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Volatile profile of Madeira wines submitted to traditional accelerated ageing

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ABSTRACT

The evolution of monovarietal fortified Madeira wines forced-aged by traditional thermal processing (*estufagem*) were studied in terms of volatiles. SPE extracts were analysed by GC–MS before and after heating at 45 °C for 3 months (standard) and at 70 °C for 1 month (overheating). One hundred and ninety volatile compounds were identified, 53 of which were only encountered in baked wines. Most chemical families increased after standard heating, especially furans and esters, up to 61 and 3-fold, respectively. On the contrary, alcohols, acetates and fatty acids decreased after heating. Varietal aromas, such as Malvasia's monoterpenic alcohols were not detected after baking. The accelerated ageing favoured the development of some volatiles previously reported as typical aromas of finest Madeira wines, particularly phenylacetaldeyde, β-damascenone and 5-ethoxymethylfurfural. Additionally, ethyl butyrate, ethyl 2-methylbutyrate, ethyl caproate, ethyl isovalerate, guaiacol, 5-hydroxymethylfurfural and γ-decalactone were also found as potential contributors to the global aroma of baked wines.

1. Introduction

Flavour is one of the most significant factors of wine quality, determining the consumer acceptance or rejection. Generally speaking, the aroma of wines is influenced by several different compounds, originated from grapes or resulting from winemaking, ageing and storage. In fact, these compounds act as a fingerprint of each type of wine. In some cases, the occurrence of a particular compound is enough to give the characteristic aroma of a wine (Polaskova, Herszage, & Ebeler, 2008).

Madeira wine is a well-known fortified wine distinguished for its superior quality and it is characterised by marked and intense flavours (V. Pereira, 2011). Its winemaking can include a peculiar maturation process, a heating step known as *estufagem*. This step consists of heating the fortified wine to about 45 °C, for at least 3 months. Then, the oxidative ageing goes further, since wine is placed in wooden casks (regularly used casks), for at least 3 years. A premature ageing takes place along with heating, being acquired some of the aroma characteristics considered typical of the finest Madeiras (older wines only matured in oak casks for several years).

It is well known that heating promotes important changes in the aroma of foods. Up to date, there are some studies dealing with the accelerated oxidative ageing, promoted by thermal processing, on the volatile profile of wines. Deibner and Bernard, in 1956, as referenced by Cutzach, Chatonnet, and Dubourdieu (1999), studied the effect of heat treatment on wine, pointing out the important role of Maillard reactions in the formation of the aroma of thermally processed sweet fortified wines, but at that time, they were unable to identify the respective compounds. Cutzach et al. (1999) investigated the ageing of red and white sweet fortified wines (*Vins doux Naturels*) following an experimental laboratory study, in which, wines were forced-aged through heating at 37 °C for 12 months. Among the developed molecules during the accelerated ageing, the same authors found that sotolon (3-hydroxy-4,5-dimethyl-2(5H)-furanone), 5-ethoxymethylfurfural, 5-hydroxymethylfurfural (HMF), furfural acetylformoin and hydroxymaltol were involved in the aroma of sweet fortified wines. Sotolon has also been considered as a key odorant of the typical aroma of oxidative aged Port wine (Silva Ferreira, Barbe, & Bertrand, 2003). Escudero, Cacho, and Ferreira (2000) also performed studies dealing with wine oxidative ageing, through laboratory-oxidised samples at 20 °C for several weeks. According to olfactometric studies (GC-O analysis), they found that the impact odorants of oxidised white wines were essentially 2,4,5-trimethyldioxolane, methional, sotolon and eugenol. Changes in

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the volatile content of Fino Sherry wines, exposed to heating (45 °C) and UV–Vis radiation, have also been reported (Benítez, Castro, Natera, & Barroso, 2006). These experiments revealed the decrease of most esters, acids and alcohols, and the increase of furfural and benzaldehyde. López de Lerma, Peinado, Moreno, and Peinado (2010) thermally processed sweet Pedro Ximénez wines at 65 °C for up to 30 days and reported the increase of volatile Maillard products, specifically of HMF, 5-ethoxymethylfurfural, dihydromaltol, 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one (DDMP), 2-methyltetrahydrofuran-3-one, furaneol, dihydro-2-methyl-3(2H)-furanone and cyclotene. Loscos, Hernández-Orte, Cacho, and Ferreira (2010) reported that accelerated ageing, at 50 °C for 9 weeks, of wines supplemented with grape flavour precursors also introduced important changes in the volatile composition. The same study showed that the main differences were observed in the first week of accelerated ageing. Most compounds first showed a significant increase and later a steady reduction, including Riesling acetal, 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), and (*E*)-1-(2,3,6-trimethylphenyl)buta-1,3-diene (TPB). However, vanillin derivatives, furan linalool oxides, 3-oxo-β-ionone, actinidols, 4-ethylphenol, and guaiacol showed a continuous increase during the ageing process.

Fedrizzi et al. (2011) studied the effect of accelerated ageing (30 °C for 60 days) on the fermentative, varietal and sulfur compounds of a dry red Botrytis Amarone wine and found out that benzaldehyde, phenylacetaldehyde, syringaldehyde and vanillin showed a perceptible increase, while several sulfur compounds disappeared after just 15 days, under oxidative conditions. They also tentatively identified methionol-S-oxide for the first time in this kind of wine. More recently, Cejudo-Bastante, Hermosín-Gutiérrez, and Pérez-Coello (2013) also compared accelerated ageing (50 °C during 7 days) with conventional storage (18 °C) analysing the volatile composition of Chardonnay white wines. They concluded that dioxanes, dioxolanes, and TDN were developed while some alcohols, terpenes, and furanic compounds disappear with accelerated ageing. Moreover, their results demonstrated that *β*-damascenone and TDN levels were quite higher in the accelerated-aged wine.

In the case of Madeira wines, which are traditionally forced-aged, few studies were done regarding the effect of the baking step on their volatile profile. The first study, carried out by Oliveira e Silva et al. (2008) was based on GC-O analysis and highlighted the occurrence of particular volatiles that imparted notes considered typical of finest Madeiras bouquet. Those volatiles were identified as sotolon, furfural, 5-methylfurfural, 5-ethoxymethylfurfural, methional, and phenylacetaldehyde.

The aim of the current work is to study the impact of *estufagem* on the global GC–MS volatile profile of Madeira wines, focusing to a large extent on individual volatile compounds, namely some that are barely reported in Madeira wines, in order to highlight the global ageing process. For this purpose, three young Madeira wines: dry Tinta Negra (TN, red variety), sweet TN and sweet Malvasia (white variety) were heated at 45 °C for 3 months. Additionally, overheating conditions, 70 °C for 1 month, were also studied to force the development of heating-specific volatiles.

2. Experimental

2.1. Wine samples

Three Madeira wines from two *Vitis vinifera* L. grape varieties of 2007 harvest were studied: dry TN, sweet TN and sweet Malvasia. The wines were produced using the winemaking practices of a Madeira wine producer. The elaboration of these wines was conducted in separated stainless steel tanks. The alcoholic fermentation was conducted under controlled temperature and without adding any commercial yeast. The fermentation for TN sweet wine was stopped adding alcohol (95% v/v) when the must specific gravity attained 1.025 g/mL, which corresponded to 115 g/L of reducing sugars in the wine, while for TN dry it was allowed to reach a specific gravity of 0.986 g/mL before fortification, allowing a low level of residual sugars in the wine (about 4 g/L). Malvasia sweet wine must was fermented up to 1.019 g/mL, keeping the reducing sugars at 96 g/L. After post-fermentation treatments, each wine was heated at 45 °C for 3 months in a special pilot scale system, equipped with 200-L stainless steel tanks, fitted with heat coils that allow hot water to circulate inside the container. To force the development of volatiles specific from overheating, each wine was also submitted to 70 °C for 1 month (overheating conditions). All samples were kept at −20 °C before being analysed.

2.2. Chemicals

All reagents were of analytical grade. Dichloromethane HPLC-grade was from Fisher Scientific (Loughborough, UK) while absolute ethanol was supplied by Sigma–Aldrich (St. Louis, MO). Ultra-pure water was obtained from a Milli-Q system (Millipore, Milford, MA). Solid anhydrous sodium sulfate was from JMGS (Lisbon, Portugal) while the 3-octanol standard was from Sigma–Aldrich. LiChrolut EN resin was supplied by Merck Co. (Darmstadt, Germany), while the 6-mL polypropylene cartridges and respective frits were obtained from Supelco (Bellefonte, PA). Solid-phase extraction was carried out in a 12-port Visiprep™ SPE vacuum manifold from Supelco.

2.3. Sample extraction

The screening of volatiles was accomplished based on the solid-phase extraction (SPE) method proposed by López, Aznar, Cacho, and Ferreira (2002). Briefly, 120 mg of LiChrolut EN resin were packed in a 6-mL cartridge. After conditioning the resin, in the SPE station, with 4 mL of dichloromethane, 4 mL of methanol and 4 mL of ethanolic solution (18%, v/v), 50 mL of wine spiked with 25 μL of 3-octanol (491 mg/L) were passed through the resin at about 2 mL/min. Then, the sorbent was dried by passing a small flow of air through it for 15 min. Finally, wine volatiles were eluted with 1.3 mL of dichloromethane and the extract dried with sodium sulfate, being kept at −20 °C until analysis. All samples were extracted in duplicate.

2.4. GC–MS analysis

The extracts were analysed using a TRACE GC Ultra gas chromatograph equipped with the ISQ single quadrupole (electron impact mode) and the TriPlus autosampler (liquid mode) from Thermo Scientific (Hudson, NH). One microlitre of extract was vaporised in the injector port at 230 °C in splitless mode (1 min). All extracts were injected twice. The column was a DB-WAXetr 30 m × 0.32 mm with 0.5 μm film thickness from Agilent J&W (Folsom, CA) and the carrier gas was He at 1 mL/min. The ionisation voltage was 70 eV with transfer line and ion source temperatures kept at 230 and 240 °C, respectively. The oven temperature program started at 40 °C for 5 min then increased up to 230 °C at 3 °C/min and finally was kept at 230 °C for 15 min. The m/z 30–400 mass range was recorded.

The identification of compounds was made by comparison of the mass spectra obtained with those present in NIST08 and Wiley 6.0 MS library databases, and comparing the obtained Kovats indexes with those stated on NIST Chemistry WebBook (Stein, 2008). The compounds, namely those that were only identified comparing the obtained mass spectra with those present in the

MS library databases, were just considered when a fair match was achieved (>70%). A C_7–C_{30} *n*-alkanes mixture (Supelco) was used to calculate the Kovats indexes. 3-Octanol was added to each sample as internal standard (IS). The amount of each volatile compound was estimated, semi-quantitatively, regarding the added amount of IS (246 μg/L) and the relative concentrations of the investigated compounds were measured as follows:

Semi-quantitative concentrations = (peak area/IS peak area) × IS concentration. The coefficient of variation (% CV) was on average 7%.

