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Identification and quantification of phenolic compounds of selected fruits from Madeira Island by HPLC-DAD–ESI-MS^n and screening for their antioxidant activity

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ABSTRACT

Five fruits species commonly cultivated and consumed in Madeira Island (Portugal) were investigated for their phenolic profile by means of reversed phase high-performance liquid chromatography coupled to diode array detection and electrospray ionisation mass spectrometry (HPLC-DAD–ESI/MS^n) and antioxidant potential. A large number of compounds were characterised, flavonoids and phenolic acids being the major components found in target samples, 39 compounds (flavonoids, phenolic acids, terpenoids, cyanogenic glycosides and organic acids) were identified in cherimoyas, lemons, papayas, passion-fruits and strawberries for the first time.

Furthermore, all samples were systematically analysed for their total phenolic and flavonoid contents along with two radical scavenging methods (ABTS and ORAC) for antioxidant activity measurement. Target fruits presented high phenolic contents which is responsible for most of the antioxidant activity against radical reactive species ($R^2 > 0.80$). Quantitative data showed that anthocyanins, in particular pelargonidin-3-*O*-hexoside (>300 mg/100 mL), present only in strawberries were the compounds in largest amounts but are the ones which contribute less to the antioxidant activity.

1. Introduction

Fruits have long been regarded as having considerable health benefits (anti-cancer, anti-cardiovascular or anti-diabetes) which are due, at least in part, to high amounts of phenolic compounds, since they alleviate oxidative stress produced by free radicals and subsequently cellular damage (Fu et al., 2013; Isabelle et al., 2010; Kevers et al., 2007; Vasco, Ruales, & Kamal-Eldin, 2008). These properties have increased the interest of the scientific community to investigate fruits' antioxidant composition and function.

Several assays have been frequently used to evaluate free radical scavenging capacity and total antioxidant ability of single compounds and/or complex mixtures such as plants, food and biological samples. The most common and widely used methods involve the determination of the disappearance of free radicals using UV–vis spectrometry, namely ABTS, DDPH, FRAP, ORAC, amongst others. Classical methods, such as Folin–Ciocalteu and aluminium chloride complexation, are used to measure overall "total" phenolic and flavonoids contents (Loizzo et al., 2012; Wolfe et al., 2008).

Currently, HPLC coupled to diode array detector with mass spectrometry has proved to be the best tool in the separation and identification of phenolics in several food commodities. This technique provides a rich amount of qualitative information from which compound identity may be inferred unequivocally (Gonzalez-Molina, Dominguez-Perles, Moreno, & Garcia-Viguera, 2010; Simirgiotis, Caligari, & Schmeda-Hirschmann, 2009).

The edaphoclimatic conditions of the Madeira Island are favourable for the production of european and tropical fruits. Lemons (*Citrus limon* (L.) Burm. F.) and strawberries (*Fragaria* × *ananassa*) are two of the most important fruit crops in the world and have a well known polyphenol composition (Aaby, Mazur, Nes, & Skrede, 2012; Dugo et al., 2005; Gonzalez-Molina et al., 2010; Ornelas-Paz et al., 2013), being an appreciable source of flavonoids (in particular flavanones and anthocyanins). However, relatively little information is available regarding the phenolic profile of exotic fruits like cherimoyas (*Annona cherimola* Mill.), papayas (*Carica papaya* L.) and passion fruits (*Passiflora edulis* Sims.) traditionally part of the Madeiran diet.

To our knowledge, only very few flavonoids were characterised in cherimoyas' juice, namely proanthocyanidin dimers and trimers,

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cathechin monomer and rutin (Barreca et al., 2011). Recent studies have demonstrated that papayas are rich in phenolic (hydroxycinnamic acids derivatives, HCAs) and carotenoid compounds (Gayosso-Garcia Sancho, Yahia, & González-Aguilar, 2011; Rivera-Pastrana, Yahia, & Gonzalez-Aguilar, 2010). Flavonoids have been described as the major components of *Passiflora* species, mainly *C*-glycosylflavones, such as apigenin and luteolin glycoside derivatives. However, most literature data on these species have been obtained not in fruit juice but on leaf extracts, due to their use in folk medicine (Zeraik & Yariwake, 2010; Zucolotto et al., 2012). The limited information in literature highlights the importance, from a nutritional point of view, of antioxidant screening in these fruits.

