8 | 11.6 | 1595.6 | 6.0 | 67.6 | 4.3 |
| 1,3-Dihydroxy-2-Propanone | 534971.4 | 10.8 | 574093.3 | 1.0 | 432035.9 | 3.6 |
| Tetrahydro-5-Methyl-2-Furanmethanol | 24988.6 | 4.5 | 27991.3 | 8.5 | 20.1 | 13.9 |
| 4,5-Dimethyl Vinylene Carbonate | 9102.2 | 10.4 | 14827.7 | 0.7 | 3690.0 | 8.3 |
| 2-Hydroxy-Dihydro-2(3H)-Furanone | 35815.5 | 4.9 | 29518.2 | 2.7 | 32920.6 | 13.8 |
| 5-Acetoxymethyl-2-Furfural A | 5644.7 | 2.3 | 3317.1 | 6.9 | 2500.9 | 5.5 |
| 5-Acetoxymethyl-2-Furfural B | 6605.7 | 9.8 | 6362.9 | 0.6 | 4392.0 | 10.1 |
| 2-Methoxy-4-Vinyl-Phenol | 1588.9 | 7.2 | 1317.5 | 3.6 | 1076.9 | 9.4 |
| 3-Methyl-2,4(3H,5H)-Furandione | 2141.9 | 7.7 | 3997.5 | 1.3 | 1310.9 | 10.5 |
| 3-Hydroxy-2,3-Dihydro-Maltol | 25425.9 | 2.3 | 30343.9 | 4.3 | 2150.2 | 12.4 |
| Decanoic Acid | 1520.2 | 7.9 | 17128.8 | 7.4 | 0.0 | |
| 5-Hydroxy-Maltol | 9891.2 | 13.0 | 11660.8 | 1.4 | 103.5 | 5.8 |
| 2,3-Dihydro-Benzofuran | 2327.1 | 15.7 | 1721.7 | 4.1 | 2326.0 | 1.5 |
| 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | 2470.2 | 13.4 | 9885.4 | 5.7 | 4319.2 | 14.4 |
| 4-Pyridinol | 212.9 | 5.0 | 524.4 | 2.6 | 643.2 | 8.5 |
| 4-Amino-Phenol | 1112.4 | 6.7 | 1073.4 | 2.3 | 1723.0 | 8.0 |
| Benzoic Acid | 207.5 | 2.2 | 49854.7 | 6.1 | 18.2 | 13.5 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Dimethylhydrazone 3-Pentanone | 9050.6 | 6.1 | 6763.8 | 3.2 | 2072.0 | 9.9 |
| Undecanoic Acid | 0.0 | | 0.0 | | 0.0 | |
| 5-(Hydroxymethyl)-Dihydro-2(3H)-Furanone | 25179.9 | 4.4 | 27077.2 | 6.2 | 16016.6 | 3.0 |
| Dodecanoic Acid | 3057.4 | 6.1 | 1496.3 | 0.6 | 0.0 | |
| 5-(Hydroxymethyl)-2-Furfural | 166665.3 | 5.9 | 63429.4 | 7.3 | 136780.2 | 4.7 |
| 3-Methoxy-1,2-Benzenediol | 236.3 | 11.9 | 423.2 | 8.1 | 81.5 | 7.4 |
| 1-(2-Furanyl)-1,2-Ethanediol | 42681.8 | 6.7 | 43532.9 | 4.9 | 23323.9 | 5.3 |
| 4-Hydroxy-Dihydro-2(3H)-Furanone | 5502.0 | 12.2 | 12161.4 | 2.3 | 5550.6 | 5.3 |

**Table 38. Mean, minimum and maximum peak area values of identified VOCs in SC-based syrups samples.**

| Volatile Organic Compounds | Relative Peak Areas (x $10^3$) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | CERT | | | NCERT | | | MED | | | STH | | |
| | Mean | Min | Max | Mean | Min | Max | Mean | Min | Max | Mean | Min | Max |
| Pentane | 16.8 | 99.9 | 46.9 | 39.0 | 137.7 | 68.8 | 84.3 | 387.4 | 255.8 | 262.0 | 552.2 | 367.9 |
| Hexane | 60.4 | 265.0 | 130.5 | 69.3 | 242.9 | 139.2 | 62.8 | 483.0 | 279.9 | 42.2 | 351.4 | 214.0 |
| 1,4-Pentadiene | 0.0 | 0.0 | 0.0 | 0.0 | 2.8 | 0.9 | 0.0 | 0.0 | 0.0 | 36.4 | 120.8 | 66.6 |
| Methanethiol | 118.2 | 1088.5 | 345.5 | 151.8 | 514.4 | 277.7 | 15.0 | 1139.9 | 435.5 | 117.3 | 703.6 | 392.5 |
| Ethanal | 1703.7 | 13999.5 | 7444.6 | 48.1 | 10363.4 | 5020.8 | 1175.8 | 7541.0 | 3665.5 | 1833.1 | 6500.3 | 4128.6 |
| Dimethyl Sulfide | 575.5 | 8188.6 | 2205.2 | 511.1 | 8414.8 | 3701.1 | 30.2 | 17048.5 | 11024.7 | 270.7 | 29191.9 | 13592.9 |
| Propanal | 261.2 | 1550.1 | 586.4 | 293.6 | 1513.2 | 854.6 | 257.6 | 1365.7 | 719.8 | 223.9 | 2797.8 | 1094.5 |
| Furan | 525.2 | 6043.5 | 2359.2 | 1964.8 | 3022.8 | 2292.8 | 554.7 | 3252.5 | 1870.1 | 2618.9 | 7488.0 | 4178.5 |
| 2-Methyl-Propanal | 6228.8 | 38319.5 | 15491.3 | 6151.6 | 13601.3 | 9493.4 | 4375.9 | 11873.6 | 8056.4 | 3049.1 | 8691.3 | 6359.2 |
| Ethyl Formate | 0.0 | 7519.6 | 2265.5 | 0.0 | 3467.6 | 1770.7 | 0.0 | 815.9 | 159.4 | 0.0 | 1365.4 | 436.0 |
| 2-Propenal | 145.2 | 578.2 | 323.7 | 26.0 | 561.6 | 299.1 | 38.0 | 783.2 | 369.2 | 262.2 | 1435.7 | 699.1 |
| 2-Methyl-Furan | 624.9 | 7432.3 | 2883.0 | 165.7 | 2490.6 | 1591.6 | 425.0 | 5223.8 | 2028.0 | 1527.6 | 11554.7 | 6207.4 |
| Ethyl Acetate | 267.0 | 25835.5 | 8965.4 | 7.2 | 21438.9 | 10134.9 | 70.5 | 9679.4 | 2234.1 | 51.5 | 752.1 | 292.9 |
| 2-Butanone | 189.2 | 4610.6 | 1104.4 | 64.1 | 594.2 | 332.8 | 187.3 | 724.3 | 395.1 | 315.0 | 1299.7 | 864.9 |
| 2-Methyl-Butanal | 12490.3 | 41222.5 | 24426.1 | 8928.2 | 23464.0 | 15632.6 | 5645.1 | 14326.7 | 10378.1 | 8293.5 | 11858.9 | 10404.6 |
| 3-Methyl-Butanal | 6399.9 | 47345.2 | 20221.3 | 1469.6 | 28625.9 | 12914.9 | 3153.2 | 28465.0 | 11330.5 | 4128.8 | 7007.2 | 5289.4 |
| Ethanol | 99041.5 | 217029.4 | 135755.4 | 2969.7 | 62772.1 | 36784.4 | 11808.6 | 105622.4 | 51163.9 | 15240.6 | 71477.3 | 39789.3 |
| Benzene | 17.1 | 209.1 | 98.9 | 3.4 | 123.5 | 52.7 | 44.4 | 136.1 | 67.6 | 30.1 | 386.5 | 154.8 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3-Buten-2-one | 263.5 | 5320.6 | 1872.2 | 41.3 | 3506.7 | 1527.3 | 43.2 | 2674.7 | 958.2 | 284.6 | 4895.1 | 1999.6 |
| 2,5-Dimethyl-Furan | 482.8 | 4274.2 | 1575.0 | 83.4 | 2949.2 | 1360.3 | 136.4 | 1640.3 | 895.8 | 1709.4 | 3112.4 | 2570.2 |
| Ethyl Propanoate | 0.0 | 1964.7 | 472.3 | 0.0 | 10426.2 | 3442.4 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2,3-Butanedione | 1212.6 | 55294.5 | 19465.7 | 196.3 | 21154.3 | 11029.1 | 1347.7 | 17963.1 | 9368.8 | 6567.0 | 32420.5 | 16292.3 |
| 2-Methylpropyl Acetate | 0.0 | 0.0 | 0.0 | 0.0 | 2128.9 | 681.8 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1-Propanol | 0.0 | 98.7 | 49.6 | 0.0 | 10496.4 | 3971.8 | 0.0 | 712.5 | 129.9 | 0.0 | 0.0 | 0.0 |
| 2-Ethyl-5-Methyl-Furan | 24.6 | 595.7 | 234.2 | 0.0 | 746.9 | 239.6 | 7.0 | 510.3 | 176.7 | 314.3 | 434.1 | 398.4 |
| Toluene | 637.2 | 59213.8 | 12908.9 | 1145.8 | 5093.7 | 3410.6 | 19.6 | 6999.8 | 1982.7 | 8.0 | 2481.4 | 1037.7 |
| Ethyl Butanoate | 0.0 | 0.0 | 0.0 | 0.0 | 1353.1 | 423.6 | 0.0 | 145.3 | 30.4 | 0.0 | 0.0 | 0.0 |
| 2-Methyl-3-Buten-2-ol | 0.0 | 3196.8 | 425.2 | 0.0 | 916.1 | 286.4 | 0.0 | 0.0 | 0.0 | 0.0 | 1975.6 | 769.4 |
| Nonomethyl Succinate | 0.0 | 3780.2 | 801.4 | 0.0 | 328.1 | 116.0 | 0.0 | 3212.1 | 832.8 | 0.0 | 891.8 | 282.1 |
| 2,3-Pentanedione | 831.9 | 18346.9 | 5430.2 | 120.9 | 10026.0 | 4881.9 | 276.3 | 8295.7 | 4012.6 | 1754.0 | 16224.4 | 6903.6 |
| Dimethyl Disulfide | 0.0 | 325.6 | 137.1 | 0.0 | 2285.6 | 726.5 | 34.5 | 484.0 | 219.4 | 0.0 | 2002.5 | 620.0 |
| 2-Ethenyl-Furan | 25.3 | 290.1 | 148.7 | 27.4 | 224.4 | 94.1 | 32.7 | 645.0 | 256.1 | 0.0 | 522.3 | 190.1 |
| 2,5-Diethyltetrahydro-Furan | 0.0 | 1432.1 | 176.9 | 0.0 | 231.6 | 70.1 | 0.0 | 0.0 | 0.0 | 0.0 | 446.6 | 154.9 |
| Hexanal | 0.0 | 0.0 | 0.0 | 0.0 | 13.7 | 4.4 | 0.0 | 678.5 | 221.7 | 0.0 | 8303.8 | 2676.7 |
| 2-Methyl-1-Propanol | 0.0 | 21211.9 | 3570.4 | 7.3 | 42253.3 | 13699.9 | 13.7 | 149.0 | 59.5 | 35.1 | 155.0 | 82.0 |
| 5-Butyl-Dihydro-2(3H)-Furanone | 497.7 | 10094.7 | 2377.8 | 14.4 | 1199.5 | 376.1 | 6.5 | 103.0 | 59.9 | 1076.1 | 22802.6 | 8386.1 |
| m-Cresol | 147.6 | 3783.7 | 1268.6 | 18.7 | 1001.3 | 379.4 | 4.5 | 385.3 | 127.6 | 3.9 | 27.0 | 13.3 |
| 1-Butanol | 16.8 | 1100.7 | 254.0 | 0.0 | 1090.0 | 375.9 | 0.0 | 19.0 | 7.2 | 0.0 | 0.0 | 0.0 |
| 5-Propyl-Dihydro-2(3H)-Furanone | 270.6 | 2789.5 | 920.9 | 9.4 | 770.2 | 250.9 | 10.3 | 691.5 | 168.0 | 45.7 | 19515.9 | 6219.9 |
| 3-Methyl-Pyridazine | 1524.7 | 9115.2 | 3702.9 | 11.5 | 2551.9 | 1087.4 | 2.6 | 1125.1 | 334.7 | 125.7 | 566.4 | 333.1 |
| 2-Heptanone | 0.0 | 0.0 | 0.0 | 0.0 | 8.8 | 2.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| m-Menthane | 3.1 | 155.7 | 38.1 | 0.0 | 0.0 | 0.0 | 0.0 | 438.5 | 120.0 | 0.0 | 18.8 | 5.9 |
| 1,3-Diazine | 20.1 | 364.7 | 111.8 | 1.6 | 1036.8 | 451.5 | 11.0 | 1812.5 | 585.4 | 3.2 | 308.6 | 122.1 |
| 2-Methyl-1-Butanol | 0.0 | 23747.0 | 8132.2 | 888.0 | 19408.9 | 8565.2 | 0.0 | 4714.5 | 956.1 | 73.6 | 304.0 | 199.2 |
| 2-Propyl-Furan | 77.2 | 3680.4 | 1146.9 | 6.8 | 566.0 | 197.1 | 7.7 | 305.4 | 84.6 | 7.8 | 25.7 | 15.1 |
| Ethyl Hexanoate | 0.0 | 0.0 | 0.0 | 0.0 | 340.8 | 98.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 2-Pentyl-Furan | 2.3 | 117.3 | 24.9 | 0.0 | 11.7 | 3.6 | 6.1 | 52.7 | 28.8 | 16.8 | 646.3 | 218.3 |
| 2-Methyl-Pyrazine | 187.8 | 2296.5 | 1017.2 | 34.1 | 1954.3 | 888.0 | 0.0 | 1603.9 | 581.1 | 0.0 | 2781.5 | 889.0 |
| 2-Methyl-Dihydro-2(3H)-Furanone | 10436.3 | 34517.2 | 19037.4 | 59.7 | 18762.0 | 6801.4 | 1487.6 | 5508.2 | 3357.9 | 4613.8 | 14410.4 | 9894.7 |
| p-Cymene | 19.5 | 120.9 | 56.5 | 0.0 | 230.8 | 88.8 | 0.0 | 5.9 | 1.1 | 0.0 | 9.8 | 4.0 |
| Mesitylene | 2.8 | 3835.9 | 499.7 | 0.0 | 120.6 | 40.2 | 0.0 | 3.6 | 0.7 | 0.0 | 6.0 | 3.4 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3,5-Xylenol | 43.4 | 396.3 | 167.4 | 0.0 | 89.6 | 29.5 | 0.0 | 11.0 | 2.1 | 0.0 | 180.8 | 57.5 |
| 3-Hydroxy-2-Butanone | 1250.4 | 5427.4 | 2817.2 | 321.1 | 1961.9 | 1001.1 | 66.2 | 2179.5 | 875.1 | 201.4 | 4844.3 | 1642.0 |
| Vinylene Carbonate | 3994.6 | 27223.9 | 14822.8 | 79.6 | 13224.2 | 5634.9 | 771.3 | 8132.9 | 4476.1 | 2115.9 | 11693.9 | 6014.8 |
| 2,6-Xylenol | 118.1 | 1679.0 | 660.4 | 4.6 | 289.2 | 153.6 | 4.1 | 275.8 | 91.0 | 4.0 | 840.5 | 259.8 |
| 1-Hydroxy-2-Propanone | 5359.8 | 30542.4 | 14325.7 | 3669.8 | 21425.1 | 11092.4 | 1530.2 | 15728.7 | 7598.7 | 2133.8 | 37495.1 | 21436.1 |
| 2,5-Dimethyl-Pyrazine | 36.4 | 1529.7 | 579.4 | 90.2 | 133.0 | 110.3 | 4.8 | 311.8 | 118.3 | 14.0 | 2316.6 | 764.4 |
| 2,6-Dimethyl-Pyrazine | 1022.0 | 3449.8 | 1605.0 | 26.8 | 1510.4 | 822.4 | 19.0 | 1029.1 | 394.5 | 93.0 | 2130.2 | 752.4 |
| 2-Cyclopenten-1-one | 1105.5 | 5960.4 | 2661.3 | 16.6 | 1134.8 | 494.5 | 92.6 | 578.5 | 231.0 | 248.5 | 13157.0 | 4557.0 |
| 1,2,3,4-Tetramethyl-4-(1-methylethenyl)-Benzene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 48.9 | 11.1 | 0.0 | 981.9 | 327.1 |
| 2-Methyl-2-Cyclopenten-1-one | 322.9 | 2259.1 | 1160.0 | 18.3 | 436.1 | 203.4 | 16.7 | 439.7 | 203.1 | 95.7 | 1538.7 | 569.7 |
| 5-Methyl-2-Furanmethanethiol | 25.3 | 8606.1 | 2489.1 | 11.1 | 13804.7 | 5140.8 | 5.9 | 2855.6 | 631.0 | 5.4 | 747.5 | 239.8 |
| 1-Hydroxy-2-Butanone | 625.6 | 10894.9 | 4798.4 | 98.9 | 4834.4 | 2054.1 | 447.4 | 4613.5 | 1635.5 | 372.5 | 14242.7 | 6189.3 |
| 2-Ethyl-6-Methyl-Pyrazine | 115.0 | 432.8 | 183.7 | 13.8 | 158.0 | 63.3 | 0.0 | 8.8 | 1.7 | 0.0 | 985.6 | 323.4 |
| 2-Ethyl-5-Methyl-Pyrazine | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 430.0 | 137.1 |
| Nonanal | 471.5 | 2652.2 | 1048.9 | 187.1 | 2195.8 | 917.8 | 228.7 | 988.4 | 644.2 | 53.5 | 746.9 | 413.8 |
| Trimethyl-Pyrazine | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 361.6 | 116.4 |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 23.8 | 4.3 | 0.0 | 892.4 | 292.8 |
| 2-Cyclohexen-1-one | 8.6 | 793.4 | 212.7 | 22.9 | 109.7 | 69.1 | 13.3 | 460.8 | 162.6 | 5.7 | 9355.0 | 3096.6 |
| 5-Methyl-2(3H)-Furanone | 2863.0 | 13000.4 | 7643.6 | 156.9 | 4543.1 | 2074.9 | 335.2 | 3296.3 | 1570.0 | 950.3 | 4811.3 | 2363.6 |
| 1,3-Dihydro-4-Methyl-2H-Imidazol-2-one | 1338.2 | 7356.9 | 3449.7 | 72.4 | 2446.3 | 1125.0 | 309.8 | 2025.7 | 1055.3 | 541.1 | 5730.1 | 2439.7 |
| Ethyl Octanoate | 0.0 | 0.0 | 0.0 | 0.0 | 1306.2 | 415.9 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | 15.4 | 727.2 | 324.4 | 3.1 | 117.1 | 61.8 | 8.7 | 1613.5 | 976.1 | 61.2 | 7401.7 | 2546.0 |
| Furfural | 22947.6 | 41364.6 | 30033.0 | 22178.0 | 42904.6 | 30159.9 | 25433.9 | 51301.2 | 35420.2 | 25738.5 | 36254.7 | 30182.5 |
| Ethanoic Acid | 63131.0 | 636409.9 | 259844.9 | 214264.9 | 439351.3 | 341352.6 | 180455.2 | 740414.3 | 371792.0 | 242461.9 | 462065.1 | 349759.6 |
| 1,2,3,4-Tetrahydro-1,6,8-Trimethyl-Naphthalene | 443.0 | 1463.8 | 738.5 | 4.8 | 370.0 | 192.5 | 37.0 | 1017.1 | 614.4 | 182.0 | 5283.0 | 2588.3 |
| 2-Ethyl-1-Hexanol | 344.4 | 3128.3 | 1135.9 | 63.6 | 11756.1 | 4024.1 | 292.5 | 825.8 | 432.7 | 483.9 | 1452.0 | 895.9 |
| 3-Methyl-Furfural | 167.8 | 909.7 | 437.5 | 218.8 | 4810.0 | 2234.7 | 25.9 | 176.8 | 109.9 | 41.8 | 355.2 | 175.3 |
| Furfuryl Formate | 756.1 | 4858.7 | 2427.0 | 54.6 | 1531.8 | 637.5 | 284.1 | 1173.4 | 700.7 | 233.6 | 711.3 | 522.2 |
| Decanal | 74.5 | 3543.2 | 1376.0 | 76.2 | 498.9 | 227.0 | 45.9 | 172.7 | 98.0 | 91.5 | 142.1 | 121.4 |
| 1-(2-Furanyl)-Ethanone | 10211.4 | 17692.6 | 13246.7 | 40.4 | 16726.1 | 8782.4 | 4500.8 | 15752.8 | 10122.0 | 1073.1 | 14185.8 | 7910.3 |
| Benzaldehyde | 463.1 | 1921.5 | 1087.5 | 5.3 | 1255.3 | 548.5 | 58.3 | 446.0 | 246.8 | 17.4 | 12037.0 | 3887.4 |
| Furfuryl Acetate | 517.7 | 3495.2 | 1799.4 | 104.1 | 962.1 | 421.3 | 24.5 | 559.9 | 332.7 | 283.9 | 805.7 | 535.9 |
| Propanoic Acid | 207.0 | 7345.3 | 1616.1 | 0.0 | 7097.5 | 2632.4 | 975.2 | 4879.5 | 2551.8 | 52.0 | 10821.9 | 5149.2 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Dimethyl Sulfoxide | 43.0 | 768.2 | 381.9 | 44.4 | 350.8 | 151.0 | 15.8 | 1833.6 | 776.5 | 70.5 | 1743.1 | 633.9 |
| 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | 113.2 | 633.5 | 318.6 | 5.0 | 305.1 | 135.3 | 0.0 | 450.8 | 139.4 | 0.0 | 1567.4 | 549.5 |
| 5-Methyl-Furfural | 11661.3 | 24544.6 | 17921.8 | 359.4 | 19111.9 | 8116.8 | 5228.9 | 21728.0 | 13984.7 | 5824.5 | 11803.7 | 8010.2 |
| 4-Cyclopentene-1,3-dione | 11200.1 | 23433.1 | 17369.9 | 242.1 | 13012.0 | 5437.2 | 2473.2 | 6775.3 | 4345.0 | 1334.4 | 14408.7 | 7375.4 |
| 2-Methyl-Benzofuran | 2204.8 | 14920.2 | 7068.4 | 19.5 | 3604.7 | 1954.3 | 14.2 | 776.1 | 341.4 | 81.0 | 612.6 | 296.0 |
| 1-(5-Methyl-2-Furanyl)-Ethanone | 499.1 | 4383.4 | 1901.4 | 103.5 | 978.6 | 449.4 | 367.3 | 1056.2 | 727.5 | 367.2 | 1003.3 | 646.5 |
| Diethylene Glycol Ethyl Ether | 1653.0 | 5846.8 | 3019.8 | 22.5 | 2187.8 | 1032.7 | 634.0 | 3656.2 | 2184.9 | 239.7 | 3930.2 | 1415.9 |
| 3-Methyl-Dihydro-2(3H)-Furanone | 662.4 | 2081.1 | 1330.4 | 127.7 | 1955.1 | 826.5 | 291.4 | 1491.3 | 743.2 | 433.8 | 4291.6 | 1985.5 |
| 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | 29.4 | 136.5 | 68.8 | 0.0 | 0.0 | 0.0 | 0.0 | 185.8 | 62.9 | 25.9 | 1524.8 | 703.1 |
| Benzeneacetaldehyde | 726.6 | 19142.8 | 7726.2 | 92.0 | 5877.1 | 2014.1 | 17.3 | 3141.0 | 1178.4 | 180.7 | 934.2 | 442.5 |
| 3,5-Dimethyl-Dihydro-2-Furanone | 425.6 | 3416.5 | 1287.3 | 396.9 | 17618.1 | 5820.0 | 336.7 | 1036.6 | 805.6 | 982.3 | 4002.7 | 2051.3 |
| 2-Propenoic Acid | 40.1 | 13502.8 | 5851.7 | 825.5 | 8050.9 | 3329.4 | 49.9 | 11447.5 | 2467.8 | 60.5 | 9187.0 | 4479.4 |
| Ethyl Decanoate | 0.0 | 0.0 | 0.0 | 0.0 | 2326.1 | 750.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Acetophenone | 107.9 | 884.9 | 344.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 522.5 | 172.1 |
| 2-Furanmethanol | 18118.3 | 56912.8 | 27308.2 | 21939.2 | 29450.6 | 25539.9 | 19309.6 | 33178.7 | 23990.8 | 18906.9 | 43825.7 | 27033.1 |
| 3-Furanmethanol | 15255.1 | 68830.6 | 33416.9 | 29472.8 | 39746.2 | 33933.0 | 11151.0 | 26502.6 | 18649.9 | 11628.5 | 45494.0 | 24864.3 |
| 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | 82.7 | 570.6 | 306.8 | 0.0 | 298.8 | 101.5 | 58.2 | 1183.9 | 539.2 | 134.7 | 5207.1 | 2471.1 |
| 2-(2-Furanylmethyl)-5-Methyl-Furan | 111.6 | 1122.5 | 531.9 | 0.0 | 21.5 | 11.6 | 0.0 | 13.7 | 2.5 | 0.0 | 9.0 | 4.2 |
| 3-Methyl-2(5H)-Furanone | 246.7 | 1021.2 | 668.3 | 100.9 | 748.6 | 392.7 | 97.8 | 879.8 | 425.6 | 147.9 | 2215.4 | 897.1 |
| 5-Methyl-2-Furanmethanol | 1243.5 | 6078.3 | 3056.2 | 154.7 | 1767.5 | 1149.8 | 0.0 | 2360.1 | 822.7 | 997.0 | 4046.3 | 2193.4 |
| Benzyl Acetate | 0.0 | 394.8 | 203.6 | 13.7 | 2072.9 | 690.1 | 0.0 | 0.0 | 0.0 | 0.0 | 4.6 | 1.5 |
| 2(5H)-Furanone | 7621.7 | 38051.3 | 21720.5 | 4133.1 | 18361.9 | 10541.1 | 3165.6 | 13227.8 | 6597.2 | 2757.0 | 27733.0 | 12581.6 |
| 2,2'-Methylenebis[5-Methyl-Furan | 292.6 | 1584.4 | 729.4 | 7.7 | 370.0 | 169.5 | 5.9 | 132.7 | 70.5 | 23.8 | 377.2 | 140.9 |
| 1,2-Cyclopentanedione | 14388.7 | 42812.3 | 29007.4 | 583.7 | 25973.6 | 12616.9 | 15152.4 | 26088.5 | 20144.7 | 10871.3 | 33119.7 | 23597.7 |
| 2-Cyclohexenol | 5070.0 | 18808.9 | 11409.9 | 161.8 | 7349.5 | 3108.9 | 700.4 | 5371.1 | 2854.4 | 2282.9 | 5136.6 | 3603.0 |
| 2-Phenylethyl Acetate | 346.7 | 6315.9 | 2050.6 | 12.0 | 9227.2 | 3215.8 | 5.9 | 12566.9 | 2747.5 | 0.0 | 23.4 | 7.6 |
| 3-Methyl-1,2-Cyclopentanedione | 6163.4 | 27187.7 | 14228.9 | 121.0 | 9928.3 | 4382.5 | 2675.4 | 8165.4 | 4797.8 | 2890.3 | 25139.6 | 10836.9 |
| 2-Ethyl-Hexanoic Acid | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 2464.6 | 1120.8 | 0.0 | 1117.2 | 371.5 |
| β-Damascenone | 195.2 | 11239.0 | 3725.2 | 314.9 | 1874.2 | 848.0 | 20.0 | 1003.5 | 466.2 | 910.5 | 2036.5 | 1442.8 |
| Ethyl Undecanoate | 0.0 | 0.0 | 0.0 | 0.0 | 4584.4 | 1465.6 | 0.0 | 0.0 | 0.0 | 0.0 | 1177.4 | 383.9 |
| 2-Methyl-Propanoic Acid | 2174.0 | 13352.8 | 6316.8 | 183.5 | 7906.7 | 3655.6 | 110.8 | 5747.2 | 2487.9 | 641.2 | 27382.6 | 10044.7 |
| 2,4,6-Trihydroxypyrimidine | 16209.4 | 34488.3 | 23333.6 | 105.2 | 209.3 | 136.4 | 89.8 | 413.0 | 228.2 | 149.0 | 805.3 | 384.1 |
| Mequinol | 539.1 | 3372.2 | 1440.6 | 82.3 | 1103.5 | 584.9 | 110.4 | 1517.0 | 576.6 | 120.3 | 1277.9 | 559.7 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,2-Diethyl-3-Methyl-Oxazolidine | 1957.4 | 14005.0 | 6563.0 | 13.9 | 7309.8 | 2907.1 | 298.1 | 6861.3 | 3079.2 | 72.9 | 2497.2 | 1376.0 |
| Oxypurinol | 4387.7 | 15475.8 | 9210.9 | 86.1 | 6130.5 | 2566.2 | 477.5 | 5888.6 | 3161.7 | 736.5 | 4018.5 | 2459.4 |
| Benzenemethanol | 235.8 | 10917.3 | 2000.8 | 89.9 | 6338.7 | 2281.9 | 18.9 | 107.6 | 62.9 | 26.5 | 240.7 | 112.9 |
| 4-Methyl-2(5H)-Furanone | 1403.4 | 7690.9 | 3718.5 | 172.2 | 1659.3 | 680.8 | 385.5 | 1525.8 | 883.7 | 584.6 | 5255.1 | 2212.5 |
| 3-Ethyl-2-Hydroxy-2-Cyclopenten-1-one | 858.6 | 7308.4 | 2738.3 | 52.6 | 150.8 | 87.9 | 18.0 | 1042.9 | 542.3 | 222.5 | 6902.3 | 2595.4 |
| Benzeneethanol | 53.3 | 522.9 | 225.0 | 18.5 | 3986.0 | 1397.0 | 100.2 | 1812.8 | 614.8 | 60.1 | 621.0 | 328.2 |
| Acrylamide | 1148.6 | 7504.0 | 4439.0 | 149.8 | 4972.6 | 1789.9 | 20.5 | 5020.1 | 1321.4 | 54.3 | 456.9 | 285.5 |
| Erythritol | 3583.0 | 18880.0 | 9237.9 | 156.4 | 11885.3 | 5262.1 | 305.2 | 7624.6 | 2857.2 | 171.5 | 34330.0 | 12124.6 |
| 2,3-Dimethyl-3-Pyrazolin-5-one | 501.9 | 2303.3 | 1283.1 | 227.6 | 965.4 | 525.8 | 0.0 | 646.9 | 284.4 | 0.0 | 1386.7 | 452.9 |
| Furfural Acetone | 455.0 | 2233.9 | 1191.5 | 23.4 | 700.5 | 327.0 | 149.7 | 332.3 | 256.0 | 178.6 | 679.4 | 378.8 |
| Cyclotene | 1418.7 | 8271.0 | 4290.3 | 33.5 | 2469.2 | 1134.9 | 193.6 | 2328.4 | 862.8 | 39.1 | 4095.2 | 1564.6 |
| 2-Methyl-1,4-Benzenediol | 865.7 | 10124.3 | 3443.8 | 49.1 | 2852.0 | 1109.2 | 190.2 | 1719.6 | 720.5 | 280.2 | 803.1 | 540.1 |
| Heptanoic Acid | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 129.5 | 23.8 | 0.0 | 2097.7 | 665.0 |
| Maltol | 7069.3 | 25568.3 | 15486.6 | 450.4 | 19398.6 | 7637.0 | 2651.9 | 9435.4 | 6963.4 | 1533.1 | 6249.6 | 3959.7 |
| 2-Acetylpyrrole | 6981.8 | 31047.7 | 12772.3 | 160.6 | 13478.9 | 6275.4 | 655.7 | 4113.7 | 2450.3 | 582.9 | 2540.4 | 1430.9 |
| 2,5-Furandicarboxaldehyde | 10985.7 | 48056.4 | 24639.8 | 191.0 | 11443.4 | 4255.9 | 1884.8 | 10496.9 | 6232.9 | 1871.2 | 3581.0 | 2546.5 |
| 2H-Pyran-2,6(3H)-Dione | 1900.4 | 17495.8 | 10140.6 | 365.4 | 8890.3 | 4313.2 | 2375.4 | 7681.1 | 4755.0 | 61.0 | 7382.9 | 3005.2 |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | 11782.3 | 57616.5 | 26518.6 | 269.4 | 22036.7 | 10363.2 | 6271.4 | 31068.2 | 14333.8 | 2423.6 | 10484.3 | 6825.8 |
| Phenol | 1793.7 | 12809.3 | 5289.8 | 232.3 | 3267.5 | 1549.6 | 1474.3 | 4781.3 | 2790.7 | 2507.7 | 9774.6 | 5153.0 |
| 1H-Pyrrole-2-Carboxaldehyde | 599.2 | 6263.3 | 2929.6 | 263.4 | 776.2 | 500.3 | 269.1 | 1957.7 | 797.1 | 150.0 | 8692.2 | 3079.3 |
| Phloroglucinol | 2419.3 | 17924.6 | 9850.4 | 184.7 | 12170.1 | 5032.8 | 191.4 | 8508.4 | 3639.1 | 122.8 | 4123.1 | 1672.3 |
| Furaneol | 13072.7 | 19674.3 | 15660.9 | 188.0 | 17818.0 | 9951.6 | 8938.7 | 15074.7 | 11751.2 | 6801.4 | 21954.1 | 14258.0 |
| Octanoic Acid | 170.8 | 416.8 | 302.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 5411.1 | 1680.4 |
| 5-Acetyl-Dihydro-2(3H)-Furanone | 10982.6 | 18325.1 | 13960.6 | 3975.2 | 13460.5 | 9264.7 | 5494.9 | 14655.9 | 9471.6 | 5688.6 | 18675.1 | 11808.0 |
| 2-Furanpropionic Acid | 2201.0 | 11946.6 | 7426.0 | 234.3 | 4166.8 | 1916.4 | 1754.1 | 4878.2 | 2997.4 | 64.7 | 2575.1 | 1323.3 |
| 1,3-Dihydroxy-2-Propanone | 277416.1 | 475218.7 | 374715.3 | 367532.2 | 608245.8 | 488678.4 | 389857.3 | 968707.3 | 573672.2 | 416352.8 | 592855.4 | 513700.2 |
| Tetrahydro-5-Methyl-2-Furanmethanol | 55.0 | 16816.7 | 7363.7 | 21888.5 | 27542.0 | 23664.7 | 13750.2 | 29202.3 | 21004.8 | 17.3 | 30368.1 | 17666.6 |
| 4,5-Dimethyl Vinylene Carbonate | 5605.3 | 21117.7 | 11900.9 | 766.3 | 21915.2 | 10673.2 | 1323.4 | 18560.2 | 8673.2 | 3382.6 | 14934.6 | 9206.6 |
| 2-Hydroxy-Dihydro-2(3H)-Furanone | 3724.0 | 36063.3 | 19282.0 | 1726.5 | 36461.2 | 20645.4 | 19202.1 | 34656.0 | 28079.0 | 28392.7 | 37588.3 | 32751.5 |
| 5-Acetoxymethyl-2-Furfural A | 9370.2 | 18952.0 | 13291.1 | 456.3 | 16969.4 | 6821.7 | 3283.5 | 15535.7 | 8959.7 | 2363.1 | 5772.0 | 3820.9 |
| 5-Acetoxymethyl-2-Furfural B | 12210.8 | 21938.5 | 16893.8 | 155.3 | 15901.9 | 7119.3 | 4686.6 | 15936.5 | 9690.1 | 3946.5 | 7251.3 | 5786.9 |
| 2-Methoxy-4-Vinyl-Phenol | 731.7 | 6924.5 | 2914.0 | 30.2 | 2209.0 | 848.7 | 157.8 | 1438.1 | 767.7 | 975.7 | 1703.7 | 1327.8 |
| 3-Methyl-2,4(3H,5H)-Furandione | 2926.3 | 11587.8 | 6993.8 | 99.4 | 4594.4 | 2176.1 | 1317.8 | 3020.6 | 2004.9 | 1173.6 | 4050.5 | 2483.4 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 3-Hydroxy-2,3-Dihydro-Maltol | 6671.7 | 15163.6 | 10715.9 | 343.3 | 18409.8 | 9107.7 | 5941.1 | 26463.5 | 14722.5 | 1883.8 | 31652.9 | 19306.6 |
| Decanoic Acid | 191.4 | 3628.6 | 1223.7 | 0.0 | 1882.2 | 933.2 | 0.0 | 1559.2 | 669.6 | 0.0 | 18403.4 | 6216.3 |
| 5-Hydroxy-Maltol | 9425.1 | 52877.1 | 27044.4 | 258.8 | 16051.4 | 8965.4 | 2035.9 | 29930.3 | 12242.0 | 97.4 | 11826.0 | 7218.5 |
| 2,3-Dihydro-Benzofuran | 821.3 | 5941.1 | 2460.7 | 15.2 | 2306.8 | 956.5 | 570.5 | 2039.6 | 1152.0 | 1650.4 | 2693.5 | 2124.9 |
| 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | 2560.9 | 8896.0 | 5570.4 | 190.7 | 5604.9 | 2498.0 | 1934.8 | 6758.8 | 3962.9 | 2138.2 | 10448.9 | 5558.3 |
| 4-Pyridinol | 3745.0 | 17161.6 | 9516.8 | 154.3 | 780.0 | 380.6 | 138.0 | 959.8 | 508.1 | 202.2 | 697.9 | 460.2 |
| 4-Amino-Phenol | 1996.1 | 12202.3 | 6197.1 | 320.9 | 6613.5 | 2735.1 | 112.9 | 8155.0 | 3085.8 | 1038.1 | 1860.4 | 1302.9 |
| Benzoic Acid | 14.8 | 15964.1 | 3453.6 | 82.2 | 4784.0 | 1638.9 | 121.6 | 1842.8 | 757.5 | 15.7 | 52908.6 | 16693.5 |
| Dimethylhydrazone 3-Pentanone | 4837.5 | 22438.0 | 11102.9 | 354.9 | 23158.2 | 9722.6 | 3032.3 | 19449.6 | 9802.9 | 1866.9 | 9603.2 | 5962.1 |
| Undecanoic Acid | 72.0 | 11261.9 | 1971.3 | 0.0 | 771.5 | 250.3 | 0.0 | 2547.3 | 845.9 | 0.0 | 0.0 | 0.0 |
| 5-(Hydroxymethyl)-Dihydro-2(3H)-Furanone | 19514.0 | 84401.1 | 37307.9 | 344.9 | 36947.0 | 20667.1 | 16365.9 | 36332.5 | 26922.0 | 15533.5 | 28762.7 | 22757.9 |
| Dodecanoic Acid | 68.7 | 3884.3 | 1750.3 | 0.0 | 1147.1 | 694.0 | 0.0 | 0.0 | 0.0 | 0.0 | 3244.1 | 1517.9 |
| 5-(Hydroxymethyl)-2-Furfural | 151000.3 | 218661.0 | 177830.0 | 123179.0 | 155732.7 | 140907.9 | 100520.2 | 233092.4 | 172166.2 | 58828.0 | 176461.4 | 122291.6 |
| 3-Methoxy-1,2-Benzenediol | 1870.1 | 15054.5 | 6072.2 | 106.1 | 587.4 | 288.5 | 54.2 | 809.2 | 397.4 | 75.5 | 457.4 | 247.0 |
| 1-(2-Furanyl)-1,2-Ethanediol | 10279.8 | 43585.0 | 19107.1 | 20013.6 | 50379.3 | 32342.2 | 423.6 | 86629.7 | 36970.8 | 22088.8 | 45659.7 | 36512.9 |
| 4-Hydroxy-Dihydro-2(3H)-Furanone | 6259.5 | 33221.5 | 18445.0 | 294.7 | 20803.5 | 9263.4 | 4221.8 | 38141.8 | 20755.9 | 4830.4 | 12436.1 | 7738.0 |