3. Results and discussion

Typical chromatograms of the current Madeira wine extracts are depicted in Fig. 1. Table 1 summarises the data of the volatile compounds encountered in the studied Madeira wines, before and after the heating at standard (45 °C for 3 months) and overheating (70 °C for 1 month) conditions. The concentrations given in Table 1 are rough estimates, but still give an idea of which order of magnitude the compounds are sensorially active and information about the evolution of each compound with heating.

The GC–MS analyses of the current sample set allowed the identification of 190 volatile compounds, including 42 esters, 29 alcohols, 18 carbonyl compounds, 19 volatile phenols, 17 fatty acids, 15 furan compounds, 15 monoterpenes, 8 acetals, 7 lactones, 4 sulfur compounds, 6 norisoprenoids and 10 other compounds. At least 171 other compounds could not be identified by the regular strategies and will require specific methods of isolation and characterisation.

The current study also revealed that a large number of compounds were developed during the traditional heating of Madeira wines (Fig. 2); 53 of the identified compounds were exclusively found in baked wines. The results showed that young TN dry wine presented the highest fraction of volatiles, about 52 mg/L (before heating), which is in agreement with the fermentation degree, essentially due to the higher levels of esters and higher alcohols

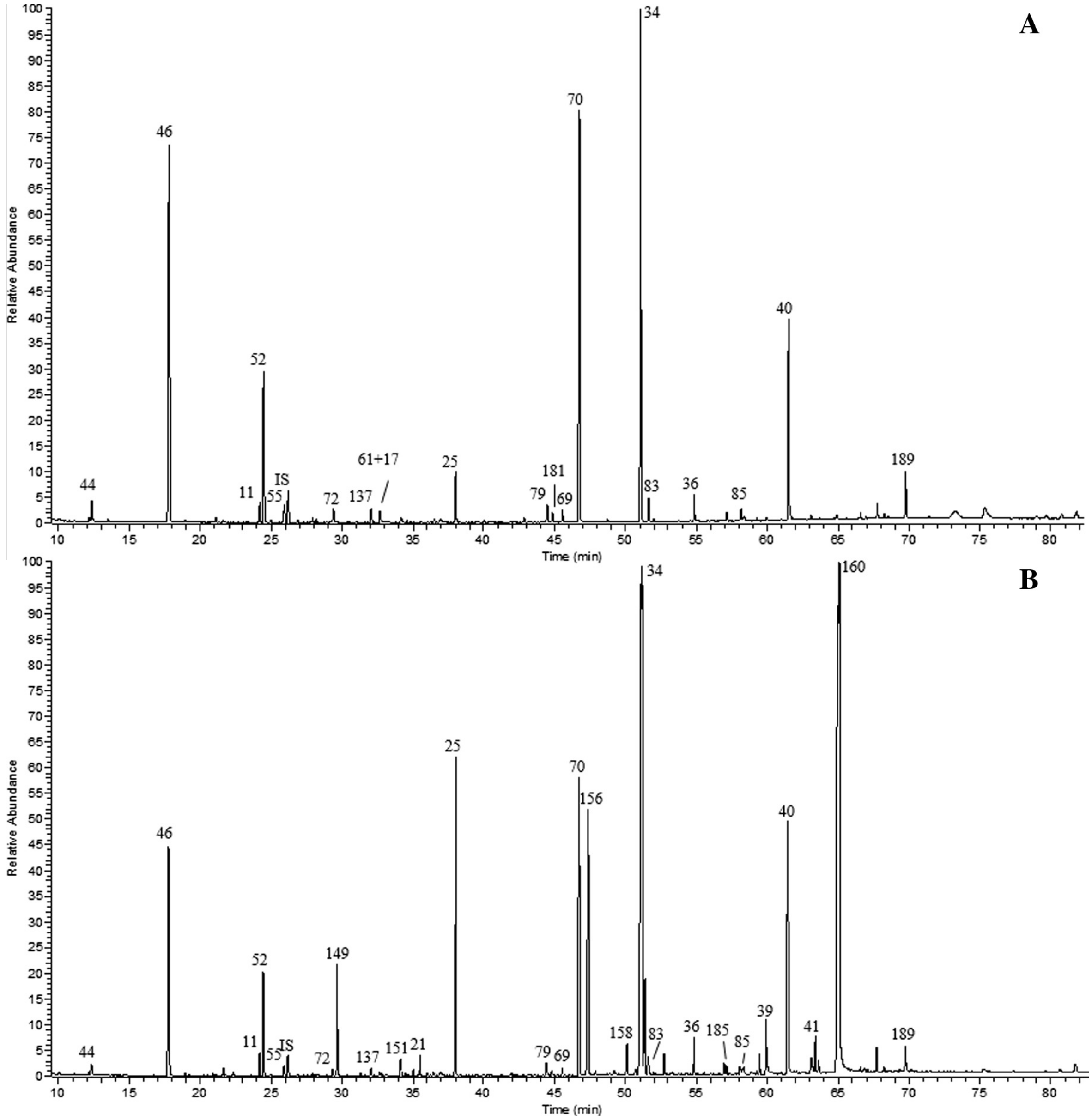

Fig. 1. Typical chromatograms of the current Madeira wine extracts. Here is presented the corresponding chromatograms of sweet TN wine before (A) and after (B) heating at 70 °C for 1 month. For peak identification see Table 1. Only the major peaks are highlighted.

Table 1
Volatile compounds identified in TN sweet, TN dry and Malvasia wines before and after the heating at 45 °C (3 months) and 70 °C (1 month).

#	Compounds	KI	TN sweet (μg/L)						TN dry (μg/L)						Malvasia (μg/L)						Common descriptors[a]
			0 m	±SD	3 m, 45 °C	±SD	1 m, 70 °C	±SD	0 m	±SD	3 m, 45 °C	±SD	1 m, 70 °C	±SD	0 m	±SD	3 m, 45 °C	±SD	1 m, 70 °C	±SD	
	Esters (42)																				
1	Ethyl butyrate*	1053	6.2	0.2	9.5	0.5	11.5	0.5	19.2	1.3	**27.5**	**0.6**	**52.7**	**20.8**	4.8	0.3	7.8	0.1	9.5	0.3	Fruity
2	Monomethyl succinate***	1062	n.d.		n.d.		n.d.		n.d.		n.d.		28.6	8.7	n.d.		n.d.		n.d.		–
3	Ethyl methylbutyrate**	1069	n.d.		n.d.		n.d.		n.d.		8.4	0.4	**25.3**	**8.5**	n.d.		n.d.		6.7	1.0	Fruity
4	Ethyl isovalerate*	1085	n.d.		n.d.		**6.9**	**1.0**	n.d.		**14.1**	**0.8**	**47.5**	**18.4**	n.d.		**4.3**	**0.4**	**9.2**	1.3	Fruity, apple
5	Isoamyl acetate*	1141	10.6	0.3	3.1	0.5	n.d.		91.7	5.0	19.8	1.9	22.2	0.2	16.1	1.5	4.3	0.6	n.d.		Banana
6	Ethyl caproate*	1251	**25.7**	**0.5**	**30.0**	**1.7**	**37.4**	**2.6**	**96.6**	**5.4**	**96.4**	**2.4**	**150.8**	**3.5**	**33.0**	**3.5**	**43.8**	**0.6**	**48.9**	**1.7**	Fruity
7	Hexyl acetate*	1289	2.9	0.2	n.d.		n.d.		6.7	0.6	n.d.		n.d.		3.0	0.4	0.0	0.0	n.d.		Fruity, pear
8	Ethyl pyruvate*	1293	10.9	0.2	10.8	0.6	28.3	0.9	26.4	0.9	27.9	0.8	20.7	1.4	34.4	0.1	26.6	1.0	39.0	1.1	Herbaceous, oil painting
9	Ethyl 3-hexenoate**	1320	n.d.		n.d.		n.d.		n.d.		2.8	0.5	n.d.		3.1	0.3	3.7	0.4	3.7	0.3	–
10	Ethyl 3-ethoxypropionate*	1354	n.d.		n.d.		7.9	0.3	n.d.		n.d.		n.d.		n.d.		1.8	0.3	8.1	0.3	–
11	Ethyl lactate*	1368	168.2	3.2	251.3	3.0	298.5	3.8	1033.7	15.2	1349.8	29.3	1228.0	34.5	290.1	5.8	381.8	4.7	447.4	9.6	Strawberry, raspberry
12	Ethyl glycolate*	1445	n.d.		5.6	0.4	9.2	0.3	n.d.		4.5	0.4	4.6	0.4	46.8	4.2	12.2	0.8	11.2	0.7	–
13	Ethyl 2-hydroxyisovalerate**	1450	2.2	0.1	6.2	0.1	9.7	0.2	11.3	0.7	34.4	1.8	52.1	0.2	n.d.		21.1	0.3	30.3	0.8	–
14	Ethyl caprylate**	1452	14.3	0.4	12.0	0.7	14.0	1.3	95.9	3.4	57.8	1.3	92.0	2.2	20.1	2.5	30.5	0.6	20.6	0.6	Fruity, apple
15	Isobutyl lactate***	1483	n.d.		n.d.		n.d.		12.9	0.7	32.3	2.3	23.3	2.9	n.d.		n.d.		n.d.		–
16	Ethyl 3-hydroxybutyrate*	1544	n.d.		3.3	0.2	4.1	0.2	13.0	0.4	14.0	0.8	14.3	1.0	n.d.		n.d.		n.d.		–
17	Ethyl leucate**	1568	9.1	0.1	15.0	0.1	18.3	0.4	46.5	0.8	83.6	1.6	95.8	1.4	24.0	0.2	32.6	0.8	42.5	0.3	–
18	Ethyl 4-oxobutyrate***	1576	5.5	0.1	7.1	0.0	9.4	0.5	3.3	0.3	5.2	0.3	4.6	0.1	2.5	0.2	5.3	0.2	5.8	0.8	–
19	Isoamyl lactate**	1593	n.d.		n.d.		n.d.		37.7	0.6	49.6	1.1	60.3	2.9	n.d.		4.3	0.5	4.7	0.3	–
20	Diethyl malonate**	1602	4.6	0.1	5.4	0.1	2.5	0.1	n.d.		n.d.		n.d.		2.0	0.1	6.9	0.1	n.d.		–
21	Ethyl levulinate**	1636	n.d.		6.4	0.0	131.7	0.8	n.d.		7.6	0.1	24.8	1.4	1.1	0.1	9.4	0.1	145.3	2.2	–
22	Ethyl caprate**	1655	5.9	0.2	4.8	0.2	3.6	0.4	92.8	2.2	36.3	3.0	30.1	0.6	6.5	1.2	7.0	0.5	3.5	0.3	Grape
23	Ethyl methyl succinate***	1662	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		2.6	0.1	9.1	0.2	13.4	0.3	–
24	Diethyl methylsuccinate***	1665	n.d.		3.4	0.3	12.1	1.2	n.d.		8.7	1.0	26.0	0.4	n.d.		n.d.		n.d.		–
25	Diethyl succinate*	1699	253.3	4.6	1627.4	13.3	2643.4	74.3	1277.8	14.9	4677.0	49.0	6240.2	988.7	691.2	6.9	3170.3	33.9	4742.7	20.1	Fruity, wine
26	Ethyl 9-decenoate**	1708	n.d.		n.d.		n.d.		6.1	0.6	n.d.		n.d.		n.d.		n.d.		n.d.		–
27	Diethyl glutarate***	1803	1.3	0.0	5.2	0.0	7.6	0.3	4.1	0.1	17.7	0.2	23.4	0.8	2.4	0.0	9.2	0.0	12.5	0.3	–
28	Ethyl phenylacetate**	1812	4.4	0.5	8.0	0.5	9.5	0.3	11.9	0.5	22.7	1.0	15.7	1.0	13.9	0.6	19.2	1.0	30.1	2.3	Fruity, sweet, honey-like
29	Ethyl 4-hydroxybutyrate**	1834	11.5	1.1	23.0	2.7	26.2	1.9	159.5	6.8	74.2	2.4	51.8	3.2	38.4	1.4	3.6	0.4	26.2	0.3	–
30	Phenylethyl acetate*	1844	7.8	0.1	n.d.		n.d.		39.0	0.7	11.7	0.5	10.4	0.3	14.9	0.3	3.7	0.2	n.d.		Roses, apple, honey, sweet
31	Ethyl laurate**	1858	5.6	0.8	n.d.		n.d.		12.2	1.1	n.d.		n.d.		4.6	0.9	n.d.		n.d.		Sweet, floral, fruity, cream
32	Diethyl adipate***	1921	n.d.		n.d.		n.d.		4.7	0.7	4.0	0.5	n.d.		n.d.		3.9	0.4	6.3	0.4	–
33	Ethyl 3-methylbutyl butanedioate***	1925	3.3	0.4	7.7	0.3	7.4	0.7	28.2	1.6	46.6	1.8	75.5	4.5	n.d.		9.0	0.7	15.9	1.4	–
34	Diethyl malate*	2077	4824.1	50.1	13657.0	815.7	16017.9	1186.2	3836.4	150.2	11597.3	210.8	13007.9	1967.0	4935.0	264.9	13125.3	291.4	15906.6	51.8	Over-ripe, peach, cut grass
35	Propyl ethyl hydroxybutanedioate***	2159	n.d.		n.d.		n.d.		n.d.		n.d.		12.5	0.9	n.d.		n.d.		n.d.		–
36	Diethyl 2-hydroxyglutarate**	2196	232.7	4.0	524.1	12.1	486.8	18.5	1037.1	45.1	2208.5	89.4	2127.1	74.6	420.9	4.2	900.5	14.6	849.6	13.5	Cotton candy
37	Ethyl palmitate**	2268	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		11.7	2.1	n.d.		n.d.		–
38	Ethyl phenyl lactate**	2314	52.5	1.7	90.2	3.2	99.3	6.5	408.3	17.7	534.6	16.2	529.7	23.9	137.7	3.3	242.4	7.1	313.4	5.1	–
39	Diethyl tartrate*	2371	49.5	3.7	406.5	7.5	947.9	30.8	70.7	7.4	330.5	24.2	759.9	17.4	38.6	7.3	409.1	27.2	1139.4	30.8	Earth, must
40	Ethyl hydrogen succinate**	2426	1928.7	25.8	3997.2	241.7	3620.3	229.2	6723.4	880.5	8836.9	236.3	8001.3	1172.6	4354.1	239.0	6487.2	106.9	6435.1	83.7	Sweet, sour, fruity
41	Ethyl citrate**	2499	n.d.		46.3	0.3	239.8	12.0	n.d.	0.0	59.0	3.0	239.7	12.0	n.d.		92.2	16.1	219.6	9.9	–
42	Ethyl 4-hydroxyphenylacetate***	2958	n.d.		n.d.		n.d.		24.6	1.9	39.4	5.6	42.9	1.5	31.3	2.0	42.9	7.4	43.7	3.7	–
	Higher alcohols (29)																				
43	1-Propanol**	1056	7.1	0.6	7.2	0.8	7.7	0.6	49.1	6.7	81.0	28.2	52.6	17.9	19.1	0.6	16.7	1.1	22.5	1.2	Fresh, alcohol
44	Isobutyl alcohol**	1108	234.7	4.7	224.8	3.2	196.0	12.5	1227.6	36.6	1337.7	187.8	998.5	44.8	441.3	18.9	403.3	5.9	412.1	11.1	Fusel, alcohol
45	1-Butanol**	1163	5.8	0.4	6.9	0.5	4.6	0.6	21.3	1.6	22.0	2.0	15.9	1.3	5.6	0.6	12.8	0.7	7.1	0.5	Medicinal, alcohol
46	Active amyl alcohol**	1228	4181.4	93.0	4335.6	198.2	3679.7	168.7	16556.2	1580.6	15336.1	353.7	13465.9	1512.1	7448.5	578.4	6937.7	170.9	6988.2	251.6	Fusel