The present work is a follow-up investigation of vitamin C content determination of various foodstuffs from Madeira Island (Spínola, Mendes, Câmara, & Castilho, 2013). Juices that had been prepared for vitamin C analysis and stored at −80 °C were now investigated for their phytochemical composition by HPLC-DAD–ESI/MS^n and antioxidant activities.

2. Experimental

2.1. Chemicals and reagents

The following reagents were purchased from Panreac (Barcelona, Spain): Folin–Ciocalteu's phenol reagent, sodium chloride, potassium chloride, L-ascorbic acid (L-AA), gallic acid (GA), quercetin (QC), and potassium acetate. Cyanidin-3-glucoside chloride (>98%) was obtained from Biopurify phytochemicals LTD (Chengdu, China). Ellagic acid, 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) and 2,2′azinobis-(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS) were obtained from Fluka (Lisbon, Portugal) and methanol from Fisher Scientific (Geel, Belgium). Apigenin, hesperidin and (+) catechin hydrated were obtained from Extrasynthese (Genay, France). Protocatechuic acid, caffeic acid, fluorescein disodium salt, potassium persulfate, sodium carbonate, metaphosphoric acid, and 2,20-azobis(2-methyl propionamidine) dihydrochloride (AAPH) from Sigma–Aldrich (St. Louis, MO, USA). Aluminium chloride hexahydrate and sodium hydrogen phosphate were obtained from Riedel-de Haën (Hanover, Germany), and potassium dihydrogen phosphate was purchased from Merck (Darmstadt, Germany). LC–MS^n grade acetonitrile (CH_3CN) (LabScan; Dublin, Ireland), formic acid (Sigma–Aldrich) and ultrapure water (Milli-Q water purification system, Millipore, USA) were used for analysis.

2.2. Sample preparation

Five fruit species, all grown by local registered producers, were obtained for this study at their peak season in 2011: passion-fruits (February), cherimoyas (March), lemons, papayas, and strawberries (April/May) (Spínola et al., 2013). Batches contained foodstuffs collected on the same day by different producers, and were delivered to Organic Chemistry and Natural Products Laboratory (Madeira Chemistry Center, CQM) by SONAE distributor 1 or 2 days after harvest. For comparison proposes, the distributor also supplied imported fruit specimens (about 1 kg each). This was not achieved for cherimoyas. Edible portions of several specimens of each fruit variety were homogenised in a pre-chilled blender and the homogenates were centrifuged at 10,000 rpm (2–4 °C; 30 min). The pellet was discharged and the supernatant was filtered to remove any solid residues. The resulting liquid (from now on designed as "juice") was stored at −80 °C until further analysis.

2.3. Chromatographic conditions

The HPLC analysis was carried out on a Dionex ultimate 3000 series instrument coupled to a binary pump, a diode-array detector, an autosampler and a column compartment (kept at 20 °C). Separation was performed on a Phenomenex Gemini C_{18} column (5 μm, 250 × 3.0 mm i.d.) using a mobile phase composed by CH_3CN (A) and water/formic acid (0.1%, v/v) at a flow rate of 0.4 mL/min. The following gradient program was used: 25% A (10 min), 25% A (20 min), 50% A (40 min), 100% A (42–47 min) and 20% A (49–55 min). Spectral data for all peaks were accumulated in the range of 190–400 nm. Fruit juices (dilution 1/10) were prepared with the initial eluent gradient, filtered through 0.45 μm PTFE membrane filters and 10 μL were injected directly. The chromatographic analysis was performed in triplicate ($n = 3$) for each sample.