**Table S39. VOCs identified in samples from this study and previously identified in others SC-based syrups from other studies.**

| Volatile Organic Compounds | Sugarcane-Based Syrups | | | | | | |
|---|---|---|---|---|---|---|---|
| | Portugal (Madeira)[1] | Egypt[2] | USA[3] | Dominican Republic[4] | China[5] | Japan[6] | Japan[7] |
| Pentane | | | | | | | |
| Hexane | | | | | | | |
| 1,4-Pentadiene | | | | | | | |
| Methanethiol | | | | | | | |
| Ethanal | X | | | | | | X |
| Dimethyl Sulfide | X | X | | | | | X |
| Propanal | X | | | | | | X |
| Furan | X | | | | | | |
| 2-Methyl-Propanal | X | X | | | | | X |
| Ethyl Formate | | | | | | | |
| 2-Propenal | | | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 2-Methyl-Furan | X | | | | |
| Ethyl Acetate | X | | | | |
| 2-Butanone | X | X | | | |
| 2-Methyl-Butanal | X | X | X | | X |
| 3-Methyl-Butanal | X | X | X | | X |
| Ethanol | X | X | | | X |
| Benzene | | | | | |
| 3-Buten-2-one | | | | | |
| 2,5-Dimethyl-Furan | X | | | | |
| Ethyl Propanoate | X | | | | |
| 2,3-Butanedione | X | | X | | X |
| 2-Methylpropyl Acetate | | | | | |
| 1-Propanol | X | | | | |
| 2-Ethyl-5-Methyl-Furan | X | | | | |
| Toluene | | | | | |
| Ethyl Butanoate | | | | | |
| 2-Methyl-3-Buten-2-ol | X | X | | | |
| Nonomethyl Succinate | | | | | |
| 2,3-Pentanedione | X | | | | |
| Dimethyl Disulfide | X | | | | |
| 2-Ethenyl-Furan | | | | | |
| 2,5-Diethyltetrahydro-Furan | | | | | |
| Hexanal | X | | | X | |
| 2-Methyl-1-Propanol | X | X | X | | |
| 5-Butyl-Dihydro-2(3H)-Furanone | X | | | | |
| m-Cresol | | | X | | |
| 1-Butanol | X | | | | |
| 5-Propyl-Dihydro-2(3H)-Furanone | | | | | |
| 3-Methyl-Pyridazine | | | | | |
| 2-Heptanone | | | | | |
| m-Menthane | | | | | |
| 1,3-Diazine | | | | | |
| 2-Methyl-1-Butanol | X | X | X | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 2-Propyl-Furan | | | | | | |
| Ethyl Hexanoate | | | | | | |
| 2-Pentyl-Furan | | | | | | |
| 2-Methyl-Pyrazine | | | | | X | |
| 2-Methyl-Dihydro-2(3H)-Furanone | X | | | | | X |
| p-Cymene | X | | | | | |
| Mesitylene | | | | | | |
| 3,5-Xylenol | | | | | | |
| 3-Hydroxy-2-Butanone | | X | X | | | X |
| Vinylene Carbonate | | | | | | |
| 2,6-Xylenol | | | | | | |
| 1-Hydroxy-2-Propanone | X | X | | | | X |
| 2,5-Dimethyl-Pyrazine | | | X | | X | X |
| 2,6-Dimethyl-Pyrazine | X | | | | X | X |
| 2-Cyclopenten-1-one | | | | | | |
| 1,2,3,4-Tetramethyl-4-(1-methylethenyl)-Benzene | | | | | | |
| 2-Methyl-2-Cyclopenten-1-one | X | | | | | |
| 5-Methyl-2-Furanmethanethiol | X | | | | | |
| 1-Hydroxy-2-Butanone | | | | | | |
| 2-Ethyl-6-Methyl-Pyrazine | X | | | | X | |
| 2-Ethyl-5-Methyl-Pyrazine | | | | | | |
| Nonanal | X | | | | X | |
| Trimethyl-Pyrazine | | | | | | |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | | | | | | |
| 2-Cyclohexen-1-one | | | | | | |
| 5-Methyl-2(3H)-Furanone | | | | | | |
| 1,3-Dihydro-4-Methyl-2H-Imidazol-2-one | | | | | | |
| Ethyl Octanoate | | | | | | |
| 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | X | | | | | |
| Furfural | X | X | | | | |
| Ethanoic Acid | X | X | X | X | | X |
| 1,2,3,4-Tetrahydro-1,6,8-Trimethyl-Naphthalene | | | | | | |
| 2-Ethyl-1-Hexanol | | | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 3-Methyl-Furfural | | | | | | |
| Furfuryl Formate | | | | | | |
| Decanal | X | | | X | X | |
| 1-(2-Furanyl)-Ethanone | X | | | | X | |
| Benzaldehyde | X | | | | | |
| Furfuryl Acetate | X | | | | | |
| Propanoic Acid | | X | | | | |
| Dimethyl Sulfoxide | | | | X | | |
| 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | X | | | | | |
| 5-Methyl-Furfural | X | X | | | X | |
| 4-Cyclopentene-1,3-dione | | | | | | |
| 2-Methyl-Benzofuran | X | | | | | |
| 1-(5-Methyl-2-Furanyl)-Ethanone | | | | | X | |
| Diethylene Glycol Ethyl Ether | | | | | | |
| 3-Methyl-Dihydro-2(3H)-Furanone | | | | | | |
| 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | | | | | | |
| Benzeneacetaldehyde | X | | | | | |
| 3,5-Dimethyl-Dihydro-2-Furanone | | | | | | |
| 2-Propenoic Acid | | | | | | |
| Ethyl Decanoate | | | | | | |
| Acetophenone | | | | | | |
| 2-Furanmethanol | X | X | X | X | X | X |
| 3-Furanmethanol | | | | | | |
| 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | | | | | | |
| 2-(2-Furanylmethyl)-5-Methyl-Furan | | | | | | |
| 3-Methyl-2(5H)-Furanone | | | | | | |
| 5-Methyl-2-Furanmethanol | X | | | X | | |
| Benzyl Acetate | X | | | | | |
| 2(5H)-Furanone | | | | | | |
| 2,2'-Methylenebis[5-Methyl-Furan | X | | | | | |
| 1,2-Cyclopentanedione | | | | | | |
| 2-Cyclohexenol | | | | | | |
| 2-Phenylethyl Acetate | X | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| 3-Methyl-1,2-Cyclopentanedione | | | | | |
| 2-Ethyl-Hexanoic Acid | | | | | |
| β-Damascenone | | | X | | X |
| Ethyl Undecanoate | | | | | |
| 2-Methyl-Propanoic Acid | | | | | |
| 2,4,6-Trihydroxypyrimidine | | | | | |
| Mequinol | X | | X | | X |
| 2,2-Diethyl-3-Methyl-Oxazolidine | | | | | |
| Oxypurinol | | | | | |
| Benzenemethanol | X | | | | X |
| 4-Methyl-2(5H)-Furanone | | | | | |
| 3-Ethyl-2-Hydroxy-2-Cyclopenten-1-one | | | | | |
| Benzeneethanol | X | | X | | X |
| Acrylamide | | X | | | |
| Erythritol | | | | | |
| 2,3-Dimethyl-3-Pyrazolin-5-one | | | | | |
| Furfural Acetone | | | | | |
| Cyclotene | | X | | | X |
| 2-Methyl-1,4-Benzenediol | | | | | |
| Heptanoic Acid | | | | | |
| Maltol | | | | | |
| 2-Acetylpyrrole | X | X | | X | X |
| 2,5-Furandicarboxaldehyde | | | | | |
| 2H-Pyran-2,6(3H)-Dione | | | | | |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | | | | | |
| Phenol | X | | | | |
| 1H-Pyrrole-2-Carboxaldehyde | | | | | |
| Phloroglucinol | | | | | |
| Furaneol | | X | X | | |
| Octanoic Acid | | | | | |
| 5-Acetyl-Dihydro-2(3H)-Furanone | | X | | | |
| 2-Furanpropionic Acid | | | | | |
| 1,3-Dihydroxy-2-Propanone | | | | | |

| | | | | | |
|---|---|---|---|---|---|
| Tetrahydro-5-Methyl-2-Furanmethanol | | | | | |
| 4,5-Dimethyl Vinylene Carbonate | | | | | |
| 2-Hydroxy-Dihydro-2(3H)-Furanone | | | | | |
| 5-Acetoxymethyl-2-Furfural A | | | | | |
| 5-Acetoxymethyl-2-Furfural B | | | | | |
| 2-Methoxy-4-Vinyl-Phenol | | | X | | X |
| 3-Methyl-2,4(3H,5H)-Furandione | | | | | |
| 3-Hydroxy-2,3-Dihydro-Maltol | | | | | |
| Decanoic Acid | | | | X | |
| 5-Hydroxy-Maltol | | | | | |
| 2,3-Dihydro-Benzofuran | | | X | | |
| 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | | | X | | |
| 4-Pyridinol | | | | | |
| 4-Amino-Phenol | | | | | |
| Benzoic Acid | | | X | | X |
| Dimethylhydrazone 3-Pentanone | | | | | |
| Undecanoic Acid | | | | | |
| 5-(Hydroxymethyl)-Dihydro-2(3H)-Furanone | | | | | |
| Dodecanoic Acid | | | | | |
| 5-(Hydroxymethyl)-2-Furfural | X | X | | | X |
| 3-Methoxy-1,2-Benzenediol | | | | | |
| 1-(2-Furanyl)-1,2-Ethanediol | | | | | |
| 4-Hydroxy-Dihydro-2(3H)-Furanone | | | X | | |

X – Identified in sugarcane based-product.

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**Table S40A. Summary of number of VOCs identified, RPA and TRPA values of main chemical classes identified in SC-based syrups samples.**

| Main Chemical Class | FRS07 | | | FRS13 | | | FRS14 | | | FRS15 | | | FRS16 | | | FRS17 | | | FRS18 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) |
| Alcohol | 9 | 238926 | 8.56 | 8 | 141489 | 9.48 | 8 | 117867 | 7.14 | 8 | 125395 | 9.33 | 8 | 177046 | 10.39 | 8 | 193986 | 9.25 | 5 | 195084 | 8.42 |
| Aldehyde | 8 | 110261 | 3.95 | 8 | 45983 | 3.08 | 8 | 36391 | 2.20 | 8 | 31888 | 2.37 | 8 | 57729 | 3.39 | 8 | 93030 | 4.44 | 8 | 121146 | 5.23 |
| Benzene | 13 | 64694 | 2.32 | 13 | 13223 | 0.89 | 13 | 10510 | 0.64 | 13 | 19716 | 1.47 | 13 | 49834 | 2.92 | 13 | 82987 | 3.96 | 12 | 39840 | 1.72 |
| Benzofuran | 2 | 16623 | 0.60 | 2 | 5103 | 0.34 | 2 | 3991 | 0.24 | 2 | 3832 | 0.29 | 2 | 9945 | 0.58 | 2 | 12791 | 0.61 | 2 | 14420 | 0.62 |
| Carboxylic Acid | 8 | 652840 | 23.38 | 8 | 321528 | 21.55 | 8 | 358502 | 21.71 | 8 | 80140 | 5.97 | 8 | 105433 | 6.19 | 8 | 211106 | 10.07 | 8 | 222590 | 9.61 |
| Ester | 6 | 59876 | 2.14 | 6 | 20255 | 1.36 | 6 | 22649 | 1.37 | 6 | 22873 | 1.70 | 6 | 57831 | 3.39 | 6 | 53139 | 2.54 | 3 | 37974 | 1.64 |
| Ether | 1 | 3325 | 0.12 | 1 | 1714 | 0.11 | 1 | 1815 | 0.11 | 1 | 2018 | 0.15 | 1 | 1869 | 0.11 | 1 | 5243 | 0.25 | 1 | 5155 | 0.22 |
| Furan | 45 | 711917 | 25.50 | 44 | 499327 | 33.47 | 44 | 551374 | 33.38 | 44 | 517432 | 38.52 | 44 | 624600 | 36.66 | 44 | 604150 | 28.82 | 44 | 750447 | 32.40 |
| Hydrocarbon | 2 | 358 | 0.01 | 2 | 134 | 0.01 | 2 | 83 | 0.01 | 2 | 97 | 0.01 | 2 | 195 | 0.01 | 2 | 147 | 0.01 | 2 | 228 | 0.01 |
| Indene | 2 | 323 | 0.01 | 2 | 136 | 0.01 | 2 | 286 | 0.02 | 2 | 319 | 0.02 | 2 | 353 | 0.02 | 2 | 600 | 0.03 | 2 | 612 | 0.03 |
| Ketone | 16 | 627082 | 22.46 | 16 | 354013 | 23.73 | 16 | 430465 | 26.06 | 16 | 399621 | 29.75 | 16 | 432674 | 25.39 | 16 | 587460 | 28.02 | 16 | 642068 | 27.72 |
| Naphthalene | 3 | 1290 | 0.05 | 3 | 1038 | 0.07 | 3 | 1334 | 0.08 | 3 | 810 | 0.06 | 3 | 1571 | 0.09 | 3 | 2531 | 0.12 | 3 | 1096 | 0.05 |
| Nitrogen | 16 | 136025 | 4.87 | 16 | 47471 | 3.18 | 16 | 59396 | 3.60 | 16 | 62281 | 4.64 | 16 | 86140 | 5.06 | 16 | 123170 | 5.88 | 16 | 128124 | 5.53 |
| Phenol | 8 | 45120 | 1.62 | 8 | 8409 | 0.56 | 8 | 12521 | 0.76 | 8 | 15127 | 1.13 | 8 | 29237 | 1.72 | 8 | 34839 | 1.66 | 8 | 49265 | 2.13 |
| Pyran | 5 | 104079 | 3.73 | 5 | 30917 | 2.07 | 5 | 42422 | 2.57 | 5 | 56803 | 4.23 | 5 | 65921 | 3.87 | 5 | 87172 | 4.16 | 5 | 95391 | 4.12 |
| Sulfur | 3 | 9225 | 0.33 | 4 | 864 | 0.06 | 4 | 1815 | 0.11 | 4 | 1585 | 0.12 | 4 | 2305 | 0.14 | 4 | 3538 | 0.17 | 3 | 2155 | 0.09 |
| Terpene | 3 | 10290 | 0.37 | 3 | 393 | 0.03 | 3 | 268 | 0.02 | 3 | 3357 | 0.25 | 3 | 1264 | 0.07 | 3 | 341 | 0.02 | 3 | 10826 | 0.47 |

[1]Number of volatile organic compounds identified.
[2]Relative Peak Areas values.
[3]Total Relative Peak Areas percentage values.

**Table S40B. Summary of number of VOCs identified, RPA and TRPA values of main chemical classes identified in SC-based syrups samples.**

| Main Chemical Class | ECAL14 | | | ENCAL14 | | | GLA14 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) |
| Alcohol | 9 | 74710 | 4.68 | 7 | 48908 | 4.68 | 8 | 104618 | 4.82 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Aldehyde | 8 | 72891 | 4.56 | 9 | 17437 | 1.67 | 8 | 45767 | 2.11 |
| Benzene | 12 | 6628 | 0.41 | 11 | 2663 | 0.25 | 12 | 40772 | 1.88 |
| Benzofuran | 2 | 4074 | 0.25 | 2 | 38 | 0.00 | 2 | 4621 | 0.21 |
| Carboxylic Acid | 6 | 359032 | 22.47 | 4 | 237798 | 22.74 | 6 | 461712 | 21.26 |
| Ester | 6 | 28397 | 1.78 | 4 | 965 | 0.09 | 11 | 77463 | 3.57 |
| Ether | 1 | 1028 | 0.06 | 1 | 24 | 0.00 | 1 | 2046 | 0.09 |
| Furan | 43 | 436967 | 27.34 | 43 | 330082 | 31.56 | 43 | 583090 | 26.85 |
| Hydrocarbon | 2 | 155 | 0.01 | 3 | 114 | 0.01 | 2 | 358 | 0.02 |
| Indene | 0 | 0 | 0.00 | 1 | 7 | 0.00 | 1 | 298 | 0.01 |
| Ketone | 17 | 537614 | 33.64 | 16 | 394890 | 37.76 | 16 | 702576 | 32.35 |
| Naphthalene | 3 | 428 | 0.03 | 3 | 14 | 0.00 | 3 | 727 | 0.03 |
| Nitrogen | 16 | 29900 | 1.87 | 16 | 1823 | 0.17 | 16 | 56333 | 2.59 |
| Phenol | 7 | 8104 | 0.51 | 7 | 921 | 0.09 | 8 | 24915 | 1.15 |
| Pyran | 5 | 30634 | 1.92 | 5 | 1758 | 0.17 | 5 | 65172 | 3.00 |
| Sulfur | 4 | 5666 | 0.35 | 3 | 7870 | 0.75 | 3 | 1033 | 0.05 |
| Terpene | 2 | 1843 | 0.12 | 1 | 420 | 0.04 | 2 | 548 | 0.03 |

[1]Number of volatile organic compounds identified.
[2]Relative Peak Areas values.
[3]Total Relative Peak Areas percentage values.

**Table S40C. Summary of number of VOCs identified, RPA and TRPA values of main chemical classes identified in SC-based syrups samples.**

| Main Chemical Class | ESP16 | | | EGP17 | | | EGPA16 | | | EGPB16 | | | EGPC16 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) |
| Alcohol | 7 | 51207 | 4.22 | 5 | 114539 | 5.23 | 5 | 65927 | 2.53 | 7 | 46370 | 3.09 | 7 | 14261 | 1.27 |
| Aldehyde | 8 | 17653 | 1.46 | 9 | 40377 | 1.84 | 9 | 63256 | 2.43 | 9 | 33742 | 2.25 | 9 | 22389 | 2.00 |
| Benzene | 12 | 2261 | 0.19 | 10 | 19924 | 0.91 | 10 | 14686 | 0.56 | 11 | 5452 | 0.36 | 10 | 1618 | 0.14 |
| Benzofuran | 2 | 1392 | 0.11 | 2 | 2018 | 0.09 | 2 | 1977 | 0.08 | 2 | 1465 | 0.10 | 2 | 614 | 0.05 |
| Carboxylic Acid | 5 | 206945 | 17.06 | 7 | 538636 | 24.58 | 7 | 684737 | 26.26 | 6 | 274028 | 18.28 | 7 | 205452 | 18.37 |
| Ester | 3 | 10623 | 0.88 | 5 | 37504 | 1.71 | 5 | 23277 | 0.89 | 5 | 5496 | 0.37 | 4 | 5128 | 0.46 |
| Ether | 1 | 650 | 0.05 | 1 | 2313 | 0.11 | 1 | 3373 | 0.13 | 1 | 3420 | 0.23 | 1 | 1169 | 0.10 |
| Furan | 43 | 361628 | 29.81 | 43 | 623287 | 28.44 | 42 | 655896 | 25.15 | 44 | 477822 | 31.87 | 43 | 366930 | 32.80 |

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hydrocarbon | 2 | 379 | 0.03 | 2 | 668 | 0.03 | 2 | 797 | 0.03 | 2 | 320 | 0.02 | 2 | 515 | 0.05 |
| Indene | 2 | 655 | 0.05 | 1 | 1137 | 0.05 | 1 | 273 | 0.01 | 2 | 877 | 0.06 | 2 | 69 | 0.01 |
| Ketone | 16 | 514880 | 42.44 | 16 | 670634 | 30.60 | 16 | 958064 | 36.74 | 16 | 561424 | 37.45 | 16 | 444025 | 39.69 |
| Naphthalene | 3 | 2465 | 0.20 | 2 | 2482 | 0.11 | 2 | 921 | 0.04 | 3 | 2731 | 0.18 | 2 | 50 | 0.00 |
| Nitrogen | 16 | 10739 | 0.89 | 15 | 48065 | 2.19 | 15 | 42134 | 1.62 | 15 | 12995 | 0.87 | 15 | 9588 | 0.86 |
| Phenol | 8 | 5446 | 0.45 | 7 | 23060 | 1.05 | 7 | 17230 | 0.66 | 7 | 6915 | 0.46 | 7 | 2753 | 0.25 |
| Pyran | 5 | 25529 | 2.10 | 5 | 48277 | 2.20 | 5 | 55116 | 2.11 | 5 | 51234 | 3.42 | 5 | 33073 | 2.96 |
| Sulfur | 4 | 227 | 0.02 | 4 | 17167 | 0.78 | 4 | 19469 | 0.75 | 4 | 14369 | 0.96 | 4 | 11049 | 0.99 |
| Terpene | 2 | 484 | 0.04 | 2 | 1414 | 0.06 | 2 | 572 | 0.02 | 3 | 464 | 0.03 | 2 | 25 | 0.00 |

[1]Number of volatile organic compounds identified.
[2]Relative Peak Areas values.
[3]Total Relative Peak Areas percentage values.

**Table S40D. Summary of number of VOCs identified, RPA and TRPA values of main chemical classes identified in SC-based syrups samples.**

| Main Chemical Class | MCBR14 | | | MDBR14 | | | AUS17 | | |
|---|---|---|---|---|---|---|---|---|---|
| | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) | Nº[1] | RPA[2] | TRPA[3] (%) |
| Alcohol | 7 | 43836 | 2.60 | 7 | 58615 | 2.74 | 6 | 69939 | 5.67 |
| Aldehyde | 8 | 24916 | 1.48 | 9 | 39631 | 1.85 | 8 | 29015 | 2.35 |
| Benzene | 11 | 2941 | 0.17 | 11 | 68107 | 3.19 | 11 | 819 | 0.07 |
| Benzofuran | 2 | 2515 | 0.15 | 2 | 2333 | 0.11 | 2 | 2415 | 0.20 |
| Carboxylic Acid | 6 | 348716 | 20.68 | 9 | 531506 | 24.86 | 4 | 259430 | 21.04 |
| Ester | 6 | 17328 | 1.03 | 3 | 26475 | 1.24 | 3 | 6046 | 0.49 |
| Ether | 1 | 3573 | 0.21 | 1 | 264 | 0.01 | 1 | 411 | 0.03 |
| Furan | 45 | 526628 | 31.23 | 44 | 473805 | 22.16 | 43 | 355368 | 28.82 |
| Hydrocarbon | 3 | 374 | 0.02 | 3 | 937 | 0.04 | 3 | 635 | 0.05 |
| Indene | 2 | 2834 | 0.17 | 2 | 6516 | 0.30 | 2 | 172 | 0.01 |
| Ketone | 16 | 629608 | 37.34 | 16 | 778171 | 36.40 | 16 | 461884 | 37.46 |
| Naphthalene | 3 | 2848 | 0.17 | 3 | 13931 | 0.65 | 2 | 273 | 0.02 |
| Nitrogen | 15 | 19440 | 1.15 | 15 | 29924 | 1.40 | 18 | 15939 | 1.29 |
| Phenol | 8 | 8292 | 0.49 | 7 | 15839 | 0.74 | 7 | 6908 | 0.56 |
| Pyran | 5 | 50882 | 3.02 | 5 | 58064 | 2.72 | 5 | 8199 | 0.66 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Sulfur | 3 | 496 | 0.03 | 3 | 31002 | 1.45 | 4 | 14220 | 1.15 |
| Terpene | 2 | 969 | 0.06 | 4 | 2893 | 0.14 | 2 | 1374 | 0.11 |

[1]Number of volatile organic compounds identified.
[2]Relative Peak Areas values.
[3]Total Relative Peak Areas percentage values.

**Table S41. One-way ANOVA test results based on the RPA of the identified VOCs in SC-based syrups samples.**

| Volatile Organic Compounds | One-way ANOVA Test | | | | | |
|---|---|---|---|---|---|---|
| | All Samples | | Tukey Test[3] ($\alpha < 0.05$) | | | |
| | F[1] | P[2] | CERT (A) | NCERT (B) | MED (C) | STH (D) |
| Pentane | 48.69 | 7.22E-15 | C; D | C; D | A; B; D | A; B; C |
| Hexane | 6.19 | 1.17E-03 | C | C | A; B | |
| 1,4-Pentadiene | 49.98 | 4.44E-15 | D | D | D | A; B; C |
| Methanethiol | 0.55 | 6.48E-01 | | | | |
| Ethanal | 3.90 | 1.39E-02 | C | | A | |
| Dimethyl Sulfide | 10.62 | 1.63E-05 | C; D | C; D | A; B | A; B |
| Propanal | 1.66 | 1.87E-01 | | | | |
| Furan | 4.36 | 8.35E-03 | D | | D | A; C |
| 2-Methyl-Propanal | 6.29 | 1.05E-03 | C; D | | A | A |
| Ethyl Formate | 6.50 | 8.41E-04 | C; D | | A | A |
| 2-Propenal | 4.14 | 1.07E-02 | D | D | D | A; B; C |
| 2-Methyl-Furan | 7.02 | 4.96E-04 | D | D | D | A; B; C |
| Ethyl Acetate | 6.88 | 5.71E-04 | C; D | C; D | A; B | A; B |
| 2-Butanone | 2.67 | 5.76E-02 | | | | |
| 2-Methyl-Butanal | 17.62 | 6.14E-08 | B; C; D | A | A | A |
| 3-Methyl-Butanal | 4.84 | 4.90E-03 | D | | | A |
| Ethanol | 38.57 | 4.72E-13 | B; C; D | A | A | A |
| Benzene | 2.93 | 4.25E-02 | | | | |
| 3-Buten-2-one | 1.00 | 4.00E-01 | | | | |
| 2,5-Dimethyl-Furan | 6.32 | 1.02E-03 | D | D | D | A; B; C |
| Ethyl Ester Propanoic Acid | 6.06 | 1.34E-03 | B | A; C; D | B | B |

| | | | | | | |
|---|---|---|---|---|---|---|
| 2,3-Butanedione | 1.97 | 1.30E-01 | | | | |
| 2-Methylpropyl Acetate | 7.54 | 2.96E-04 | B | A; C; D | B | B |
| 1-Propanol | 10.48 | 1.85E-05 | B | A; C; D | B | B |
| 2-Ethyl-5-Methyl-Furan | 2.34 | 8.43E-02 | | | | |
| Toluene | 3.73 | 1.69E-02 | C | | A | |
| Ethyl Butanoate | 6.54 | 8.12E-04 | B | A; C; D | B | B |
| 2-Methyl-3-Buten-2-ol | 1.98 | 1.29E-01 | | | | |
| Nonomethyl Succinate | 1.48 | 2.32E-01 | | | | |
| 2,3-Pentanedione | 0.67 | 5.73E-01 | | | | |
| Dimethyl Disulfide | 3.01 | 3.86E-02 | | | | |
| 2-Ethenyl-Furan | 1.81 | 1.57E-01 | | | | |
| 2,5-Diethyltetrahydro-Furan | 1.17 | 3.32E-01 | | | | |
| Hexanal | 6.57 | 7.86E-04 | D | D | D | A; B; C |
| 2-Methyl-1-Propanol | 4.77 | 5.31E-03 | B | A; C; D | B | B |
| 5-Butyl-Dihydro-2(3H)-Furanone | 7.17 | 4.29E-04 | D | D | D | A; B; C |
| m-Cresol | 7.92 | 2.04E-04 | B; C; D | A | A | A |
| 1-Butanol | 4.26 | 9.35E-03 | | C | B | |
| 5-Propyl-Dihydro-2(3H)-Furanone | 6.25 | 1.10E-03 | D | D | D | A; B; C |
| 3-Methyl-Pyridazine | 17.95 | 4.85E-08 | B; C; D | A | A | A |
| 2-Heptanone | 6.94 | 5.37E-04 | B | A; C; D | B | B |
| m-Menthane | 4.49 | 7.22E-03 | | C | B; D | C |
| 1,3-Diazine | 4.21 | 9.93E-03 | C | | A | |
| 2-Methyl-1-Butanol | 7.80 | 2.29E-04 | C; D | C; D | A; B | A; B |
| 2-Propyl-Furan | 8.62 | 1.03E-04 | B; C; D | A | A | A |
| Ethyl Hexanoate | 6.79 | 6.29E-04 | B | A; C; D | B | B |
| 2-Pentyl-Furan | 6.50 | 8.47E-04 | D | D | D | A; B; C |
| 2-Methyl-Pyrazine | 0.91 | 4.45E-01 | | | | |
| 2-Methyl-Dihydro-2(3H)-Furanone | 23.37 | 1.35E-09 | B; C; D | A | A | A |
| p-Cymene | 11.15 | 1.02E-05 | C; D | C; D | A; B | A; B |
| Mesitylene | 1.67 | 1.85E-01 | | | | |
| 3,5-Xylenol | 15.25 | 3.56E-07 | B; C; D | A | A | A |
| 3-Hydroxy-2-Butanone | 7.23 | 4.00E-04 | B; C | A | A | |
| Vinylene Carbonate | 11.87 | 5.49E-06 | B; C; D | A | A | A |