(*continued on next page*)

Table 1 (*continued*)

#	Compounds	KI	TN sweet (µg/L)						TN dry (µg/L)						Malvasia (µg/L)						Common descriptors[a]
			0 m	±SD	3 m, 45 °C	±SD	1 m, 70 °C	±SD	0 m	±SD	3 m, 45 °C	±SD	1 m, 70 °C	±SD	0 m	±SD	3 m, 45 °C	±SD	1 m, 70 °C	±SD	
47	1-Pentanol[**]	1270	4.8	0.4	4.1	0.5	2.7	0.1	13.2	0.7	9.6	0.5	6.6	0.2	6.9	0.9	6.1	0.4	5.2	0.3	Fruity, balsamic
48	4-Methyl-1-pentanol[**]	1334	3.0	0.2	3.3	0.1	3.9	0.5	13.5	0.9	13.7	0.5	15.9	0.5	5.7	0.4	4.6	0.3	6.1	0.4	Almond, toasted
49	2-Heptanol[**]	1339	1.8	0.1	1.7	0.0	1.7	0.1	2.3	0.1	2.4	0.1	2.5	0.1	n.d.		n.d.		n.d.		Fruity, mouldy, musty
50	(*Z*)-2-penten-1-ol[**]	1343	2.1	0.3	1.8	0.3	2.3	0.3	2.7	0.4	2.9	0.5	2.9	0.4	3.6	0.6	3.3	0.6	3.6	0.5	–
51	3-Methyl-1-pentanol[**]	1348	4.0	0.3	3.6	0.3	4.5	0.5	19.3	0.3	19.1	0.7	19.5	0.3	7.7	0.6	6.8	0.7	7.9	0.6	–
52	1-Hexanol[**]	1374	1247.5	13.9	1268.4	23.6	1255.3	27.6	1088.4	8.1	1054.1	14.7	1090.7	10.0	1117.6	36.6	992.8	11.1	1058.9	10.5	Green, grass
53	(*E*)-3-hexen-1-ol[**]	1385	22.6	0.9	21.7	0.6	22.2	1.2	17.6	0.2	19.8	0.7	17.3	0.4	21.6	0.7	25.2	0.5	22.3	0.3	Green, floral
54	3-Ethoxy-1-propanol[**]	1396	2.1	0.3	1.7	0.1	n.d.		14.7	0.4	13.5	0.8	11.7	0.3	6.0	0.3	5.3	0.2	6.2	0.4	Fruity
55	(*Z*)-3-hexen-1-ol[**]	1405	150.9	2.6	142.6	1.9	132.0	0.7	164.0	1.3	147.0	4.0	142.4	1.5	291.6	3.7	253.1	1.5	251.0	4.8	Grass, green
56	(*E*)-2-hexen-1-ol[**]	1429	18.4	0.4	18.1	0.1	20.5	0.7	3.2	0.1	3.8	0.5	4.7	0.5	17.7	0.2	17.0	0.3	17.1	0.4	Grass, herb
57	(*Z*)-2-hexen-1-ol[**]	1439	7.3	0.7	7.3	0.5	8.0	0.3	4.1	0.3	4.9	0.7	5.1	0.4	5.0	0.7	4.9	0.6	4.2	0.5	Grass, herb
58	1-Heptanol[**]	1476	4.8	0.3	4.3	0.1	4.5	0.3	9.9	0.1	9.7	0.5	10.6	0.3	5.9	0.5	4.9	0.2	5.9	0.2	Grape, sweet
59	2-Ethyl-1-hexanol[**]	1510	5.0	0.2	8.7	0.2	4.1	0.1	5.8	0.2	13.7	0.3	8.4	0.6	5.4	0.6	10.5	0.6	4.6	0.3	Mushroom, sweet fruit
60	3,5,5-Trimethylhexanol[***]	1527	2.9	0.1	3.4	0.4	4.3	0.2	6.7	0.4	6.7	0.5	9.1	0.5	n.d.		n.d.		4.1	0.2	–
61	2,3-Butanediol, isomer 1[*]	1566	81.0	1.4	69.7	16.1	28.5	6.5	173.7	72.2	267.2	111.4	255.2	4.3	n.d.		n.d.		n.d.		Butter, cream
62	1-Octanol[*]	1578	8.2	0.9	8.3	0.9	9.3	0.6	14.4	1.4	12.8	0.9	11.6	1.9	16.4	2.1	9.3	0.7	7.7	1.3	Citrus, roses
63	2,3-Butanediol, isomer 2[**]	1602	n.d.		n.d.		n.d.		28.7	14.3	50.1	25.6	43.8	1.9	n.d.		n.d.		n.d.		–
64	1,2-Propanediol[**]	1619	3.9	0.4	n.d.		n.d.		4.1	1.4	10.9	5.4	8.3	1.4	n.d.		n.d.		n.d.		–
65	1-Nonanol[**]	1680	1.6	0.1	1.7	0.1	2.0	0.1	4.0	0.1	4.1	0.2	4.4	0.1	2.9	0.0	2.7	0.1	n.d.		Fat, green
66	1-Methoxy-2-butanol[***]	1683	n.d.		n.d.		n.d.		8.5	2.5	10.1	2.5	10.3	0.3	n.d.		n.d.		n.d.		–
67	1-Decanol[*]	1783	n.d.		n.d.		n.d.		2.6	0.2	2.7	0.6	5.4	0.9	2.7	0.2	n.d.		n.d.		Orange flowery, fatty
68	Buthoxyethoxyethanol[***]	1819	35.1	0.9	7.0	0.5	8.7	0.8	6.9	0.6	n.d.		n.d.		12.9	1.6	12.3	1.1	13.3	1.8	–
69	Benzyl alcohol[*]	1909	120.7	2.5	111.5	0.7	114.5	5.6	219.8	6.9	198.2	9.8	198.8	4.5	117.0	1.7	115.3	2.3	128.4	2.5	Citrusy, sweet, almonds
70	Phenylethyl alcohol[*]	1945	3782.2	41.9	4148.3	88.5	4062.6	130.6	13672.5	2289.4	12982.1	360.7	12244.3	2053.4	8027.4	648.7	7,832.3	149.9	8263.5	114.1	Flowery, pollen, perfumed, roses
71	2-Ethoxybenzyl alcohol[**]	1978	n.d.		25.3	0.3	62.0	0.2	n.d.		30.0	1.7	49.9	1.4	n.d.		32.0	2.4	108.9	5.1	–
	Fatty acids (17)																				
72	Acetic acid[*]	1488	106.9	5.0	108.5	16.8	67.6	13.5	88.4	30.9	156.1	76.9	138.3	7.1	55.0	4.6	65.8	0.6	125.5	1.2	Vinegar, acid, fatty
73	Propionic acid[**]	1573	n.d.		n.d.		2.5	0.2	5.5	0.8	3.8	0.4	n.d.		n.d.		n.d.		n.d.		Vinegarish
74	Isobutyric acid[*]	1601	14.8	0.2	11.5	0.5	9.3	0.5	46.4	2.0	45.2	4.0	41.9	1.1	19.0	3.5	19.4	0.6	19.9	0.4	Rancid, butter, cheese
75	Butyric acid[*]	1664	10.2	0.2	9.0	0.1	8.4	0.2	22.0	0.5	21.1	0.5	19.6	0.7	8.8	0.1	8.2	0.2	9.1	0.1	Cheese, rancid, sweat
76	Isovaleric acid[*]	1704	n.d.		n.d.		n.d.		32.2	1.0	n.d.		n.d.		15.6	0.3	13.8	0.5	12.2	0.0	Fatty, rancid
77	2-Methyl butyric acid[**]	1704	13.1	0.3	n.d.		n.d.		69.7	1.6	47.9	6.3	n.d.		31.8	0.5	30.9	1.4	24.8	0.4	Cheese, sweat
78	Valeric acid[**]	1773	0.9	0.1	0.8	0.1	1.1	0.0	1.9	0.1	1.5	0.1	1.6	0.1	1.3	0.0	1.5	0.1	1.5	0.0	–
79	Caproic acid[*]	1880	92.9	3.4	88.2	1.0	103.5	4.1	308.61	6.65	301.32	12.31	294.95	3.78	152.3	2.3	140.7	3.2	148.2	2.1	Cheese, rancid, fatty
80	2-Ethylhexanoic acid[**]	1981	13.0	1.3	n.d.		n.d.		n.d.		n.d.		17.8	2.4	19.5	1.8	11.5	1.6	0.0	0.0	–
81	(*E*)-4-Hexenoic acid[***]	1996	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		13.0	1.1	8.5	1.4	12.4	1.7	–
82	(*E*)-2-Hexenoic acid[**]	2003	28.8	1.7	33.6	0.2	36.6	1.2	16.2	1.4	18.5	1.1	17.8	0.7	15.0	0.8	10.0	1.5	21.6	0.8	Musty, fatty
83	Caprylic acid[*]	2094	200.7	6.6	199.7	7.4	240.3	17.4	**953.7**	**47.6**	**946.0**	**76.5**	**856.6**	**12.4**	448.9	2.2	371.3	10.7	317.5	9.2	Rancid, harsh, cheese, fatty acid
84	Pelargonic acid[*]	2202	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		13.9	1.8	n.d.		n.d.		Green, fatty
85	Capric acid[*]	2307	109.4	5.1	107.6	3.6	94.1	9.4	304.4	21.0	355.5	20.8	284.9	13.5	216.6	4.1	186.0	5.6	155.1	1.0	Rancid, fatty
86	Benzoic acid[**]	2482	30.8	3.7	26.7	5.0	36.2	2.4	25.2	1.2	33.0	4.7	40.6	2.8	45.3	1.1	37.3	7.0	29.5	3.2	Urine
87	Lauric acid[**]	2519	n.d.		26.4	2.5	n.d.		53.1	9.4	40.8	3.5	60.4	9.0	44.9	2.2	n.d.		58.8	4.4	Metal
88	Phenylacetic acid[**]	2608	12.1	0.5	12.8	0.1	13.9	0.6	31.5	2.5	32.0	2.0	28.5	2.0	32.3	0.9	33.2	1.9	32.3	1.1	Honey, flower
	Volatile phenols (19)																				
89	Ethyl salicylate[**]	1839	17.4	0.3	10.0	0.2	9.0	0.8	6.7	0.4	6.2	0.6	7.8	0.6	n.d.		29.9	1.0	5.1	0.4	Wintergreen, mint
90	Guaiacol[**]	1892	2.2	0.2	4.3	0.3	**27.8**	**1.2**	n.d.		n.d.		**22.4**	**0.4**	n.d.		n.d.		n.d.		Smoky, sweet, medicine
91	4-Ethylguaiacol[*]	2065	n.d.		n.d.		n.d.		1.9	0.1	1.8	0.1	2.2	0.1	5.7	0.2	5.3	0.2	6.8	0.2	Spice, clove
92	*m*-Cresol[**]	2120	n.d.		n.d.		7.3	1.3	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		Leather