For HPLC-DAD/ESI-MS^n analysis, a Bruker Esquire model 6000 ion trap mass spectrometer (Bremen, Germany) with an ESI source was used. MS^n analysis worked in negative and positive mode and scan range was set at m/z 100–1000 with speed of 13,000 Da/s. The conditions of ESI were as follows: drying and nebulizer gas (N_2) flow rate and pressure, 10 mL/min and 50 psi; capillary temperature, 325 °C; capillary voltage, 4.5 keV; collision gas (He) pressure and energy, 1×10^{-5} mbar and 40 eV; and fragmentor, 1.0 eV. Esquire control software was used for the data acquisition and data analysis for processing.

2.4. Quantitative analysis of individual phenolic compounds

For this quantitative analysis, the method described by Díaz-García, Obón, Castellar, Collado, and Alacid (2013) was adopted. One standard polyphenol of each group was used to calculate individual concentration present in juices by HPLC-DAD. Caffeic and gallic acids were used for hydroxycinnamic and hydroxybenzoic acids, respectively. Anthocyanins standard was cyanidin 3-*O*-glucoside and hesperidin, quercetin and apigenin standards for flavanones, flavonols and flavones, respectively. (+) Catechin hydrated and ellagic acid were used as standards for quantification of flavanols and ellagitannins. Stock standard solutions (1 g/L) were prepared in methanol and calibration curves were prepared for quantitative analysis of phenolic compounds in the target samples by diluting the stock solutions with initial mobile phase. Six concentrations (5–100 mg/L) were used for the calibration, plotting peak area *vs*. concentration, with $R^2 \geqslant 0.967$. The quantification of polyphenols was calculated by the extrapolation of the peak area values obtained for the components of every juice analysed from the calibration curve of the standard for each polyphenol group. Total individual phenolic Contents (TIPC) was defined as the sum of the quantified phenolic compounds.

2.5. Total phenolic and flavonoid contents and antioxidant capacities assays

2.5.1. Total phenolic content (TPC)

Before all the antioxidant activity determinations, juices were diluted (1:10 with distilled water). TPC was determined by the Folin–Ciocalteu method (Gouveia & Castilho, 2011): 50 μL of sample was mixed with 1.25 mL of FCR (diluted 1:10) and 1 mL of 7.5% Na_2CO_3, were added to a 5 mL test tube, and mixed. After 30 min in darkness and room temperature, the absorbance of the reaction mixture was measured at 765 nm ($n = 3$). The amounts of total phenolics in fruits were expressed as mg of gallic acid equivalents (GAE)/100 g of juice.

2.5.2. Total flavonoid content (TFC)

The flavonoid content was evaluated using the aluminium chloride colorimetric method (Gouveia & Castilho, 2011): 0.5 mL of diluted sample was mixed with 1.5 mL of methanol, 2.8 mL of deionized water, 0.1 mL of CH_3COOK (1 M) and 0.1 mL of $AlCl_3{\cdot}6H_2O$. The reaction mixture was allowed to react for 30 min in darkness and room temperature, and then the absorbance at 415 nm was measured ($n = 3$). The results were expressed as mg of quercetin equivalent (QCE)/100 g of juice.

2.5.3. ABTS radical scavenging activity

The $ABTS^{\cdot+}$ assay was performed according to the procedures of Gouveia and Castilho (2011). For each analysis, 40 μL of sample solution was added to 1.96 mL of the $ABTS^{\cdot+}$ solution (diluted in phosphate buffered saline, PBS; absorbance 0.700 ± 0.021). The reduction of absorbance at 734 nm was measured during 10 min. Results were expressed as μmol Trolox equivalent (TE)/100 g of juice and as mg Vitamin C equivalent (VCE)/100 g of juice.

2.5.4. Oxygen radical absorbance capacity (ORAC) assay

The ORAC assay was performed according to Cíž et al. (2010), with slight modifications. Briefly, 25 μL of sample was transferred to the microplate, which also contained a blank (200 μL of PBS) and a control (25 μL of PBS). Then 150 μL of 40 nmol fluorescein (in PBS) was added to the control and sample wells. After incubation (37 °C, 30 min), 25 μL AAPH (153 mmol/L in PBS) was added to all of the wells with the exception of the blank. Fluorescence readings were taken every minute for 60 min and results were expressed as μmol TE/100 g of juice.