| | | | | | | |
|---|---|---|---|---|---|---|
| 2,6-Xylenol | 7.97 | 1.93E-04 | B; C | A | A | |
| 1-Hydroxy-2-Propanone | 4.87 | 4.76E-03 | | | D | C |
| 2,5-Dimethyl-Pyrazine | 3.76 | 1.64E-02 | | | | |
| 2,6-Dimethyl-Pyrazine | 9.80 | 3.41E-05 | B; C; D | A | A | A |
| 2-Cyclopenten-1-one | 6.76 | 6.49E-04 | C | D | A, D | B; C |
| 1,2,3,4-Tetramethyl-4-(1-methylethenyl)-Benzene | 6.78 | 6.33E-04 | D | D | D | A; B; C |
| 2-Methyl-2-Cyclopenten-1-one | 12.45 | 3.36E-06 | B; C; D | A | A | A |
| 5-Methyl-2-Furanmethanethiol | 5.25 | 3.17E-03 | | C; D | B | B |
| 1-Hydroxy-2-Butanone | 4.92 | 4.51E-03 | C | | A; D | C |
| 2-Ethyl-6-Methyl-Pyrazine | 5.56 | 2.25E-03 | A | D | A; D | B; C |
| 2-Ethyl-5-Methyl-Pyrazine | 6.93 | 5.44E-04 | D | D | D | A; B; C |
| Nonanal | 3.02 | 3.83E-02 | D | | | A |
| Trimethyl-Pyrazine | 6.94 | 5.41E-04 | D | D | D | A; B; C |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | 6.87 | 5.77E-04 | D | D | D | A; B; C |
| 2-Cyclohexen-1-one | 6.19 | 1.16E-03 | D | D | D | A; B; C |
| 5-Methyl-2(3H)-Furanone | 29.65 | 3.71E-11 | B; C; D | A | A | A |
| 1,3-Dihydro-4-Methyl-2H-Imidazol-2-one | 8.43 | 1.24E-04 | B; C | A | A | |
| Ethyl Octanoate | 6.93 | 5.44E-04 | B | A; C; D | B | B |
| 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | 6.21 | 1.14E-03 | D | D | | A; B |
| Furfural | 2.57 | 6.44E-02 | | | | |
| Ethanoic Acid | 1.59 | 2.03E-01 | | | | |
| 1,2,3,4-Tetrahydro-1,6,8-Trimethyl-Naphthalene | 12.54 | 3.13E-06 | D | D | D | A; B; C |
| 2-Ethyl-1-Hexanol | 4.98 | 4.23E-03 | B | A; C; D | B | B |
| 3-Methyl-Furfural | 16.94 | 1.01E-07 | B | A; C; D | B | B |
| Furfuryl Formate | 17.23 | 8.15E-08 | B; C; D | A | A | A |
| Decanal | 14.47 | 6.54E-07 | B; C; D | A | A | A |
| 1-(2-Furanyl)-Ethanone | 3.94 | 1.33E-02 | D | | | A |
| Benzaldehyde | 4.98 | 4.21E-03 | D | D | D | A; B; C |
| Furfuryl Acetate | 20.88 | 6.61E-09 | B; C; D | A | A | A |
| Propanoic Acid | 3.32 | 2.70E-02 | D | | | A |
| Dimethyl Sulfoxide | 3.01 | 3.87E-02 | | C | B | |
| 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | 3.47 | 2.28E-02 | | | D | C |
| 5-Methyl-Furfural | 12.90 | 2.31E-06 | B; D | A; C | B; D | A; C |

| | | | | | | |
|---|---|---|---|---|---|---|
| 4-Cyclopentene-1,3-dione | 42.70 | 7.89E-14 | B; C; D | A | A | A |
| 2-Methyl-Benzofuran | 27.39 | 1.27E-10 | B; C; D | A | A | A |
| 1-(5-Methyl-2-Furanyl)-Ethanone | 11.80 | 5.84E-06 | B; C; D | A | A | A |
| Diethylene Glycol Ethyl Ether | 5.67 | 2.00E-03 | B; D | A | | A |
| 3-Methyl-Dihydro-2(3H)-Furanone | 4.62 | 6.25E-03 | | D | D | B; C |
| 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | 17.05 | 9.30E-08 | D | D | D | A; B; C |
| Benzeneacetaldehyde | 11.51 | 7.47E-06 | B; C; D | A | A | A |
| 3,5-Dimethyl-Dihydro-2-Furanone | 5.54 | 2.31E-03 | B | A; C | B | |
| 2-Propenoic Acid | 2.09 | 1.14E-01 | | | | |
| Ethyl Decanoate | 6.94 | 5.40E-04 | B | A; C; D | B | B |
| Acetophenone | 13.09 | 1.98E-06 | B; C | A | A | |
| 2-Furanmethanol | 0.50 | 6.84E-01 | | | | |
| 3-Furanmethanol | 5.07 | 3.82E-03 | C | C | A; B | |
| 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | 14.77 | 5.16E-07 | D | D | D | A; B; C |
| 2-(2-Furanylmethyl)-5-Methyl-Furan | 28.08 | 8.70E-11 | B; C; D | A | A | A |
| 3-Methyl-2(5H)-Furanone | 2.66 | 5.80E-02 | | | | |
| 5-Methyl-2-Furanmethanol | 13.31 | 1.65E-06 | B; C | A | A; D | C |
| Benzyl Acetate | 6.18 | 1.18E-03 | B | A; C; D | B | B |
| 2(5H)-Furanone | 10.38 | 2.02E-05 | B; C; D | A | A | A |
| 2,2'-Methylenebis[5-Methyl-Furan | 24.37 | 7.39E-10 | B; C; D | A | A | A |
| 1,2-Cyclopentanedione | 9.93 | 3.05E-05 | B; C | A; D | A | B |
| 2-Cyclohexenol | 23.74 | 1.08E-09 | B; C; D | A | A | A |
| 2-Phenylethyl Acetate | 1.70 | 1.78E-01 | | | | |
| 3-Methyl-1,2-Cyclopentanedione | 8.89 | 7.98E-05 | B; C | A | A | |
| 2-Ethyl-Hexanoic Acid | 16.91 | 1.03E-07 | C | C | A; B; D | C |
| β-Damascenone | 4.62 | 6.25E-03 | C | | A | |
| Ethyl Undecanoate | 6.25 | 1.09E-03 | B | A; C | B | |
| 2-Methyl-Propanoic Acid | 3.65 | 1.86E-02 | | | D | C |
| 2,4,6-Trihydroxypyrimidine | 180.09 | ≤1.00E-19 | B; C; D | A | A | A |
| Mequinol | 7.19 | 4.20E-04 | B; C; D | A | A | A |
| 2,2-Diethyl-3-Methyl-Oxazolidine | 7.29 | 3.79E-04 | B; C; D | A | A | A |
| Oxypurinol | 23.80 | 1.04E-09 | B; C; D | A | A | A |
| Benzenemethanol | 3.17 | 3.23E-02 | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 4-Methyl-2(5H)-Furanone | 13.71 | 1.19E-06 | B; C | A | A | |
| 3-Ethyl-2-Hydroxy-2-Cyclopenten-1-one | 8.08 | 1.74E-04 | B; C | A; D | A; D | B; C |
| Benzeneethanol | 4.25 | 9.45E-03 | B | A; D | | C |
| Acrylamide | 13.60 | 1.30E-06 | B; C; D | A | A | A |
| Erythritol | 3.43 | 2.40E-02 | | | D | C |
| 2,3-Dimethyl-3-Pyrazolin-5-one | 13.49 | 1.43E-06 | B; C; D | A | A | A |
| Furfural Acetone | 22.71 | 2.03E-09 | B; C; D | A | A | A |
| Cyclotene | 17.59 | 6.30E-08 | B; C; D | A | A | A |
| 2-Methyl-1,4-Benzenediol | 7.42 | 3.32E-04 | B; C; D | A | A | A |
| Heptanoic Acid | 6.74 | 6.57E-04 | D | D | D | A; B; C |
| Maltol | 15.39 | 3.21E-07 | B; C; D | A | A | A |
| 2-Acetylpyrrole | 17.38 | 7.30E-08 | B; C; D | A | A | A |
| 2,5-Furandicarboxaldehyde | 30.06 | 2.98E-11 | B; C; D | A | A | A |
| 2H-Pyran-2,6(3H)-Dione | 9.16 | 6.17E-05 | B; C; D | A | A | A |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | 9.33 | 5.29E-05 | B; C; D | A | A | A |
| Phenol | 6.26 | 1.08E-03 | B; C | A; D | A | B |
| 1H-Pyrrole-2-Carboxaldehyde | 4.50 | 7.14E-03 | B; C | A | A | |
| Phloroglucinol | 10.07 | 2.69E-05 | B; C; D | A | A | A |
| Furaneol | 5.05 | 3.91E-03 | B; C | A | A | |
| Octanoic Acid | 6.11 | 1.26E-03 | D | D | D | A; B; C |
| 5-Acetyl-Dihydro-2(3H)-Furanone | 6.80 | 6.22E-04 | B; C | A | A | |
| 2-Furanpropionic Acid | 19.07 | 2.23E-08 | B; C; D | A | A | A |
| 1,3-Dihydroxy-2-Propanone | 10.30 | 2.18E-05 | C; D | | A | A |
| Tetrahydro-5-Methyl-2-Furanmethanol | 15.38 | 3.23E-07 | B; C; D | A | A | A |
| 4,5-Dimethyl Vinylene Carbonate | 0.89 | 4.55E-01 | | | | |
| 2-Hydroxy-Dihydro-2(3H)-Furanone | 4.53 | 6.94E-03 | D | | | A |
| 5-Acetoxymethyl-2-Furfural A | 11.55 | 7.21E-06 | B; C; D | A | A; D | A; C |
| 5-Acetoxymethyl-2-Furfural B | 22.74 | 2.00E-09 | B; C; D | A | A | A |
| 2-Methoxy-4-Vinyl-Phenol | 10.71 | 1.51E-05 | B; C; D | A | A | A |
| 3-Methyl-2,4(3H,5H)-Furandione | 22.67 | 2.09E-09 | B; C; D | A | A | A |
| 3-Hydroxy-2,3-Dihydro-Maltol | 4.00 | 1.25E-02 | D | D | | A; B |
| Decanoic Acid | 6.02 | 1.39E-03 | D | D | D | A; B; C |
| 5-Hydroxy-Maltol | 13.13 | 1.92E-06 | B; C; D | A | A | A |

| | | | | | | |
|---|---|---|---|---|---|---|
| 2,3-Dihydro-Benzofuran | 6.15 | 1.22E-03 | B; C | A | A | |
| 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | 4.60 | 6.39E-03 | B | A; D | | B |
| 4-Pyridinol | 45.77 | 2.25E-14 | B; C; D | A | A | A |
| 4-Amino-Phenol | 7.14 | 4.38E-04 | B; C; D | A | A | A |
| Benzoic Acid | 4.98 | 4.22E-03 | D | D | D | A; B; C |
| Dimethylhydrazone 3-Pentanone | 1.27 | 2.96E-01 | | | | |
| Undecanoic Acid | 2.03 | 1.21E-01 | | | | |
| 5-(Hydroxymethyl)-Dihydro-2(3H)-Furanone | 4.65 | 6.04E-03 | B; D | A | | A |
| Dodecanoic Acid | 8.96 | 7.45E-05 | C | | A; D | C |
| 5-(Hydroxymethyl)-2-Furfural | 8.22 | 1.51E-04 | B; D | A | D | A; C |
| 3-Methoxy-1,2-Benzenediol | 22.36 | 2.55E-09 | B; C; D | A | A | A |
| 1-(2-Furanyl)-1,2-Ethanediol | 3.47 | 2.28E-02 | C | | A | |
| 4-Hydroxy-Dihydro-2(3H)-Furanone | 6.27 | 1.07E-03 | D | C | B; D | A; C |

[1]F Value - Fischer value from One-way ANOVA test.
[2]P Value - Probability value from One-way ANOVA test.
[3]Samples with significantly different relative peak area values determined by one-way ANOVA with Post-hoc Tukey test ($\alpha < 0.05$).

**Table S42. Information summary of PCA and PLS based on the RPA of the identified VOCs in SC-based syrups samples.**

| Analysis | Component | $R^2X$ | Eigenvalues | $R^2Y$ | $Q^2$ | Significance | Iterations |
|---|---|---|---|---|---|---|---|
| PCA | 1 | 0.3542 | 57.37 | n.a. | 0.322 | S | 6 |
| | 2 | 0.1846 | 29.90 | n.a. | 0.020 | S | 13 |
| | 3 | 0.1105 | 17.90 | n.a. | 0.109 | S | 11 |
| | 4 | 0.0533 | 8.64 | n.a. | 0.019 | S | 8 |
| | 5 | 0.0485 | 7.86 | n.a. | 0.055 | S | 12 |
| | 6 | 0.0374 | 6.06 | n.a. | -0.002 | UNKNOWN | 50 |
| PLS | 1 | 0.3856 | 57.07 | 0.058 | 0.014 | S | 10 |
| | 2 | 0.1982 | 29.34 | 0.059 | 0.001 | S | 9 |
| | 3 | 0.1158 | 17.14 | 0.059 | 0.019 | S | 11 |
| | 4 | 0.0562 | 8.31 | 0.059 | 0.006 | S | 8 |
| | 5 | 0.0479 | 7.09 | 0.059 | 0.012 | S | 12 |
| | 6 | 0.0361 | 5.35 | 0.059 | 0.011 | S | 25 |
| | 7 | 0.0307 | 4.55 | 0.058 | 0.020 | S | 33 |

| | | | | | | |
|---|---|---|---|---|---|---|
| 8 | 0.0290 | 4.29 | 0.059 | 0.023 | S | 13 |
| 9 | 0.0211 | 3.12 | 0.059 | 0.019 | S | 24 |
| 10 | 0.0206 | 3.05 | 0.059 | 0.041 | S | 15 |
| 11 | 0.0147 | 2.17 | 0.058 | 0.026 | S | 50 |
| 12 | 0.0138 | 2.04 | 0.059 | 0.086 | S | 13 |
| 13 | 0.0091 | 1.35 | 0.058 | 0.084 | S | 16 |
| 14 | 0.0072 | 1.07 | 0.058 | 0.117 | S | 10 |
| 15 | 0.0043 | 0.64 | 0.058 | 0.068 | S | 21 |
| 16 | 0.0030 | 0.45 | 0.058 | 0.117 | S | 3 |
| 17 | 0.0026 | 0.39 | 0.058 | 0.900 | S | 3 |
| 18 | 0.0007 | 0.09 | 0.002 | 0.094 | S | 10 |

**Table S43. Loading results and VIP scores of variables from PCA and Partial Least Squares Analysis PLS based on the RPA of the identified VOCs in samples SC-based syrups samples.**

| Volatile Organic Compounds | Abbreviations | PCA | | | | | PLS | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | VIP[1] | | | | | VIP[1] | |
| | | 1 | 2 | 3 | Importance | Power (x 100) | 1 | 2 | 3 | Importance | Power (x 100) |
| Pentane | PTANE | -0.254 | -0.731 | 0.050 | 112 | 78.55 | -0.03 | -0.14 | 0.01 | 21 | 10.79 |
| Hexane | HXANE | 0.026 | -0.253 | 0.145 | 110 | 80.04 | 0.00 | -0.05 | 0.03 | 12 | 11.76 |
| 1,4-Pentadiene | PT14DIENE | -0.065 | -0.904 | -0.026 | 50 | 94.19 | -0.01 | -0.17 | -0.01 | 98 | 6.05 |
| Ethanal | ETAL | 0.900 | 0.001 | 0.232 | 34 | 95.60 | 0.12 | 0.00 | 0.06 | 116 | 5.40 |
| Dimethyl Sulfide | DMSULFI | -0.158 | -0.763 | -0.106 | 106 | 82.37 | -0.02 | -0.14 | -0.03 | 32 | 9.61 |
| Furan | FUR | 0.244 | -0.062 | -0.130 | 134 | 55.20 | 0.03 | -0.01 | -0.03 | 15 | 11.50 |
| 2-Methyl-Propanal | MPPAL | 0.782 | 0.281 | -0.213 | 72 | 90.37 | 0.10 | 0.05 | -0.05 | 61 | 7.73 |
| Ethyl Formate | EESTFA | 0.363 | 0.280 | 0.237 | 136 | 51.32 | 0.05 | 0.05 | 0.06 | 17 | 11.06 |
| 2-Propenal | PPENAL | 0.163 | -0.790 | 0.136 | 108 | 80.59 | 0.02 | -0.15 | 0.03 | 30 | 9.70 |
| 2-Methyl-Furan | M2FUR | 0.314 | -0.248 | -0.175 | 49 | 94.21 | 0.04 | -0.05 | -0.04 | 27 | 9.83 |
| Ethyl Acetate | EESTAA | 0.380 | 0.307 | 0.586 | 124 | 67.97 | 0.05 | 0.05 | 0.14 | 37 | 9.51 |
| 2-Methyl-Butanal | M2BTAL | 0.857 | 0.252 | -0.197 | 94 | 85.46 | 0.11 | 0.05 | -0.04 | 43 | 9.03 |
| 3-Methyl-Butanal | M3BTAL | 0.729 | 0.191 | -0.194 | 126 | 66.86 | 0.10 | 0.03 | -0.04 | 41 | 9.20 |
| Ethanol | ETOL | 0.742 | 0.340 | -0.435 | 91 | 85.94 | 0.10 | 0.06 | -0.10 | 53 | 8.35 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Benzene | BNZ | 0.490 | -0.787 | -0.096 | 84 | 87.55 | 0.06 | -0.15 | -0.02 | 56 | 8.13 |
| 2,5-Dimethyl-Furan | DM25FUR | 0.268 | -0.024 | 0.379 | 100 | 83.90 | 0.04 | -0.01 | 0.09 | 19 | 10.87 |
| Ethyl Propanoate | EESTPA | 0.142 | 0.153 | 0.947 | 2 | 99.00 | 0.02 | 0.02 | 0.23 | 97 | 6.21 |
| 2-Methylpropyl Acetate | MP2ESTAA | 0.064 | 0.120 | 0.934 | 30 | 96.00 | 0.01 | 0.02 | 0.23 | 90 | 6.60 |
| 1-Propanol | P1POL | 0.037 | 0.135 | 0.922 | 48 | 94.25 | 0.00 | 0.02 | 0.23 | 77 | 6.91 |
| Toluene | TOLNE | 0.416 | 0.134 | 0.042 | 140 | 40.09 | 0.06 | 0.02 | 0.01 | 9 | 12.22 |
| Ethyl Butanoate | EESTBA | 0.062 | 0.117 | 0.943 | 24 | 96.27 | 0.01 | 0.02 | 0.23 | 85 | 6.62 |
| Dimethyl Disulfide | DMDSFD | -0.274 | 0.141 | -0.175 | 137 | 49.62 | -0.04 | 0.03 | -0.04 | 14 | 11.58 |
| Hexanal | HXAL | 0.060 | -0.985 | 0.045 | 10 | 97.94 | 0.01 | -0.18 | 0.01 | 129 | 4.97 |
| 2-Methyl-1-Propanol | M2PP1OL | 0.167 | 0.183 | 0.927 | 21 | 96.57 | 0.02 | 0.03 | 0.22 | 83 | 6.65 |
| 5-Butyl-Dihydro-2(3H)-Furanone | BDH2FURONE | 0.295 | -0.897 | -0.063 | 29 | 96.03 | 0.04 | -0.17 | -0.02 | 109 | 5.61 |
| m-Cresol | MCREOL | 0.882 | 0.200 | -0.079 | 101 | 83.58 | 0.12 | 0.04 | -0.02 | 92 | 6.57 |
| 1-Butanol | BT1OL | 0.371 | 0.236 | 0.734 | 87 | 87.20 | 0.05 | 0.04 | 0.18 | 57 | 8.10 |
| 5-Propyl-Dihydro-2(3H)-Furanone | PDH2FURONE | 0.173 | -0.961 | 0.004 | 14 | 97.51 | 0.02 | -0.18 | 0.00 | 127 | 5.02 |
| 3-Methyl-Pyridazine | M3PYRDZNE | 0.881 | 0.234 | -0.052 | 95 | 85.43 | 0.12 | 0.04 | -0.01 | 96 | 6.26 |
| 2-Heptanone | HPT2ONE | -0.151 | 0.087 | -0.064 | 144 | 6.95 | -0.02 | 0.02 | -0.01 | 8 | 12.53 |
| m-Menthane | MMTHANE | 0.170 | -0.002 | -0.031 | 130 | 62.40 | 0.02 | 0.00 | -0.01 | 3 | 14.24 |
| 1,3-Diazine | D13ZINE | 0.001 | 0.067 | 0.438 | 97 | 84.45 | 0.00 | 0.01 | 0.10 | 22 | 9.98 |
| 2-Methyl-1-Butanol | M2BT1OL | 0.315 | 0.298 | 0.609 | 105 | 82.49 | 0.04 | 0.05 | 0.15 | 50 | 8.66 |
| 2-Propyl-Furan | PP2FUR | 0.751 | 0.225 | -0.068 | 129 | 64.35 | 0.10 | 0.04 | -0.01 | 28 | 9.81 |
| Ethyl Hexanoate | EESTHA | 0.068 | 0.116 | 0.928 | 47 | 94.60 | 0.01 | 0.02 | 0.23 | 89 | 6.60 |
| 2-Pentyl-Furan | PT2FUR | 0.067 | -0.973 | 0.018 | 31 | 95.81 | 0.01 | -0.18 | 0.00 | 70 | 7.19 |
| 2-Methyl-Dihydro-2(3H)-Furanone | MDH2FURONE | 0.710 | 0.227 | -0.345 | 116 | 75.37 | 0.09 | 0.04 | -0.08 | 45 | 8.96 |
| p-Cymene | PCYMNE | 0.346 | 0.306 | 0.769 | 73 | 89.84 | 0.05 | 0.05 | 0.19 | 75 | 7.00 |
| 3,5-Xylenol | XYL35NOL | 0.816 | 0.247 | -0.072 | 104 | 82.90 | 0.11 | 0.04 | -0.02 | 86 | 6.61 |
| 3-Hydroxy-2-Butanone | HXY3BT2ONE | 0.902 | -0.336 | -0.034 | 45 | 94.70 | 0.12 | -0.06 | -0.01 | 113 | 5.48 |
| Vinylene Carbonate | VYLESTCA | 0.977 | -0.013 | 0.064 | 23 | 96.47 | 0.13 | 0.00 | 0.02 | 112 | 5.49 |
| 2,6-Xylenol | XYL26NOL | 0.671 | 0.230 | -0.104 | 122 | 71.31 | 0.09 | 0.04 | -0.02 | 47 | 8.85 |
| 1-Hydroxy-2-Propanone | HXY1PP2ONE | 0.574 | -0.524 | 0.263 | 120 | 72.83 | 0.08 | -0.10 | 0.06 | 46 | 8.91 |
| 2,5-Dimethyl-Pyrazine | DM25PYZNE | 0.111 | 0.206 | -0.193 | 117 | 74.78 | 0.02 | 0.04 | -0.05 | 2 | 16.06 |
| 2,6-Dimethyl-Pyrazine | DM26PYZNE | 0.571 | 0.316 | -0.157 | 114 | 76.08 | 0.08 | 0.06 | -0.04 | 49 | 8.77 |
| 2-Cyclopenten-1-one | CY2PT1EONE | 0.514 | -0.819 | -0.055 | 3 | 98.59 | 0.07 | -0.15 | -0.01 | 134 | 4.86 |
| 1,2,3,4-Tetramethyl-4-(1-methylethenyl)-Benzene | TM4MEYL1BNZ | 0.059 | -0.981 | 0.039 | 5 | 98.56 | 0.01 | -0.18 | 0.01 | 131 | 4.96 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2-Methyl-2-Cyclopenten-1-one | M2CY2PT1EONE | 0.935 | -0.232 | -0.143 | 18 | 96.85 | 0.12 | -0.04 | -0.03 | 110 | 5.59 |
| 5-Methyl-2-Furanmethanethiol | M2FURTHOL | 0.209 | 0.248 | 0.879 | 56 | 93.22 | 0.03 | 0.04 | 0.21 | 67 | 7.50 |
| 1-Hydroxy-2-Butanone | H1BT2ONE | 0.658 | -0.604 | 0.008 | 99 | 84.04 | 0.09 | -0.11 | 0.00 | 76 | 7.00 |
| 2-Ethyl-6-Methyl-Pyrazine | E6MPYZNE | 0.096 | 0.172 | -0.278 | 65 | 91.81 | 0.01 | 0.03 | -0.07 | 38 | 9.33 |
| 2-Ethyl-5-Methyl-Pyrazine | E5MPYZNE | -0.230 | 0.045 | -0.171 | 52 | 94.12 | -0.03 | 0.01 | -0.04 | 35 | 9.57 |
| Nonanal | NONAL | 0.582 | 0.167 | -0.206 | 139 | 44.99 | 0.08 | 0.03 | -0.05 | 29 | 9.71 |
| Trimethyl-Pyrazine | TMPYZNE | -0.230 | 0.045 | -0.172 | 51 | 94.12 | -0.03 | 0.01 | -0.04 | 34 | 9.57 |
| 3-Ethyl-2-Methyl-1,3-Hexadiene | E3M2HX13DENE | 0.067 | -0.981 | 0.041 | 4 | 98.58 | 0.01 | -0.18 | 0.01 | 132 | 4.94 |
| 2-Cyclohexen-1-one | C2HEXONE | 0.102 | -0.971 | 0.049 | 12 | 97.80 | 0.01 | -0.18 | 0.01 | 124 | 5.12 |
| 5-Methyl-2(3H)-Furanone | M5FURONE | 0.952 | 0.054 | -0.039 | 58 | 92.91 | 0.13 | 0.01 | -0.01 | 108 | 5.63 |
| 1,3-Dihydro-4-Methyl-2H-Imidazol-2-one | M4IMDZONE | 0.900 | -0.358 | 0.011 | 37 | 95.41 | 0.12 | -0.07 | 0.00 | 136 | 4.81 |
| Ethyl Octanoate | EESTOA | 0.068 | 0.117 | 0.936 | 28 | 96.05 | 0.01 | 0.02 | 0.23 | 88 | 6.60 |
| 1,2,3,4-Tetrahydro-1,1,6-Trimethyl-Naphthalene | T116TNP | 0.035 | -0.962 | 0.029 | 44 | 94.72 | 0.00 | -0.18 | 0.00 | 80 | 6.82 |
| 1,2,3,4-Tetrahydro-1,6,8-Trimethyl-Naphthalene | T168TNP | 0.163 | -0.917 | 0.018 | 71 | 90.84 | 0.02 | -0.17 | 0.00 | 66 | 7.50 |
| 2-Ethyl-1-Hexanol | E2HX1OL | 0.223 | 0.074 | 0.929 | 35 | 95.44 | 0.03 | 0.01 | 0.23 | 84 | 6.63 |
| 3-Methyl-Furfural | M3FURAL | -0.081 | 0.113 | -0.134 | 143 | 15.04 | -0.01 | 0.02 | -0.02 | 11 | 11.78 |
| Furfuryl Formate | FURYLFMTE | 0.831 | 0.231 | 0.045 | 53 | 93.86 | 0.11 | 0.04 | 0.01 | 72 | 7.04 |
| Decanal | DECAL | 0.877 | 0.212 | -0.176 | 89 | 86.20 | 0.12 | 0.04 | -0.04 | 33 | 9.61 |
| 1-(2-Furanyl)-Ethanone | FURYLONE | 0.740 | -0.115 | 0.344 | 93 | 85.50 | 0.10 | -0.02 | 0.08 | 58 | 8.10 |
| Benzaldehyde | BENZAL | 0.265 | -0.936 | 0.070 | 11 | 97.90 | 0.03 | -0.17 | 0.02 | 122 | 5.22 |
| Furfuryl Acetate | FURYLACTE | 0.948 | 0.135 | -0.076 | 39 | 95.15 | 0.13 | 0.02 | -0.02 | 125 | 5.10 |
| Propanoic Acid | PPANOIC | 0.030 | -0.633 | 0.543 | 111 | 79.82 | 0.00 | -0.12 | 0.13 | 26 | 9.90 |
| Dimethyl Sulfoxide | DMSULFO | 0.202 | -0.569 | 0.091 | 90 | 86.14 | 0.03 | -0.11 | 0.02 | 42 | 9.07 |
| 1,2,3,4-Tetrahydro-1,5,8-Trimethyl-Naphthalene | T158TNP | 0.327 | -0.817 | 0.113 | 81 | 88.32 | 0.04 | -0.15 | 0.03 | 52 | 8.43 |
| 5-Methyl-Furfural | M5FURAL | 0.734 | 0.262 | 0.209 | 92 | 85.63 | 0.10 | 0.05 | 0.05 | 60 | 7.93 |
| 4-Cyclopentene-1,3-dione | CPT4E13DONE | 0.909 | -0.019 | 0.018 | 67 | 91.48 | 0.12 | 0.00 | 0.00 | 102 | 5.91 |
| 2-Methyl-Benzofuran | M2BNZFUR | 0.885 | 0.253 | -0.139 | 64 | 91.89 | 0.12 | 0.05 | -0.03 | 91 | 6.57 |
| 1-(5-Methyl-2-Furanyl)-Ethanone | M5FURYLONE | 0.923 | 0.088 | -0.107 | 78 | 88.73 | 0.12 | 0.01 | -0.02 | 101 | 5.95 |
| Diethylene Glycol Ethyl Ether | DENGOLEETHR | 0.669 | 0.275 | -0.068 | 119 | 73.05 | 0.09 | 0.05 | -0.02 | 44 | 9.01 |
| 3-Methyl-Dihydro-2(3H)-Furanone | M3DHFURONE | 0.513 | -0.737 | 0.244 | 76 | 89.11 | 0.07 | -0.14 | 0.06 | 40 | 9.22 |
| 2,3-Dihydro-1,1,4,6-Tetramethyl-1H-Indene | DHT1146MIDNE | 0.047 | -0.926 | 0.004 | 70 | 90.95 | 0.01 | -0.17 | 0.00 | 79 | 6.83 |
| Benzeneacetaldehyde | BENZACETAL | 0.926 | 0.198 | -0.013 | 55 | 93.26 | 0.12 | 0.04 | 0.00 | 104 | 5.80 |
| 3,5-Dimethyl-Dihydro-2-Furanone | DM35DHFURONE | -0.182 | -0.107 | -0.131 | 142 | 23.36 | -0.02 | -0.02 | -0.03 | 4 | 14.09 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ethyl Ester Decanoic Acid | EESTDA | 0.068 | 0.117 | 0.936 | 26 | 96.10 | 0.01 | 0.02 | 0.23 | 87 | 6.61 |
| Acetophenone | ACETPHONE | 0.873 | -0.284 | -0.250 | 57 | 92.92 | 0.12 | -0.05 | -0.06 | 115 | 5.41 |
| 3-Furanmethanol | FUR3OL | 0.521 | 0.156 | -0.153 | 138 | 46.31 | 0.07 | 0.03 | -0.03 | 7 | 12.56 |
| 2,3-Dihydro-1,1,5,6-Tetramethyl-1H-Indene | DHT1156MIDNE | 0.067 | -0.938 | 0.054 | 68 | 91.23 | 0.01 | -0.17 | 0.01 | 81 | 6.74 |
| 2-(2-Furanylmethyl)-5-Methyl-Furan | FURYLMFUR | 0.891 | 0.239 | -0.237 | 60 | 92.42 | 0.12 | 0.04 | -0.06 | 99 | 6.01 |
| 5-Methyl-2-Furanmethanol | M5FUR2OL | 0.874 | -0.238 | -0.098 | 80 | 88.58 | 0.12 | -0.05 | -0.02 | 59 | 7.98 |
| Benzyl Acetate | PMESTAA | 0.193 | 0.183 | 0.910 | 19 | 96.76 | 0.03 | 0.03 | 0.22 | 65 | 7.54 |
| 2(5H)-Furanone | FURONE | 0.839 | -0.240 | 0.005 | 107 | 81.85 | 0.11 | -0.05 | 0.00 | 64 | 7.56 |
| 2,2'-Methylenebis[5-Methyl-Furan | MNEB5MFUR | 0.840 | 0.273 | -0.079 | 83 | 87.86 | 0.11 | 0.05 | -0.02 | 74 | 7.04 |
| 1,2-Cyclopentanedione | CPT12DONE | 0.838 | -0.115 | 0.004 | 113 | 78.44 | 0.11 | -0.02 | 0.00 | 55 | 8.18 |
| 2-Cyclohexenol | CHEX2E1OL | 0.977 | 0.134 | -0.077 | 13 | 97.78 | 0.13 | 0.02 | -0.02 | 142 | 4.00 |
| 3-Methyl-1,2-Cyclopentanedione | M3CPT12DONE | 0.895 | -0.419 | -0.039 | 1 | 99.15 | 0.12 | -0.08 | -0.01 | 144 | 3.93 |
| 2-Ethyl-Hexanoic Acid | E2HXNOIC | -0.219 | -0.367 | 0.004 | 127 | 66.09 | -0.03 | -0.07 | 0.00 | 5 | 13.32 |
| β-Damascenone | DAMSNONE | 0.741 | 0.024 | -0.313 | 109 | 80.57 | 0.10 | 0.00 | -0.07 | 31 | 9.69 |
| Ethyl Undecanoate | EESTUNDA | 0.033 | 0.105 | 0.918 | 74 | 89.49 | 0.00 | 0.02 | 0.22 | 73 | 7.04 |
| 2-Methyl-Propanoic Acid | M2PPOICA | 0.571 | -0.786 | 0.146 | 15 | 97.30 | 0.08 | -0.15 | 0.03 | 137 | 4.66 |
| 2,4,6-Trihydroxypyrimidine | THDXYPYMNE | 0.823 | 0.277 | -0.245 | 75 | 89.13 | 0.11 | 0.05 | -0.06 | 107 | 5.74 |
| Mequinol | MEQNOL | 0.800 | 0.246 | -0.098 | 86 | 87.21 | 0.11 | 0.04 | -0.02 | 51 | 8.59 |
| 2,2-Diethyl-3-Methyl-Oxazolidine | DEMOXZDNE | 0.857 | 0.215 | 0.171 | 69 | 91.08 | 0.11 | 0.04 | 0.04 | 93 | 6.54 |
| Oxypurinol | OXYPUROL | 0.947 | 0.198 | -0.039 | 41 | 95.01 | 0.13 | 0.04 | -0.01 | 103 | 5.90 |
| Benzenemethanol | BENZMTOL | 0.484 | 0.131 | 0.330 | 98 | 84.08 | 0.06 | 0.02 | 0.08 | 23 | 9.96 |
| 4-Methyl-2(5H)-Furanone | M4FUR2ONE | 0.924 | -0.264 | -0.165 | 25 | 96.21 | 0.12 | -0.05 | -0.04 | 140 | 4.51 |
| 3-Ethyl-2-Hydroxy-2-Cyclopenten-1-one | E3H2C2PT1ONE | 0.724 | -0.574 | -0.215 | 46 | 94.70 | 0.10 | -0.11 | -0.05 | 111 | 5.58 |
| Benzeneethanol | BENZETOL | 0.020 | 0.082 | 0.919 | 82 | 88.06 | 0.00 | 0.01 | 0.22 | 48 | 8.80 |
| Acrylamide | ACRYLMDE | 0.863 | 0.284 | 0.214 | 77 | 89.00 | 0.11 | 0.05 | 0.05 | 63 | 7.65 |
| Erythritol | ERYTOL | 0.630 | -0.727 | 0.150 | 32 | 95.76 | 0.08 | -0.14 | 0.04 | 119 | 5.26 |
| 2,3-Dimethyl-3-Pyrazolin-5-one | DM23PYZLONE | 0.961 | -0.127 | -0.004 | 27 | 96.07 | 0.13 | -0.02 | 0.00 | 138 | 4.59 |
| Furfural Acetone | FURALTONE | 0.977 | 0.079 | -0.094 | 6 | 98.21 | 0.13 | 0.01 | -0.02 | 143 | 3.94 |
| Cyclotene | CYTENE | 0.956 | -0.063 | -0.025 | 38 | 95.24 | 0.13 | -0.01 | 0.00 | 117 | 5.33 |
| 2-Methyl-1,4-Benzenediol | M2BNZ14DIOL | 0.864 | 0.165 | -0.072 | 42 | 94.98 | 0.11 | 0.03 | -0.01 | 82 | 6.68 |
| Heptanoic Acid | HPTOIC | 0.056 | -0.979 | 0.038 | 9 | 98.08 | 0.01 | -0.18 | 0.01 | 120 | 5.24 |
| Maltol | MALTOL | 0.901 | 0.272 | 0.233 | 33 | 95.67 | 0.12 | 0.05 | 0.06 | 126 | 5.09 |
| 2-Acetylpyrrole | ACTLPYROLE | 0.804 | 0.289 | -0.139 | 88 | 86.75 | 0.11 | 0.05 | -0.03 | 78 | 6.86 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2,5-Furandicarboxaldehyde | FUR25DIAL | 0.920 | 0.260 | -0.143 | 40 | 95.13 | 0.12 | 0.05 | -0.03 | 135 | 4.82 |
| 2H-Pyran-2,6(3H)-Dione | PYR26DIONE | 0.884 | 0.272 | 0.106 | 66 | 91.73 | 0.12 | 0.05 | 0.03 | 71 | 7.10 |
| 1-(2-Furanyl)-2-Hydroxy-Ethanone | H2FURYLONE | 0.654 | 0.211 | 0.219 | 125 | 67.73 | 0.09 | 0.04 | 0.05 | 39 | 9.32 |
| Phenol | PHEOL | 0.819 | -0.441 | -0.111 | 63 | 91.98 | 0.11 | -0.08 | -0.03 | 100 | 5.95 |
| 1H-Pyrrole-2-Carboxaldehyde | PYRLE2AL | 0.727 | -0.593 | -0.166 | 59 | 92.66 | 0.10 | -0.11 | -0.04 | 105 | 5.78 |
| Phloroglucinol | PHLOGLNOL | 0.913 | 0.189 | 0.233 | 43 | 94.82 | 0.12 | 0.03 | 0.06 | 130 | 4.96 |
| Furaneol | FUREOL | 0.627 | -0.370 | 0.279 | 128 | 64.81 | 0.08 | -0.07 | 0.06 | 24 | 9.95 |
| Octanoic Acid | OCTOIC | 0.159 | -0.954 | 0.007 | 20 | 96.71 | 0.02 | -0.18 | 0.00 | 118 | 5.33 |
| 5-Acetyl-Dihydro-2(3H)-Furanone | ACYLDHFURONE | 0.828 | -0.343 | 0.134 | 96 | 84.60 | 0.11 | -0.06 | 0.03 | 68 | 7.26 |
| 2-Furanpropionic Acid | FURPPIONIC | 0.927 | 0.244 | -0.053 | 36 | 95.42 | 0.12 | 0.04 | -0.01 | 121 | 5.24 |
| 1,3-Dihydroxy-2-Propanone | DHYPPAONE | -0.075 | -0.292 | 0.297 | 115 | 75.70 | -0.01 | -0.06 | 0.07 | 13 | 11.74 |
| Tetrahydro-5-Methyl-2-Furanmethanol | TEHYMFUROL | -0.414 | -0.379 | 0.433 | 118 | 73.62 | -0.06 | -0.07 | 0.10 | 18 | 11.01 |
| 2-Hydroxy-Dihydro-2(3H)-Furanone | HY2DHFURONE | -0.511 | -0.163 | 0.311 | 135 | 53.19 | -0.07 | -0.03 | 0.07 | 20 | 10.86 |
| 5-Acetoxymethyl-2-Furfural A | ACTYMFURALA | 0.696 | 0.307 | 0.290 | 103 | 82.98 | 0.09 | 0.05 | 0.07 | 54 | 8.29 |
| 5-Acetoxymethyl-2-Furfural B | ACTYMFURALB | 0.839 | 0.261 | 0.139 | 79 | 88.70 | 0.11 | 0.05 | 0.03 | 95 | 6.32 |
| 2-Methoxy-4-Vinyl-Phenol | MXY2VYL4PHEOL | 0.942 | 0.121 | -0.054 | 61 | 92.28 | 0.12 | 0.02 | -0.01 | 133 | 4.89 |
| 3-Methyl-2,4(3H,5H)-Furandione | M3FURDIONE | 0.985 | 0.081 | -0.055 | 7 | 98.20 | 0.13 | 0.01 | -0.01 | 141 | 4.42 |
| 3-Hydroxy-2,3-Dihydro-Maltol | HX3DH23MALTOL | 0.100 | -0.585 | 0.246 | 133 | 56.55 | 0.01 | -0.11 | 0.06 | 10 | 12.00 |
| Decanoic Acid | DECOIC | 0.175 | -0.957 | 0.079 | 17 | 97.17 | 0.02 | -0.18 | 0.02 | 123 | 5.15 |
| 5-Hydroxy-Maltol | HX5MALTOL | 0.912 | 0.126 | -0.085 | 54 | 93.32 | 0.12 | 0.02 | -0.02 | 69 | 7.20 |
| 2,3-Dihydro-Benzofuran | DHBNZFUR | 0.840 | 0.029 | -0.062 | 102 | 83.20 | 0.11 | 0.00 | -0.01 | 94 | 6.37 |
| 1,4:3,6-Dianhydro-.alpha.-d-Glucopyranose | GLUPYROSE | 0.750 | -0.489 | 0.041 | 85 | 87.40 | 0.10 | -0.09 | 0.01 | 62 | 7.66 |
| 4-Pyridinol | PYRDINOL | 0.905 | 0.242 | -0.258 | 22 | 96.57 | 0.12 | 0.04 | -0.06 | 139 | 4.55 |
| 4-Amino-Phenol | AMIPHEOL | 0.861 | 0.231 | 0.055 | 16 | 97.25 | 0.11 | 0.04 | 0.01 | 106 | 5.75 |
| Benzoic Acid | BNZOIC | 0.269 | -0.930 | 0.056 | 8 | 98.18 | 0.04 | -0.17 | 0.01 | 128 | 4.99 |
| 5-(Hydroxymethyl)-Dihydro-2(3H)-Furanone | HM5FURONE | 0.703 | 0.083 | 0.055 | 132 | 60.18 | 0.09 | 0.01 | 0.01 | 36 | 9.56 |
| Dodecanoic Acid | DODECOIC | 0.748 | -0.069 | -0.056 | 131 | 61.80 | 0.10 | -0.01 | -0.01 | 25 | 9.95 |
| 5-(Hydroxymethyl)-2-Furfural | HM5FURAL | 0.107 | 0.611 | -0.141 | 123 | 69.81 | 0.01 | 0.11 | -0.04 | 6 | 12.56 |
| 3-Methoxy-1,2-Benzenediol | M3BNZDIOL | 0.890 | 0.219 | -0.249 | 62 | 92.06 | 0.12 | 0.04 | -0.06 | 114 | 5.45 |
| 1-(2-Furanyl)-1,2-Ethanediol | FURYLETDIOL | 0.048 | -0.264 | 0.282 | 121 | 71.33 | 0.01 | -0.05 | 0.07 | 16 | 11.49 |
| 4-Hydroxy-Dihydro-2(3H)-Furanone | DHYHYFURONE | 0.523 | 0.078 | 0.080 | 141 | 38.18 | 0.07 | 0.01 | 0.02 | 1 | 16.66 |