93	4-Ethylphenol**	2215	n.d.		n.d.		6.0	0.9	8.6	0.4	6.7	0.8	9.0	0.9	8.5	1.4	10.1	0.6	11.1	1.0	Phenolic
94	4-Vinylguaiacol**	2234	n.d.		1.7	0.0	4.5	0.6	n.d.		1.6	0.3	13.9	0.3	n.d.		n.d.		40.6	2.1	Clove-like, smoky
95	Syringol**	2301	n.d.		16.1	2.1	107.2	7.6	n.d.		n.d.		118.6	17.4	n.d.		n.d.		n.d.		–
96	2,4-Di-tert-butylphenol**	2346	25.9	1.4	31.1	1.8	35.8	2.1	43.9	6.3	38.8	2.8	40.0	5.2	50.7	3.9	36.4	1.7	49.9	1.4	–
97	4-Vinylphenol**	2440	n.d.		n.d.		n.d.		n.d.		n.d.		144.8	10.8	n.d.		n.d.		166.7	10.2	Almond shell
98	4-Allylsyringol**	2579	n.d.		n.d.		n.d.		n.d.		n.d.		18.8	0.2	n.d.		n.d.		n.d.		–
99	4-Ethoxymethylphenol***	2586	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		14.0	2.4	n.d.		–
100	Vanillin**	2613	38.4	1.0	42.5	0.8	39.5	1.4	13.7	0.9	27.1	0.7	17.0	0.9	22.2	0.5	54.4	2.2	28.2	1.3	Vanilla-like, sweet
101	Methyl vanillate**	2650	9.9	1.4	11.2	1.3	16.2	1.8	20.0	2.6	16.6	1.6	20.1	2.6	12.3	1.5	12.8	2.5	23.3	3.6	Caramel, butterscotch, vanilla
102	Ethyl vanillate**	2676	47.7	2.8	n.d.		n.d.		51.7	4.3	96.0	6.5	86.7	5.0	n.d.		n.d.		n.d.		Flowery, fruity, sweet, vanilla
103	Acetovanillone*	2687	17.7	1.8	24.3	0.6	18.3	1.4	26.9	4.2	31.1	6.2	33.7	4.0	26.7	2.0	66.7	6.4	49.4	4.4	Vanilla
104	Vanillyl ethyl ether***	2780	n.d.		n.d.		n.d.		30.7	3.7	32.8	4.4	65.7	12.9	n.d.		n.d.		n.d.		–
105	3,4-Dimethoxyphenol***	2816	n.d.		n.d.		n.d.		14.8	2.3	n.d.		n.d.		n.d.		n.d.		n.d.		–
106	Syringaldehyde**	2989	54.6	4.8	94.3	29.2	60.1	3.2	n.d.		63.5	14.3	42.2	11.8	n.d.		27.6	5.3	n.d.		Chocolate, grape, woody, smoky, wine-like
107	4-Hydroxybenzaldehyde***	3015	101.8	11.1	105.0	7.8	104.2	10.0	51.3	7.6	177.1	15.9	107.9	12.0	139.5	2.0	268.8	21.7	46.5	5.2	–
	Monoterpenes (15)																				
108	Eucalyptol**	1218	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		2.4	0.2	Eucalyptus, fresh, cool, camphoraceous, medicinal
109	(*E*)-Linalool oxide*	1462	n.d.		6.5	0.5	19.7	0.6	4.0	0.2	10.7	0.7	26.8	0.2	4.4	0.6	13.1	0.4	31.7	1.2	–
110	(*Z*)-Linalool oxide*	1490	n.d.		n.d.		n.d.		n.d.		n.d.		10.0	0.3	n.d.		n.d.		n.d.		Flowery
111	Linalool*	1569	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		19.4	0.3	n.d.		n.d.		Flowery, citrus-like, bergamot
112	3-Terpinen-1-ol**	1597	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		2.2	0.3	Musty
113	Hotrienol**	1634	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		3.3	0.3	n.d.		n.d.		Hyacinth
114	α-Terpineol**	1720	3.7	0.4	8.0	0.7	8.0	1.3	5.9	0.4	8.0	0.3	8.0	0.7	42.4	0.5	39.9	1.2	18.1	1.8	Pine, oil, anise, mint
115	3,7-Dimethyl-1,5-octadien-3,7-diol***	1723	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		7.3	0.1	n.d.		n.d.		–
116	Citronellol*	1788	n.d.		n.d.		n.d.		3.9	0.3	n.d.		n.d.		n.d.		n.d.		n.d.		Citronella, rose, green, lemon
117	Nerol*	1825	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		4.1	0.5	n.d.		n.d.		Sweet
118	Geraniol**	1872	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		6.3	0.2	n.d.		n.d.		Rose-like, citrus-like, geranium
119	2,6-Dimethyl-3,7-octadien-2,6-diol**	1974	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		49.5	0.9	7.2	1.0	n.d.		–
120	Linalool hydrate**	2004	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		18.8	0.8	24.1	0.6	n.d.		–
121	*p*-Menthane-3,8-diol***	2127	n.d.		n.d.		n.d.		n.d.		13.2	0.7	22.4	1.8	n.d.		n.d.		n.d.		–
122	3,7-Dimethyl-1,7-octanediol***	2235	n.d.		n.d.		n.d.		8.2	1.4	n.d.		n.d.		11.5	0.7	n.d.		n.d.		–
	Norisoprenoids (6)																				
123	2,6,6-Trimethyl-2-cyclohexen-1-one***	1422	n.d.		n.d.		2.8	0.2	n.d.		n.d.		3.7	0.6	n.d.		n.d.		2.6	0.4	–
0.3	Vitispirane**	1546	n.d.		2.5		2.9	0.3	n.d.		n.d.		4.7	0.5	n.d.		13.8	0.7	11.5	0.4	Camphor, eucalyptus
	1-(2,4,6-Trimethylphenyl)buta-1,3-diene***	1768	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		1.4	0.1	1.8	0.1	–
0.1	1,1,6-Trimethyl-1,2-dihydronaphthalene (TDN)**	1770	n.d.		0.8		1.2	0.1	n.d.		n.d.		1.9	0.1	n.d.		n.d.		n.d.		Petrol, kerosene-like
0.3	β-Damascenone**	1846	n.d.		**3.5**		**12.0**	**1.7**	n.d.		n.d.		n.d.		n.d.		n.d.		**14.9**	**1.8**	Baked apple, rose, honey
128	1-(2,3,6-Trimethylphenyl)-3-buten-2-one**	2146	n.d.		n.d.		36.9	4.9	n.d.		n.d.		53.7	4.4	n.d.		n.d.		51.5	1.2	–
	Carbonyl compounds (18)																				
129	3-Hexanone**	1079	6.2	0.6	5.3	0.7	17.4	0.7	n.d.		n.d.		n.d.		n.d.		5.0	1.0	19.2	1.3	Ether, grape
130	Hexanal**	1098	6.2	0.4	5.3	0.6	4.8	0.5	n.d.		n.d.		n.d.		5.6	0.5	4.7	0.8	5.8	0.9	Grass, tallow, fatty
131	(*E*)-3-Penten-2-one**	1145	4.9	0.3	3.7	0.5	4.7	0.8	n.d.		8.7	0.8	n.d.		5.5	0.7	5.4	0.2	5.3	0.7	–