2.6. Statistical analysis

Data analysis was carried out with SPSS for Windows, IBM SPSS Statistics 20 (SPSS, Inc., USA). Analysis of variance (ANOVA) and simple linear regression analysis (R^2) was used to evaluate the results obtained in TPC, TFC and the two antioxidant capacities assays, for the fruit samples. A value of $p < 0.05$ was considered statistically significant.

3. Results and discussion

A phenolic screening of five fruits species commonly consumed was performed. Typical base peak chromatograms (BPC) of analysed fruits are shown in Fig. 1. Identification of compounds was assigned by comparison of their UV–Vis spectra and mass spectrometric data obtained under both negative and positive electron spray ionisation (ESI^-/ESI^+) conditions and with scientific literature.

Tables 1 and 2 reports all of the identified compounds with their UV absorptions and MS^n fragmentation pattern in negative and positive mode, respectively. Compounds were numbered by their elution order since most of them were not found in all samples. A great variety of components was found, being characterised 114 of phenolic nature, mainly flavonoids (*O*- and *C*-glycosylated), HCAs derivatives, and 24 other phytochemicals. Additionally, anthocyanins were also characterised in strawberries (positive mode), mainly glycosides and rutinosides of pelargonidin and cyanindin. The phenolic composition obtained by our HPLC-UV/DAD–MS^n analysis was in agreement with previous works (Aaby et al., 2012; Barreca et al., 2011; Gayosso-Garcia Sancho et al., 2011; Gonzalez-Molina et al., 2010; Ornelas-Paz et al., 2013; Rivera-Pastrana et al., 2010; Zeraik & Yariwake, 2010; Zucolotto et al., 2012). However, despite their well established profiles, we were still able to identify some unreported compounds in lemons and strawberries. The majority of compounds characterised on tropical fruits are here reported for the first time, including isorhamnetin, terpenoids, cyanogenic glycosides, caffeic, quinic, malic and glucaric acids derivatives. The presence of unreported compounds in this species could be related not only to the lack of scientific studies on them, but also to the extraction procedures performed by previous analytical works. A significant amount of bioactive compounds can remain in the solid residues after such extractions and are not taken into account in further analysis.

3.1. Negative mode ionisation

The use of ESI as ionisation source operating in the negative mode has proved to be more efficient and sensitive for phenolic compounds and flavonoids characterisation.

3.1.1. Identification of hydroxycinnamic acids

Caffeic acids conjugated with one or more sugar moieties were detected in all analysed fruits. The nature of the glycosides groups was identified based on the neutral losses of rutinoside, hexoside, caffeoyl, rhamnoside and pentoside moieties (−308, −162, −162, −146, −132, respectively).

Some compounds were characterised based on literature comparison (Gouveia & Castilho, 2010; Rivera-Pastrana et al., 2010): caffeic acid-*O*-hexoside-*O*-rhamnoside (**1**), caffeic acid-*O*-hexoside-*O*-pentoside (**2**), caffeic acid-*O*-hexoside derivative (**3** and **52**), dimmer of caffeic acid-*O*-hexoside (**4**) and caffeic acid-*O*-hexoside (**19**).

Compound **17** (t_R = 4.2 min) with $[M-H]^-$ ion at *m/z* 565 under fragmentation lost a hexoside residue followed by a sinapic acid moiety (224 Da). Hence, was tentatively characterised for the first time in strawberries as caffeic acid-*O*-(sinapoyl-*O*-hexoside).

Caffeoylshikimic acid with $[M-H]^-$ at *m/z* 335 (compound **54**) was previously described in mate (Bravo, Goya, & Lecumberri, 2007) and our characterisation was based on their report. To our best knowledge, this is the first time that this compound is identified in passion fruits juice.