**Table S44. Loading results of samples and variables from PCA and PLS based on the RPA of the identified VOCs in SC-based syrups samples**.

| ID Sample Code | ID Group Code | PCA | | | PLS | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 1 | 2 | 3 |
| FRS07 | CERT | 0.01 | 0.07 | -0.06 | n.a. | n.a. | n.a. |
| FRS13 | CERT | 0.21 | 0.14 | 0.14 | n.a. | n.a. | n.a. |
| FRS14 | CERT | 0.35 | 0.08 | -0.06 | n.a. | n.a. | n.a. |
| FRS15 | CERT | 0.53 | 0.10 | -0.22 | n.a. | n.a. | n.a. |
| FRS16 | CERT | -0.08 | 0.10 | -0.06 | n.a. | n.a. | n.a. |
| FRS17 | CERT | -0.03 | 0.10 | -0.09 | n.a. | n.a. | n.a. |
| FRS18 | CERT | 0.48 | 0.05 | -0.18 | n.a. | n.a. | n.a. |
| ECAL14 | NCERT | -0.15 | 0.09 | -0.06 | n.a. | n.a. | n.a. |
| ENCAL14 | NCERT | -0.32 | 0.08 | -0.13 | n.a. | n.a. | n.a. |
| GLA14 | NCERT | 0.07 | 0.12 | 0.94 | n.a. | n.a. | n.a. |
| ESP16 | MED | -0.23 | 0.02 | -0.05 | n.a. | n.a. | n.a. |
| EGP17 | MED | -0.05 | -0.01 | 0.06 | n.a. | n.a. | n.a. |
| EGPA16 | MED | -0.08 | -0.01 | 0.01 | n.a. | n.a. | n.a. |
| EGPB16 | MED | -0.18 | 0.01 | -0.04 | n.a. | n.a. | n.a. |
| EGPC16 | MED | -0.25 | 0.03 | -0.06 | n.a. | n.a. | n.a. |
| MCBR14 | STH | -0.13 | -0.04 | 0.00 | n.a. | n.a. | n.a. |
| MDBR14 | STH | 0.07 | -0.98 | 0.04 | n.a. | n.a. | n.a. |
| AUS17 | STH | -0.23 | 0.05 | -0.17 | n.a. | n.a. | n.a. |
| Centroid (CERT) | CERT | n.a. | n.a. | n.a. | 0.09 | 0.06 | -0.06 |
| Centroid (NCERT) | NCERT | n.a. | n.a. | n.a. | -0.03 | 0.03 | 0.12 |
| Centroid (MED) | MED | n.a. | n.a. | n.a. | -0.05 | 0.01 | -0.01 |
| Centroid (STH) | STH | n.a. | n.a. | n.a. | -0.02 | -0.11 | -0.02 |

**Table S35. Scores results of all cases from PCA and PLS based on the RPA of the identified VOCs in SC-based syrups samples.**

| ID Replicate Number | ID Replicate Code | PCA | | | PLS | | |
|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 1 | 2 | 3 |
| 1 | S1-15A | 6.71 | -0.90 | 0.26 | 6.73 | -1.39 | 0.24 |
| 2 | S1-15B | 6.74 | -1.30 | 0.38 | 6.76 | -1.80 | 0.37 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 3 | S1-15C | 6.73 | -1.10 | 0.32 | 6.74 | -1.60 | 0.31 |
| 4 | S1-16A | 6.95 | -3.41 | 0.22 | 6.97 | -3.76 | 0.19 |
| 5 | S1-16B | 6.94 | -3.38 | 0.20 | 6.96 | -3.73 | 0.17 |
| 6 | S1-16C | 6.95 | -3.40 | 0.21 | 6.96 | -3.75 | 0.18 |
| 7 | S1-17A | 8.29 | -12.36 | 1.66 | 8.31 | -12.09 | 1.51 |
| 8 | S1-17B | 8.13 | -11.06 | 1.53 | 8.15 | -10.80 | 1.39 |
| 9 | S1-17C | 8.21 | -11.71 | 1.60 | 8.23 | -11.45 | 1.45 |
| 10 | S1-18A | 7.45 | -10.41 | -0.15 | 7.47 | -10.29 | -0.21 |
| 11 | S1-18B | 7.40 | -9.25 | -0.14 | 7.42 | -9.14 | -0.20 |
| 12 | S1-18C | 7.43 | -9.83 | -0.14 | 7.44 | -9.71 | -0.21 |
| 13 | S2-15A | 6.50 | -0.20 | 0.59 | 6.51 | -0.18 | 0.55 |
| 14 | S2-15B | 6.52 | 0.13 | 0.56 | 6.53 | 0.14 | 0.52 |
| 15 | S2-15C | 6.51 | -0.04 | 0.57 | 6.52 | -0.02 | 0.54 |
| 16 | S2-16A | 6.11 | 1.26 | 0.05 | 6.12 | 1.21 | 0.05 |
| 17 | S2-16B | 6.04 | 1.12 | 0.01 | 6.05 | 1.08 | 0.01 |
| 18 | S2-16C | 6.07 | 1.19 | 0.03 | 6.08 | 1.14 | 0.03 |
| 19 | S2-17A | 6.65 | -0.04 | 0.46 | 6.66 | 0.01 | 0.43 |
| 20 | S2-17B | 6.64 | 0.00 | 0.44 | 6.64 | 0.05 | 0.41 |
| 21 | S2-17C | 6.65 | -0.02 | 0.45 | 6.65 | 0.03 | 0.42 |
| 22 | S2-18A | 6.36 | 1.20 | -0.09 | 6.37 | 1.17 | -0.09 |
| 23 | S2-18B | 6.38 | 0.94 | -0.10 | 6.38 | 0.91 | -0.10 |
| 24 | S2-18C | 6.37 | 1.07 | -0.10 | 6.37 | 1.04 | -0.10 |
| 25 | S3-15A | 4.20 | 2.73 | 0.21 | 4.20 | 2.83 | 0.22 |
| 26 | S3-15B | 4.26 | 2.71 | 0.26 | 4.26 | 2.81 | 0.28 |
| 27 | S3-15C | 4.23 | 2.72 | 0.23 | 4.23 | 2.82 | 0.25 |
| 28 | S3-16A | 3.39 | 3.58 | 0.27 | 3.40 | 3.64 | 0.30 |
| 29 | S3-16B | 3.27 | 3.72 | 0.31 | 3.28 | 3.78 | 0.34 |
| 30 | S3-16C | 3.33 | 3.65 | 0.29 | 3.34 | 3.71 | 0.32 |
| 31 | S3-17A | 3.89 | 3.36 | 0.31 | 3.89 | 3.44 | 0.33 |
| 32 | S3-17B | 3.71 | 3.45 | 0.24 | 3.71 | 3.52 | 0.26 |
| 33 | S3-17C | 3.80 | 3.41 | 0.28 | 3.80 | 3.48 | 0.30 |
| 34 | S3-18A | 3.68 | 3.33 | 0.23 | 3.68 | 3.41 | 0.26 |
| 35 | S3-18B | 3.64 | 3.31 | 0.17 | 3.65 | 3.38 | 0.20 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 36 | S3-18C | 3.66 | 3.32 | 0.20 | 3.66 | 3.39 | 0.23 |
| 37 | S4-15A | 1.55 | 4.01 | 0.56 | 1.56 | 4.07 | 0.58 |
| 38 | S4-15B | 2.35 | 3.83 | 0.47 | 2.36 | 3.89 | 0.49 |
| 39 | S4-15C | 1.95 | 3.92 | 0.52 | 1.96 | 3.98 | 0.54 |
| 40 | S4-16A | 3.06 | 3.51 | 0.27 | 3.06 | 3.58 | 0.28 |
| 41 | S4-16B | 2.66 | 3.67 | 0.36 | 2.66 | 3.74 | 0.38 |
| 42 | S4-16C | 2.86 | 3.59 | 0.31 | 2.86 | 3.66 | 0.33 |
| 43 | S4-17A | 3.78 | 3.09 | 0.00 | 3.78 | 3.17 | 0.03 |
| 44 | S4-17B | 3.59 | 3.21 | -0.06 | 3.58 | 3.30 | -0.03 |
| 45 | S4-17C | 3.69 | 3.15 | -0.03 | 3.68 | 3.23 | 0.00 |
| 46 | S4-18A | 3.18 | 3.48 | -0.02 | 3.18 | 3.55 | 0.01 |
| 47 | S4-18B | 2.84 | 3.51 | 0.03 | 2.84 | 3.58 | 0.06 |
| 48 | S4-18C | 3.01 | 3.50 | 0.01 | 3.01 | 3.56 | 0.03 |
| 49 | S5-15A | -9.18 | 1.46 | -2.55 | -9.32 | 1.28 | -2.51 |
| 50 | S5-15B | -10.59 | 1.31 | -2.61 | -10.72 | 1.13 | -2.57 |
| 51 | S5-15C | -9.89 | 1.38 | -2.58 | -10.02 | 1.20 | -2.54 |
| 52 | S5-16A | -20.09 | -1.99 | -12.39 | -20.14 | -1.90 | -11.98 |
| 53 | S5-16B | -17.36 | -1.72 | -11.78 | -17.41 | -1.63 | -11.35 |
| 54 | S5-16C | -18.72 | -1.85 | -12.08 | -18.77 | -1.76 | -11.66 |
| 55 | S5-17A | -25.33 | -2.03 | -1.50 | -25.32 | -1.99 | -1.39 |
| 56 | S5-17B | -24.97 | -1.89 | -1.81 | -24.96 | -1.85 | -1.72 |
| 57 | S5-17C | -25.15 | -1.96 | -1.66 | -25.14 | -1.92 | -1.56 |
| 58 | S5-18A | -25.18 | -0.78 | 10.67 | -25.13 | -0.83 | 10.23 |
| 59 | S5-18B | -30.16 | -1.21 | 12.44 | -30.10 | -1.26 | 12.07 |
| 60 | S5-18C | -27.67 | -0.99 | 11.56 | -27.61 | -1.05 | 11.15 |

**Table S46. Results of variables from LDA after matrix reduction method to 20 % of original dimension according with higher on the VIP scores values from the PLS analysis based on the RPA of the identified VOCs in SC-based syrups samples.**

| Volatile Organic Compounds | Abbreviations | PLS | | LDA | |
|---|---|---|---|---|---|
| | | VIP[1] | | W[2] | F[3] |
| | | Importance | Power (x 100) | | |
| 4-Hydroxy-Dihydro-2(3H)-Furanone | DHYHYFURONE | 1 | 16.66 | 3.65E-01 | 11.01 |
| 2,5-Dimethyl-Pyrazine | DM25PYZNE | 2 | 16.06 | 1.08E-01 | 52.36 |
| m-Menthane | MMTHANE | 3 | 14.24 | 1.52E-01 | 35.32 |
| 3,5-Dimethyl-Dihydro-2-Furanone | DM35DHFURONE | 4 | 14.09 | 7.00E-02 | 84.12 |
| 2-Ethyl-Hexanoic Acid | E2HXNOIC | 5 | 13.32 | 1.74E-01 | 30.00 |
| 5-(Hydroxymethyl)-2-Furfural | HM5FURAL | 6 | 12.56 | 9.88E-02 | 57.78 |
| 3-Furanmethanol | FUR3OL | 7 | 12.56 | 3.37E-01 | 12.46 |
| 2-Heptanone | HPT2ONE | 8 | 12.53 | 1.25E-01 | 44.35 |
| Toluene | TOLNE | 9 | 12.22 | 1.70E-01 | 30.92 |
| 3-Hydroxy-2,3-Dihydro-Maltol | HX3DH23MALTOL | 10 | 12.00 | 5.06E-02 | 118.94 |
| 3-Methyl-Furfural | M3FURAL | 11 | 11.78 | 5.51E-02 | 108.69 |
| Hexane | HXANE | 12 | 11.76 | 7.81E-02 | 74.72 |
| 1,3-Dihydroxy-2-Propanone | DHYPPAONE | 13 | 11.74 | 1.39E-01 | 39.10 |
| Dimethyl Disulfide | DMDSFD | 14 | 11.58 | Removed from analysis. | |
| Furan | FUR | 15 | 11.50 | 5.16E-02 | 116.40 |
| 1-(2-Furanyl)-1,2-Ethanediol | FURYLETDIOL | 16 | 11.49 | 1.52E-01 | 35.27 |
| Ethyl Formate | EESTFA | 17 | 11.06 | 9.00E-02 | 64.02 |
| Tetrahydro-5-Methyl-2-Furanmethanol | TEHYMFUROL | 18 | 11.01 | 2.45E-01 | 19.50 |
| 2,5-Dimethyl-Furan | DM25FUR | 19 | 10.87 | 3.60E-01 | 11.28 |
| 2-Hydroxy-Dihydro-2(3H)-Furanone | HY2DHFURONE | 20 | 10.86 | 5.74E-02 | 104.08 |
| Pentane | PTANE | 21 | 10.79 | 1.47E-01 | 36.65 |
| 1,3-Diazine | D13ZINE | 22 | 9.98 | 2.12E-01 | 23.53 |
| Benzenemethanol | BENZMTOL | 23 | 9.96 | 7.13E-02 | 82.55 |
| Furaneol | FUREOL | 24 | 9.95 | 2.44E-01 | 19.66 |
| Dodecanoic Acid | DODECOIC | 25 | 9.95 | 4.00E-02 | 151.93 |
| Propanoic Acid | PPANOIC | 26 | 9.90 | 2.88E-01 | 15.69 |
| 2-Methyl-Furan | M2FUR | 27 | 9.83 | 2.44E-01 | 19.67 |

| | | | | | |
|---|---|---|---|---|---|
| 2-Propyl-Furan | PP2FUR | 28 | 9.81 | 1.35E-01 | 40.60 |
| Nonanal | NONAL | 29 | 9.71 | 1.69E-01 | 31.04 |
| 2-Propenal | PPENAL | 30 | 9.70 | 1.16E-01 | 48.21 |
| β-Damascenone | DAMSNONE | 31 | 9.69 | 2.90E-01 | 15.50 |
| Dimethyl Sulfide | DMSULFI | 32 | 9.61 | 1.43E-01 | 38.09 |
| Decanal | DECAL | 33 | 9.61 | 1.45E-01 | 37.49 |

[1]F - Fischer value from One-way ANOVA test.
[2]W - Wilks value from Linear Discriminant Analysis.
[3]F - Fischer value from Linear Discriminant Analysis.
[4]CDF - Canonical Discriminant Function Coefficients.

**Table S47. CDF Coefficients and Highest Probability Classification results of samples from LDA after matrix reduction method obtained from One-way ANOVA test based on the RPA of identified VOCs in SC-based syrups samples.**

| ID Replicate Code | ID Group Code | LDA | | | | | | | | | PLS | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | CDF[1] | | | CDF[1] Class Means | | | Highest Probability Classification | | | Score Value | | | Loading Value | | |
| | | 1 | 2 | 3 | 1 | 2 | 3 | First | Second | Third | 1 | 2 | 3 | 1 | 2 | 3 |
| FRS07A | CERT | -367.3 | -4.6 | -2.0 | -367.5 | -4.8 | -2.6 | CERT | MED | STH | 1.51 | 0.73 | -0.09 | 0.18 | 0.04 | 0.02 |
| FRS07B | | -367.4 | -5.2 | -2.0 | | | | CERT | MED | STH | 2.15 | 0.57 | -0.21 | | | |
| FRS07C | | -367.4 | -4.9 | -2.0 | | | | CERT | MED | STH | 1.83 | 0.65 | -0.15 | | | |
| FRS13A | | -367.3 | -4.8 | -1.9 | | | | CERT | MED | STH | 5.66 | -0.03 | -0.35 | | | |
| FRS13B | | -367.8 | -4.9 | -3.4 | | | | CERT | MED | STH | 4.50 | 0.26 | -0.17 | | | |
| FRS13C | | -367.6 | -4.8 | -2.6 | | | | CERT | MED | STH | 5.08 | 0.11 | -0.26 | | | |
| FRS14A | | -367.5 | -4.6 | -1.9 | | | | CERT | MED | STH | 7.78 | -0.58 | -0.11 | | | |
| FRS14B | | -367.6 | -5.0 | -3.0 | | | | CERT | MED | STH | 7.80 | -0.45 | -0.12 | | | |
| FRS14C | | -367.5 | -4.8 | -2.4 | | | | CERT | MED | STH | 7.79 | -0.52 | -0.11 | | | |
| FRS15A | | -367.3 | -5.5 | -2.4 | | | | CERT | MED | STH | 8.87 | -0.55 | 0.01 | | | |
| FRS15B | | -367.7 | -4.4 | -3.0 | | | | CERT | MED | STH | 11.10 | -0.93 | -0.08 | | | |
| FRS15C | | -367.5 | -4.9 | -2.7 | | | | CERT | MED | STH | 9.99 | -0.74 | -0.04 | | | |
| FRS16A | | -366.7 | -5.7 | -3.4 | | | | CERT | MED | STH | 0.38 | 1.23 | 0.48 | | | |
| FRS16B | | -368.4 | -4.2 | -2.1 | | | | CERT | MED | STH | 0.84 | 1.16 | 0.46 | | | |
| FRS16C | | -367.6 | -4.9 | -2.8 | | | | CERT | MED | STH | 0.61 | 1.19 | 0.47 | | | |
| FRS17A | | -367.6 | -3.6 | -1.4 | | | | CERT | MED | STH | 0.85 | 1.01 | 0.35 | | | |

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| FRS17B | | -367.5 | -5.9 | -4.7 | | | | CERT | MED | STH | 1.72 | 0.82 | 0.33 | | | |
| FRS17C | | -367.6 | -4.8 | -3.1 | | | | CERT | MED | STH | 1.28 | 0.92 | 0.34 | | | |
| FRS18A | | -367.8 | -4.4 | -2.4 | | | | CERT | MED | STH | 8.01 | 0.13 | 0.20 | | | |
| FRS18B | | -367.4 | -5.2 | -2.8 | | | | CERT | MED | STH | 10.18 | -0.02 | 0.21 | | | |
| FRS18C | | -367.6 | -4.8 | -2.6 | | | | CERT | MED | STH | 9.09 | 0.05 | 0.20 | | | |
| ECAL14A | | 189.2 | -31.1 | 43.8 | | | | NCERT | MED | STH | -2.31 | 2.92 | 3.48 | | | |
| ECAL14B | | 189.0 | -29.4 | 44.2 | | | | NCERT | MED | STH | -2.60 | 2.81 | 3.27 | | | |
| ECAL14C | | 189.1 | -30.2 | 44.0 | | | | NCERT | MED | STH | -2.46 | 2.87 | 3.37 | | | |
| ENCAL14A | | 192.3 | -27.6 | 44.2 | | | | NCERT | MED | STH | -4.85 | 2.48 | 2.10 | | | |
| ENCAL14B | NCERT | 185.6 | -32.6 | 42.8 | 189.1 | -30.2 | 43.7 | NCERT | MED | STH | -4.83 | 2.47 | 2.10 | -0.05 | 0.22 | 0.34 |
| ENCAL14C | | 189.0 | -30.1 | 43.5 | | | | NCERT | MED | STH | -4.84 | 2.48 | 2.10 | | | |
| GLA14A | | 189.8 | -31.3 | 43.4 | | | | NCERT | MED | STH | -0.56 | 0.93 | 0.43 | | | |
| GLA14B | | 188.4 | -29.3 | 44.0 | | | | NCERT | MED | STH | -0.87 | 0.88 | 0.40 | | | |
| GLA14C | | 189.1 | -30.3 | 43.7 | | | | NCERT | MED | STH | -0.71 | 0.91 | 0.41 | | | |
| ESP16A | | 217.2 | 75.4 | -5.2 | | | | MED | NCERT | STH | -3.88 | 1.07 | -0.76 | | | |
| ESP16B | | 217.2 | 74.8 | -9.3 | | | | MED | NCERT | STH | -3.95 | 1.09 | -0.70 | | | |
| ESP16C | | 217.2 | 75.1 | -7.2 | | | | MED | NCERT | STH | -3.91 | 1.08 | -0.73 | | | |
| EGP17A | | 219.3 | 71.9 | -5.0 | | | | MED | NCERT | STH | -2.42 | 0.22 | -2.38 | | | |
| EGP17B | | 215.2 | 77.7 | -9.1 | | | | MED | NCERT | STH | -2.17 | -0.05 | -2.50 | | | |
| EGP17C | | 217.3 | 74.8 | -7.0 | | | | MED | NCERT | STH | -2.29 | 0.08 | -2.44 | | | |
| EGPA16A | | 216.9 | 76.2 | -5.8 | | | | MED | NCERT | STH | -2.80 | 0.19 | -2.65 | | | |
| EGPA16B | MED | 216.8 | 74.7 | -8.6 | 217.1 | 75.0 | -7.0 | MED | NCERT | STH | -2.81 | 0.29 | -2.95 | -0.09 | 0.06 | -0.50 |
| EGPA16C | | 216.8 | 75.4 | -7.2 | | | | MED | NCERT | STH | -2.81 | 0.24 | -2.80 | | | |
| EGPB16A | | 217.8 | 74.2 | -6.6 | | | | MED | NCERT | STH | -3.73 | 0.02 | -2.77 | | | |
| EGPB16B | | 216.7 | 75.8 | -7.2 | | | | MED | NCERT | STH | -3.59 | 0.13 | -2.60 | | | |
| EGPB16C | | 217.3 | 75.0 | -6.9 | | | | MED | NCERT | STH | -3.66 | 0.08 | -2.69 | | | |
| EGPC16A | | 219.7 | 75.3 | -9.0 | | | | MED | NCERT | STH | -4.27 | 0.64 | -1.69 | | | |
| EGPC16B | | 214.6 | 73.8 | -4.5 | | | | MED | NCERT | STH | -4.35 | 0.84 | -1.51 | | | |
| EGPC16C | | 217.2 | 74.6 | -6.8 | | | | MED | NCERT | STH | -4.31 | 0.74 | -1.60 | | | |
| MCBR14A | | 306.0 | -82.6 | -25.8 | | | | STH | MED | NCERT | -3.24 | -2.55 | 1.40 | | | |
| MCBR14B | STH | 307.1 | -84.4 | -26.4 | 306.6 | -83.4 | -26.0 | STH | MED | NCERT | -3.02 | -2.69 | 1.27 | -0.07 | -0.35 | 0.23 |
| MCBR14C | | 306.6 | -83.5 | -26.1 | | | | STH | MED | NCERT | -3.13 | -2.62 | 1.34 | | | |
| MDBR14A | | 306.1 | -82.4 | -24.3 | | | | STH | MED | NCERT | -3.59 | -7.09 | 1.31 | | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| MDBR14B | 307.1 | -84.6 | -27.8 | STH | MED | NCERT | -3.71 | -6.96 | 1.22 |
| MDBR14C | 306.6 | -83.5 | -26.1 | STH | MED | NCERT | -3.65 | -7.02 | 1.27 |
| AUS17A | 307.4 | -84.6 | -25.5 | STH | MED | NCERT | -3.81 | -0.56 | 1.32 |
| AUS17B | 305.9 | -82.0 | -26.1 | STH | MED | NCERT | -3.99 | -0.45 | 1.33 |
| AUS17C | 306.6 | -83.3 | -25.8 | STH | MED | NCERT | -3.90 | -0.50 | 1.33 |

**Table S48. Information summary of PLS based only on the RPA of the most predictive VOCs identified in SC-based syrups samples.**

| Analysis | Component | $R^2X$ | Eigenvalues | $R^2Y$ | $Q^2$ | Significance | Iterations |
|---|---|---|---|---|---|---|---|
| PLS | 1 | 0.6370 | 22.931 | 0.0585 | 0.0104 | S | 5 |
| | 2 | 0.1211 | 4.359 | 0.0588 | 0.0224 | S | 8 |
| | 3 | 0.0720 | 2.590 | 0.0588 | 0.0209 | S | 16 |
| | 4 | 0.0479 | 1.725 | 0.0585 | 0.0169 | S | 11 |
| | 5 | 0.0332 | 1.196 | 0.0580 | 0.0214 | S | 14 |
| | 6 | 0.0228 | 0.822 | 0.0581 | 0.0346 | S | 10 |
| | 7 | 0.0158 | 0.569 | 0.0584 | 0.0242 | S | 14 |
| | 8 | 0.0122 | 0.440 | 0.0582 | 0.0340 | S | 20 |
| | 9 | 0.0089 | 0.321 | 0.0579 | 0.0271 | S | 8 |
| | 10 | 0.0069 | 0.250 | 0.0581 | 0.0350 | S | 10 |
| | 11 | 0.0054 | 0.194 | 0.0561 | 0.0454 | S | 37 |
| | 12 | 0.0046 | 0.164 | 0.0578 | 0.0584 | S | 18 |
| | 13 | 0.0035 | 0.126 | 0.0571 | 0.0721 | S | 18 |
| | 14 | 0.0030 | 0.107 | 0.0569 | 0.1358 | S | 19 |
| | 15 | 0.0023 | 0.083 | 0.0554 | 0.1979 | S | 8 |
| | 16 | 0.0011 | 0.040 | 0.0551 | 0.3034 | S | 8 |
| | 17 | 0.0005 | 0.017 | 0.0488 | 0.5225 | S | 5 |
| | 18 | 0.0006 | 0.018 | 0.0060 | 0.0654 | S | 9 |

**Table S49. Analytical methods based in LC for determination of FDs in processed food matrices.**

| Furanic Derivatives | Food Matrix | Sample Dilution | Extraction Technique | Chromatography Analysis | Optimization Strategy | Validation Parameters | Reference |
|---|---|---|---|---|---|---|---|
| 5HMF, FURL | Coffee | 1/75 (v/v) | LLE | HPLC-DAD | n. p. | accuracy, precision, LOD, LOQ | [14] |
| 5HMF | Corn and Cane Syrup | 1/50 (w/v) | DI | HPLC-UV | n. p. | linearity, accuracy, precision, LOD, LOQ | [5] |
| 5HMF, 5MF, FURL, 3FURL, 2FA, 3FA | Fruit juices | 1/25 (v/v) | LLME | HPLC-DAD | Univariate (only HPLC) | linearity, accuracy, precision, LOD, LOQ | [17] |
| 5HMF | Fruit Molasses | 1/5 (w/v) | LLE | HPLC-DAD | n. p. | n. p. | [6] |
| 5HMF, 4HMDF, 2FA, FURL, 3FURL, 2AF, 5MF, MFT, EFT | Apple Cider and Wine | 1/10 (v/v) | SPE | HPLC-DAD-MS | Univariate (only SPE) | linearity, accuracy, precision, LOD, LOQ | [9] |
| 5HMF, 2FA, FURL, 2FMK, 5MF | Agave and Tequila | 1/10 (v/v) | LLE | HPLC-DAD | n. p. | n. p. | [18] |
| 5HMF, 2FA, 3FA, FURL, 3FURL | Honey | 1/10 (w/v) | LLE | HPLC-DAD | Univariate (only HPLC) | linearity, accuracy, precision, LOD, LOQ | [4] |
| 5HMF | Treacle | 1/100 (w/v) | DI | HPLC-DAD | n. p. | n. p. | [7] |
| F2A, 5HMF, DMHF, 2FA, 2AF, FAL | Balsamic Vinegar | 1/10 (v/v) | DI | HPLC-DAD | n. p. | linearity, accuracy, precision, LOD, LOQ | [15] |