(*continued on next page*)

Table 1 (*continued*)

#	Compounds	KI	TN sweet (µg/L)						TN dry (µg/L)						Malvasia (µg/L)						Common descriptors[a]
			0 m	±SD	3 m, 45 °C	±SD	1 m, 70 °C	±SD	0 m	±SD	3 m, 45 °C	±SD	1 m, 70 °C	±SD	0 m	±SD	3 m, 45 °C	±SD	1 m, 70 °C	±SD	
132	4-Ethoxy-2-pentanone***	1258	2.2	0.1	3.1	0.1	2.1	0.1	n.d.		4.8	0.2	0.9	0.0	3.1	0.0	7.7	0.1	3.3	0.1	–
133	4-ethoxy-2-butanone***	1280	n.d.		n.d.		4.5	0.3	n.d.		n.d.		n.d.		n.d.		n.d.		3.6	0.1	–
134	Acetoin**	1309	20.0	0.2	20.1	0.4	19.9	0.4	11.9	0.2	12.0	0.6	10.1	0.0	n.d.		n.d.		38.8	1.0	Butter, cream, flowery, wet
135	Acetol**	1326	n.d.		5.0	0.2	52.8	1.8	n.d.		n.d.		n.d.		n.d.		n.d.		55.2	2.2	Sweet, caramel
136	Cyclopenten-3-one***	1379	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		3.6	0.6	–
137	Benzaldehyde*	1551	127.6	1.5	102.9	1.3	103.0	2.6	10.2	0.2	50.6	2.9	22.0	2.2	71.8	0.9	77.2	1.1	62.5	1.6	Almond, burnt sugar
138	2-Cyclopentene-1,4-dione**	1616	n.d.		n.d.		7.1	0.5	n.d.		n.d.		n.d.		n.d.		n.d.		9.8	0.7	–
139	Phenylacetaldehyde**	1673	79.2	0.5	54.6	1.3	98.2	2.1	12.5	1.2	28.3	0.8	46.6	2.0	28.7	1.6	38.8	2.6	31.4	2.0	Green, honey
140	Phenylacetone***	1756	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		6.0	0.2	3.7	0.1	–
141	Ethyl nicotinate**	1843	n.d.		3.5	0.1	7.6	0.3	n.d.		n.d.		10.0	0.2	n.d.		n.d.		6.9	0.1	–
142	Cyclotene***	1859	n.d.		n.d.		9.6	1.2	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		Sweet, burnt
143	Ethyl picolinate***	2028	n.d.		n.d.		13.8	0.5	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		–
144	2H-Pyran-2,6(3H)-dione***	2033	n.d.		n.d.		n.d.		11.1	0.7	5.8	0.8	18.1	1.5	n.d.		n.d.		n.d.		
145	3-Hydroxy-4-phenyl-2-butanone**	2302	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		20.6	1.7	27.0	5.7	25.7	1.2	–
146	Hydroxymaltol***	2332	n.d.		49.8	4.8	81.9	10.7	n.d.		n.d.		n.d.		n.d.		119.4	8.8	31.7	3.3	–
	Furan compounds (15)																				
147	2,2-Dimethyl-5-(1-methyl-1-propenyl)-tetrahydrofuran***	1258	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		3.0	0.1	–
148	Dihydro-2-methyl-3(2H)-furanone***	1286	n.d.		n.d.		8.5	0.3	n.d.		n.d.		n.d.		n.d.		n.d.		9.7	0.2	–
149	Furfural*	1492	8.0	0.1	159.4	3.3	987.5	16.1	5.6	0.0	98.8	1.6	563.1	18.0	9.2	0.2	143.9	2.2	1038.2	14.4	Almonds, pungent, bread, sweet
150	2-Acetylfuran*	1533	n.d.		3.3	0.0	29.1	0.9	n.d.		2.3	0.1	15.8	0.4	n.d.		3.5	0.0	26.3	0.4	Balsamic
151	5-Methylfurfural*	1600	n.d.		6.9	0.1	116.7	3.3	n.d.		4.2	0.1	50.1	1.7	n.d.		5.2	0.1	98.1	2.8	Almond, caramel, burnt sugar
152	2-Furyl ethyl ketone***	1602	n.d.		n.d.		16.3	0.4	n.d.		n.d.		n.d.		n.d.		n.d.		25.9	0.3	–
153	2-Acetyl-5-methylfuran***	1642	n.d.		n.d.		6.7	0.4	n.d.		n.d.		6.8	1.6	n.d.		n.d.		10.8	0.6	–
154	Ethyl 2-furoate*	1650	5.8	0.8	12.7	0.4	44.1	0.8	5.5	1.0	12.0	0.5	57.9	1.4	12.3	0.6	21.6	1.5	76.9	1.6	Vanilla, scorched
155	Furfuryl alcohol**	1690	n.d.		2.6	0.4	9.7	0.6	4.9	0.9	n.d.		n.d.		n.d.		n.d.		13.5	2.0	Burnt
156	5-Ethoxymethylfurfural***	1962	n.d.		52.3	1.5	**3616.4**	**114.8**	n.d.		n.d.		**117.7**	**9.8**	n.d.		26.2	1.7	**3551.3**	**33.1**	–
157	2,5-Furandicarboxaldehyde***	2018	n.d.		6.6	0.4	101.5	7.4	n.d.		n.d.		n.d.		n.d.		n.d.		128.8	9.7	–
158	Furyl hydroxymethyl ketone***	2046	1.3	0.0	29.0	0.3	355.4	13.4	n.d.		n.d.		9.4	0.3	1.3	0.0	18.6	0.4	458.5	9.2	–
159	2,3-Dihydrobenzofuran***	2437	n.d.		21.2	1.4	44.2	4.2	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		–
160	5-Hydroxymethylfurfural (HMF)*	2551	41.3	0.8	3124.7	141.3	**20738.1**	**1533.3**	35.7	14.8	82.0	5.4	868.7	49.7	32.0	2.3	1518.1	97.7	**19571.7**	**284.4**	Caramel
161	1-(5-Hydroxymethyl-2-furanyl)-1-propanone***	2623	n.d.		n.d.		37.0	1.9	n.d.		n.d.		n.d.		n.d.		n.d.		131.7	6.7	–
	Lactones (7)																				
162	γ-Butyrolactone**	1661	16.1	0.2	17.4	0.6	17.0	0.4	40.6	0.8	44.1	0.6	44.3	1.6	13.0	0.3	13.1	0.1	14.3	0.3	Caramel, sweet
163	α-Angelica lactone***	1460	n.d.		n.d.		3.9	0.4	n.d.		n.d.		n.d.		n.d.		n.d.		7.9	1.2	–
164	β-Angelica lactone***	1709	n.d.		n.d.		6.1	0.1	n.d.		n.d.		n.d.		n.d.		n.d.		6.9	0.2	–
165	γ-Ethoxybutyrolactone***	1756	14.4	0.2	13.2	0.2	17.5	0.2	9.7	0.5	14.9	0.4	13.2	0.6	5.2	0.1	9.4	0.7	11.4	0.3	–
166	γ-Nonalactone**	2060	n.d.		9.8	1.3	n.d.		8.7	2.2	10.1	0.5	20.0	2.0	n.d.		7.1	0.7	9.0	1.7	Coconut, peach
167	γ-Decalactone**	2112	n.d.		n.d.		2.6	0.1	2.9	0.1	3.4	0.3	8.4	0.5	n.d.		n.d.		n.d.		Peach, fatty, coconut
168	γ-Carboethoxy-γ-butyrolactone**	2273	79.9	1.0	118.4	1.8	125.0	3.8	364.9	16.7	467.9	9.3	539.3	23.5	140.4	3.9	190.5	2.8	235.3	10.4	Roast, smoke
	Sulphur compounds (4)																				
169	2-Methyl-3-thiolanone***	1556	n.d.		n.d.		n.d.		8.4	0.2	6.3	0.5	12.5	1.1	n.d.		n.d.		4.9	0.6	–
170	Ethyl 3-(methylthio) propionate***	1591	n.d.		n.d.		n.d.		11.3	0.7	14.2	2.0	17.4	2.2	n.d.		3.1	0.4	3.4	0.3	–
171	Methionol*	1747	n.d.		n.d.		n.d.		161.9	4.0	135.4	4.9	137.9	3.3	10.5	0.4	9.4	1.3	10.1	0.7	Sweet, potato
172	4-(Methylthio)-1-butanol***	1870	n.d.		n.d.		n.d.		9.3	0.4	7.2	0.8	8.5	0.9	n.d.		n.d.		n.d.		–
	Acetals (8)																				
173	Isovaleraldehyde diethyl acetal***	1090	n.d.		n.d.		20.4	0.7	n.d.		n.d.		10.9	3.3	n.d.		n.d.		7.0	0.5	–