Compounds **102** (t_R = 13.7 min) and **117** (t_R = 17.8 min) with different $[M-H]^-$ ions (at *m/z* 513 and 527, respectively) were tentatively identified as caffeoyltartaric acid derivatives, according to their fragment ions 311, 179, 149 and 135. They were only found in cherimoyas and are reported for the first time.

Ten other caffeic acid derivatives (**56**, **73**, **78**, **83**, **85**, **97**, **121**, **135**, **136** and **141**) were found, distributed in all samples. They gave different fragmentation patterns but all had in common the fragment ion at *m/z* 179 [caffeic acid$-H^-$]. However, based only on the data available it was not possible to completely characterise these compounds.

The presence of 3-*O*-caffeoylquinic acid and 4-*O*-caffeoylquinic acid (compounds **8** and **16**, respectively) was confirmed by their MS^n spectra (Gouveia & Castilho, 2010). While 3-*O* isomer exhibited fragmentation pattern *m/z* 353 → 191, indicating the presence of a monocaffeoylquinic acid (loss of caffeic acid moiety), the 4-*O* isomer showed distinct product ions (173 and 111), but not the negative ion at *m/z* 191 [quinic acid$-H]^-$. 4,5-Dicaffeoylquinic acid (compound **9**) with $[M-H]^-$ at *m/z* 515 was also characterised in lemons and passion fruits, based on literature comparison (Gouveia & Castilho, 2011).

Compounds **34**, **43**, **87** and **99** with deprotonated molecular ions at *m/z* 385, 355, 371 and 563, respectively, were characterised as conjugates of ferulic, coumaric and caffeic acids with glucaric acid, according to Simirgiotis et al. (2009). Compounds **34** and **43** have been previously described in mountain papayas (*Carica pubescens* (A. DC.)), but never in *C. papaya* L. Compounds **87** and **99** are reported in passion fruits for the first time. Caffeoylglucaric acid (compound **87**) occurred again at 11.5 min with a formate adduct.