**Table S50. TPA and IP results for all runs (n = 3) of the MEPS-KS screening model based on Full Factorial Design (3^2-level and 1^9-level factors).**

| Run Number | Factor (CCP) | | | | 5HMF | | FURL | | FAL | | 2FMK | | 5MF | | Sum | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Sorbent (1) | Elution Solvent (2) | Loading Cycles (3) | Loading Volume (4) | Total Peak Area ( $10^3$) | RSD (%) | Total Peak Area ($\times 10^3$) | RSD (%) | Total Peak Area ($\times 10^3$) | RSD (%) | Total Peak Area ($\times 10^3$) | RSD (%) | Total Peak Area ($\times 10^3$) | RSD (%) | Total Peak Area ($\times 10^3$) | Mean RSD (%) |
| 1 | C2 | ACN | 3 x | 250 µL | 54.6 | 4.1 | 38.5 | 4.5 | 101.7 | 3.7 | 31.4 | 3.0 | 57.2 | 3.0 | 283.5 | 3.7 |
| 2 | C2 | ACN | 3 x | 500 µL | 51.8 | 1.3 | 35.8 | 1.1 | 93.6 | 1.3 | 29.1 | 0.6 | 54.4 | 0.5 | 264.8 | 1.0 |
| 3 | C2 | ACN | 5 x | 250 µL | 50.2 | 1.4 | 33.8 | 1.3 | 92.1 | 0.3 | 27.8 | 1.3 | 51.7 | 1.2 | 255.6 | 1.1 |
| 4 | C2 | ACN | 5 x | 500 µL | 51.0 | 6.3 | 34.2 | 5.9 | 96.2 | 3.7 | 28.6 | 4.8 | 54.7 | 4.3 | 264.7 | 5.0 |
| 5 | C2 | MeOH | 3 x | 250 µL | 53.4 | 3.7 | 35.5 | 4.0 | 101.4 | 2.6 | 29.5 | 2.4 | 54.9 | 3.2 | 274.7 | 3.2 |
| 6 | C2 | MeOH | 3 x | 500 µL | 45.8 | 2.9 | 31.4 | 2.1 | 85.0 | 2.2 | 26.4 | 1.6 | 49.1 | 1.7 | 237.7 | 2.1 |
| 7 | C2 | MeOH | 5 x | 250 µL | 56.1 | 3.6 | 37.9 | 3.3 | 104.4 | 3.3 | 31.6 | 2.3 | 57.9 | 2.5 | 287.9 | 3.0 |
| 8 | C2 | MeOH | 5 x | 500 µL | 63.9 | 3.5 | 43.7 | 3.8 | 119.8 | 1.2 | 36.1 | 2.6 | 65.9 | 1.3 | 329.4 | 2.5 |
| 9 | C8 | ACN | 3 x | 250 µL | 75.0 | 4.0 | 60.0 | 2.6 | 168.3 | 1.9 | 53.8 | 2.8 | 101.8 | 1.2 | 459.0 | 2.5 |
| 10 | C8 | ACN | 3 x | 500 µL | 63.8 | 5.9 | 54.5 | 5.3 | 143.8 | 5.3 | 52.0 | 3.6 | 98.7 | 3.2 | 412.8 | 4.7 |
| 11 | C8 | ACN | 5 x | 250 µL | 73.9 | 1.0 | 59.8 | 1.3 | 152.6 | 0.2 | 55.0 | 2.4 | 103.2 | 2.2 | 444.4 | 1.4 |
| 12 | C8 | ACN | 5 x | 500 µL | 68.3 | 4.9 | 56.9 | 4.3 | 143.8 | 1.2 | 53.6 | 2.5 | 102.5 | 2.5 | 425.2 | 3.1 |
| 13 | C8 | MeOH | 3 x | 250 µL | 82.4 | 5.8 | 65.8 | 3.8 | 179.9 | 2.1 | 59.3 | 2.9 | 105.1 | 2.4 | 492.5 | 3.4 |
| 14 | C8 | MeOH | 3 x | 500 µL | 71.3 | 6.2 | 60.3 | 4.6 | 166.5 | 2.8 | 56.4 | 2.2 | 102.8 | 2.6 | 457.4 | 3.7 |
| 15 | C8 | MeOH | 5 x | 250 µL | 68.3 | 4.1 | 58.5 | 2.7 | 149.2 | 0.6 | 57.8 | 2.6 | 105.2 | 2.4 | 439.0 | 2.5 |
| 16 | C8 | MeOH | 5 x | 500 µL | 50.5 | 2.5 | 49.5 | 1.8 | 113.1 | 1.9 | 51.8 | 1.7 | 97.0 | 1.8 | 362.0 | 1.9 |
| 17 | C18 | ACN | 3 x | 250 µL | 72.8 | 6.4 | 69.5 | 3.7 | 197.6 | 0.5 | 65.1 | 1.4 | 117.9 | 1.6 | 522.9 | 2.7 |
| 18 | C18 | ACN | 3 x | 500 µL | 69.0 | 3.5 | 70.6 | 2.5 | 186.9 | 1.7 | 67.8 | 0.5 | 124.6 | 0.2 | 519.0 | 1.7 |
| 19 | C18 | ACN | 5 x | 250 µL | 65.3 | 1.9 | 64.4 | 1.0 | 175.9 | 1.4 | 62.4 | 1.1 | 116.7 | 0.9 | 484.6 | 1.3 |
| 20 | C18 | ACN | 5 x | 500 µL | 49.3 | 2.3 | 60.6 | 1.4 | 133.1 | 1.2 | 70.2 | 1.3 | 136.4 | 1.5 | 449.7 | 1.5 |
| 21 | C18 | MeOH | 3 x | 250 µL | 71.3 | 4.0 | 66.1 | 2.7 | 189.3 | 0.6 | 60.5 | 2.6 | 109.1 | 1.4 | 496.3 | 2.3 |
| 22 | C18 | MeOH | 3 x | 500 µL | 62.4 | 3.3 | 66.2 | 1.8 | 172.8 | 1.8 | 66.7 | 1.0 | 125.0 | 0.1 | 493.2 | 1.6 |
| 23 | C18 | MeOH | 5 x | 250 µL | 72.4 | 3.5 | 66.7 | 2.5 | 135.0 | 2.7 | 66.7 | 2.1 | 119.6 | 2.6 | 460.3 | 2.7 |
| 24 | C18 | MeOH | 5 x | 500 µL | 76.5 | 2.7 | 74.4 | 2.0 | 140.1 | 3.4 | 71.8 | 1.7 | 130.9 | 1.6 | 493.8 | 2.3 |
| 25 | M1 | ACN | 3 x | 250 µL | 93.0 | 2.4 | 70.1 | 1.2 | 138.6 | 3.4 | 63.4 | 0.6 | 117.7 | 1.0 | 482.7 | 1.7 |
| 26 | M1 | ACN | 3 x | 500 µL | 86.8 | 1.5 | 71.5 | 2.1 | 127.1 | 1.3 | 65.9 | 1.8 | 125.8 | 3.4 | 477.1 | 2.0 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 27 | M1 | ACN | 5 x | 250 µL | 110.8 | 2.7 | 81.7 | 3.5 | 164.0 | 2.4 | 66.2 | 1.9 | 129.9 | 2.7 | 552.7 | 2.6 |
| 28 | M1 | ACN | 5 x | 500 µL | 91.7 | 1.7 | 71.7 | 2.3 | 133.8 | 1.1 | 66.5 | 2.5 | 128.1 | 2.3 | 491.8 | 2.0 |
| 29 | M1 | MeOH | 3 x | 250 µL | 80.0 | 2.7 | 64.3 | 4.2 | 112.1 | 3.0 | 57.6 | 4.4 | 113.3 | 1.9 | 427.3 | 3.3 |
| 30 | M1 | MeOH | 3 x | 500 µL | 107.7 | 2.7 | 74.6 | 2.5 | 150.1 | 2.6 | 60.6 | 2.2 | 113.6 | 2.0 | 506.7 | 2.4 |
| 31 | M1 | MeOH | 5 x | 250 µL | 84.5 | 2.3 | 68.9 | 7.0 | 119.2 | 3.0 | 62.4 | 5.4 | 110.1 | 2.2 | 445.2 | 4.0 |
| 32 | M1 | MeOH | 5 x | 500 µL | 101.3 | 2.7 | 72.7 | 3.4 | 127.4 | 3.6 | 63.6 | 2.6 | 128.6 | 3.1 | 493.6 | 3.1 |
| 33 | SIL | ACN | 3 x | 250 µL | 56.2 | 1.5 | 28.8 | 1.2 | 61.3 | 1.5 | 19.5 | 1.5 | 37.8 | 0.7 | 203.5 | 1.3 |
| 34 | SIL | ACN | 3 x | 500 µL | 52.3 | 6.0 | 27.1 | 5.5 | 58.2 | 4.9 | 18.3 | 7.4 | 35.7 | 4.4 | 191.5 | 5.6 |
| 35 | SIL | ACN | 5 x | 250 µL | 112.0 | 1.3 | 55.7 | 5.5 | 126.5 | 2.5 | 37.4 | 5.1 | 68.9 | 3.5 | 400.5 | 3.6 |
| 36 | SIL | ACN | 5 x | 500 µL | 72.3 | 3.0 | 36.3 | 4.3 | 81.2 | 3.5 | 24.4 | 3.9 | 46.0 | 2.3 | 260.2 | 3.4 |
| 37 | SIL | MeOH | 3 x | 250 µL | 76.2 | 1.4 | 40.5 | 2.2 | 93.8 | 0.7 | 27.1 | 1.7 | 48.6 | 6.1 | 286.1 | 2.4 |
| 38 | SIL | MeOH | 3 x | 500 µL | 56.5 | 4.7 | 30.1 | 4.4 | 66.5 | 1.9 | 19.9 | 3.4 | 36.1 | 5.0 | 209.1 | 3.9 |
| 39 | SIL | MeOH | 5 x | 250 µL | 66.2 | 4.8 | 35.4 | 5.5 | 78.8 | 4.9 | 23.6 | 5.5 | 41.6 | 5.4 | 245.6 | 5.2 |
| 40 | SIL | MeOH | 5 x | 500 µL | 45.4 | 4.4 | 25.4 | 4.4 | 50.1 | 2.1 | 17.4 | 4.3 | 32.5 | 5.4 | 170.9 | 4.1 |
| 41 | PEP | ACN | 3 x | 250 µL | 147.6 | 1.2 | 165.9 | 1.5 | 266.8 | 0.6 | 124.7 | 1.7 | 187.1 | 1.3 | 892.0 | 1.3 |
| 42 | PEP | ACN | 3 x | 500 µL | 130.6 | 1.6 | 198.7 | 1.2 | 245.2 | 1.1 | 202.6 | 1.2 | 341.9 | 1.2 | 1119.0 | 1.3 |
| 43 | PEP | ACN | 5 x | 250 µL | 112.6 | 1.2 | 177.2 | 1.2 | 209.7 | 0.8 | 184.6 | 1.8 | 314.1 | 1.1 | 998.2 | 1.2 |
| 44 | PEP | ACN | 5 x | 500 µL | 127.4 | 2.3 | 146.4 | 1.4 | 217.1 | 1.2 | 149.2 | 1.6 | 282.8 | 1.7 | 922.9 | 1.6 |
| 45 | PEP | MeOH | 3 x | 250 µL | 131.1 | 2.6 | 113.7 | 2.7 | 230.8 | 2.1 | 67.2 | 2.3 | 99.7 | 3.3 | 642.5 | 2.6 |
| 46 | PEP | MeOH | 3 x | 500 µL | 118.0 | 2.5 | 119.2 | 2.4 | 215.7 | 1.4 | 84.6 | 2.1 | 142.5 | 2.1 | 680.1 | 2.1 |
| 47 | PEP | MeOH | 5 x | 250 µL | 124.5 | 3.7 | 119.3 | 3.6 | 222.2 | 1.8 | 83.4 | 2.9 | 134.4 | 2.5 | 683.8 | 2.9 |
| 48 | PEP | MeOH | 5 x | 500 µL | 96.0 | 2.6 | 113.3 | 3.8 | 174.4 | 1.7 | 89.3 | 2.5 | 161.9 | 3.3 | 634.9 | 2.8 |
| 49 | R-AX | ACN | 3 x | 250 µL | 128.0 | 1.2 | 147.7 | 1.1 | 204.3 | 1.0 | 142.8 | 3.3 | 261.8 | 1.1 | 884.6 | 1.6 |
| 50 | R-AX | ACN | 3 x | 500 µL | 122.3 | 1.7 | 151.3 | 1.5 | 196.5 | 2.4 | 169.3 | 2.5 | 347.7 | 1.9 | 987.1 | 2.0 |
| 51 | R-AX | ACN | 5 x | 250 µL | 119.5 | 1.5 | 140.7 | 1.2 | 192.4 | 1.1 | 151.5 | 1.8 | 306.4 | 1.9 | 910.5 | 1.5 |
| 52 | R-AX | ACN | 5 x | 500 µL | 117.5 | 1.7 | 167.0 | 0.8 | 186.6 | 2.0 | 186.4 | 1.5 | 402.2 | 1.7 | 1059.7 | 1.5 |
| 53 | R-AX | MeOH | 3 x | 250 µL | 98.8 | 3.4 | 111.8 | 1.4 | 241.5 | 0.8 | 70.2 | 0.7 | 101.4 | 1.6 | 623.7 | 1.6 |
| 54 | R-AX | MeOH | 3 x | 500 µL | 94.8 | 0.7 | 115.4 | 1.1 | 243.0 | 0.9 | 84.1 | 2.1 | 140.0 | 2.5 | 677.2 | 1.4 |
| 55 | R-AX | MeOH | 5 x | 250 µL | 93.2 | 1.8 | 108.7 | 0.6 | 232.0 | 1.5 | 78.0 | 0.7 | 127.1 | 0.9 | 639.0 | 1.1 |
| 56 | R-AX | MeOH | 5 x | 500 µL | 91.8 | 1.8 | 115.7 | 0.5 | 230.6 | 0.8 | 87.6 | 1.3 | 154.9 | 1.3 | 680.5 | 1.1 |
| 57 | R-CX | ACN | 3 x | 250 µL | 131.9 | 1.4 | 157.3 | 1.0 | 256.4 | 1.0 | 156.0 | 1.1 | 274.1 | 1.5 | 975.8 | 1.2 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 58 | R-CX | ACN | 3 x | 500 µL | 152.8 | 1.1 | 176.0 | 0.9 | 295.3 | 0.8 | 184.5 | 1.0 | 338.0 | 1.0 | 1146.6 | 0.9 |
| 59 | R-CX | ACN | 5 x | 250 µL | 125.9 | 1.1 | 149.6 | 1.6 | 242.6 | 1.3 | 155.7 | 1.4 | 300.7 | 1.2 | 974.4 | 1.3 |
| 60 | R-CX | ACN | 5 x | 500 µL | 132.3 | 1.4 | 151.9 | 1.2 | 248.7 | 1.1 | 159.4 | 1.6 | 337.5 | 1.0 | 1029.8 | 1.3 |
| 61 | R-CX | MeOH | 3 x | 250 µL | 96.3 | 1.7 | 101.2 | 1.7 | 228.9 | 1.3 | 66.9 | 1.9 | 96.4 | 1.5 | 589.6 | 1.6 |
| 62 | R-CX | MeOH | 3 x | 500 µL | 98.1 | 1.8 | 106.9 | 1.9 | 235.0 | 1.7 | 77.2 | 1.7 | 126.2 | 1.0 | 643.4 | 1.6 |
| 63 | R-CX | MeOH | 5 x | 250 µL | 90.1 | 1.2 | 100.8 | 0.7 | 216.1 | 1.3 | 72.4 | 1.8 | 116.5 | 1.2 | 595.9 | 1.2 |
| 64 | R-CX | MeOH | 5 x | 500 µL | 92.1 | 1.4 | 106.2 | 0.9 | 220.1 | 1.2 | 80.6 | 1.5 | 140.3 | 1.2 | 639.2 | 1.2 |
| 65 | PGC | ACN | 3 x | 250 µL | 25.3 | 5.1 | 11.3 | 4.0 | 40.1 | 4.5 | 11.0 | 5.3 | 18.9 | 4.1 | 106.6 | 4.6 |
| 66 | PGC | ACN | 3 x | 500 µL | 18.4 | 1.7 | 9.0 | 2.3 | 27.7 | 6.2 | 8.3 | 2.3 | 12.7 | 1.2 | 76.1 | 2.7 |
| 67 | PGC | ACN | 5 x | 250 µL | 28.5 | 2.6 | 14.3 | 3.3 | 45.3 | 2.6 | 12.5 | 3.2 | 19.9 | 2.1 | 120.4 | 2.8 |
| 68 | PGC | ACN | 5 x | 500 µL | 19.1 | 4.4 | 9.8 | 4.3 | 30.5 | 3.6 | 8.6 | 5.8 | 13.4 | 3.4 | 81.4 | 4.3 |
| 69 | PGC | MeOH | 3 x | 250 µL | 24.2 | 3.7 | 11.1 | 1.8 | 35.4 | 5.0 | 9.9 | 4.5 | 15.8 | 3.9 | 96.4 | 3.8 |
| 70 | PGC | MeOH | 3 x | 500 µL | 24.6 | 4.0 | 11.0 | 3.2 | 36.3 | 4.3 | 10.1 | 2.6 | 16.0 | 4.6 | 98.1 | 3.7 |
| 71 | PGC | MeOH | 5 x | 250 µL | 33.0 | 4.4 | 14.1 | 6.2 | 42.1 | 3.5 | 16.1 | 5.1 | 18.6 | 6.4 | 123.8 | 5.1 |
| 72 | PGC | MeOH | 5 x | 500 µL | 26.5 | 4.9 | 11.7 | 4.8 | 37.9 | 3.9 | 10.6 | 4.1 | 16.7 | 5.0 | 103.4 | 4.5 |

**Table S51. TPA and respective IP results for all runs (n = 3) of the UHPLC-KS screening model based on Full Factorial Design (1^2-level, 2^3-level and 1^4-level factors).**

| Run number | Factor (CPP) | | | | 5HMF | | FURL | | FAL | | 2FMK | | 5MF | | Sum | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Column Type (1) | Organic Eluent (2) | Column Flow (3) | Column Temperature (4) | Total Peak Area ($\times 10^3$) | RSD (%) | Total Peak Area ($\times 10^3$) | RSD (%) | Total Peak Area ($\times 10^3$) | RSD (%) | Total Peak Area ($\times 10^3$) | RSD (%) | Total Peak Area ($\times 10^3$) | RSD (%) | Total Peak Area ($\times 10^3$) | RSD Mean (%) |
| 1 | CORTECS | ACN | 125 µL $min^{-1}$ | 30 ºC | 118.7 | 0.7 | 344.3 | 3.0 | 326.2 | 1.6 | 163.8 | 3.2 | 522.5 | 0.9 | 1475.5 | 1.9 |
| 2 | CORTECS | ACN | 125 µL $min^{-1}$ | 40 ºC | 114.0 | 2.3 | 342.1 | 2.5 | 305.3 | 1.1 | 161.2 | 1.8 | 521.0 | 0.4 | 1443.5 | 1.6 |
| 3 | CORTECS | ACN | 125 µL $min^{-1}$ | 50 ºC | 148.1 | 1.7 | 317.0 | 2.2 | 301.4 | 2.3 | 216.9 | 1.4 | 513.4 | 1.4 | 1496.7 | 1.8 |
| 4 | CORTECS | ACN | 250 µL $min^{-1}$ | 30 ºC | 67.4 | 2.8 | 122.5 | 1.9 | 120.2 | 1.9 | 104.5 | 1.8 | 246.4 | 0.6 | 661.0 | 1.8 |
| 5 | CORTECS | ACN | 250 µL $min^{-1}$ | 40 ºC | 117.9 | 1.4 | 123.9 | 3.2 | 128.7 | 3.6 | 163.3 | 1.5 | 239.2 | 0.7 | 773.0 | 2.1 |
| 6 | CORTECS | ACN | 250 µL $min^{-1}$ | 50 ºC | 79.3 | 1.9 | 117.0 | 2.1 | 153.4 | 2.1 | 90.0 | 2.3 | 227.1 | 2.7 | 666.9 | 2.2 |
| 7 | CORTECS | ACN | 375 µL $min^{-1}$ | 30 ºC | 56.9 | 2.3 | 86.7 | 1.5 | 104.9 | 3.1 | 41.7 | 2.2 | 146.2 | 1.6 | 436.4 | 2.1 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 | CORTECS | ACN | 375 µL $min^{-1}$ | 40 ºC | 68.1 | 2.3 | 77.6 | 2.7 | 82.6 | 2.5 | 46.1 | 2.7 | 141.1 | 1.7 | 415.5 | 2.4 |
| 9 | CORTECS | ACN | 375 µL $min^{-1}$ | 50 ºC | 45.5 | 1.5 | 78.4 | 2.0 | 97.7 | 2.0 | 42.4 | 3.0 | 133.8 | 2.5 | 397.7 | 2.2 |
| 10 | CORTECS | MeOH | 125 µL $min^{-1}$ | 30 ºC | 225.5 | 1.5 | 223.3 | 0.5 | 242.9 | 3.1 | 179.9 | 2.5 | 353.7 | 0.9 | 1225.3 | 1.7 |
| 11 | CORTECS | MeOH | 125 µL $min^{-1}$ | 40 ºC | 208.7 | 0.5 | 260.5 | 2.1 | 253.2 | 1.9 | 194.1 | 3.0 | 378.2 | 1.0 | 1294.6 | 1.7 |
| 12 | CORTECS | MeOH | 125 µL $min^{-1}$ | 50 ºC | 155.7 | 1.4 | 227.1 | 2.9 | 266.5 | 0.2 | 211.2 | 2.6 | 428.0 | 0.3 | 1288.5 | 1.5 |
| 13 | CORTECS | MeOH | 250 µL $min^{-1}$ | 30 ºC | 95.4 | 2.9 | 140.5 | 2.2 | 180.0 | 1.8 | 118.2 | 1.6 | 232.4 | 1.5 | 766.5 | 2.0 |
| 14 | CORTECS | MeOH | 250 µL $min^{-1}$ | 40 ºC | 112.8 | 1.8 | 147.1 | 1.2 | 190.8 | 2.0 | 114.0 | 3.3 | 227.0 | 0.8 | 791.7 | 1.8 |
| 15 | CORTECS | MeOH | 250 µL $min^{-1}$ | 50 ºC | 110.4 | 1.8 | 135.6 | 1.4 | 184.9 | 1.6 | 114.2 | 2.2 | 232.5 | 0.6 | 777.5 | 1.5 |
| 16 | CORTECS | MeOH | 375 µL $min^{-1}$ | 30 ºC | 84.9 | 2.7 | 86.3 | 3.1 | 102.5 | 0.9 | 86.8 | 2.8 | 174.8 | 2.3 | 535.3 | 2.3 |
| 17 | CORTECS | MeOH | 375 µL $min^{-1}$ | 40 ºC | 70.5 | 2.0 | 88.8 | 3.6 | 102.7 | 2.1 | 74.5 | 1.8 | 135.7 | 0.7 | 472.3 | 2.0 |
| 18 | CORTECS | MeOH | 375 µL $min^{-1}$ | 50 ºC | 66.1 | 3.0 | 83.7 | 3.7 | 108.5 | 1.0 | 70.2 | 1.5 | 155.8 | 1.7 | 484.3 | 2.2 |
| 19 | BEH | ACN | 125 µL $min^{-1}$ | 30 ºC | 69.7 | 0.8 | 31.0 | 3.1 | 131.1 | 1.3 | 127.6 | 2.9 | 210.3 | 1.7 | 569.7 | 1.9 |
| 20 | BEH | ACN | 125 µL $min^{-1}$ | 40 ºC | 53.9 | 1.8 | 119.6 | 3.0 | 87.1 | 2.8 | 174.4 | 3.8 | 287.7 | 1.1 | 722.7 | 2.5 |
| 21 | BEH | ACN | 125 µL $min^{-1}$ | 50 ºC | 39.5 | 1.7 | 146.8 | 2.8 | 80.4 | 2.9 | 153.5 | 1.2 | 344.7 | 1.7 | 764.9 | 2.1 |
| 22 | BEH | ACN | 250 µL $min^{-1}$ | 30 ºC | 71.1 | 3.2 | 128.0 | 3.4 | 129.8 | 1.8 | 100.7 | 3.3 | 201.9 | 1.2 | 631.6 | 2.6 |
| 23 | BEH | ACN | 250 µL $min^{-1}$ | 40 ºC | 102.4 | 1.5 | 142.9 | 1.0 | 132.9 | 2.3 | 105.0 | 3.3 | 237.9 | 1.6 | 721.1 | 2.0 |
| 24 | BEH | ACN | 250 µL $min^{-1}$ | 50 ºC | 91.1 | 1.7 | 133.4 | 1.7 | 122.7 | 2.4 | 98.6 | 1.7 | 216.8 | 0.6 | 662.6 | 1.6 |
| 25 | BEH | ACN | 375 µL $min^{-1}$ | 30 ºC | 68.3 | 1.4 | 74.7 | 2.7 | 60.4 | 3.2 | 77.7 | 2.2 | 116.5 | 7.9 | 397.5 | 3.5 |
| 26 | BEH | ACN | 375 µL $min^{-1}$ | 40 ºC | 76.5 | 1.2 | 73.1 | 3.0 | 65.3 | 2.7 | 76.1 | 2.0 | 114.2 | 8.5 | 405.2 | 3.5 |
| 27 | BEH | ACN | 375 µL $min^{-1}$ | 50 ºC | 76.6 | 2.8 | 76.0 | 1.4 | 61.8 | 4.0 | 82.3 | 0.6 | 128.7 | 2.3 | 425.4 | 2.2 |
| 28 | BEH | MeOH | 125 µL $min^{-1}$ | 30 ºC | 228.9 | 1.9 | 137.5 | 1.0 | 161.2 | 0.8 | 140.7 | 2.0 | 248.4 | 3.3 | 916.7 | 1.8 |
| 29 | BEH | MeOH | 125 µL $min^{-1}$ | 40 ºC | 228.4 | 1.2 | 171.7 | 3.9 | 158.4 | 3.5 | 139.5 | 2.4 | 308.9 | 3.4 | 1006.9 | 2.9 |
| 30 | BEH | MeOH | 125 µL $min^{-1}$ | 50 ºC | 215.9 | 1.1 | 255.8 | 3.5 | 132.5 | 3.3 | 173.8 | 2.2 | 342.7 | 1.0 | 1120.6 | 2.2 |
| 31 | BEH | MeOH | 250 µL $min^{-1}$ | 30 ºC | 117.5 | 2.0 | 131.9 | 2.1 | 68.1 | 2.3 | 109.6 | 2.9 | 208.6 | 3.0 | 635.8 | 2.4 |
| 32 | BEH | MeOH | 250 µL $min^{-1}$ | 40 ºC | 110.3 | 1.7 | 125.0 | 1.2 | 74.0 | 2.8 | 110.7 | 3.0 | 208.5 | 3.0 | 628.5 | 2.3 |
| 33 | BEH | MeOH | 250 µL $min^{-1}$ | 50 ºC | 121.7 | 1.6 | 140.5 | 2.9 | 63.8 | 1.9 | 117.0 | 2.5 | 230.0 | 0.3 | 673.0 | 1.9 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 34 | BEH | MeOH | 375 µL $min^{-1}$ | 30 ºC | 80.6 | 2.1 | 85.7 | 2.9 | 84.8 | 4.0 | 84.6 | 1.0 | 170.0 | 3.7 | 505.7 | 2.7 |
| 35 | BEH | MeOH | 375 µL $min^{-1}$ | 40 ºC | 95.5 | 3.8 | 77.4 | 4.5 | 84.1 | 3.5 | 91.1 | 1.4 | 168.0 | 4.7 | 516.0 | 3.6 |
| 36 | BEH | MeOH | 375 µL $min^{-1}$ | 50 ºC | 85.8 | 2.8 | 76.6 | 3.7 | 78.2 | 3.7 | 84.0 | 1.6 | 161.0 | 4.2 | 485.6 | 3.2 |
| 37 | HSS | ACN | 125 µL $min^{-1}$ | 30 ºC | 186.0 | 1.3 | 177.9 | 1.4 | 238.2 | 2.7 | 84.1 | 0.9 | 297.4 | 1.3 | 983.6 | 1.5 |
| 38 | HSS | ACN | 125 µL $min^{-1}$ | 40 ºC | 219.4 | 2.4 | 221.7 | 1.7 | 240.6 | 2.7 | 179.8 | 2.3 | 368.1 | 1.9 | 1229.7 | 2.2 |
| 39 | HSS | ACN | 125 µL $min^{-1}$ | 50 ºC | 181.5 | 1.6 | 244.0 | 2.1 | 198.6 | 3.6 | 162.3 | 2.3 | 390.4 | 0.2 | 1176.8 | 2.0 |
| 40 | HSS | ACN | 250 µL $min^{-1}$ | 30 ºC | 99.4 | 1.5 | 137.1 | 2.5 | 116.5 | 3.5 | 117.3 | 3.3 | 239.4 | 0.6 | 709.7 | 2.3 |
| 41 | HSS | ACN | 250 µL $min^{-1}$ | 40 ºC | 94.1 | 2.6 | 141.8 | 0.4 | 115.7 | 1.5 | 95.0 | 2.0 | 242.6 | 0.4 | 689.2 | 1.4 |
| 42 | HSS | ACN | 250 µL $min^{-1}$ | 50 ºC | 102.4 | 3.5 | 131.3 | 1.8 | 114.0 | 4.3 | 118.1 | 2.8 | 263.4 | 2.4 | 729.2 | 3.0 |
| 43 | HSS | ACN | 375 µL $min^{-1}$ | 30 ºC | 71.9 | 3.8 | 93.0 | 2.5 | 70.8 | 3.4 | 73.6 | 2.2 | 127.8 | 2.7 | 437.1 | 2.9 |
| 44 | HSS | ACN | 375 µL $min^{-1}$ | 40 ºC | 85.0 | 0.9 | 89.7 | 1.5 | 70.1 | 2.3 | 76.1 | 2.0 | 127.6 | 2.4 | 448.5 | 1.8 |
| 45 | HSS | ACN | 375 µL $min^{-1}$ | 50 ºC | 81.4 | 4.6 | 99.2 | 0.6 | 72.9 | 3.3 | 70.8 | 1.8 | 123.6 | 2.5 | 447.9 | 2.5 |
| 46 | HSS | MeOH | 125 µL $min^{-1}$ | 30 ºC | 209.8 | 2.2 | 260.3 | 0.4 | 277.0 | 1.7 | 197.7 | 1.6 | 383.1 | 2.5 | 1328.0 | 1.7 |
| 47 | HSS | MeOH | 125 µL $min^{-1}$ | 40 ºC | 212.8 | 3.3 | 260.7 | 1.8 | 263.5 | 3.0 | 211.6 | 1.6 | 415.3 | 0.9 | 1364.0 | 2.1 |
| 48 | HSS | MeOH | 125 µL $min^{-1}$ | 50 ºC | 199.7 | 1.3 | 267.8 | 3.4 | 274.2 | 1.0 | 203.7 | 1.8 | 428.1 | 1.5 | 1373.4 | 1.8 |
| 49 | HSS | MeOH | 250 µL $min^{-1}$ | 30 ºC | 108.7 | 1.7 | 135.1 | 2.0 | 131.2 | 0.5 | 101.6 | 3.6 | 195.6 | 2.5 | 672.1 | 2.1 |
| 50 | HSS | MeOH | 250 µL $min^{-1}$ | 40 ºC | 127.5 | 0.4 | 132.3 | 1.9 | 141.3 | 2.4 | 99.1 | 2.3 | 185.6 | 1.4 | 685.8 | 1.7 |
| 51 | HSS | MeOH | 250 µL $min^{-1}$ | 50 ºC | 114.7 | 1.8 | 120.6 | 2.4 | 139.8 | 3.0 | 99.3 | 1.9 | 201.7 | 0.8 | 676.0 | 2.0 |
| 52 | HSS | MeOH | 375 µL $min^{-1}$ | 30 ºC | 76.5 | 1.5 | 72.5 | 4.7 | 93.1 | 4.6 | 65.3 | 1.2 | 134.6 | 1.9 | 441.9 | 2.8 |
| 53 | HSS | MeOH | 375 µL $min^{-1}$ | 40 ºC | 79.4 | 0.4 | 66.3 | 4.1 | 79.0 | 2.7 | 62.1 | 0.8 | 127.1 | 1.6 | 413.9 | 1.9 |
| 54 | HSS | MeOH | 375 µL $min^{-1}$ | 50 ºC | 68.2 | 2.7 | 81.0 | 3.2 | 94.4 | 2.9 | 62.0 | 1.4 | 112.2 | 2.0 | 417.8 | 2.4 |
| 55 | HILIC | ACN | 125 µL $min^{-1}$ | 30 ºC | 22.4 | 2.7 | 124.8 | 2.1 | 3.4 | 8.0 | 42.1 | 3.8 | 151.3 | 1.0 | 344.0 | 3.5 |
| 56 | HILIC | ACN | 125 µL $min^{-1}$ | 40 ºC | 15.7 | 6.9 | 119.0 | 0.6 | 2.7 | 6.5 | 40.7 | 3.5 | 203.2 | 4.3 | 381.3 | 4.4 |
| 57 | HILIC | ACN | 125 µL $min^{-1}$ | 50 ºC | 10.9 | 3.8 | 113.3 | 2.2 | 3.2 | 3.5 | 41.8 | 2.7 | 244.2 | 0.7 | 413.4 | 2.6 |
| 58 | HILIC | ACN | 250 µL $min^{-1}$ | 30 ºC | 37.3 | 6.4 | 115.2 | 0.1 | 12.8 | 2.3 | 31.0 | 1.1 | 133.8 | 1.3 | 330.1 | 2.2 |
| 59 | HILIC | ACN | 250 µL $min^{-1}$ | 40 ºC | 38.1 | 4.8 | 121.1 | 1.7 | 17.6 | 3.7 | 34.4 | 1.2 | 134.2 | 2.5 | 345.4 | 2.8 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 60 | HILIC | ACN | 250 µL min$^{-1}$ | 50 ºC | 38.4 | 3.5 | 119.9 | 0.9 | 11.4 | 6.1 | 28.5 | 4.1 | 135.7 | 0.6 | 333.8 | 3.0 |
| 61 | HILIC | ACN | 375 µL min$^{-1}$ | 30 ºC | 18.8 | 5.8 | 64.9 | 2.0 | 10.3 | 5.4 | 15.3 | 2.1 | 78.6 | 1.3 | 187.9 | 3.3 |
| 62 | HILIC | ACN | 375 µL min$^{-1}$ | 40 ºC | 25.0 | 1.7 | 69.3 | 0.8 | 10.4 | 1.0 | 16.4 | 1.1 | 69.5 | 1.8 | 190.6 | 1.3 |
| 63 | HILIC | ACN | 375 µL min$^{-1}$ | 50 ºC | 20.9 | 3.1 | 65.9 | 2.8 | 12.1 | 4.8 | 12.4 | 1.9 | 70.4 | 1.1 | 181.6 | 2.7 |
| 64 | HILIC | MeOH | 125 µL min$^{-1}$ | 30 ºC | 32.0 | 1.2 | 198.5 | 6.7 | 52.4 | 4.3 | 74.9 | 3.6 | 219.6 | 1.0 | 577.5 | 3.3 |
| 65 | HILIC | MeOH | 125 µL min$^{-1}$ | 40 ºC | 22.5 | 4.1 | 225.3 | 1.4 | 43.3 | 2.3 | 97.9 | 2.4 | 271.0 | 2.7 | 660.0 | 2.6 |
| 66 | HILIC | MeOH | 125 µL min$^{-1}$ | 50 ºC | 15.9 | 7.1 | 223.7 | 2.8 | 36.4 | 2.1 | 88.2 | 1.8 | 285.3 | 1.0 | 649.6 | 3.0 |
| 67 | HILIC | MeOH | 250 µL min$^{-1}$ | 30 ºC | 77.2 | 1.0 | 112.0 | 2.3 | 25.3 | 2.4 | 64.3 | 0.7 | 170.3 | 2.9 | 449.1 | 1.9 |
| 68 | HILIC | MeOH | 250 µL min$^{-1}$ | 40 ºC | 79.7 | 1.6 | 115.0 | 1.6 | 12.9 | 8.1 | 68.7 | 1.5 | 181.7 | 0.3 | 457.9 | 2.6 |
| 69 | HILIC | MeOH | 250 µL min$^{-1}$ | 50 ºC | 62.1 | 3.7 | 120.8 | 0.9 | 14.8 | 3.1 | 69.6 | 0.3 | 173.9 | 1.8 | 441.3 | 1.9 |
| 70 | HILIC | MeOH | 375 µL min$^{-1}$ | 30 ºC | 52.0 | 4.5 | 66.9 | 3.6 | 19.0 | 4.2 | 44.7 | 1.1 | 110.0 | 2.0 | 292.5 | 3.1 |
| 71 | HILIC | MeOH | 375 µL min$^{-1}$ | 40 ºC | 56.3 | 2.1 | 62.6 | 0.8 | 19.1 | 2.9 | 46.3 | 2.1 | 120.1 | 2.0 | 304.3 | 2.0 |
| 72 | HILIC | MeOH | 375 µL min$^{-1}$ | 50 ºC | 49.4 | 1.7 | 59.5 | 3.2 | 20.5 | 6.5 | 44.9 | 0.8 | 110.3 | 3.1 | 284.5 | 3.0 |