174	Acetaldehyde ethyl amyl acetal***	1121	n.d.		n.d.		n.d.		6.4	0.9	8.6	0.7	11.9	1.7	n.d.		3.2	0.4	n.d.		–
175	Glycolaldehyde diethyl acetal***	1482	11.2	0.9	6.0	0.1	5.1	0.5	n.d.		n.d.		n.d.		6.5	0.5	13.3	1.1	5.7	0.6	–
176	Furfural diethyl acetal***	1484	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		20.3	0.7	–
177	*cis*-5-Hydroxy-2-methyl-1,3-dioxane***	1525	6.8	0.3	9.9	0.4	5.4	0.5	22.2	0.7	78.6	1.0	23.9	2.0	20.1	0.4	45.5	2.8	11.6	0.3	–
178	*cis*-4-Hydroxymethyl-2-methyl-1,3-dioxolane***	1639	5.2	0.2	7.0	0.2	61.7	1.3	31.2	0.5	39.6	0.6	19.3	0.4	11.1	0.2	20.2	1.0	5.2	0.4	–
179	Phenylacetaldehyde diethyl acetal***	1740	7.7	0.2	5.0	0.1	8.4	0.2	n.d.		n.d.		n.d.		6.3	1.0	2.0	0.1	2.9	0.4	–
180	*trans*-5-Hydroxy-2-methyl-1,3-dioxane***	1854	4.1	0.6	9.2	0.6	11.9	1.8	19.5	0.3	87.2	4.2	85.5	2.0	20.3	1.9	18.7	0.8	n.d.		–
	Other compounds (10)																				
181	N-(3-Methylbutyl)acetamide***	1889	n.d.		81.1	0.9	70.2	2.3	330.0	12.9	261.1	22.1	236.5	23.8	91.2	2.1	260.9	4.7	68.3	1.8	–
182	3,7-Dimethyl-2,3-epoxy-6-octanyl-1-oxythiocarbonylimidazolide***	2083	n.d.		61.6	1.5	1351.7	47.1	n.d.		n.d.		60.4	4.5	n.d.		44.2	4.7	1264.4	8.6	–
183	Ethyl pyrrole-2-carboxylate***	2117	n.d.		n.d.		7.5	0.7	n.d.		n.d.		n.d.		n.d.		n.d.		n.d.		–
184	2,3-Dihydroxypyrazine***	2254	n.d.		n.d.		11.7	0.7	n.d.		14.9	1.6	26.9	2.3	n.d.		n.d.		9.5	0.5	–
185	Curvulol***	2267	n.d.		24.1	1.6	150.4	5.8	n.d.		n.d.		76.3	1.2	n.d.		26.1	3.0	410.8	8.5	–
186	Ethyl 2-formylpyrrole-1-acetate***	2308	n.d.		n.d.		n.d.		n.d.		n.d.		118.1	12.2	n.d.		n.d.		n.d.		–
187	Diethyl phthalate**	2404	16.3	1.5	32.4	1.1	n.d.		24.4	3.9	n.d.		n.d.		17.8	5.3	n.d.		n.d.		–
188	Isobutyl phthalate***	2574	14.1	2.0	11.9	1.0	n.d.		18.4	3.0	17.2	2.6	13.3	4.1	11.9	1.8	n.d.		n.d.		–
189	Dibutyl phthalate**	2729	457.3	8.0	325.8	3.4	403.2	48.6	113.8	9.7	139.8	6.4	91.7	12.8	165.6	2.8	150.2	7.5	127.5	9.0	–
190	Phthalimide***	2975	63.9	5.3	n.d.		n.d.		59.7	8.9	n.d.		n.d.		n.d.		n.d.		n.d.		–

KI – Kovats index; SD – standard deviation; n.d. – not detected. In **bold** are highlighted the compounds above the odour threshold.

[a] Based on flavournet (www.flavornet.org/) and pherobase (www.pherobase.com/) online databases.

[*] MS data and Kovats index in agreement with those of authentic compound.

[**] MS data and Kovats index in agreement with those in literature.

[***] MS data in agreement with those in NIST08 and Wiley 6.0 libraries.

(Fig. 3). This study also showed that the volatile fraction of these Madeira wines increased after the heating process, up to 88% in sweet wines and up to 28% in the dry wine.

3.1. Esters

Esters are usually considered important to the sensory properties of wines, contributing with positive aromas, essentially with fruity notes (Ebeler, 2001). The results showed that esters were one of the most abundant groups (representing at least 30%) as they are secondary aromas (Fig. 3). As expected, they appeared at higher amounts in the dry wine because it was more fermented.

Most esters increased with the heating step, mainly the most abundant (Table 1), which were diethyl malate (odour threshold (Oth) of 760 mg/L, (Sánchez-Palomo, Gómez García-Carpintero, Alonso-Villegas, & González-Viñas, 2010)), ethyl hydrogen succinate, diethyl succinate and ethyl lactate (Oth of 200 and 155 mg/L, respectively (Campo, Ferreira, Escudero, Marques, & Cacho, 2006), but none seem to contribute to the flavour of the current wines, because they were below their Oth. Other minor esters also increased (ethyl butyrate and ethyl caproate) or were formed (ethyl 2-methylbutyrate and ethyl isovalerate) after the heating step. These ethyl esters might impart positive fruity notes to the aroma of these wines since they were above their Oth (20, 18, 3 and 14 μg/L, respectively; Campo et al., 2006; Gómez-Míguez, Cacho, Ferreira, Vicario, & Heredia, 2007). Ethyl caproate has been reported as an important odorant of young TN wines (Perestrelo, Fernandes, Albuquerque, Marques, & Câmara, 2006), as well as of aged Madeira wines (Campo et al., 2006).

Other minor esters revealed a great increase with baking. Some might even be important for the aroma definition of older Madeira wines, such as diethyl 2-hydroxyglutarate that was found to increase up to 125% after *estufagem*. Lee and Noble (2003) found that this ester contributes a cotton candy aroma to Californian Chardonnay wines. This compound has also been found in wines made from botrytised berries (Accordini, 2013). Another ester that showed a marked development was diethyl tartrate, which increased to almost 30-fold its initial value. On the other hand, some esters decreased after thermal processing, e.g., isoamyl acetate, which was present at levels higher than its Oth (30 μg/L, (Campo et al., 2006)) in the young TN dry wine, nevertheless its banana-like scent diminished due its decline.

There are several esters that only appeared after baking, namely the previously mentioned ethyls 2-methylbutyrate and isovalerate, but also ethyl levulinate, ethyl 3-ethoxypropionate, propyl ethyl hydroxypentanedioate, diethyl methylsuccinate and ethyl citrate. Ethyl levulinate was also encountered in sweet fortified wines by Cutzach et al. (1999), at forced-ageing conditions (heating at 37 °C for 12 months). According to them, levulinic acid, which can be formed by the heat breakdown of glucose, furfuryl alcohol or HMF in acidic medium, reacts with ethanol, to form ethyl levulinate. Ethyl 3-ethoxypropionate, as far as we know, has only been identified in brandies (Ledauphin et al., 2004), while propyl ethyl hydroxypentanedioate has not been identified in beverages. Diethyl methylsuccinate was previously identified in oak-aged Madeira wines by A. C. Pereira, Reis, Saraiva, and Marques (2010). Actually, these authors, according to chemometric studies, found out that this ester, together with ethyl lactate, ethyl methylsuccinate, diethyl succinate and ethyl hydrogen succinate, were especially important in the aged wines. Ethyl citrate was also found by Schneider, Baumes, Bayonove, and Razungles (1998) in sweet fortified wines from Grenache Noir.

Some esters are not commonly reported in wines, namely ethyl phenylacetate and ethyl 4-hydroxyphenylacetate, which indeed increased after *estufagem*, however it has been found in Aglianico del Vulture wines by Tat, Comuzzo, Battistutta, and Zironi (2007)

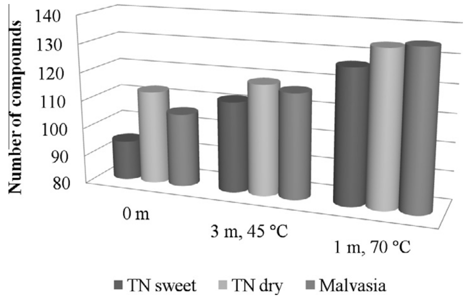

Fig. 2. Number of compounds identified before and after the heating at standard (3 months, 45 °C) and overheating (1 month, 70 °C) conditions of the Madeira wines in study.

and in Riesling wines by Güntert, Rapp, Takeoka, and Jennings (1986). Ethyl phenylacetate occurrence might be related with shikimate (phenylalanine and tyrosine) and cinnamate pathways during alcoholic fermentation by enzymatic esterification of phenylacetic acid (Tat et al., 2007). Likewise, the occurrence of 4-hydroxyphenylacetate might be related with the esterification of 4-hydroxyphenylacetic acid, a product of tyrosine metabolism (Güntert et al., 1986). Despite its positive development, the concentration of ethyl phenylacetate never attained its odour threshold, of 73 μg/L (Tat et al., 2007).

3.2. Higher alcohols

Higher alcohols were quantitatively the largest group of volatiles accumulated during the fermentation of these Madeira wines, representing in average 57% of the total content (Fig. 3). However, taking into account that they generally have high perception threshold, they did not seem to influence the aroma of these fortified wines.

These secondary aromas are essentially formed either from sugar catabolism or from amino acid decarboxylation and deamination. In this sense, unsurprisingly, sweet wines (short fermentation) presented the lowest content of alcohols (Fig. 3). From the 29 alcohols identified, active amyl alcohol, phenylethyl alcohol and 1-hexanol were by far the most abundant higher alcohols, with concentrations between 1.0 and 16.5 mg/L (Table 1). After the thermal processing of these wines, alcohols did not change very much, only small variations were encountered, thus it was not possible to identify a clear tendency. Actually, only 2-ethoxybenzyl alcohol was formed during the heating step. As far as we know, this compound is rarely reported in wines and may be derived from the reaction of ethanol with benzyl alcohol, which indeed slightly decreased after *estufagem* (Table 1).

3.3. Fatty acids

Fatty acids in wines may have origin in grapes or can be formed during the fermentative step by microbial organisms. Several compounds belonging to this chemical family were identified in these wines, including short chain (propionic, butyric and valeric acids), medium chain (caproic, caprylic, pelargonic and capric acids), long chain (lauric acid) and branched-chain fatty acids (isobutyric, isovaleric, 2-methylbutyric, 2-ethylhexanoic, 4-hexenoic and (*E*)-2-hexenoic acids). Together, they did not represent more than 3.5% of the volatile fraction of these wines (Fig. 3). Fatty acids were more abundant in TN dry wine (Table 1) due to the longer fermentation time.

The most abundant was caprylic acid, with levels ranging from 199.7 to 953.7 μg/L. Actually it was the only fatty acid exceeding its odour threshold (500 μg/L), but only in TN dry wine. Uncommonly, 4-hexenoic acid was encountered in Malvasia wine. According to deMan (1999), the presence of this acid in wines is usually related with the microbial degradation of sorbate, generating a geranium off-flavour note. In general, fatty acids decreased after the baking step (Fig. 3), probably due to their participation in esterification reactions with ethanol.