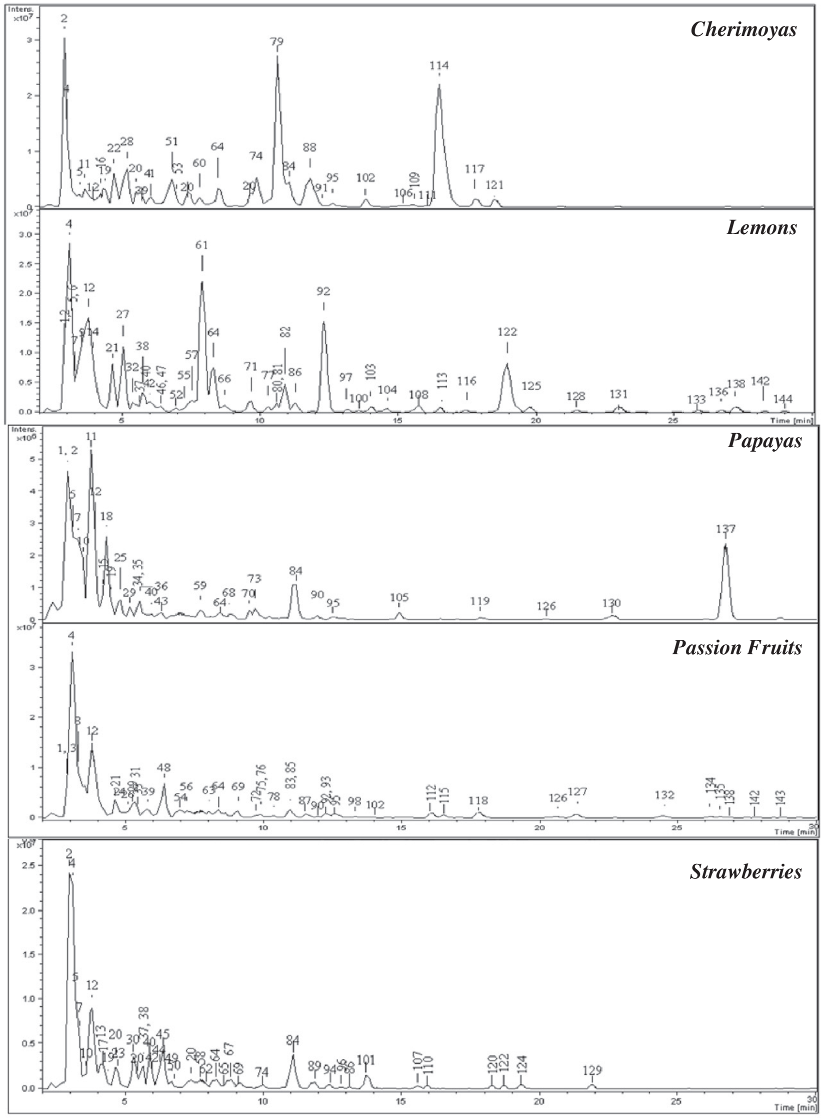

Fig. 1. HPLC-DAD–ESI/MS^n base peak chromatograms (BPC) of juice from cherimoyas, lemons, papayas, passion fruits and strawberries.

Compounds **59** and **68** with [M−H]$^-$ at *m*/*z* 309 and 209 were identified in papayas for the first time as feruloyl-malic acid caffeoyl-malic acid, respectively.

Compound **121** (t_R = 18.9 min) and **123** (t_R = 19.8 min) exhibited [M−H]$^-$ ions at *m*/*z* 499 and 529, respectively and showed identical fragmentation pattern as 4-*O*-caffeoyl-5-*O*-*p*-coumaroylquinic acid and 1-*O*-caffeoyl-5-*O*-feruloylquinic acid (Gouveia & Castilho, 2010).

Compounds **116** (t_R = 17.4 min), **133** (t_R = 25.9 min) and **144** (t_R = 29.0 min) with [M−H]$^-$ ions at *m*/*z* 517, 459 and 417 showed similar fragmentation and were tentatively classified as *p*-coumaroylquinic acid derivatives, according to their fragmentation behaviour. This is the first time that these quinic acid conjugates (**121**, **123**, **116**, **133** and **144**) are reported in lemons.

Compounds **37** and **143** showed both a base peak at *m*/*z* 163 [coumaryl−H]$^-$ after loss of glycoside residues and were identified as *p*-coumaric acid-*O*-hexoside and *p*-coumaric acid-*O*-dihexoside, respectively (Aaby et al., 2012; Gayosso-Garcia Sancho et al., 2011). Moreover, in the absence of more specific data, some compounds were tentatively characterised as coumaric acid derivatives (**48**, **53**, **75**, **76**, **93**, **98**, **115**, **134** and **140**).

Ferulic acid-*O*-hexoside and ferulic acid were attributed to compounds **38** and **95**, respectively, showing typical fragment at *m*/*z* 193 (Gayosso-Garcia Sancho et al., 2011). Additionally, compounds **45**, **67**, **128** and **142** with [M−H]$^-$ ions at *m*/*z* 449, 397, 555 and 643, respectively, were identified as ferulic acid-*O*-hexoside derivative (**45**) based on Aaby et al. (2012) and ferulic acid derivatives (**67**, **128** and **142**).

Sinapic acid and sinapic acid-*O*-hexoside (compounds **38** and **40**) exhibited [M−H]$^-$ ions at *m*/*z* 223 and 385, respectively, being identified according to previous reports in mountain papaya (*C. pubescens* (A. DC.)) (Simirgiotis et al., 2009). However, these compounds have not been, so far, reported in common papaya (*C. papaya* L.).

3.1.2. Hydroxybenzoic acid derivatives

Compound **25** (t_R = 4.8 min) showed a [M−H]$^-$ at *m*/*z* 315 and displayed the same fragmentation pattern as protocatechuic acid-*O*-hexoside (Rivera-Pastrana et al., 2010).