**Table S52. PR and respective IP results for all runs (n = 3) of the UHPLC-KS screening model based on Full Factorial Design (1^2-level, 2^3-level and 1^4-level factors).**

| Run number | Factor (CPP) | | | | 5HMF | | FURL | | FAL | | 2FMK | | 5MF | | Sum | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Column Type (1) | Organic Eluent (2) | Column Flow (3) | Column Temperature (4) | Peak Resolution | RSD (%) | Peak Resolution | RSD (%) | Peak Resolution | RSD (%) | Peak Resolution | RSD (%) | Peak Resolution | RSD (%) | Peak Resolution Mean | RSD Mean (%) |
| 1 | CORTECS | ACN | 125 µL min$^{-1}$ | 30 ºC | 3.9 | 0.5 | 2.9 | 0.6 | 2.3 | 0.6 | 2.2 | 0.6 | 1.7 | 0.7 | 2.6 | 0.6 |
| 2 | CORTECS | ACN | 125 µL min$^{-1}$ | 40 ºC | 4.6 | 0.6 | 2.7 | 0.6 | 1.5 | 0.8 | 2.1 | 0.7 | 1.7 | 0.7 | 2.5 | 0.7 |
| 3 | CORTECS | ACN | 125 µL min$^{-1}$ | 50 ºC | 5.4 | 0.5 | 2.3 | 0.5 | 1.5 | 0.5 | 1.6 | 0.5 | 1.8 | 0.5 | 2.5 | 0.5 |
| 4 | CORTECS | ACN | 250 µL min$^{-1}$ | 30 ºC | 1.6 | 0.4 | 1.9 | 1.1 | 1.7 | 1.2 | 1.6 | 1.2 | 2.1 | 0.5 | 1.8 | 0.9 |
| 5 | CORTECS | ACN | 250 µL min$^{-1}$ | 40 ºC | 1.6 | 1.0 | 1.9 | 0.6 | 1.7 | 0.7 | 1.6 | 0.7 | 2.2 | 0.6 | 1.8 | 0.7 |
| 6 | CORTECS | ACN | 250 µL min$^{-1}$ | 50 ºC | 2.3 | 1.2 | 1.6 | 0.8 | 1.6 | 0.8 | 1.5 | 0.8 | 2.4 | 0.6 | 1.9 | 0.8 |
| 7 | CORTECS | ACN | 375 µL min$^{-1}$ | 30 ºC | 1.7 | 0.7 | 1.8 | 0.5 | 1.2 | 0.6 | 1.6 | 0.5 | 1.7 | 0.5 | 1.6 | 0.6 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 8 | CORTECS | ACN | 375 µL $min^{-1}$ | 40 ºC | 1.9 | 0.9 | 1.7 | 1.2 | 1.4 | 1.4 | 1.5 | 1.3 | 1.7 | 0.5 | 1.7 | 1.1 |
| 9 | CORTECS | ACN | 375 µL $min^{-1}$ | 50 ºC | 2.3 | 0.8 | 1.6 | 0.7 | 1.5 | 0.7 | 1.4 | 0.7 | 2.0 | 0.6 | 1.8 | 0.7 |
| 10 | CORTECS | MeOH | 125 µL $min^{-1}$ | 30 ºC | 3.1 | 0.7 | 1.7 | 0.8 | 1.9 | 0.7 | 1.8 | 0.8 | 1.7 | 0.7 | 2.0 | 0.7 |
| 11 | CORTECS | MeOH | 125 µL $min^{-1}$ | 40 ºC | 3.5 | 0.8 | 1.5 | 0.5 | 1.8 | 0.5 | 1.6 | 0.5 | 1.6 | 0.5 | 2.0 | 0.6 |
| 12 | CORTECS | MeOH | 125 µL $min^{-1}$ | 50 ºC | 3.5 | 0.5 | 1.4 | 1.3 | 1.6 | 1.2 | 1.4 | 1.4 | 1.5 | 0.6 | 1.9 | 1.0 |
| 13 | CORTECS | MeOH | 250 µL $min^{-1}$ | 30 ºC | 1.1 | 1.2 | 1.6 | 0.7 | 1.5 | 0.7 | 1.8 | 0.6 | 1.5 | 0.7 | 1.5 | 0.8 |
| 14 | CORTECS | MeOH | 250 µL $min^{-1}$ | 40 ºC | 1.3 | 0.7 | 1.5 | 0.8 | 1.5 | 0.9 | 1.4 | 0.9 | 1.5 | 0.7 | 1.4 | 0.8 |
| 15 | CORTECS | MeOH | 250 µL $min^{-1}$ | 50 ºC | 1.5 | 0.7 | 1.5 | 0.6 | 1.3 | 0.6 | 1.4 | 0.6 | 1.5 | 0.6 | 1.4 | 0.6 |
| 16 | CORTECS | MeOH | 375 µL $min^{-1}$ | 30 ºC | 1.2 | 0.8 | 2.0 | 1.1 | 1.3 | 1.5 | 1.6 | 1.2 | 1.3 | 0.6 | 1.5 | 1.0 |
| 17 | CORTECS | MeOH | 375 µL $min^{-1}$ | 40 ºC | 1.2 | 0.8 | 1.6 | 0.7 | 1.5 | 0.7 | 2.5 | 0.6 | 1.5 | 0.7 | 1.7 | 0.7 |
| 18 | CORTECS | MeOH | 375 µL $min^{-1}$ | 50 ºC | 1.6 | 0.7 | 1.4 | 0.9 | 1.8 | 0.8 | 2.6 | 0.7 | 1.4 | 0.7 | 1.7 | 0.7 |
| 19 | BEH | ACN | 125 µL $min^{-1}$ | 30 ºC | 1.4 | 1.0 | 1.2 | 0.6 | 1.5 | 0.5 | 1.5 | 0.6 | 1.1 | 0.6 | 1.3 | 0.7 |
| 20 | BEH | ACN | 125 µL $min^{-1}$ | 40 ºC | 1.4 | 1.1 | 1.6 | 1.3 | 1.7 | 1.2 | 1.6 | 1.3 | 1.2 | 0.6 | 1.5 | 1.1 |
| 21 | BEH | ACN | 125 µL $min^{-1}$ | 50 ºC | 1.4 | 1.1 | 1.6 | 0.7 | 1.8 | 0.7 | 1.6 | 0.7 | 1.3 | 0.8 | 1.5 | 0.8 |
| 22 | BEH | ACN | 250 µL $min^{-1}$ | 30 ºC | 2.3 | 0.8 | 1.5 | 0.8 | 1.1 | 1.0 | 1.8 | 0.8 | 1.4 | 0.7 | 1.6 | 0.8 |
| 23 | BEH | ACN | 250 µL $min^{-1}$ | 40 ºC | 2.3 | 0.8 | 1.6 | 0.5 | 1.2 | 0.6 | 1.8 | 0.5 | 1.4 | 0.6 | 1.6 | 0.6 |
| 24 | BEH | ACN | 250 µL $min^{-1}$ | 50 ºC | 2.2 | 0.8 | 1.6 | 1.3 | 1.5 | 1.3 | 2.0 | 1.1 | 1.3 | 0.6 | 1.7 | 1.0 |
| 25 | BEH | ACN | 375 µL $min^{-1}$ | 30 ºC | 1.7 | 0.9 | 1.0 | 0.8 | 1.8 | 0.7 | 1.1 | 0.8 | 1.5 | 0.7 | 1.4 | 0.8 |
| 26 | BEH | ACN | 375 µL $min^{-1}$ | 40 ºC | 1.8 | 0.9 | 1.3 | 0.9 | 1.9 | 0.7 | 1.1 | 1.0 | 1.6 | 0.7 | 1.6 | 0.8 |
| 27 | BEH | ACN | 375 µL $min^{-1}$ | 50 ºC | 1.7 | 0.9 | 1.4 | 0.6 | 2.0 | 0.5 | 1.2 | 0.6 | 1.7 | 0.5 | 1.6 | 0.6 |
| 28 | BEH | MeOH | 125 µL $min^{-1}$ | 30 ºC | 1.1 | 1.3 | 1.3 | 1.5 | 1.2 | 1.6 | 1.3 | 1.5 | 1.3 | 0.6 | 1.2 | 1.3 |
| 29 | BEH | MeOH | 125 µL $min^{-1}$ | 40 ºC | 1.4 | 1.0 | 1.2 | 0.8 | 1.2 | 0.8 | 1.2 | 0.8 | 1.4 | 0.7 | 1.3 | 0.8 |
| 30 | BEH | MeOH | 125 µL $min^{-1}$ | 50 ºC | 1.5 | 1.0 | 1.7 | 0.8 | 1.3 | 0.9 | 1.5 | 0.8 | 1.2 | 0.8 | 1.4 | 0.9 |
| 31 | BEH | MeOH | 250 µL $min^{-1}$ | 30 ºC | 1.2 | 1.2 | 1.5 | 0.6 | 1.1 | 0.6 | 1.7 | 0.5 | 1.4 | 0.6 | 1.4 | 0.7 |
| 32 | BEH | MeOH | 250 µL $min^{-1}$ | 40 ºC | 1.3 | 1.1 | 1.4 | 1.4 | 1.4 | 1.4 | 1.8 | 1.1 | 1.4 | 0.6 | 1.5 | 1.1 |
| 33 | BEH | MeOH | 250 µL $min^{-1}$ | 50 ºC | 1.6 | 1.0 | 1.5 | 0.7 | 1.6 | 0.7 | 1.9 | 0.6 | 1.8 | 0.6 | 1.7 | 0.7 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 34 | BEH | MeOH | 375 µL $min^{-1}$ | 30 ºC | 1.2 | 1.2 | 1.2 | 1.0 | 1.1 | 1.0 | 1.1 | 1.0 | 1.4 | 0.7 | 1.2 | 1.0 |
| 35 | BEH | MeOH | 375 µL $min^{-1}$ | 40 ºC | 1.2 | 1.1 | 1.4 | 0.6 | 1.1 | 0.6 | 1.2 | 0.6 | 1.5 | 0.5 | 1.3 | 0.7 |
| 36 | BEH | MeOH | 375 µL $min^{-1}$ | 50 ºC | 1.7 | 0.9 | 1.5 | 1.3 | 1.4 | 1.4 | 1.7 | 1.2 | 1.7 | 0.5 | 1.6 | 1.1 |
| 37 | HSS | ACN | 125 µL $min^{-1}$ | 30 ºC | 1.6 | 0.7 | 1.5 | 0.7 | 2.2 | 0.6 | 1.1 | 0.8 | 1.7 | 0.7 | 1.6 | 0.7 |
| 38 | HSS | ACN | 125 µL $min^{-1}$ | 40 ºC | 1.5 | 0.7 | 1.4 | 0.9 | 2.0 | 0.7 | 1.3 | 0.9 | 1.9 | 0.6 | 1.6 | 0.8 |
| 39 | HSS | ACN | 125 µL $min^{-1}$ | 50 ºC | 1.3 | 0.7 | 1.3 | 0.6 | 2.0 | 0.5 | 1.7 | 0.5 | 1.9 | 0.5 | 1.7 | 0.6 |
| 40 | HSS | ACN | 250 µL $min^{-1}$ | 30 ºC | 1.9 | 0.6 | 2.3 | 1.0 | 2.4 | 1.0 | 1.7 | 1.2 | 1.3 | 0.6 | 1.9 | 0.9 |
| 41 | HSS | ACN | 250 µL $min^{-1}$ | 40 ºC | 1.9 | 0.6 | 2.1 | 0.6 | 2.6 | 0.6 | 1.6 | 0.7 | 1.3 | 0.7 | 1.9 | 0.6 |
| 42 | HSS | ACN | 250 µL $min^{-1}$ | 50 ºC | 1.9 | 0.6 | 1.2 | 1.0 | 2.0 | 0.7 | 1.7 | 0.8 | 1.5 | 0.7 | 1.7 | 0.8 |
| 43 | HSS | ACN | 375 µL $min^{-1}$ | 30 ºC | 2.4 | 0.8 | 1.7 | 0.5 | 1.4 | 0.6 | 1.8 | 0.5 | 1.4 | 0.6 | 1.7 | 0.6 |
| 44 | HSS | ACN | 375 µL $min^{-1}$ | 40 ºC | 2.1 | 0.6 | 1.7 | 1.2 | 2.0 | 1.1 | 2.0 | 1.1 | 1.7 | 0.5 | 1.9 | 0.9 |
| 45 | HSS | ACN | 375 µL $min^{-1}$ | 50 ºC | 1.3 | 0.8 | 2.6 | 0.6 | 2.0 | 0.6 | 2.8 | 0.6 | 2.0 | 0.6 | 2.1 | 0.6 |
| 46 | HSS | MeOH | 125 µL $min^{-1}$ | 30 ºC | 2.3 | 0.6 | 2.1 | 0.7 | 2.2 | 0.7 | 1.8 | 0.8 | 1.3 | 0.7 | 1.9 | 0.7 |
| 47 | HSS | MeOH | 125 µL $min^{-1}$ | 40 ºC | 2.4 | 0.6 | 2.2 | 0.5 | 2.0 | 0.5 | 1.8 | 0.5 | 1.3 | 0.6 | 1.9 | 0.5 |
| 48 | HSS | MeOH | 125 µL $min^{-1}$ | 50 ºC | 2.4 | 1.1 | 2.3 | 1.0 | 1.4 | 1.4 | 2.1 | 1.0 | 1.4 | 1.4 | 1.9 | 1.2 |
| 49 | HSS | MeOH | 250 µL $min^{-1}$ | 30 ºC | 1.6 | 0.7 | 1.6 | 0.7 | 1.8 | 0.7 | 1.4 | 0.7 | 2.1 | 0.6 | 1.7 | 0.7 |
| 50 | HSS | MeOH | 250 µL $min^{-1}$ | 40 ºC | 2.2 | 0.6 | 1.7 | 0.8 | 1.8 | 0.8 | 1.5 | 0.8 | 2.0 | 0.7 | 1.8 | 0.8 |
| 51 | HSS | MeOH | 250 µL $min^{-1}$ | 50 ºC | 1.6 | 0.7 | 1.9 | 0.5 | 1.4 | 0.6 | 1.9 | 0.5 | 1.5 | 0.6 | 1.7 | 0.6 |
| 52 | HSS | MeOH | 375 µL $min^{-1}$ | 30 ºC | 2.5 | 0.6 | 1.8 | 1.2 | 1.5 | 1.3 | 1.4 | 1.4 | 1.8 | 1.1 | 1.8 | 1.1 |
| 53 | HSS | MeOH | 375 µL $min^{-1}$ | 40 ºC | 2.4 | 0.6 | 1.8 | 0.6 | 1.8 | 0.6 | 1.5 | 0.7 | 2.0 | 0.6 | 1.9 | 0.6 |
| 54 | HSS | MeOH | 375 µL $min^{-1}$ | 50 ºC | 1.3 | 0.7 | 1.6 | 0.8 | 2.0 | 0.7 | 1.6 | 0.8 | 2.1 | 0.7 | 1.7 | 0.8 |
| 55 | HILIC | ACN | 125 µL $min^{-1}$ | 30 ºC | 1.2 | 1.3 | 3.5 | 0.9 | 1.4 | 8.0 | 1.6 | 2.4 | 2.1 | 0.5 | 2.0 | 2.6 |
| 56 | HILIC | ACN | 125 µL $min^{-1}$ | 40 ºC | 1.1 | 0.6 | 3.2 | 6.6 | 1.4 | 5.9 | 1.3 | 8.0 | 1.9 | 4.6 | 1.8 | 5.1 |
| 57 | HILIC | ACN | 125 µL $min^{-1}$ | 50 ºC | 1.1 | 0.8 | 2.8 | 3.6 | 1.5 | 6.4 | 1.3 | 4.5 | 1.3 | 1.7 | 1.6 | 3.4 |
| 58 | HILIC | ACN | 250 µL $min^{-1}$ | 30 ºC | 2.3 | 3.6 | 2.7 | 1.2 | 1.6 | 4.7 | 1.7 | 15.8 | 1.5 | 4.6 | 2.0 | 6.0 |
| 59 | HILIC | ACN | 250 µL $min^{-1}$ | 40 ºC | 2.3 | 3.7 | 2.2 | 4.9 | 1.4 | 5.2 | 1.9 | 4.1 | 1.4 | 1.9 | 1.9 | 4.0 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 60 | HILIC | ACN | 250 µL min$^{-1}$ | 50 ºC | 2.0 | 2.9 | 2.4 | 3.1 | 1.5 | 13.8 | 1.6 | 8.2 | 1.3 | 3.4 | 1.8 | 6.3 |
| 61 | HILIC | ACN | 375 µL min$^{-1}$ | 30 ºC | 1.5 | 2.9 | 1.7 | 5.8 | 1.3 | 8.0 | 1.9 | 12.6 | 1.3 | 6.5 | 1.5 | 7.1 |
| 62 | HILIC | ACN | 375 µL min$^{-1}$ | 40 ºC | 1.9 | 3.5 | 1.8 | 3.1 | 1.3 | 2.6 | 1.6 | 2.0 | 1.3 | 3.0 | 1.6 | 2.9 |
| 63 | HILIC | ACN | 375 µL min$^{-1}$ | 50 ºC | 2.1 | 2.9 | 1.8 | 2.6 | 1.2 | 4.9 | 2.0 | 13.0 | 1.2 | 3.7 | 1.7 | 5.4 |
| 64 | HILIC | MeOH | 125 µL min$^{-1}$ | 30 ºC | 1.9 | 5.8 | 1.6 | 7.6 | 1.9 | 7.7 | 1.8 | 6.4 | 1.2 | 2.6 | 1.7 | 6.0 |
| 65 | HILIC | MeOH | 125 µL min$^{-1}$ | 40 ºC | 1.8 | 4.1 | 1.4 | 1.7 | 1.9 | 4.4 | 1.8 | 8.4 | 1.2 | 1.9 | 1.6 | 4.1 |
| 66 | HILIC | MeOH | 125 µL min$^{-1}$ | 50 ºC | 2.3 | 3.0 | 1.4 | 2.7 | 1.7 | 3.0 | 1.4 | 14.0 | 1.2 | 5.6 | 1.6 | 5.7 |
| 67 | HILIC | MeOH | 250 µL min$^{-1}$ | 30 ºC | 1.8 | 2.8 | 1.4 | 7.2 | 1.2 | 3.7 | 2.4 | 5.1 | 1.2 | 4.1 | 1.6 | 4.6 |
| 68 | HILIC | MeOH | 250 µL min$^{-1}$ | 40 ºC | 1.8 | 2.9 | 1.4 | 6.1 | 1.6 | 2.6 | 2.6 | 4.2 | 1.3 | 1.5 | 1.7 | 3.4 |
| 69 | HILIC | MeOH | 250 µL min$^{-1}$ | 50 ºC | 1.8 | 3.7 | 1.5 | 5.6 | 1.5 | 2.7 | 2.1 | 8.3 | 1.2 | 2.9 | 1.6 | 4.6 |
| 70 | HILIC | MeOH | 375 µL min$^{-1}$ | 30 ºC | 1.8 | 1.3 | 1.4 | 8.0 | 1.2 | 7.8 | 2.5 | 13.3 | 1.3 | 5.7 | 1.7 | 7.2 |
| 71 | HILIC | MeOH | 375 µL min$^{-1}$ | 40 ºC | 1.8 | 0.6 | 1.4 | 5.9 | 1.4 | 6.3 | 2.9 | 2.5 | 1.4 | 1.1 | 1.8 | 3.3 |
| 72 | HILIC | MeOH | 375 µL min$^{-1}$ | 50 ºC | 1.8 | 2.2 | 1.5 | 6.4 | 1.9 | 3.1 | 2.6 | 7.8 | 1.3 | 2.8 | 1.8 | 4.5 |

**Table S53. Verification data of MEPS$_{R\text{-}CX}$-MODR through analysis of agreement between the predicted and observed values.**

| FDs | Total Peak Area (× 10$^3$) | | | | | | Intermediate Precision (% RSD) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Observed Value 1 | Observed Value 2 | Observed Value 3 | Predicted Value | 95% CI[a] Low | 95% CI[a] High | Observed Value 1 | Observed Value 2 | Observed Value 3 | Predicted Value | 95% CI[a] Low | 95% CI[a] High |
| 5HMF | 151.7 | 151.7 | 155.2 | 152.8 | 150.1 | 155.6 | 1.02 | 1.08 | 1.13 | 1.08 | 0.99 | 1.16 |
| FURL | 173.8 | 176.8 | 177.2 | 176.0 | 172.9 | 179.0 | 0.85 | 0.90 | 0.81 | 0.85 | 0.77 | 0.93 |
| FAL | 296.9 | 297.2 | 291.8 | 295.3 | 290.8 | 299.9 | 0.83 | 0.79 | 0.87 | 0.83 | 0.76 | 0.91 |
| 2FMK | 184.3 | 182.4 | 186.9 | 184.5 | 181.1 | 188.0 | 1.05 | 0.95 | 1.00 | 1.00 | 0.91 | 1.09 |
| 5MF | 334.4 | 337.2 | 342.3 | 338.0 | 332.1 | 343.8 | 0.96 | 0.91 | 1.01 | 0.96 | 0.88 | 1.04 |
| Sum | 1141.1 | 1145.3 | 1153.4 | 1146.6 | 1134.2 | 1159.0 | 0.94 | 0.93 | 0.97 | 0.94 | 0.87 | 1.02 |

[a]CI - Confidence interval.

**Table S54. Verification data of UHPLCCORTECS-MODR through analysis of agreement between the predicted and observed values.**

| FDs | Total Peak Area (× $10^3$) | | | | | | Peak Resolution | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Observed Value 1 | Observed Value 2 | Observed Value 3 | Predicted Value | 95% CI[a] Low | 95% CI[a] High | Observed Value 1 | Observed Value 2 | Observed Value 3 | Predicted Value | 95% CI[a] Low | 95% CI[a] High |
| 5HMF | 146.5 | 146.2 | 151.5 | 127.3 | 113.2 | 141.3 | 5.44 | 5.47 | 5.42 | 5.19 | 5.03 | 5.36 |
| FURL | 306.1 | 290.3 | 295.0 | 315.4 | 304.8 | 326.0 | 2.30 | 2.31 | 2.29 | 2.41 | 2.35 | 2.47 |
| FAL | 316.0 | 320.1 | 314.8 | 323.7 | 314.9 | 332.5 | 1.51 | 1.52 | 1.51 | 1.73 | 1.53 | 1.93 |
| 2FMK | 216.6 | 213.2 | 220.9 | 182.6 | 160.6 | 204.6 | 1.64 | 1.65 | 1.63 | 1.83 | 1.73 | 1.92 |
| 5MF | 523.5 | 508.2 | 508.6 | 511.9 | 507.7 | 516.0 | 1.75 | 1.76 | 1.75 | 1.83 | 1.79 | 1.87 |
| Sum | 1508.5 | 1478.0 | 1490.8 | 1460.8 | 1428.6 | 1493.1 | 2.53 | 2.54 | 2.52 | 2.60 | 2.56 | 2.64 |

[a]CI - Confidence interval

**Table S55. TPA and PR results for all runs of the robustness screening model based on Fractional Factorial Design (2^3-level factors).**

| Run number | Column Flow | Column Temperature | 5HMF | | FURL | | FAL | | 2FMK | | 5MF | | Sum | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Total Peak Area (× $10^3$) | Peak Resolution | Total Peak Area (× $10^3$) | Peak Resolution | Total Peak Area (× $10^3$) | Peak Resolution | Total Peak Area (× $10^3$) | Peak Resolution | Total Peak Area (× $10^3$) | Peak Resolution | Total Peak Area (× $10^3$) | Peak Resolution Mean |
| 1 | 125 µL $min^{-1}$ | 50 ºC | 140.7 | 5.43 | 303.8 | 2.37 | 305.6 | 1.59 | 215.6 | 1.69 | 512.1 | 1.85 | 1477.8 | 2.59 |
| 2 | 125 µL $min^{-1}$ | 50 ºC | 139.5 | 5.43 | 308.2 | 2.39 | 303.4 | 1.60 | 214.6 | 1.70 | 514.5 | 1.86 | 1480.2 | 2.60 |
| 3 | 125 µL $min^{-1}$ | 50 ºC | 137.6 | 5.41 | 308.9 | 2.36 | 299.1 | 1.58 | 218.0 | 1.68 | 517.8 | 1.85 | 1481.4 | 2.58 |
| 4 | 115 µL $min^{-1}$ | 50 ºC | 143.9 | 5.39 | 303.5 | 2.35 | 301.9 | 1.58 | 217.4 | 1.66 | 512.8 | 1.87 | 1479.5 | 2.57 |
| 5 | 115 µL $min^{-1}$ | 50 ºC | 147.4 | 5.39 | 305.3 | 2.36 | 299.5 | 1.61 | 216.4 | 1.64 | 509.2 | 1.87 | 1477.7 | 2.57 |
| 6 | 115 µL $min^{-1}$ | 50 ºC | 145.4 | 5.41 | 301.3 | 2.39 | 303.5 | 1.58 | 215.3 | 1.68 | 513.9 | 1.90 | 1479.5 | 2.59 |
| 7 | 135 µL $min^{-1}$ | 50 ºC | 138.6 | 5.36 | 304.4 | 2.37 | 304.9 | 1.55 | 215.2 | 1.67 | 507.5 | 1.87 | 1470.6 | 2.57 |
| 8 | 135 µL $min^{-1}$ | 50 ºC | 137.3 | 5.37 | 302.5 | 2.34 | 302.4 | 1.56 | 216.9 | 1.67 | 512.0 | 1.86 | 1471.2 | 2.56 |
| 9 | 135 µL $min^{-1}$ | 50 ºC | 138.7 | 5.37 | 304.3 | 2.35 | 303.8 | 1.55 | 214.5 | 1.65 | 512.5 | 1.85 | 1473.8 | 2.55 |
| 10 | 125 µL $min^{-1}$ | 48 ºC | 138.2 | 5.35 | 304.0 | 2.40 | 301.7 | 1.54 | 216.7 | 1.65 | 515.8 | 1.88 | 1476.4 | 2.56 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 11 | 125 µL $min^{-1}$ | 48 ºC | 139.2 | 5.36 | 302.9 | 2.37 | 298.2 | 1.56 | 218.7 | 1.63 | 514.3 | 1.89 | 1473.2 | 2.56 |
| 12 | 125 µL $min^{-1}$ | 48 ºC | 139.9 | 5.34 | 300.3 | 2.39 | 303.5 | 1.57 | 215.6 | 1.67 | 510.8 | 1.87 | 1470.2 | 2.57 |
| 13 | 125 µL $min^{-1}$ | 52 ºC | 139.5 | 5.42 | 305.5 | 2.39 | 303.2 | 1.56 | 212.3 | 1.65 | 521.5 | 1.88 | 1482.0 | 2.58 |
| 14 | 125 µL $min^{-1}$ | 52 ºC | 139.9 | 5.43 | 306.0 | 2.40 | 300.4 | 1.57 | 216.0 | 1.66 | 518.6 | 1.88 | 1480.9 | 2.59 |
| 15 | 125 µL $min^{-1}$ | 52 ºC | 139.1 | 5.44 | 302.0 | 2.40 | 302.3 | 1.58 | 218.3 | 1.65 | 519.1 | 1.87 | 1480.7 | 2.59 |

**Table S56. Verification data of method robustness through analysis of agreement between the predicted and observed values.**

| FDs | Total Peak Area (× $10^3$) | | | | | | Peak Resolution | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Observed Value 1 | Observed Value 2 | Observed Value 3 | Predicted Value | 95% CI[a] Low | 95% CI[a] High | Observed Value 1 | Observed Value 2 | Observed Value 3 | Predicted Value | 95% CI[a] Low | 95% CI[a] High |
| 5HMF | 140.7 | 139.5 | 137.6 | 139.3 | 137.8 | 140.8 | 5.43 | 5.43 | 5.41 | 5.43 | 5.41 | 5.44 |
| FURL | 303.8 | 308.2 | 308.9 | 307.0 | 304.3 | 309.6 | 2.37 | 2.39 | 2.36 | 2.37 | 2.35 | 2.39 |
| FAL | 305.6 | 303.4 | 299.1 | 302.7 | 299.8 | 305.6 | 1.59 | 1.60 | 1.58 | 1.59 | 1.57 | 1.60 |
| 2FMK | 215.6 | 214.6 | 218.0 | 216.1 | 213.7 | 218.4 | 1.69 | 1.70 | 1.68 | 1.69 | 1.67 | 1.71 |
| 5MF | 512.1 | 514.5 | 517.8 | 514.8 | 511.6 | 518.0 | 1.85 | 1.86 | 1.85 | 1.85 | 1.84 | 1.87 |
| Sum | 1477.8 | 1480.2 | 1481.4 | 1479.8 | 1477.4 | 1482.2 | 2.59 | 2.60 | 2.58 | 2.59 | 2.58 | 2.60 |

**Table S57. Identification of SC-derived samples by sample name, replicate number, producer, production type, production year, geographical area and authenticity certification**.

| Sample name | Replicate number | Producer | Production type | Production year | Geographical area[a] | Authenticity |
|---|---|---|---|---|---|---|
| FRS15 | 1<br>2<br>3 | FRS | Industrial | 2013 | Funchal, Câmara de Lobos (Portugal) | Certified |
| FRS14 | 4<br>5<br>6 | FRS | Industrial | 2014 | Funchal, Câmara de Lobos (Portugal) | Certified |
| FRS13 | 7<br>8 | FRS | Industrial | 2015 | Funchal, Câmara de Lobos (Portugal) | Certified |

| | | | | | | |
|---|---|---|---|---|---|---|
| | 9 | | | | | |
| | 10 | | | | | |
| NCAL14 | 11 | NCAL | Industrial | 2014 | Calheta, Ribeira Brava (Portugal) | Non-Certified |
| | 12 | | | | | |
| | 13 | | | | | |
| CAL14 | 14 | CAL | Industrial | 2014 | Calheta, Ribeira Brava (Portugal) | Non-Certified |
| | 15 | | | | | |
| | 16 | | | | | |
| MCBR14 | 17 | MCBR | Industrial | 2014 | Brasil | Non-Certified |
| | 18 | | | | | |
| | 19 | | | | | |
| MLBR14 | 20 | MLBR | Industrial | 2014 | Brasil | Non-Certified |
| | 21 | | | | | |
| | 22 | | | | | |
| GLA14 | 23 | GLA | Home-made | 2014 | Santa Cruz, Machico (Portugal) | Non-Certified |
| | 24 | | | | | |

[a] Geographical area of sugarcanes cultivation selected to produce SCH.

**Table S58. Calibration functions of FDs for quantification proposes.**

| Furanic Derivatives | RT (min)[a] | λ max (nm)[b] | Concentration range (mg $L^{-1}$) | Regression equation | Correlation coefficient ($r^2$) |
|---|---|---|---|---|---|
| 5HMF | 4.4 | 283 | 0.13 - 17.8 | y = -0.0075x2 + 1.2054x + 0.0674 | 0.9999 |
| FURL | 5.2 | 278 | 0.12 - 15.9 | y = -0.0457x2 + 5.1996x + 0.1179 | 0.9998 |
| FAL | 5.0 | 216 | 0.53 - 72.3 | y = -0.001x2 + 0.6421x + 0.7192 | 0.9996 |
| 2FMK | 6.3 | 274 | 0.10 - 13.1 | y = -0.0719x2 + 4.2799x + 0.3299 | 0.9998 |
| 5MF | 7.0 | 291 | 0.10 - 13.4 | y = -0.0505x2 + 7.0872x + 0.067 | 0.9999 |

[a] Retention time.
[b] Maximum absorbance values obtained in the PDA system detection.