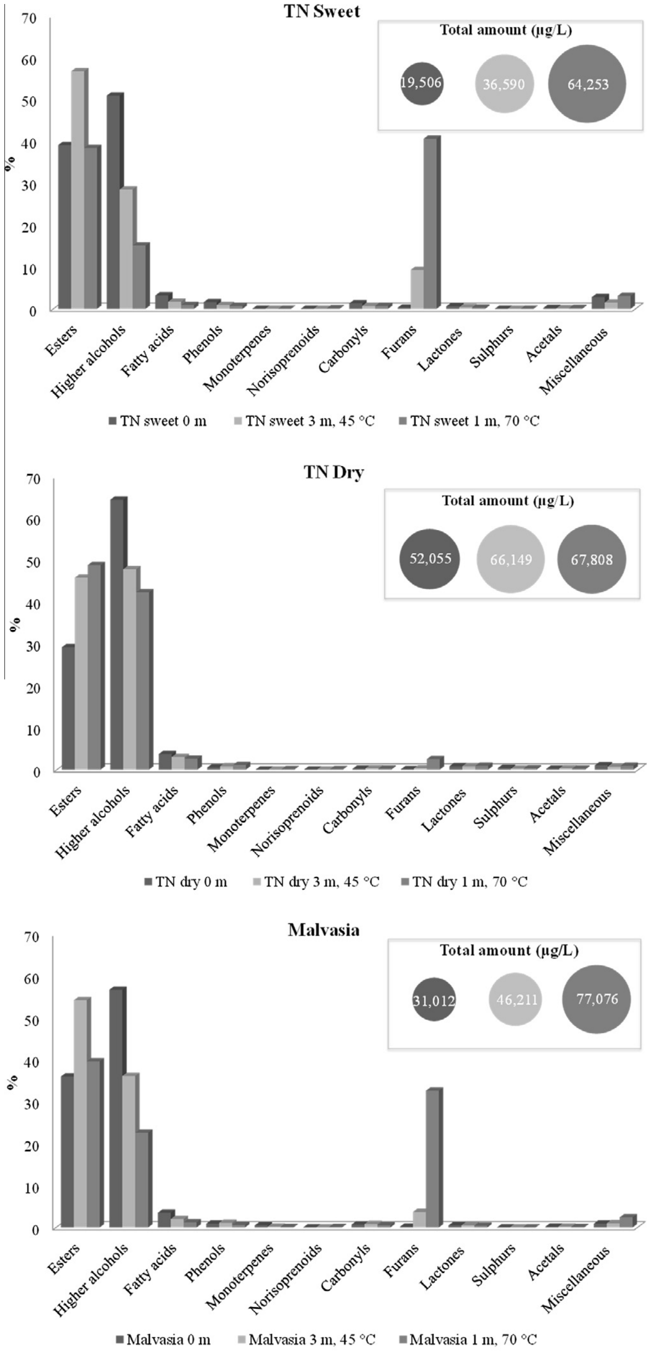

Fig. 3. Percentage of each chemical family identified in the current Madeira wines before and after heating at standard (3 months at 45 °C) and overheating (1 month at 70 °C) conditions.

3.4. Volatile phenols

Nineteen volatile phenols were identified in this sample set of Madeira wines. Quantitatively, they represent a minor group (less than 1.1%) among the volatiles encountered. However, some of them may negatively affect the overall aroma of a wine, if present at concentrations above their low odour thresholds, imparting animal, horse sweat, leather or medicinal off-flavours. The most common examples are vinylphenols and ethylphenols. Actually, 4-ethylphenol (Oth of 440 μg/L, (Campo et al., 2006)), 4-ethylguaiacol (Oth of 33 μg/L, (Gómez-Míguez et al., 2007)), 4-vinylphenol and 4-vinylguaiacol (Oth of 180 and 1100 μg/L, respectively (Campo et al., 2006)) were identified in these wines but all bellow their odour threshold (Table 1), so it seems that they might not have an impact on the aroma of these wines. Guaiacol was found above its odour threshold (up to 3-fold higher) only in TN wines heated at 70 °C. Guaiacol is frequently considered as a cause of defects in wines, imparting smoky notes. This result suggests that temperature accelerates its development; hence high temperatures should be avoided in the thermal processing. In wine, guaiacol occurrence is normally associated with oak barrel maturation, however, this route does not explain its development with the current heating. Probably, its development might be related with the thermal decarboxylation of hydroxycinnamates. Vanillin and its esters, acetovanillone, syringaldehyde and 4-hydroxybenzadehyde were also detected, but all bellow their odour perception limit. The occurrence of vanillin in wines is also commonly related with barrel maturation, but in this case this observation is not likely because these wines did not pass through wood-ageing yet. A reasonable explanation is that maybe vanillin and its esters were transferred from grapes to wines (Flamini & Traldi, 2010). The slight increase of acetovanillone after wines heating is also interesting. Similarly, Escudero et al. (2000) also found acetovanillone in laboratory oxidised white wines. According to them, wine oxidation may release the glycosylated acetovanillone extracted from grapes. Others volatile phenols were only detected after baking, namely 4-vinylguaiacol, 4-vinylphenol, 4-allylsyringol and syringol. Generally speaking, volatile phenols seem to be promoted by the thermal treatment of wines.

3.5. Monoterpenes

Monoterpenic compounds are usually considered as varietal compounds because they are present in grapes, especially in skins, or arise from grape precursors. In the current sample set were found 15 monoterpenes, representing less than 0.5% of the volatile fraction. The highest levels were found in young Malvasia wine (white variety), with at least 8-fold more.

In general, monoterpenic alcohols such as linalool, hotrienol, citronellol, nerol and geraniol, when present, disappeared with heating. It was also observed the same tendency for most monoterpenic diols, excepting *p*-menthane-3,8-diol, which was only detected in baked TN dry wine. It is known that the profile and content of monoterpenes can be altered during ageing, essentially due to acid-catalysed reactions. For example, linalool can be transformed into α-terpineol and successively to 1,8-terpines, and geraniol and nerol into linalool and α-terpineol (Versini, Dellacassa, Carlin, Fedrizzi, & Magno, 2008). Probably, this explains the arising of eucalyptol (1,8-cineole), 3-terpinen-1-ol, *p*-menthane-3,8-diol and the increasing of α-terpineol in TN wines. According to Marais (1983) review, eucalyptol was also found in wines heated at 70 °C (wine pH at 1.0). Monoterpenic oxides were also identified, namely the isomeric forms of linalool oxides, that abruptly increased after the heating process, while most monoterpenic diols tend to disappear after baking, like most monoterpenic alcohols. Linalool oxides may have been formed by linalool oxidation *via* epoxide (Marais, 1983).

3.6. Norisoprenoids

Six norisoprenoids were identified in these Madeira wines: 2,6,6-trimethyl-2-cyclohexen-1-one, vitispirane, 1-(2,4,6-trimethylphenyl)buta-1,3-diene, TDN, β-damascenone and 1-(2,3,6-trimethylphenyl)-3-buten-2-one. These compounds were only detected in baked Madeira wines, indicating that temperature accelerates their formation. Kanasawud and Crouzet (1990) demonstrated that 2,6,6-trimethyl-2-cyclohexen-1-one formation in aqueous medium is related with the thermal degradation of carotenoids, namely β-carotene. Apparently, this ketone has never been identified in wines.

In the current study, an isomer of TPB, the 1-(2,4,6-trimethylphenyl)buta-1,3-diene, was identified according to Wiley 6.0 MS library, with the following ion peaks (*m*/*z*), ordered according to their abundance: 157, 142, 141, 128, 172, 115, and eluting before β-damascenone with a KI of 1768. Janusz et al. (2003) were the first researchers to report the occurrence of TPB in wines as a potent grape-derived odorant, with a very low odour perception limit of 40 ng/L. According to them, this compound exhibits green and cut-grass notes at low concentrations and pungent or chemical scents when present at higher concentrations. They reported that TPB elutes just after the elution of β-damascenone on a Carbowax column, with a Kovats GC retention index of 1830 and a mass spectrum with the following ions, ordered according to their abundance: *m*/*z* 157, 142, 141, 172, 128, 115. Additionally, in the current study we also found another compound with structural similarities with TPB, the 1-(2,3,6-trimethylphenyl)-3-buten-2-one, which, as far as we know, was only identified by Nykanen (1986) in wine and distilled alcoholic beverages.

Finally, vitispirane and TDN were never been encountered above their odour perception; however, β-damascenone, only detected in baked sweet wines, reaching 300-fold above its odour threshold (0.05 μg/L, (Campo et al., 2006)) in wines heated at overheating conditions. This result leads us to conclude that this compound might play an important role in the aroma of Madeira baked wines. Campo et al. (2006) found that β-damascenone has a great contribution to the aroma of oak-aged Madeira wines.

3.7. Carbonyl compounds

Carbonyls group includes aldehydes and ketones. In the current sample set 18 carbonyls were found, from which 3 were aldehydes.

It is known that the major wine aldehyde is acetaldehyde; however, in the current samples it was not possible to quantify this aldehyde elutes too early to measure. However, other aldehydes were identified, namely hexanal, benzaldehyde and phenylacetaldehyde. The latter compound has reached values far above its odour perception (98-fold higher) and it seems that baking favours its development (Table 1). These results indicate that phenylacetaldehyde (honey-like scent) might be important for the aroma definition of the Madeira wines submitted to *estufagem*. Actually, Oliveira e Silva et al. (2008), through GC-O analysis, also found out that phenylacetaldehyde imparted a significant contribution to the aroma of heated Madeira wines. Comparable results were obtained by Campo et al. (2006) in oak-aged Madeira wines. The occurrence of this aldehyde in beverages has been related with Maillard reactions, specifically with Strecker degradation, through phenylalanine degradation (Soares da Costa et al., 2004). According to Campo et al. (2006) the presence of hexanal is most likely due to the direct oxidation of 1-hexanol.

Several ketones were identified in these wines, specifically some usually found in sweet fortified wines, namely cyclotene, 3-hydroxy-4-phenyl-2-butanone and hydroxymaltol (Cutzach et al., 1999; López de Lerma et al., 2010). Cyclotene and hydroxymaltol were only detected in baked wines at levels ranging from 9.6 to 119.4 μg/L. The presence of these two carbonyls in wines is usually associated with Maillard reactions (Cutzach et al., 1999). Other carbonyls that are rarely identified in wines were also identified, namely (*E*)-3-penten-2-one, 4-ethoxy-2-pentanone, 4-ethoxy-2-butanone, cyclopenten-3-one, 2-cyclopentene-1, 4-dione, phenylacetone, ethyl nicotinate, ethyl picolinate, and 2H-pyran-2,6(3H)-dione. (*E*)-3-Penten-2-one was already encountered in young Madeiras by Perestrelo et al. (2006). Cyclopenten-3-one, only detected in Malvasia heated at 70 °C, has been detected in foods submitted to thermal processing, especially in coffee (Nebesny, Budryn, Kula, & Majda, 2007). The formation of 2-cyclopentene-1,4-dione in foods has been related with sugar degradation promoted by heating, namely in Maillard reaction (Ames, Guy, & Kipping, 2001). In fact, this compound was only found in the sweet wines submitted to heating. As far as we know, this carbonyl has never been detected in wines. It seems that phenylacetone formation is also associated with the heating process since it was only detected in baked Malvasia wines. Actually, it was identified in roasted model reactions consisting of glucose and phenylalanine (Baltes & Mevissen, 1988). 2H-Pyran-2,6(3H)-dione was previously identified in oak aged Madeira wines (A. C. Pereira et al., 2010). It seems that ethyl nicotinate and picolinate were only detected in these baked wines.

3.8. Furan compounds

At least 15 furan compounds were developed in Madeira wines due to the thermal processing. Generally speaking, heating developed more furans in sweet wines than in dry wines as well as higher contents (Fig. 3). In sweet wines baked at standard conditions furans composed, on average, 7% of the volatile fraction, while in the dry wine they represent less than 0.3%. Nevertheless, after heating at 70 °C, furans comprised up to 41% in sweet wines and less than 3% in TN dry wine. These results can be explained by the fact that furans in wines are generated by the thermal degradation of sugars due to acid-catalysed reactions, or even through Maillard reaction (V. Pereira, Albuquerque, Ferreira, Cacho, & Marques, 2011). Some furans provided remarkable increases with baking, especially 5-hydroxymethylfurfural (HMF), 5-ethoxymethylfurfural, furfural, furyl hydroxymethyl ketone, 2,5-furandicarboxaldehyde and 5-methylfurfural (Table 1). Similar results were previously observed (V. Pereira et al., 2011), showing that HMF content in aged wines is extremely dependent of the heating temperature (above 50 °C) and sugar content. Two furans exceeded their odour threshold in wines baked at 70 °C (Table 1), 5-ethoxymethylfurfural (Oth of 90 μg/L, (Cutzach, Chatonnet, & Dubourdieu, 2000)) and HMF (Oth of 12 mg/L, (Hauck, Landmann, Brühlmann, & Schwab, 2003)). The former has surpassed 40-fold the odour perception and the second only almost 2-fold. This result indicates that these furans may be potential odorants of baked Madeira wines. Indeed, Oliveira e Silva et al. (2008) observed that 5-ethoxymethylfurfural had an important role in the definition of the global aroma of baked Madeira wines. Cutzach et al. (1999) observed the same in sweet fortified wines and suggested that 5-ethoxymethylfurfural can be obtained by the reaction of HMF with ethanol, catalysed by the wine acidic medium and temperature.

Other minor furans, usually reported in aged wines (Cutzach et al., 1999; A. C. Pereira et al., 2010) were also identified, such as 2-acetylfuran, 2-acetyl-5-methylfuran, ethyl 2-furoate and furfuryl alcohol. Additionally, were also detected in baked wines minor furans rarely detected in wines, namely 2,2-dimethyl-5-(1-methyl-1-propenyl)-tetrahydrofuran, dihydro-2-methyl-3(2H)-furanone, 2-furyl ethyl ketone and 1-(5-hydroxymethyl-2-furanyl)-1-propanone. 2,2-Dimethyl-5-(1-methyl-1-propenyl)-tetrahydrofuran has been detected in the volatile fraction of an ice wine (Setkova, Risticevic, & Pawliszyn, 2007).

3.9. Lactones

Lactones are essentially formed by yeast during alcoholic fermentation, though significant odorant lactones are usually accumulated during wine ageing. The most common example is sotolon, which imparts powerful nutty, sweet, burnt, curry notes to those wines in which it is present. Oliveira e Silva et al. (2008) confirmed the importance of sotolon in the typicality of Madeira wines and observed a progressive increase of sotolon in Madeira wines submitted to *estufagem*. However, in the current baked Madeiras, this lactone was not detected, probably because the used analytical procedure was not appropriate to detect this lactone. Nonetheless, 7 lactones were currently detected, most of them never surpassing their odour perception. The exception was γ-decalactone, which slightly surpassed its low flavour threshold (2.6 μg/L, (Czerny et al., 2008)) in TN dry wine. The results also showed that this lactone, as well as most lactones, suffered a slight increase after the heating step. Quantitatively, the most abundant lactone was γ-carboethoxy-γ-butyrolactone, with values ranging between 79.9 and 539.3 μg/L. Its content was higher in TN dry wine indicating that longer fermentations favour its formation. Additionally, the results also showed that γ-carboethoxy-γ-butyrolactone greatly increased after heating, indicating that temperature favours its formation. This lactone was already reported in Madeira wines aged in oak casks (A. C. Pereira et al., 2010). γ-Butyrolactone, commonly considered the most abundant wine lactone, since it is essentially derived from the fermentative process, was also detected with values ranging between 13.0 and 44.3 μg/L. γ-Ethoxybutyrolactone was also detected, probably formed by the reaction between ethanol and γ-butyrolactone. This lactone was previously identified in the volatile fraction of toasted wood chips (Fernández de Simón, Esteruelas, Mun~oz, Cadahîa, & Sanz, 2009). Other minor lactones were also detected, namely γ-nonalactone and the two isomers (α and β) of angelica lactone. Pisarnitskii (2001) has suggested that angelica lactones in wines are products of sugar decomposition. Actually, these lactones were only detected in sweet wines baked at overheating conditions.

3.10. Sulfur compounds

Volatile sulfur compounds in wines are usually responsible for unpleasant odours, even when present in trace amounts, since they possess low perception thresholds. Usually, their presence in wines is associated with the enzymatic (fermentative process) or non-enzymatic (storage or maturation processes) degradation of sulfur-containing compounds, especially amino acids (Mestres, Busto, & Guasch, 2000). In the current wines only 4 sulfur compounds were encountered and all apparently below their odour perception limit. The volatile profile of TN sweet wine did not show any sulfur compounds, even after *estufagem*. Methionol was the most abundant sulfur compound, especially in TN dry wine (135.4–161.9 μg/L). In fact, TN dry wine accumulated higher contents, probably because it was more fermented. Fedrizzi et al. (2011) also found out that methionol was the most abundant sulfur-containing aroma compound. Besides methionol, ethyl 3-(methylthio)propionate was also detected (3.1–17.4 μg/L). Both compounds are usually considered products of methionine metabolism (Mestres et al., 2000). 4-(Methylthio)-1-butanol, usually related with homomethionine metabolism (Mestres et al., 2000), was only found in TN dry wine (7.2–8.5 μg/L), but its tendency during *estufagem* could not be clearly established. According to the results of Fedrizzi et al. (2011), this compound was the second most abundant sulfur compound and has the tendency to decline under oxidative conditions. 2-Methyl-3-thiolanone, already identified in other wines (Aznar, López, Cacho, & Ferreira, 2001), was also encountered in the current Madeira wines, with values ranging from 4.9 to 12.5 μg/L. Generally speaking, it seems that the heating process did not promote significant changes in the levels of sulfur compounds. Fedrizzi et al. (2011) found out the depletion of most sulfur compounds after the first 15 days of oxidative ageing of Amarone wines.

3.11. Acetals

The origin of acetals in wines is usually associated with the reaction of aldehydes with hydroxyl groups of two alcohols. Madeira wines present favourable conditions for their production, since the alcoholic content is high and several aldehydes are present. In fact, 8 acetals were detected in the current sample set.

Heterocyclic acetals were also encountered in the current Madeiras, specifically *cis*-5-hydroxy-2-methyl-1,3-dioxane (*cis*-dioxane), *cis*-4-hydroxymethyl-2-methyl-1,3-dioxolane (*cis*-dioxolane) and *trans*-5-hydroxy-2-methyl-1,3-dioxane (*trans*-dioxane). Interestingly, *cis*-dioxane always increased when the baking was conducted at standard conditions, but not always increased when the heating took place at higher temperatures. Similar trends were usually observed for *cis*-dioxolane and *trans*-dioxane.

Four diethyl acetals were also identified, namely the diethyl acetals of isovaleraldehyde, glycolaldehyde, furfural and phenylacetaldehyde, with values ranging from 2.0 to 20.4 μg/L. Additionally, acetaldehyde ethyl amyl acetal, probably originated from the reaction of acetaldehyde with ethanol and amyl alcohol (1-pentanol), was also encountered. The acyclic acetals did not present a clear trend with the heating process.

3.12. Other compounds

Finally, 10 compounds that do not belong to the aforementioned chemical families were also found in the current Madeiras. Among them were 4 phthalates, which can be transferred to wines during winemaking from plastic materials (Carrillo, Salazar, Moreta, & Tena, 2007). In general, phthalates concentration decreased after the thermal processing.

Another compound that is often reported in wines (Oliveira, Oliveira, Baumes, & Maia, 2008; Perestrelo et al., 2006), *N*-(3-methylbutyl)acetamide, was also found, especially in TN dry wine. Other compounds were only developed after heating, which was the case of the following compounds, tentatively identified by mass spectra (comparison with NIST and Wiley libraries): 3,7-dimethyl-2,3-epoxy-6-octanyl-1-oxythiocarbonylimidazolide, ethyl pyrrole-2-carboxylate, 2,3-dihydroxypyrazine, curvulol and ethyl 2-formylpyrrole-1-acetate. Interestingly, the compound identified as 3,7-dimethyl-2,3-epoxy-6-octanyl-1-oxythiocarbonylimidazolide sharply increased after the thermal processing, from not detected up to 1351.7 μg/L. Its increase was especially high in sweet wines.

4. Conclusions

The current study showed that *estufagem* introduced significant changes in the volatile composition of Madeira wines. The heating process promoted the increase of the volatile fraction regardless of the sweetness degree, especially increasing the complexity of sweet wines up to 88%. Apparently, major differences were not observed in the volatile profile of wines obtained from different grape varieties after *estufagem*, although it was noticeable that before this step Malvasia was more abundant and richer than Tinta Negra. Moreover, the temperature increase (overheating experiment) had a great impact on the development of new volatile compounds, especially in sweet wines.

At least 190 volatile compounds were identified, 53 of which exclusively encountered in baked wines. It was observed that most chemical families increased after the heating step, especially furan compounds and esters. Thus, in quantitative terms, the volatile profile of baked Madeira wines was mostly represented by esters (more than 38%) and alcohols (more than 15%). Moreover, furan compounds (sugar by-products) play a significant role in the volatile fraction of sweet wines, especially when the heating is performed at high temperatures. Interestingly, 6 norisoprenoids were developed during baking, particularly β-damascenone, which exceeded the limit of olfactory perception, at least 70-fold more in standard heating. In opposition, alcohols and fatty acids presented a slight decrease after heating. Similarly, most acetates declined after baking contributing to the loss of fruitiness. Additionally, several varietal aromas, such as monoterpenic alcohols, usually related to the floral character of some wines and especially encountered in Malvasia wine, were not detected after baking.

In terms of odorant impact, the obtained results showed that *estufagem* favoured the development of some volatiles previously reported as typical aromas of Madeira wines, particularly phenylacetaldehyde, β-damascenone and 5-ethoxymethylfurfural. Additionally, ethyl butyrate, ethyl 2-methylbutyrate, ethyl hexanoate, ethyl isovalerate, guaiacol, HMF and γ-decalactone were also found as potential contributors to the global aroma of baked wines.

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