**Table S59. Information summary of PCA and PLS analysis based on the concentration values of FDs in SC-derived samples.**

| Analysis | Component | $R^2X$ | Eigenvalues | $R^2Y$ | $Q^2$ | Significance | Iterations |
|---|---|---|---|---|---|---|---|
| PCA | 1 | 0.80391 | 3733.93 | n.a. | 0.15 | S | 4 |
| | 2 | 0.19502 | 905.81 | n.a. | 0.62 | S | 2 |
| | 3 | 0.00082 | 3.81 | n.a. | 0.32 | S | 3 |
| | 4 | 0.00014 | 0.64 | n.a. | 0.34 | S | 3 |
| | 5 | 0.00003 | 0.15 | n.a. | -0.10 | S | 34 |
| PLS | 1 | 0.76048 | 3052.71 | 0.23171 | 0.19 | S | 11 |
| | 2 | 0.23845 | 1107.20 | 0.03208 | -0.08 | NS | 3 |

n.a. - not available in PCA.

**Table S60. Information summary of variables from PCA, PLS and LDA analysis based on the concentration values of FDs in SC-derived samples.**

| Variables | PCA | | | PLS | LDA | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | VIP value | Principal Component 1 | Principal Component 2 | Partial Least Square 1 | Wilks value | F value | p value | Canonical Discriminant Function 1 | Canonical Discriminant Function 2 |
| 5HMF | 1.000 | 0.44 | -0.76 | 0.24 | 0.09 | 83.69 | 0.000001 | 0.36 | -0.05 |
| FURL | 1.000 | -0.52 | -0.73 | 0.56 | 0.47 | 9.45 | 0.001739 | 1.37 | 4.51 |
| FAL | 1.000 | -0.81 | 0.13 | 0.31 | 0.30 | 20.16 | 0.000033 | -0.22 | -0.19 |
| 2FMK | 0.998 | 0.81 | 0.14 | -0.24 | 0.19 | 36.01 | 0.000001 | -15.05 | 0.45 |
| 5MF | 1.000 | -0.06 | 0.71 | -0.15 | 0.32 | 17.99 | 0.000064 | 3.15 | 0.26 |

[a] Variable importance in projection.
[b] Fischer value.
c Backward stepwise method (*p* value to enter 0.05, p value to remove 0.05).

**Table S61. Analytical methods for determination of SGs in food matrices.**

| Sugars | Food Product | Study Propose | Sample Preparation | Analysis | Optimization Type | Validation Parameters | Reference |
|---|---|---|---|---|---|---|---|
| Fructose, Glucose, Galactose, Sucrose, Lactulose, Lactose | Milk | Sugars Profile | LLE | LC-RI | n.p.[1] | Linearity, Accuracy, Precision, LOD, LOQ | (Chávez-Servín et al. 2004) |
| Fructose, Glucose; Sucrose, Sorbitol | Peach, Nectarine | Cultivars | LLE | LC-RI | n.p.[1] | n.p.[1] | (Cantín et al. 2009) |
| Fructose, Glucose; Sucrose, Sorbitol | Apple | Cultivars | UA-LLE | LC-RI | Box-Behnken Design (H2SO4 concentration, flow rate, column temperature) | Linearity, Accuracy, Precision, LOD, LOQ | (Filip et al. 2016) |
| Fructose, Glucose | Orange Juice | Geographical Origin | n.p.[1] | LC-RI | n.p.[1] | Linearity, Accuracy, Precision, LOD, LOQ | (Nikolaou et al. 2017) |
| Maltose, Glucose, Fructose, Rhamnose | Grape Juice, Wine | Geographical Origin | n.p.[1] | LC-RI | n.p.[1] | Linearity, Accuracy, Precision, LOD, LOQ | (Coelho et al. 2018) |
| Fructose, Glucose, Sucrose, Maltose | Honey | Geographical Origin | LLE | LC-RI | n.p.[1] | Linearity, Precision, LOD, LOQ | (Karabagias 2019) |
| Fructose, Glucose, Sucrose, Maltose, Maltotriose, Maltotetraose, Maltopentaose, Maltohexaose, Maltoheptaose | Honey | Adulteration | n.p.[1] | LC-RI | n.p.[1] | n.p.[1] | (Wang et al. 2015) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Fructose, Glucose, Sucrose | Sugarcane Molasses | Sugars Profile | SPE Clean-up | LC-RI | Univariate Design (Column Type, Mobile Phase) | Linearity, Accuracy, Precision, LOD | (Xu et al. 2015) |
| Fructose, Glucose; Sucrose; Kestose | Agave Syrup | Sugars Profile | n.p.[1] | LC-RI | n.p.[1] | n.p.[1] | (Muñiz-Márquez et al. 2015) |
| Fructose, Glucose, Sucrose, Maltose | Yacon Syrup | Sugars Profile | LLME | LC-RI | n.p.[1] | n.p.[1] | (Silva et al. 2018a) |
| Fructose, Glucose, Sucrose | Date Syrup | Sugars Profile | n.p.[1] | LC-RI | n.p.[1] | n.p.[1] | (Al Eid 2006) |
| Fructose, Glucose, Sucrose | Nectar | Sugars Profile | n.p.[1] | LC-ELSD | n.p.[1] | Linearity, Accuracy, Precision, LOD, LOQ | (Lindqvist et al. 2018) |
| Fructose, Glucose; Sucrose, Sorbitol | Peach, Apple, Watermelon, Cherry Fruits | Sugars Profile | n.p.[1] | LC-ELSD | Univariate Design (Column Temperature, Mobile Phase, Gas Flow Rate) | Linearity, Accuracy, Precision, LOD, LOQ | (Ma et al. 2014) |
| Fructose, Glucose, Sucrose | Honey | Typicality | n.p.[1] | LC-ELSD | n.p.[1] | n.p.[1] | (Kek et al. 2017) |
| Fructose, Glucose, Sucrose, Maltose, Lactose, Erythritol, Xylitol, Sorbitol, Mannitol, Inositol, Maltitol, Lactitol, Isomalt | Candies, Gum, Jelly, Chocolate | Sugars Profile | LLE | UPLC-ELSD | Univariate Design (Column Type, Mobile Phase) | Linearity, Accuracy, LOD, LOQ | (Koh et al. 2018) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Fructose, Glucose; Sucrose, Maltose, Maltotriose | Honey, Inverted Sugar Syrup | Adulteration | n.p.[1] | HPAEC-PAD | n.p.[1] | n.p.[1] | (Cordella et al. 2005) |
| Trehalose, Glucose, Fructose, Sucrose, Melezitose, Turanose, Maltose | Honey | Sugars Profile | n.p.[1] | HPAEC-PAD | n.p.[1] | LOQ | (Anjos et al. 2015) |
| Fructose, Glucose, Sucrose | Cane Honey, Jaggeries, Brown Sugar | Sugars Profile | n.p.[1] | HPAEC-PAD | n.p.[1] | n.p.[1] | (Seguí et al. 2015) |
| Fructose, Glucose, Sucrose | Maple Syrup | Typicality | n.p.[1] | HPAEC-PAD | n.p.[1] | n.p.[1] | (Mellado-Mojica et al. 2016) |
| Rhamnose, Fructose, Glucose,Sucrose, Lactose, Raffinose, Maltose, Erlose | Honeydew, Nectar | Sugars Profile | UA-LLE | HPAEC-PAD | Univariate Design (Column Type, Mobile Phase, Sample Elimination) | Linearity, LOD, LOQ | (Ni et al. 2016) |
| Fructose, Glucose, Sucrose | Potato, Strawberry | Typicality | LLE | LC-MS | Univariate Design (Extraction Method) | Selectivity, Linearity, Accuracy, Precision, LOD, LOQ | (Georgelis et al. 2018) |
| Fructose, Glucose, Sucrose, Kestose, Nystose. | Palm Fruit Dates | Sugars Profile | LLE | UPLC-MS | Univariate Design (Column Type, Mobile Phase) | Linearity, Accuracy, Precision, LOD, LOQ | (Ghfar et al. 2015) |
| Glucose, Fructose, Sucrose, Maltose, Erythritol, Mannitol, Maltitol, Sorbitol, Xylitol | Orange-Apple Juices, Black Currant-Cherry Nectars, Raspberry Syrup | Sugars Profile | n.p.[1] | LC-CAD | Univariate Design (Column Temperature, Mobile Phase, Column Flow Rate) | Linearity, Accuracy, Precision, LOD, LOQ | (Grembecka et al. 2014) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ribose, Xylose, Glucose, Maltose, Isomaltose, Maltotriose, Maltopentaose, Maltohexaose, Maltoheptaose | Beer | Sugars Profile | Derivatization | LC-FLD, LC-MS | n.p.[1] | n.p.[1] | (Rakete and Glomb 2013) |
| Isomaltose, Isomaltotriose, Panose, Maltose, Glucose | Wine Rice | Sugars Profile | Derivatization | LC-UV | n.p.[1] | Linearity, Accuracy, Precision, LOD, LOQ | (Bai et al. 2015) |
| Maltoheptose, Maltohexose, Maltopentose, Maltotetrose Maltotriose, Maltose, Sucrose, Glucose, Fructose, Xylose, Rhamnose | Beet Molasses | Sugars Profile | Derivatization | HPTLC-FLD | n.p.[1] | n.p.[1] | (Vaccari et al. 2001) |
| Ribose, Glucose, Fructose, Galactose, Inositol, Galactinol | Mulberry | Sugars Profile | LLE, Derivatization | GC-MS | Univariate Design (Derivatization Procedure) | Linearity, Accuracy, Precision, LOD, LOQ | (Rodríguez-Sánchez et al. 2011) |
| Apiose, Arabinose, Rhamnose, Fucose, Xylose, Mannose, Galactose, Glucose | Wine | Sugars Profile | Derivatization | GC-MS, GC-FID | n.p.[1] | Linearity, Accuracy, Precision, LOD, LOQ | (Guadalupe et al. 2012) |
| Glucose, Lactose, Galactose, Inositol | Milk | Sugars Profile | Derivatization | GC-FID | Univariate Design (Injection Volume) | Linearity, Accuracy, Precision, LOD, LOQ | (Idda et al. 2016) |
| Fructose, Glucose, Sucrose, Mannitol, Inositol | Agave Syrup | Authenticity | n.p.[1] | GC-FID, HPAEC-PAD | n.p.[1] | n.p.[1] | (Willems and Low 2012) |
| Fructose, Glucose, Sucrose, Maltose | Honey | Sugars Profile | n.p.[1] | Raman Spectroscopy | n.p.[1] | n.p.[1] | (Özbalci et al. 2013) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Fructose, Glucose, Sucrose, Maltose | Honey | Sugars Profile | n.p.[1] | NMR | n.p.[1] | n.p.[1] | (Jamróz et al. 2014a) |
| Maltose, Lactose, Xylose, Arabinose, Glucose, Ribose, Rhamnose, Fucose, Galactose, Mannose | Beer, Milk | Sugars Profile | LLE, Derivatization | CZE-UV | n.p.[1] | Linearity, Accuracy, Precision, LOD, LOQ | (Wang et al. 2012) |
| Cellobiose, Fructose, Fucose, Galactose, Glucose, Inositol, Mannitol, Mannose, Rhamnose, Ribose, Sorbitol, Trehalose, Xylose | Wine | Geographical Origin | n.p.[1] | CZE-UV | n.p.[1] | Linearity, Accuracy, Precision, LOD, LOQ | (Rovio et al. 2011) |

1 n.p. – not performed.

**Table S62. TPA and respective IP results for all runs (n = 3) of the $KS_{HPLC-IR}$ screening model based on Full Factorial Design (3^3-level factors).**

| Run Number | Factor (CMP) | | | GLU | | FRU | | SUC | | RHA | | XYL | | MAN | | Sum | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Acetone Content (1) | Column Flow (2) | Column Temperature (3) | Total Peak Area | RSD (%) | Total Peak Area | RSD (%) | Total Peak Area | RSD (%) | Total Peak Area | RSD (%) | Total Peak Area | RSD (%) | Total Peak Area | RSD (%) | Total Peak Area | Mean RSD (%) |
| 1 | 75% | 300 µL $min^{-1}$ | 60 ºC | 63.0 | 1.1 | 39.2 | 0.6 | 137.7 | 0.4 | 19.5 | 1.7 | 6.0 | 2.1 | n.d. | | 265.5 | 1.2 |
| 2 | 75% | 300 µL $min^{-1}$ | 70 ºC | 68.1 | 0.9 | 27.4 | 1.4 | 142.3 | 1.1 | 20.5 | 1.4 | 4.1 | 5.5 | n.d. | | 262.5 | 2.1 |
| 3 | 75% | 300 µL $min^{-1}$ | 80 ºC | 66.3 | 0.9 | 26.6 | 0.2 | 135.3 | 1.2 | 19.6 | 1.2 | 2.0 | 4.4 | n.d. | | 249.8 | 1.6 |
| 4 | 75% | 400 µL $min^{-1}$ | 60 ºC | 40.4 | 1.1 | 25.2 | 1.3 | 94.9 | 1.2 | 12.9 | 1.1 | 2.8 | 3.4 | n.d. | | 176.2 | 1.6 |
| 5 | 75% | 400 µL $min^{-1}$ | 70 ºC | 44.8 | 1.1 | 22.3 | 1.2 | 98.3 | 1.0 | 13.8 | 2.3 | 2.0 | 0.7 | n.d. | | 181.2 | 1.3 |
| 6 | 75% | 400 µL $min^{-1}$ | 80 ºC | 48.1 | 1.9 | 18.8 | 0.5 | 101.3 | 1.3 | 13.8 | 0.3 | 1.4 | 3.1 | n.d. | | 183.5 | 1.4 |
| 7 | 75% | 500 µL $min^{-1}$ | 60 ºC | 28.0 | 3.2 | 17.6 | 4.9 | 71.9 | 3.0 | 9.2 | 2.8 | 1.2 | 7.0 | n.d. | | 127.8 | 4.2 |
| 8 | 75% | 500 µL $min^{-1}$ | 70 ºC | 31.5 | 3.0 | 16.4 | 3.0 | 70.9 | 2.4 | 9.6 | 2.7 | 0.6 | 4.6 | n.d. | | 128.9 | 3.1 |
| 9 | 75% | 500 µL $min^{-1}$ | 80 ºC | 36.2 | 2.5 | 14.9 | 3.7 | 77.7 | 2.2 | 10.4 | 1.7 | 0.4 | 6.8 | n.d. | | 139.6 | 3.4 |
| 10 | 80% | 300 µL $min^{-1}$ | 60 ºC | 68.7 | 3.3 | 33.2 | 4.4 | 128.3 | 1.8 | 22.5 | 3.1 | 12.2 | 3.6 | 2.5 | 7.1 | 267.3 | 3.9 |
| 11 | 80% | 300 µL $min^{-1}$ | 70 ºC | 74.8 | 0.5 | 37.7 | 0.9 | 141.5 | 3.3 | 24.8 | 2.7 | 12.4 | 7.4 | 7.5 | 5.8 | 298.7 | 3.4 |
| 12 | 80% | 300 µL $min^{-1}$ | 80 ºC | 76.3 | 1.9 | 40.5 | 1.9 | 148.9 | 5.4 | 20.7 | 1.4 | 11.2 | 3.0 | 10.1 | 3.3 | 307.7 | 2.8 |
| 13 | 80% | 400 µL $min^{-1}$ | 60 ºC | 49.0 | 2.3 | 23.4 | 2.6 | 105.6 | 0.9 | 16.3 | 2.8 | 8.3 | 3.9 | 0.8 | 7.6 | 203.5 | 3.3 |

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 14 | 80% | 400 µL min$^{-1}$ | 70 ºC | 55.4 | 3.1 | 28.2 | 3.1 | 112.6 | 2.7 | 18.1 | 1.2 | 8.3 | 3.1 | 4.4 | 5.6 | 227.0 | 3.1 |
| 15 | 80% | 400 µL min$^{-1}$ | 80 ºC | 55.7 | 3.5 | 30.5 | 4.1 | 114.3 | 3.3 | 16.6 | 3.5 | 7.5 | 5.8 | 6.3 | 5.9 | 230.9 | 4.4 |
| 16 | 80% | 500 µL min$^{-1}$ | 60 ºC | 38.2 | 2.5 | 20.2 | 3.3 | 90.4 | 0.8 | 13.1 | 3.2 | 5.6 | 5.7 | 0.9 | 2.8 | 168.3 | 3.1 |
| 17 | 80% | 500 µL min$^{-1}$ | 70 ºC | 39.5 | 2.1 | 19.5 | 4.6 | 83.0 | 2.9 | 12.4 | 4.8 | 5.0 | 4.8 | 2.0 | 5.8 | 161.5 | 4.2 |
| 18 | 80% | 500 µL min$^{-1}$ | 80 ºC | 41.8 | 3.2 | 22.6 | 2.8 | 83.7 | 1.8 | 13.8 | 2.9 | 5.4 | 3.9 | 4.1 | 6.7 | 171.4 | 3.5 |
| 19 | 85% | 300 µL min$^{-1}$ | 60 ºC | 91.1 | 3.4 | 55.6 | 2.2 | 157.5 | 2.8 | 36.0 | 4.1 | 25.2 | 4.6 | 14.3 | 5.1 | 379.6 | 3.7 |
| 20 | 85% | 300 µL min$^{-1}$ | 70 ºC | 98.9 | 3.7 | 61.2 | 1.4 | 149.6 | 2.8 | 32.0 | 1.8 | 20.4 | 1.6 | 22.4 | 2.2 | 384.4 | 2.3 |
| 21 | 85% | 300 µL min$^{-1}$ | 80 ºC | 91.0 | 1.1 | 62.5 | 4.5 | 166.7 | 2.5 | 35.5 | 4.6 | 16.2 | 4.2 | 19.8 | 4.5 | 391.8 | 3.6 |
| 22 | 85% | 400 µL min$^{-1}$ | 60 ºC | 60.0 | 1.5 | 39.0 | 3.9 | 112.5 | 1.5 | 24.7 | 5.1 | 15.6 | 5.7 | 8.5 | 6.8 | 260.4 | 4.1 |
| 23 | 85% | 400 µL min$^{-1}$ | 70 ºC | 64.5 | 4.2 | 46.2 | 1.4 | 125.7 | 2.7 | 18.7 | 4.0 | 15.9 | 1.3 | 14.7 | 5.7 | 285.7 | 3.2 |
| 24 | 85% | 400 µL min$^{-1}$ | 80 ºC | 69.1 | 4.2 | 43.0 | 3.3 | 110.4 | 3.6 | 27.9 | 5.4 | 16.0 | 3.8 | 15.8 | 6.5 | 282.2 | 4.5 |
| 25 | 85% | 500 µL min$^{-1}$ | 60 ºC | 50.3 | 4.7 | 30.0 | 4.6 | 90.3 | 4.5 | 24.0 | 6.5 | 11.8 | 5.2 | 4.4 | 3.7 | 210.9 | 4.9 |
| 26 | 85% | 500 µL min$^{-1}$ | 70 ºC | 58.3 | 2.1 | 36.2 | 3.8 | 90.5 | 4.5 | 18.7 | 5.5 | 12.2 | 5.0 | 13.4 | 6.8 | 229.2 | 4.6 |
| 27 | 85% | 500 µL min$^{-1}$ | 80 ºC | 54.6 | 4.1 | 38.3 | 2.4 | 97.0 | 2.7 | 17.5 | 5.8 | 14.7 | 6.3 | 9.8 | 5.6 | 231.9 | 4.5 |

**Table S63. PR and respective IP results for all runs (n = 3) of the KSHPLC-IR screening model based on Full Factorial Design (3^3-level factors).**

| Run Number | Factor (CMP) | | | GLU | | FRU | | SUC | | RHA | | XYL | | MAN | | Sum | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Acetone Content (1) | Column Flow (2) | Column Temperature (3) | Peak Resolution | RSD (%) | Peak Resolution | RSD (%) | Peak Resolution | RSD (%) | Peak Resolution | RSD (%) | Peak Resolution | RSD (%) | Peak Resolution | RSD (%) | Peak Resolution | Mean RSD (%) |
| 1 | 75% | 300 µL min$^{-1}$ | 60 ºC | 1.6 | 1.3 | 1.4 | 0.7 | 2.7 | 2.3 | 1.6 | 0.8 | 0.9 | 0.5 | n.d. | | 1.6 | 1.1 |
| 2 | 75% | 300 µL min$^{-1}$ | 70 ºC | 1.7 | 0.5 | 1.7 | 0.5 | 2.8 | 4.0 | 1.8 | 1.2 | 1.0 | 0.9 | n.d. | | 1.8 | 1.4 |
| 3 | 75% | 300 µL min$^{-1}$ | 80 ºC | 1.9 | 0.9 | 1.3 | 0.4 | 2.9 | 0.8 | 1.9 | 0.7 | 1.2 | 2.2 | n.d. | | 1.8 | 1.0 |
| 4 | 75% | 400 µL min$^{-1}$ | 60 ºC | 1.5 | 2.5 | 1.2 | 2.7 | 1.9 | 4.8 | 1.5 | 0.6 | 0.9 | 1.5 | n.d. | | 1.4 | 2.4 |
| 5 | 75% | 400 µL min$^{-1}$ | 70 ºC | 1.6 | 0.8 | 1.5 | 0.6 | 2.0 | 3.6 | 1.6 | 0.7 | 0.8 | 3.5 | n.d. | | 1.5 | 1.9 |
| 6 | 75% | 400 µL min$^{-1}$ | 80 ºC | 1.7 | 0.8 | 1.2 | 1.5 | 2.7 | 5.3 | 1.7 | 2.5 | 1.1 | 2.1 | n.d. | | 1.7 | 2.4 |
| 7 | 75% | 500 µL min$^{-1}$ | 60 ºC | 1.4 | 1.2 | 1.1 | 1.1 | 2.1 | 5.5 | 1.4 | 2.2 | 1.0 | 2.7 | n.d. | | 1.4 | 2.5 |
| 8 | 75% | 500 µL min$^{-1}$ | 70 ºC | 1.5 | 0.6 | 1.3 | 1.1 | 2.0 | 3.0 | 1.6 | 6.3 | 1.0 | 3.0 | n.d. | | 1.5 | 2.8 |
| 9 | 75% | 500 µL min$^{-1}$ | 80 ºC | 1.6 | 1.2 | 1.5 | 1.1 | 2.7 | 3.0 | 1.7 | 0.7 | 1.1 | 0.7 | n.d. | | 1.7 | 1.4 |
| 10 | 80% | 300 µL min$^{-1}$ | 60 ºC | 2.6 | 2.1 | 1.0 | 3.1 | 2.3 | 3.0 | 1.7 | 1.0 | 1.1 | 1.5 | 1.3 | 1.8 | 1.7 | 2.1 |
| 11 | 80% | 300 µL min$^{-1}$ | 70 ºC | 2.8 | 0.2 | 1.2 | 2.1 | 2.4 | 0.9 | 1.8 | 2.6 | 1.1 | 0.7 | 1.2 | 0.8 | 1.8 | 1.2 |
| 12 | 80% | 300 µL min$^{-1}$ | 80 ºC | 3.1 | 1.0 | 1.3 | 0.4 | 2.5 | 1.1 | 2.1 | 0.4 | 1.2 | 0.4 | 1.2 | 1.1 | 1.9 | 0.7 |

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 13 | 80% | 400 µL min$^{-1}$ | 60 ºC | 2.4 | 0.7 | 1.2 | 1.0 | 1.9 | 4.0 | 1.6 | 1.4 | 1.1 | 0.4 | 1.2 | 1.6 | 1.6 | 1.5 |
| 14 | 80% | 400 µL min$^{-1}$ | 70 ºC | 2.7 | 1.5 | 1.2 | 1.7 | 2.0 | 5.7 | 1.8 | 1.7 | 1.1 | 2.0 | 1.2 | 2.4 | 1.7 | 2.5 |
| 15 | 80% | 400 µL min$^{-1}$ | 80 ºC | 3.0 | 1.6 | 1.3 | 0.6 | 2.2 | 2.3 | 2.0 | 1.3 | 1.2 | 1.4 | 1.2 | 0.7 | 1.8 | 1.3 |
| 16 | 80% | 500 µL min$^{-1}$ | 60 ºC | 2.3 | 1.5 | 1.1 | 1.5 | 1.9 | 4.3 | 1.6 | 0.3 | 1.1 | 0.4 | 1.1 | 0.4 | 1.5 | 1.4 |
| 17 | 80% | 500 µL min$^{-1}$ | 70 ºC | 2.5 | 1.1 | 1.2 | 1.7 | 2.2 | 3.8 | 1.7 | 1.4 | 1.1 | 2.5 | 1.2 | 1.8 | 1.7 | 2.1 |
| 18 | 80% | 500 µL min$^{-1}$ | 80 ºC | 2.8 | 1.1 | 1.3 | 0.0 | 2.6 | 2.4 | 1.9 | 1.8 | 1.1 | 1.3 | 1.1 | 0.8 | 1.8 | 1.2 |
| 19 | 85% | 300 µL min$^{-1}$ | 60 ºC | 3.9 | 1.5 | 1.2 | 1.8 | 1.3 | 5.8 | 1.8 | 1.7 | 1.3 | 0.4 | 1.4 | 2.3 | 1.8 | 2.3 |
| 20 | 85% | 300 µL min$^{-1}$ | 70 ºC | 4.1 | 1.8 | 1.4 | 1.2 | 1.4 | 5.0 | 2.1 | 1.0 | 1.3 | 1.6 | 1.4 | 1.7 | 2.0 | 2.1 |
| 21 | 85% | 300 µL min$^{-1}$ | 80 ºC | 4.5 | 1.5 | 1.5 | 2.8 | 1.7 | 4.1 | 2.2 | 1.5 | 1.3 | 0.7 | 1.4 | 2.3 | 2.1 | 2.2 |
| 22 | 85% | 400 µL min$^{-1}$ | 60 ºC | 3.7 | 0.6 | 1.2 | 4.8 | 1.3 | 1.1 | 1.7 | 1.4 | 1.3 | 1.3 | 1.3 | 8.1 | 1.7 | 2.9 |
| 23 | 85% | 400 µL min$^{-1}$ | 70 ºC | 4.0 | 2.4 | 1.3 | 1.9 | 1.4 | 4.9 | 2.0 | 3.9 | 1.3 | 0.9 | 1.3 | 2.7 | 1.9 | 2.8 |
| 24 | 85% | 400 µL min$^{-1}$ | 80 ºC | 4.4 | 2.0 | 1.5 | 1.4 | 2.3 | 3.6 | 2.1 | 2.2 | 1.4 | 2.1 | 1.3 | 1.0 | 2.2 | 2.0 |
| 25 | 85% | 500 µL min$^{-1}$ | 60 ºC | 3.4 | 3.3 | 1.1 | 3.7 | 1.4 | 4.4 | 1.6 | 8.3 | 1.2 | 1.8 | 1.2 | 8.4 | 1.7 | 5.0 |
| 26 | 85% | 500 µL min$^{-1}$ | 70 ºC | 4.0 | 2.0 | 1.3 | 1.0 | 1.8 | 3.3 | 2.0 | 4.7 | 1.2 | 1.4 | 1.2 | 1.1 | 1.9 | 2.2 |
| 27 | 85% | 500 µL min$^{-1}$ | 80 ºC | 4.3 | 1.4 | 1.5 | 0.8 | 2.0 | 2.5 | 2.1 | 4.3 | 1.3 | 1.0 | 1.3 | 1.1 | 2.1 | 1.8 |

**Table S64. ASY and respective IP results for all runs (n = 3) of the HPLC-IR-KS screening model based on Full Factorial Design (3^3-level factors).**

| | Factor (CMP) | | | GLU | | FRU | | SUC | | RHA | | XYL | | MAN | | Sum | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Run Number | Acetone Content (1) | Column Flow (2) | Column Temperature (3) | Peak Asymmetry | RSD (%) | Peak Asymmetry | RSD (%) | Peak Asymmetry | RSD (%) | Peak Asymmetry | RSD (%) | Peak Asymmetry | RSD (%) | Peak Asymmetry | RSD (%) | Peak Asymmetry | Mean RSD (%) |
| 1 | 75% | 300 µL min$^{-1}$ | 60 ºC | 1.3 | 0.6 | 1.3 | 0.7 | 1.2 | 0.4 | 1.0 | 0.9 | 0.8 | 4.7 | n.d. | | 1.1 | 1.5 |
| 2 | 75% | 300 µL min$^{-1}$ | 70 ºC | 1.2 | 0.7 | 1.1 | 2.3 | 1.2 | 0.8 | 1.1 | 0.4 | 0.7 | 1.3 | n.d. | | 1.1 | 1.1 |
| 3 | 75% | 300 µL min$^{-1}$ | 80 ºC | 1.2 | 0.4 | 1.0 | 0.8 | 1.2 | 0.7 | 1.1 | 0.4 | 0.7 | 7.7 | n.d. | | 1.0 | 2.0 |
| 4 | 75% | 400 µL min$^{-1}$ | 60 ºC | 1.3 | 0.4 | 1.2 | 1.7 | 1.3 | 0.6 | 1.0 | 1.2 | 0.7 | 3.9 | n.d. | | 1.1 | 1.6 |
| 5 | 75% | 400 µL min$^{-1}$ | 70 ºC | 1.2 | 0.3 | 1.4 | 1.2 | 1.3 | 1.9 | 1.1 | 0.0 | 0.6 | 0.7 | n.d. | | 1.1 | 0.8 |
| 6 | 75% | 400 µL min$^{-1}$ | 80 ºC | 1.2 | 0.7 | 1.0 | 1.6 | 1.3 | 1.7 | 1.1 | 0.4 | 1.0 | 9.9 | n.d. | | 1.1 | 2.9 |
| 7 | 75% | 500 µL min$^{-1}$ | 60 ºC | 1.3 | 0.8 | 1.1 | 1.9 | 1.3 | 0.4 | 1.0 | 0.0 | 0.9 | 6.1 | n.d. | | 1.1 | 1.8 |
| 8 | 75% | 500 µL min$^{-1}$ | 70 ºC | 1.2 | 1.8 | 1.2 | 2.7 | 1.2 | 0.8 | 1.0 | 0.5 | 0.9 | 2.8 | n.d. | | 1.1 | 1.7 |
| 9 | 75% | 500 µL min$^{-1}$ | 80 ºC | 1.2 | 0.7 | 1.0 | 2.0 | 1.2 | 0.0 | 1.1 | 1.2 | 0.9 | 2.4 | n.d. | | 1.1 | 1.3 |
| 10 | 80% | 300 µL min$^{-1}$ | 60 ºC | 1.3 | 4.6 | 1.0 | 0.5 | 1.2 | 1.4 | 1.1 | 4.7 | 0.9 | 2.1 | 1.6 | 9.1 | 1.2 | 3.7 |

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 11 | 80% | 300 µL min$^{-1}$ | 70 ºC | 1.2 | 4.1 | 1.1 | 1.6 | 1.1 | 0.8 | 1.2 | 2.0 | 0.9 | 0.5 | 1.1 | 2.4 | 1.1 | 1.9 |
| 12 | 80% | 300 µL min$^{-1}$ | 80 ºC | 1.1 | 1.1 | 1.1 | 0.0 | 1.2 | 6.2 | 1.1 | 2.5 | 0.9 | 0.9 | 1.0 | 0.5 | 1.1 | 1.9 |
| 13 | 80% | 400 µL min$^{-1}$ | 60 ºC | 1.3 | 5.9 | 1.1 | 1.6 | 1.2 | 2.1 | 1.2 | 1.1 | 0.9 | 0.5 | 1.0 | 4.0 | 1.1 | 2.5 |
| 14 | 80% | 400 µL min$^{-1}$ | 70 ºC | 1.2 | 4.4 | 1.0 | 0.9 | 1.2 | 1.6 | 1.2 | 2.8 | 0.9 | 2.0 | 1.1 | 3.4 | 1.1 | 2.5 |
| 15 | 80% | 400 µL min$^{-1}$ | 80 ºC | 1.1 | 1.5 | 1.1 | 0.9 | 1.2 | 1.2 | 1.1 | 3.1 | 0.8 | 2.5 | 1.0 | 2.2 | 1.1 | 1.9 |
| 16 | 80% | 500 µL min$^{-1}$ | 60 ºC | 1.1 | 1.8 | 1.1 | 1.9 | 1.2 | 1.4 | 1.1 | 3.2 | 0.8 | 1.1 | 1.3 | 0.4 | 1.1 | 1.6 |
| 17 | 80% | 500 µL min$^{-1}$ | 70 ºC | 1.2 | 1.5 | 1.0 | 0.9 | 1.2 | 2.8 | 1.1 | 4.5 | 0.8 | 0.6 | 1.1 | 5.8 | 1.1 | 2.7 |
| 18 | 80% | 500 µL min$^{-1}$ | 80 ºC | 1.2 | 2.6 | 1.1 | 0.4 | 1.1 | 1.3 | 1.1 | 1.2 | 0.8 | 1.5 | 0.9 | 1.8 | 1.0 | 1.5 |
| 19 | 85% | 300 µL min$^{-1}$ | 60 ºC | 1.1 | 4.6 | 1.0 | 0.8 | 1.0 | 3.7 | 1.2 | 3.0 | 0.9 | 6.4 | 1.1 | 2.9 | 1.0 | 3.6 |
| 20 | 85% | 300 µL min$^{-1}$ | 70 ºC | 1.1 | 8.1 | 1.1 | 1.8 | 1.0 | 5.9 | 1.3 | 4.0 | 1.0 | 1.3 | 1.0 | 1.9 | 1.1 | 3.8 |
| 21 | 85% | 300 µL min$^{-1}$ | 80 ºC | 1.0 | 2.1 | 1.1 | 2.2 | 0.9 | 2.3 | 1.1 | 2.3 | 1.0 | 2.0 | 1.0 | 2.9 | 1.0 | 2.3 |
| 22 | 85% | 400 µL min$^{-1}$ | 60 ºC | 1.1 | 2.1 | 1.0 | 0.5 | 1.1 | 1.6 | 1.3 | 6.4 | 1.0 | 2.2 | 1.1 | 9.4 | 1.1 | 3.7 |
| 23 | 85% | 400 µL min$^{-1}$ | 70 ºC | 1.0 | 2.1 | 1.1 | 1.6 | 1.0 | 5.2 | 1.1 | 3.7 | 1.0 | 3.4 | 1.0 | 0.9 | 1.0 | 2.8 |
| 24 | 85% | 400 µL min$^{-1}$ | 80 ºC | 1.0 | 1.7 | 1.1 | 0.0 | 1.0 | 2.5 | 1.2 | 8.5 | 1.0 | 2.5 | 1.0 | 1.0 | 1.0 | 2.7 |
| 25 | 85% | 500 µL min$^{-1}$ | 60 ºC | 1.2 | 4.4 | 1.0 | 0.5 | 1.1 | 3.8 | 1.2 | 9.1 | 0.9 | 2.4 | 1.1 | 7.6 | 1.1 | 4.6 |
| 26 | 85% | 500 µL min$^{-1}$ | 70 ºC | 1.2 | 3.9 | 1.0 | 1.4 | 0.9 | 0.5 | 1.0 | 8.4 | 1.0 | 0.5 | 1.0 | 1.4 | 1.0 | 2.7 |
| 27 | 85% | 500 µL min$^{-1}$ | 80 ºC | 1.0 | 1.6 | 1.1 | 1.1 | 1.0 | 1.3 | 1.2 | 2.1 | 0.9 | 2.7 | 0.9 | 1.0 | 1.0 | 1.6 |

**Table S65. Verification data of MODR through analysis of agreement between the predicted and observed values.**

| Sugars | Total Peak Area | | | | | | Peak Resolution | | | | | | Peak Asymmetry | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Observed Value 1 | Observed Value 2 | Observed Value 3 | Predicted Value | 95% CI[a] Low | 95% CI[a] High | Observed Value 1 | Observed Value 2 | Observed Value 3 | Predicted Value | 95% CI[a] Low | 95% CI[a] High | Observed Value 1 | Observed Value 2 | Observed Value 3 | Predicted Value | 95% CI[a] Low | 95% CI[a] High |
| GLU | 89.2 | 89.1 | 87.0 | 89.9 | 88.2 | 91.7 | 4.53 | 4.60 | 4.43 | 4.43 | 4.37 | 4.49 | 0.96 | 0.99 | 1.01 | 1.03 | 0.98 | 1.07 |
| FRU | 56.9 | 61.2 | 63.5 | 54.8 | 52.5 | 57.0 | 1.57 | 1.55 | 1.47 | 1.46 | 1.40 | 1.52 | 1.09 | 1.15 | 1.12 | 1.03 | 0.99 | 1.08 |
| SUC | 154.6 | 158.5 | 164.2 | 150.3 | 146.7 | 153.9 | 1.71 | 1.62 | 1.79 | 2.07 | 1.93 | 2.20 | 0.80 | 0.93 | 0.98 | 0.93 | 0.91 | 0.96 |
| RHA | 36.5 | 33.4 | 32.8 | 31.4 | 30.1 | 32.7 | 2.16 | 2.18 | 2.24 | 2.19 | 2.14 | 2.23 | 1.05 | 1.20 | 1.16 | 1.19 | 1.15 | 1.24 |
| XYL | 15.2 | 16.5 | 15.0 | 18.1 | 17.1 | 19.0 | 1.32 | 1.30 | 1.32 | 1.38 | 1.34 | 1.42 | 1.00 | 1.10 | 0.98 | 0.97 | 0.91 | 1.03 |
| MAN | 18.3 | 17.1 | 19.1 | 16.1 | 14.8 | 17.4 | 1.38 | 1.39 | 1.32 | 1.33 | 1.30 | 1.36 | 0.94 | 1.00 | 1.00 | 0.99 | 0.93 | 1.06 |
| Sum/ Mean | 370.7 | 375.8 | 381.6 | 360.6 | 353.9 | 367.2 | 2.11 | 2.11 | 2.10 | 2.14 | 2.11 | 2.17 | 0.97 | 1.06 | 1.04 | 1.03 | 1.01 | 1.04 |

**Table S66. TPA and respective IP results for all runs (n = 2) of the robustness screening model based on Fractional Factorial Design (3^3-level factors).**

| Run Number | Factor (CMP) | | | GLU | | FRU | | SUC | | RHA | | XYL | | MAN | | Sum | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Acetone Content (1) | Column Flow (2) | Column Temperature (3) | Total Peak Area | RSD (%) | Total Peak Area | RSD (%) | Total Peak Area | RSD (%) | Total Peak Area | RSD (%) | Total Peak Area | RSD (%) | Total Peak Area | RSD (%) | Total Peak Area | Mean RSD (%) |
| 1 | 85% | 300 µL $min^{-1}$ | 80 ºC | 85.1 | 0.4 | 87.1 | 0.9 | 311.9 | 0.2 | 20.1 | 3.7 | 91.7 | 0.3 | 80.1 | 1.8 | 676.0 | 1.2 |
| 2 | 85% | 300 µL $min^{-1}$ | 79 ºC | 84.0 | 1.5 | 82.3 | 1.8 | 305.2 | 0.2 | 20.0 | 3.1 | 90.7 | 0.8 | 78.0 | 1.4 | 660.2 | 1.5 |
| 3 | 85% | 300 µL $min^{-1}$ | 81 ºC | 85.4 | 1.0 | 86.7 | 2.9 | 313.6 | 0.8 | 21.3 | 2.2 | 92.1 | 2.2 | 77.1 | 1.8 | 676.2 | 1.8 |
| 4 | 84% | 300 µL $min^{-1}$ | 80 ºC | 82.1 | 1.2 | 82.6 | 1.9 | 306.8 | 0.6 | 23.1 | 1.6 | 82.7 | 2.5 | 73.8 | 1.9 | 651.1 | 1.6 |
| 5 | 86% | 300 µL $min^{-1}$ | 80 ºC | 84.9 | 0.1 | 80.7 | 1.3 | 307.5 | 1.0 | 22.9 | 1.6 | 90.0 | 0.8 | 78.9 | 2.5 | 664.9 | 1.2 |
| 6 | 85% | 290 µL $min^{-1}$ | 80 ºC | 84.8 | 1.1 | 83.3 | 1.6 | 324.0 | 0.9 | 20.2 | 3.6 | 88.8 | 2.3 | 77.3 | 1.5 | 678.3 | 1.8 |
| 7 | 85% | 310 µL $min^{-1}$ | 80 ºC | 83.9 | 1.2 | 86.6 | 1.2 | 305.4 | 1.1 | 19.8 | 5.4 | 82.9 | 1.6 | 73.6 | 1.2 | 652.1 | 1.9 |

**Table S67. PR and respective IP results for all runs (n = 2) of the robustness screening model based on Fractional Factorial Design (3^3-level factors).**

| Run Number | Factor (CMP) | | | GLU | | FRU | | SUC | | RHA | | XYL | | MAN | | Sum | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Acetone Content (1) | Column Flow (2) | Column Temperature (3) | Peak Resolution | RSD (%) | Peak Resolution | RSD (%) | Peak Resolution | RSD (%) | Peak Resolution | RSD (%) | Peak Resolution | RSD (%) | Peak Resolution | RSD (%) | Peak Resolution | Mean RSD (%) |
| 1 | 85% | 300 µL $min^{-1}$ | 80 ºC | 3.0 | 0.7 | 4.2 | 0.7 | 3.3 | 1.1 | 3.5 | 0.3 | 2.6 | 0.8 | 1.1 | 1.4 | 2.9 | 0.8 |
| 2 | 85% | 300 µL $min^{-1}$ | 79 ºC | 2.6 | 0.9 | 4.1 | 0.2 | 3.3 | 1.1 | 3.2 | 0.5 | 2.4 | 1.0 | 1.1 | 1.9 | 2.8 | 0.9 |
| 3 | 85% | 300 µL $min^{-1}$ | 81 ºC | 2.7 | 0.6 | 4.1 | 0.6 | 3.3 | 0.7 | 3.3 | 0.8 | 2.6 | 1.4 | 1.1 | 2.2 | 2.9 | 1.0 |
| 4 | 84% | 300 µL $min^{-1}$ | 80 ºC | 2.5 | 0.8 | 3.8 | 0.3 | 3.2 | 1.4 | 3.2 | 0.2 | 2.4 | 0.8 | 1.1 | 1.8 | 2.7 | 0.9 |
| 5 | 86% | 300 µL $min^{-1}$ | 80 ºC | 2.9 | 0.9 | 4.3 | 0.5 | 3.3 | 0.8 | 3.3 | 0.8 | 2.6 | 1.9 | 1.2 | 0.9 | 2.9 | 0.9 |
| 6 | 85% | 290 µL $min^{-1}$ | 80 ºC | 2.8 | 0.5 | 4.1 | 0.1 | 3.4 | 0.6 | 3.4 | 0.1 | 2.4 | 0.2 | 1.1 | 1.9 | 2.9 | 0.6 |
| 7 | 85% | 310 µL $min^{-1}$ | 80 ºC | 3.0 | 0.8 | 4.2 | 0.5 | 3.5 | 1.3 | 3.5 | 0.3 | 2.5 | 0.0 | 1.1 | 3.6 | 3.0 | 1.1 |

**Table S68. ASY and respective IP results for all runs (n = 2) of the robustness screening model based on Fractional Factorial Design (3^3-level factors).**

| Run Number | Factor (CMP) | | | GLU | | FRU | | SUC | | RHA | | XYL | | MAN | | Sum | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Acetone Content (1) | Column Flow (2) | Column Temperature (3) | Peak Asymmetry | RSD (%) | Peak Asymmetry | RSD (%) | Peak Asymmetry | RSD (%) | Peak Asymmetry | RSD (%) | Peak Asymmetry | RSD (%) | Peak Asymmetry | RSD (%) | Peak Asymmetry | Mean RSD (%) |
| 1 | 85% | 300 µL $min^{-1}$ | 80 ºC | 1.1 | 0.9 | 1.1 | 0.5 | 1.0 | 0.5 | 1.0 | 0.5 | 1.1 | 0.5 | 1.0 | 1.0 | 1.0 | 0.6 |
| 2 | 85% | 300 µL $min^{-1}$ | 79 ºC | 1.2 | 0.8 | 1.1 | 2.3 | 1.0 | 4.1 | 1.0 | 1.0 | 1.2 | 0.4 | 1.0 | 0.5 | 1.1 | 1.5 |
| 3 | 85% | 300 µL $min^{-1}$ | 81 ºC | 1.2 | 0.0 | 1.1 | 0.0 | 1.0 | 0.5 | 1.0 | 1.0 | 1.2 | 0.4 | 1.0 | 1.0 | 1.1 | 0.5 |
| 4 | 84% | 300 µL $min^{-1}$ | 80 ºC | 1.1 | 0.0 | 1.1 | 0.9 | 1.2 | 3.0 | 1.1 | 0.9 | 1.1 | 0.5 | 1.0 | 1.0 | 1.1 | 1.1 |
| 5 | 86% | 300 µL $min^{-1}$ | 80 ºC | 1.1 | 0.9 | 1.0 | 1.9 | 0.9 | 1.6 | 1.1 | 0.5 | 1.1 | 0.5 | 1.0 | 0.5 | 1.0 | 1.0 |
| 6 | 85% | 290 µL $min^{-1}$ | 80 ºC | 1.2 | 0.4 | 1.1 | 1.4 | 1.2 | 0.8 | 1.0 | 0.5 | 1.2 | 0.4 | 1.0 | 0.0 | 1.1 | 0.6 |
| 7 | 85% | 310 µL $min^{-1}$ | 80 ºC | 1.1 | 1.8 | 1.0 | 0.5 | 1.0 | 1.0 | 1.0 | 0.5 | 1.0 | 0.5 | 1.1 | 1.4 | 1.0 | 1.0 |

**Table S69. Verification data of method robustness through analysis of agreement between the predicted and observed values.**

| Sugars | Total Peak Area | | | | | Peak Resolution | | | | | Peak Asymmetry | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Observed Value 1 | Observed Value 2 | Predicted Value | 95% CI[a] Low | 95% CI[a] High | Observed Value 1 | Observed Value 2 | Predicted Value | 95% CI[a] Low | 95% CI[a] High | Observed Value 1 | Observed Value 2 | Predicted Value | 95% CI[a] Low | 95% CI[a] High |
| GLU | 85.4 | 84.8 | 85.1 | 83.1 | 87.2 | 3.05 | 3.01 | 3.03 | 2.98 | 3.08 | 1.10 | 1.12 | 1.11 | 1.09 | 1.13 |
| FRU | 87.9 | 86.3 | 87.1 | 83.6 | 90.6 | 4.15 | 4.21 | 4.18 | 4.13 | 4.23 | 1.07 | 1.06 | 1.07 | 1.03 | 1.10 |
| SUC | 312.5 | 311.2 | 311.9 | 306.2 | 317.6 | 3.28 | 3.35 | 3.32 | 3.23 | 3.40 | 0.99 | 0.98 | 0.99 | 0.93 | 1.04 |
| XYL | 91.5 | 92.0 | 91.7 | 88.2 | 95.2 | 2.57 | 2.53 | 2.55 | 2.49 | 2.61 | 1.09 | 1.10 | 1.10 | 1.08 | 1.11 |
| MAN | 81.6 | 78.6 | 80.1 | 76.8 | 83.4 | 1.09 | 1.12 | 1.11 | 1.05 | 1.16 | 1.01 | 1.03 | 1.02 | 1.00 | 1.04 |
| Sum/Mean | 658.9 | 653.0 | 655.9 | 645.8 | 666.1 | 2.83 | 2.84 | 2.84 | 2.81 | 2.87 | 1.05 | 1.06 | 1.06 | 1.04 | 1.07 |

[a]CI - Confidence interval.

**Table S70. Mean concentration values of sugars found in SCH samples by USA-LLE/HPLC-RI.**

| Samples | FRU | | GLU | | SUC | |
|---|---|---|---|---|---|---|
| | Conc. Mean (g $Kg^{-1}$)[a] | RSD (%) | Conc. Mean (g $Kg^{-1}$)[a] | RSD (%) | Conc. Mean (g $Kg^{-1}$)[a] | RSD (%) |
| FRS16 | 163,9 | 0,7 | 152,8 | 0,7 | 303,5 | 0,6 |
| FRS17 | 168,9 | 3,2 | 151,1 | 1,4 | 307,0 | 1,2 |
| FRS18 | 173,4 | 0,5 | 164,0 | 0,2 | 304,7 | 0,7 |

a Average values (n = 3).

**Table S71. ID replicate number, ID replicate code, ID sample code, ID group code, processing year, processing type, geographic origin and regional certification of SC-based syrups samples.**

| ID Replicate Number | ID Replicate Code | ID Sample Code | ID Group Code | Processing Year | Processing Type | Geographic Origin | Regional Certification |
|---|---|---|---|---|---|---|---|
| 1 | FRS07A | FRS07 | CERT | 2007 | Industrial | Madeira Island, Portugal, Atlantic Region | Certified |
| 2 | FRS07B | | | | | | |
| 3 | FRS07C | | | | | | |
| 4 | FRS13A | FRS13 | CERT | 2013 | Industrial | Madeira Island, Portugal, Atlantic Region | Certified |
| 5 | FRS13B | | | | | | |
| 6 | FRS13C | | | | | | |
| 7 | FRS14A | FRS14 | CERT | 2014 | Industrial | Madeira Island, Portugal, Atlantic Region | Certified |
| 8 | FRS14B | | | | | | |
| 9 | FRS14C | | | | | | |
| 10 | FRS15A | FRS15 | CERT | 2015 | Industrial | Madeira Island, Portugal, Atlantic Region | Certified |
| 11 | FRS15B | | | | | | |
| 12 | FRS15C | | | | | | |
| 13 | FRS16A | FRS16 | CERT | 2016 | Industrial | | Certified |
| 14 | FRS16B | | | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 15 | FRS16C | | | | | Madeira Island, Portugal, Atlantic Region | |
| 16 | FRS17A | | | | | | |
| 17 | FRS17B | FRS17 | CERT | 2017 | Industrial | Madeira Island, Portugal, Atlantic Region | Certified |
| 18 | FRS17C | | | | | | |
| 19 | FRS18A | | | | | | |
| 20 | FRS18B | FRS18 | CERT | 2018 | Industrial | Madeira Island, Portugal, Atlantic Region | Certified |
| 21 | FRS18C | | | | | | |
| 22 | ECAL14A | | | | | | |
| 23 | ECAL14B | ECAL14 | NCERT | 2014 | Industrial | Madeira Island, Portugal, Atlantic Region | Non-Certified |
| 24 | ECAL14C | | | | | | |
| 25 | ENCAL14A | | | | | | |
| 26 | ENCAL14B | ENCAL14 | NCERT | 2014 | Industrial | Madeira Island, Portugal, Atlantic Region | Non-Certified |
| 27 | ENCAL14C | | | | | | |
| 28 | GLA14A | | | | | | |
| 29 | GLA14B | ECAL16 | NCERT | 2014 | Home-made | Madeira Island, Portugal, Atlantic Region | Non-Certified |
| 30 | GLA14C | | | | | | |
| 31 | ESP16A | | | | | | |
| 32 | ESP16B | ESP16 | MED | 2016 | Industrial | Spain, Mediterranean Region | Not Applicable |
| 33 | ESP16C | | | | | | |
| 34 | EGP17A | | | | | | |
| 35 | EGP17B | EGP17 | MED | 2017 | Industrial | Spain, Mediterranean Region | Not Applicable |
| 36 | EGP17C | | | | | | |
| 37 | EGPA16A | | | | | | |
| 38 | EGPA16B | EGPA16 | MED | 2016 | Industrial | Spain, Mediterranean Region | Not Applicable |
| 39 | EGPA16C | | | | | | |
| 40 | EGPB16A | | | | | | |
| 41 | EGPB16B | EGPB16 | MED | 2016 | Industrial | Spain, Mediterranean Region | Not Applicable |
| 42 | EGPB16C | | | | | | |
| 43 | EGPC16A | | | | | | |
| 44 | EGPC16B | EGPC16 | MED | 2016 | Industrial | Egypt, Mediterranean Region | Not Applicable |
| 45 | EGPC16C | | | | | | |
| 46 | MCBR14A | MCBR14 | STH | 2014 | Industrial | | Not Applicable |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 47 | MCBR14B | | | | | Brazil, Southern Hemisphere Region | |
| 48 | MCBR14C | | | | | | |
| 49 | MDBR14A | | | | | | |
| 50 | MDBR14B | MDBR14 | STH | 2014 | Industrial | Brazil, Southern Hemisphere Region | Not Applicable |
| 51 | MDBR14C | | | | | | |
| 52 | AUS17A | | | | | | |
| 53 | AUS17B | AUS17 | STH | 2017 | Industrial | Australia, Southern Hemisphere Region | Not Applicable |
| 54 | AUS17C | | | | | | |

**Table S72. Calibration functions of SGs for quantification proposes.**

| Sugar | RT (min)[a] | Concentration range (g $L^{-1}$) | Regression equation | Correlation coefficient ($r^2$) |
|---|---|---|---|---|
| GLU | 8.5 | 157.30 - 3.09 | y = -0.00004x2 + 0.1031x + 0.2725 | 0.9980 |
| FRU | 10.4 | 156.44 - 3.04 | y = 0.00002x2 + 0.0895x + 0.2587 | 0.9992 |
| SUC | 14.3 | 178.06 - 7.65 | y = -0.00004x2 + 0.133x + 0.0023 | 0.9993 |

[a] Retention time.

**Table S73. Information summary of PCA and PLS based on the on the concentration values of SGs in SC-based syrup samples.**

| Analysis | Component | $R^2X$ | Eigenvalues | $R^2Y$ | $Q^2$ | Significance | Iterations |
|---|---|---|---|---|---|---|---|
| PCA | 1 | 0.1799 | 3.96 | n.a. | 0.0595 | S | 6 |
| | 2 | 0.0936 | 2.06 | n.a. | 0.0120 | S | 12 |
| PLS | 1 | 0.4233 | 3.39 | 0.0294 | 0.0300 | S | 11 |
| | 2 | 0.2083 | 1.67 | 0.0294 | 0.0251 | S | 15 |

**Table S74. Information summary of PCA, PLS and LDA analysis based on the concentration values of SGs in SC-based syrups.**

| Sugar | ANOVA | | PCA | | | PLS | | | LDA | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | F value[a] | P value[b] | VIP value[c] | Principal Component 1 | Principal Component 2 | VIP value[c] | Partial Least Square 1 | Partial Least Square 2 | Wilks value | F value[a] | P value[b] | Canonical Function 1 | Canonical Function 2 |
| FRU | 183.30 | 1.11E-16 | 0.992 | 0.963 | 0.187 | 0.268 | -0.503 | 0.168 | 0.55 | 13.27 | 2.00E-06 | -0.095 | -0.996 |
| GLU | 268.39 | 2.93E-21 | 0.966 | 0.961 | -0.201 | 0.293 | -0.515 | -0.144 | 0.48 | 17.45 | 8.52E-08 | -0.450 | -0.833 |
| SUC | 72.33 | 4.13E-13 | 0.962 | -0.704 | -0.707 | 0.322 | 0.372 | -0.264 | 0.75 | 5.42 | 2.73E-03 | 0.128 | 0.750 |
| TOTAL | 40.42 | 6.50E-11 | 0.992 | 0.742 | -0.661 | 0.383 | -0.394 | -0.232 | removed[d] | removed[d] | removed[d] | removed[d] | removed[d] |

[a]F Value - Fischer value from One-way ANOVA test.
[b]P Value - Probability value from One-way ANOVA test.
[c]Variable Importance in Projection (VIP) value.
[d]Removed by backward stepwise regression (p > 0,05).
n.a. - not available in Principal Component Analysis.

**Table S75. Loading results of samples and variables from PCA and PLS based on the concentrations of SGs in SC-based syrups samples.**

| ID Sample Code | ID Group Code | PCA | | PLS | |
|---|---|---|---|---|---|
| | | 1 | 2 | 1 | 2 |
| FRS13 | CERT | -0.04 | 0.19 | n.a. | n.a. |
| FRS14 | CERT | 0.00 | 0.10 | n.a. | n.a. |
| FRS15 | CERT | 0.02 | -0.02 | n.a. | n.a. |
| FRS16 | CERT | 0.05 | 0.06 | n.a. | n.a. |
| FRS17 | CERT | 0.06 | 0.04 | n.a. | n.a. |
| FRS18 | CERT | 0.10 | 0.00 | n.a. | n.a. |
| FRS07 | CERT | 0.00 | 0.09 | n.a. | n.a. |
| GLA14 | NCERT | -0.02 | -0.19 | n.a. | n.a. |
| CAL14 | NCERT | 0.04 | -0.05 | n.a. | n.a. |
| NCAL14 | NCERT | -0.51 | -0.07 | n.a. | n.a. |
| MDBR14 | STH | -0.07 | -0.24 | n.a. | n.a. |
| MCBR14 | STH | 0.21 | 0.20 | n.a. | n.a. |
| EGPTA16 | MED | 0.20 | -0.68 | n.a. | n.a. |
| EGPTB16 | MED | 0.23 | -0.01 | n.a. | n.a. |

| | | | | | |
|---|---|---|---|---|---|
| EGPTC16 | MED | -0.05 | -0.31 | n.a. | n.a. |
| EGPT17 | MED | -0.07 | 0.43 | n.a. | n.a. |
| ESP16 | MED | 0.48 | 0.31 | n.a. | n.a. |
| AUS18 | STH | -0.63 | 0.13 | n.a. | n.a. |
| Centroid (CERT) | CERT | n.a. | n.a. | -0.06 | 0.72 |
| Centroid (NCERT) | NCERT | n.a. | n.a. | 0.22 | -0.28 |
| Centroid (MED) | MED | n.a. | n.a. | 0.22 | -0.11 |
| Centroid (STH) | STH | n.a. | n.a. | -0.30 | -0.47 |

**Table S76. Scores results of all cases from PCA and PLS based on the concentrations of SGs in SC-based syrups samples.**

| ID Sample Number | ID Sample Code | PCA | | PLS | |
|---|---|---|---|---|---|
| | | 1 | 2 | 1 | 2 |
| 1 | FRS13A | -0.24 | 1.00 | 0.10 | 1.61 |
| 2 | FRS13B | -0.31 | 1.16 | 0.17 | 1.69 |
| 3 | FRS13B | -0.35 | 1.18 | 0.21 | 1.70 |
| 4 | FRS14A | -0.08 | 0.62 | 0.00 | 1.55 |
| 5 | FRS14B | 0.04 | 0.50 | -0.12 | 1.48 |
| 6 | FRS14C | -0.07 | 0.69 | -0.01 | 1.58 |
| 7 | FRS15A | 0.20 | -0.17 | -0.24 | 1.33 |
| 8 | FRS15B | 0.13 | -0.11 | -0.17 | 1.35 |
| 9 | FRS15C | 0.11 | -0.01 | -0.14 | 1.40 |
| 10 | FRS16A | 0.38 | 0.37 | -0.37 | 1.48 |
| 11 | FRS16B | 0.46 | 0.29 | -0.44 | 1.44 |
| 12 | FRS16C | 0.31 | 0.43 | -0.29 | 1.51 |
| 13 | FRS17A | 0.63 | 0.11 | -0.60 | 1.41 |
| 14 | FRS17B | 0.37 | 0.31 | -0.33 | 1.49 |
| 15 | FRS17C | 0.39 | 0.32 | -0.35 | 1.50 |
| 16 | FRS18A | 0.87 | 0.01 | -0.75 | 1.40 |
| 17 | FRS18B | 0.91 | -0.07 | -0.79 | 1.36 |
| 18 | FRS18C | 0.77 | 0.08 | -0.64 | 1.43 |
| 19 | FRS07A | 0.04 | 0.42 | -0.11 | 1.51 |
| 20 | FRS07B | -0.03 | 0.54 | -0.04 | 1.55 |

| | | | | | |
|---|---|---|---|---|---|
| 21 | FRS07C | -0.07 | 0.58 | 0.00 | 1.58 |
| 22 | GLA14A | -0.01 | -1.33 | 0.59 | -1.26 |
| 23 | GLA14B | -0.18 | -0.91 | 0.76 | -1.03 |
| 24 | GLA14C | -0.20 | -1.01 | 0.78 | -1.09 |
| 25 | CAL14A | 0.40 | -0.49 | 0.28 | -0.97 |
| 26 | CAL14B | 0.29 | -0.24 | 0.40 | -0.87 |
| 27 | CAL14C | 0.29 | -0.22 | 0.40 | -0.85 |
| 28 | NCAL14A | -4.09 | -0.28 | 3.75 | -0.97 |
| 29 | NCAL14B | -4.12 | -0.57 | 3.78 | -1.13 |
| 30 | NCAL14C | -4.12 | -0.28 | 3.79 | -0.97 |
| 31 | MDBR14A | -0.48 | -1.67 | 0.96 | -0.99 |
| 32 | MDBR14B | -0.59 | -1.25 | 1.07 | -0.78 |
| 33 | MDBR14C | -0.63 | -1.34 | 1.12 | -0.83 |
| 34 | MCBR14A | 1.69 | 1.28 | -0.67 | 0.00 |
| 35 | MCBR14B | 1.81 | 1.02 | -0.79 | -0.12 |
| 36 | MCBR14C | 1.68 | 1.27 | -0.66 | 0.01 |
| 37 | EGPTA16A | 1.90 | -4.07 | -2.17 | -2.23 |
| 38 | EGPTA16B | 1.50 | -3.96 | -1.75 | -2.18 |
| 39 | EGPTA16C | 1.57 | -3.88 | -1.82 | -2.14 |
| 40 | EGPTB16A | 2.11 | -0.28 | -2.33 | -1.32 |
| 41 | EGPTB16B | 1.76 | 0.06 | -1.96 | -1.13 |
| 42 | EGPTB16C | 1.80 | 0.01 | -2.00 | -1.17 |
| 43 | EGPTC16A | -0.51 | -1.72 | -0.22 | -1.64 |
| 44 | EGPTC16B | -0.27 | -2.01 | -0.47 | -1.77 |
| 45 | EGPTC16C | -0.45 | -1.71 | -0.29 | -1.62 |
| 46 | EGPT17A | -0.47 | 2.62 | -0.31 | -0.42 |
| 47 | EGPT17B | -0.67 | 2.34 | -0.09 | -0.59 |
| 48 | EGPT17C | -0.67 | 2.57 | -0.10 | -0.47 |
| 49 | ESP16A | 3.90 | 1.74 | -3.64 | -0.67 |
| 50 | ESP16B | 3.98 | 1.79 | -3.73 | -0.63 |
| 51 | ESP16C | 3.74 | 1.93 | -3.48 | -0.57 |
| 52 | AUS18A | -5.09 | 0.49 | 4.53 | -0.47 |
| 53 | AUS18B | -5.16 | 0.97 | 4.61 | -0.23 |

| | | | | | |
|---|---|---|---|---|---|
| 54 | AUS18C | -5.15 | 0.88 | 4.59 | -0.27 |

**Table S77. CDF Coefficients and Highest Probability Classification results of samples from LDA based on the concentrations of SGs in SC-based syrups samples**.

| ID Replicate Code | ID Group Code | LDA | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | CDF[1] | | | CDF[1] Class Means | | | Highest Probability Classification | | |
| | | 1 | 2 | 3 | 1 | 2 | 3 | First | Second | Third |
| FRS13A | | 0.9 | -0.2 | -0.5 | | | | CERT | CERT | NCERT |
| FRS13B | | 0.7 | -0.1 | -0.8 | | | | CERT | CERT | NCERT |
| FRS13B | | 0.5 | -0.1 | -0.8 | | | | CERT | CERT | STH |
| FRS14A | | 0.7 | -0.2 | -0.3 | | | | CERT | CERT | NCERT |
| FRS14B | | 0.6 | -0.2 | -0.2 | | | | CERT | CERT | NCERT |
| FRS14C | | 0.7 | -0.2 | -0.4 | | | | CERT | CERT | NCERT |
| FRS15A | | 1.0 | -0.4 | 0.4 | | | | CERT | CERT | NCERT |
| FRS15B | | 0.9 | -0.3 | 0.3 | | | | CERT | CERT | NCERT |
| FRS15C | | 0.5 | -0.2 | 0.0 | | | | CERT | CERT | NCERT |
| FRS16A | | 0.5 | -0.4 | -0.1 | | | | CERT | CERT | NCERT |
| FRS16B | CERT | 0.6 | -0.5 | 0.0 | 0.9 | -0.4 | -0.1 | CERT | CERT | NCERT |
| FRS16C | | 0.4 | -0.3 | -0.3 | | | | CERT | CERT | NCERT |
| FRS17A | | 1.5 | -0.8 | 0.4 | | | | CERT | CERT | NCERT |
| FRS17B | | 0.8 | -0.4 | -0.1 | | | | CERT | CERT | NCERT |
| FRS17C | | 1.0 | -0.5 | -0.1 | | | | CERT | CERT | NCERT |
| FRS18A | | 0.6 | -0.7 | 0.2 | | | | CERT | CERT | NCERT |
| FRS18B | | 0.7 | -0.7 | 0.3 | | | | CERT | CERT | NCERT |
| FRS18C | | 0.5 | -0.6 | 0.1 | | | | CERT | CERT | NCERT |
| FRS07A | | 2.9 | -0.8 | 0.3 | | | | CERT | CERT | NCERT |
| FRS07B | | 2.0 | -0.6 | 0.0 | | | | CERT | CERT | NCERT |
| FRS07C | | 2.1 | -0.6 | 0.0 | | | | CERT | CERT | NCERT |
| GLA14A | | 0.2 | 0.1 | 1.1 | | | | NCERT | CERT | NCERT |
| GLA14B | NCERT | 0.3 | 0.1 | 0.5 | 0.6 | 0.7 | 0.4 | NCERT | CERT | NCERT |
| GLA14C | | 0.1 | 0.2 | 0.6 | | | | NCERT | CERT | NCERT |
| CAL14A | | 1.4 | -0.5 | 0.8 | | | | NCERT | CERT | NCERT |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| CAL14B | | 0.2 | -0.2 | 0.2 | | | | NCERT | CERT | NCERT |
| CAL14C | | 0.8 | -0.4 | 0.3 | | | | NCERT | CERT | NCERT |
| NCAL14A | | 1.0 | 2.1 | -0.1 | | | | NCERT | NCERT | STH |
| NCAL14B | | 0.7 | 2.3 | 0.2 | | | | NCERT | NCERT | STH |
| NCAL14C | | 0.7 | 2.2 | -0.2 | | | | NCERT | NCERT | STH |
| MDBR14A | | -1.8 | 1.0 | 0.9 | | | | STH | MED | STH |
| MDBR14B | | -2.6 | 1.2 | 0.2 | | | | STH | MED | STH |
| MDBR14C | | -2.3 | 1.1 | 0.4 | | | | STH | MED | STH |
| MCBR14A | | 0.5 | -1.3 | -0.7 | | | | STH | CERT | MED |
| MCBR14B | STH | 0.9 | -1.4 | -0.2 | -0.3 | 0.8 | -0.3 | STH | CERT | NCERT |
| MCBR14C | | 0.8 | -1.3 | -0.6 | | | | STH | CERT | NCERT |
| AUS18A | | 0.9 | 2.7 | -0.5 | | | | STH | NCERT | STH |
| AUS18B | | 0.3 | 2.8 | -1.3 | | | | STH | STH | NCERT |
| AUS18C | | 0.4 | 2.8 | -1.2 | | | | STH | STH | NCERT |
| EGPTA16A | | -0.5 | -0.5 | 3.0 | | | | MED | MED | NCERT |
| EGPTA16B | | -0.5 | -0.3 | 2.8 | | | | MED | MED | NCERT |
| EGPTA16C | | -0.7 | -0.3 | 2.7 | | | | MED | MED | NCERT |
| EGPTB16A | | -3.5 | -0.3 | -0.1 | | | | MED | MED | STH |
| EGPTB16B | | -3.2 | -0.2 | -0.6 | | | | MED | MED | STH |
| EGPTB16C | | -3.5 | -0.1 | -0.5 | | | | MED | MED | STH |
| EGPTC16A | | -1.8 | 1.0 | 0.7 | | | | MED | MED | STH |
| EGPTC16B | MED | -0.8 | 0.6 | 1.4 | -1.5 | -0.3 | 0.1 | MED | MED | NCERT |
| EGPTC16C | | -1.3 | 0.8 | 0.8 | | | | MED | MED | STH |
| EGPT17A | | 0.3 | -0.2 | -1.9 | | | | MED | CERT | STH |
| EGPT17B | | -0.1 | 0.2 | -1.6 | | | | MED | STH | CERT |
| EGPT17C | | -0.1 | 0.1 | -1.9 | | | | MED | CERT | STH |
| ESP16A | | -2.2 | -1.9 | -1.1 | | | | MED | MED | CERT |
| ESP16B | | -2.1 | -2.0 | -1.2 | | | | MED | MED | CERT |
| ESP16C | | -2.2 | -1.8 | -1.4 | | | | MED | MED | STH |

[1]CDF - Canonical Discriminant Function Coefficients.