Compound **58** (t_R = 7.7 min) displayed [M−H]$^-$ at *m*/*z* 447 and showed a loss of 146 Da could be attributed to a deoxyhexoside unit. According to literature (Ornelas-Paz et al., 2013), **58** was

Table 1
Characterisation of phenolic and organic compounds of juice from five fruit crop species by HPLC-DAD–ESI$^-$/MS^n.

N°	t_R (min)	λ_{max} (nm)	$[M-H]^-$ (m/z)	HPLC-DAD–ESI/MS^n m/z (% base peak)	Identification	Fruit
1	2.9	267	487	MS^2 [487]: 341 (100), 146 (10.4) MS^3 [487 → 341]: 179 (100), 143 (68.2), 127 (13.4), 102 (19.3) MS^4 [487 → 341 → 179]: 143 (100), 119 (49.9), 135 (76.3), 89 (36.7)	Caffeic acid-*O*-hexoside-*O*-rhamnoside	Lemons[1] Papayas Passion fruits[1]
2	2.9	–	473	MS^2 [473]: 342 (19.4), 341 (100), 132 (23.6), 131 (19.1) MS^3 [473 → 341]: 179 (100), 149 (77.3), 119 (62.3), 113 (28.1) MS^3 [473 → 341 → 179]: 161 (80.5), 149 (100), 119 (78.6), 135 (72.5)	Caffeic acid hexoside-*O*-pentoside	Strawberries[1] Lemons[1] Cherimoyas[1] Papayas[1]
3	2.9	261	446	MS^2 [446]: 341 (100) MS^3 [446 → 341]: 239 (45.5), 179 (100), 161 (41.3), 113 (18.8) MS^4 [446 → 341 → 179]: 161 (62.3), 149 (52.2), 135 (100)	Caffeic acid-*O*-hexoside derivative	Passion fruits
4	3.1	–	683	MS^2 [683]: 342 (17.0), 341 (100) MS^3 [683 → 341]: 179 (100), 161 (35.8), 143 (16.6), 119 (16.6), 113 (16.2) MS^4 [683 → 341 → 179]: 161 (40.9), 119 (100); 135 (43.8), 113 (38.1)	Caffeic acid hexoside dimer	Strawberries Lemons Cherimoyas[1] Passion fruits[1]
5	3.2	–	191	MS^2 [191]: 127 (100), 173 (59.8), 111 (38.7), 85 (62.3) MS^3 [191 → 127]: 111 (100), 85 (73.2)	Quinic acid	Strawberries Lemons Cherimoyas Papayas
6	3.2	–	533	MS^2 [533]: 191 (100) MS^3 [533 → 191]: 127 (100), 173 (74.1), 111 (74.4), 85 (63.5)	Quinic acid derivative	Lemons
7	3.3	245	175	MS^2 [175]: 115 (100) MS^3 [175 → 115]: 88 (25.2), 87 (100), 85 (10.5) MS^4 [175 → 115 → 87]: 59 (100)	L-Ascorbic acid	Strawberries Lemons Papayas
8	3.3	246	515	MS^2 [515]: 353 (100), 191 (19.4), 179 (5.1) MS^3 [515 → 353]: 191 (100), 179 (33.7), 173 (4.5), 135 (11.0)	3,5-*O*-dicaffeoylquinic acid	Passion fruits[1]
9	3.6	–	515	MS^2 [515]: 479 (11.8), 191 (52.1), 179 (32.6), 173 (100) MS^3 [515 → 173]: 127 (15.9), 111 (100)	4,5-*O*-dicafeoylquinic acid	Lemons[1]
10	3.6	–	133	MS^2 [133]: 115 (100) MS^3 [133 → 115]: 71 (100)	Malic acid	Strawberries Cherimoyas Papayas
11	3.7	–	209	MS^2 [209]: 191 (100), 85 (25.9) MS^3 [209 → 191]: 147 (100), 85 (12.3)	Glucaric acid	Cherimoyas Papayas
12	3.9	–	191	MS^2 [191]: 173 (18.5), 111 (100) MS^3 [191 → 111]: 67 (100)	Citric acid	All samples
13	4.1	–	529	MS^2 [529]: 432 (20.6),431 (100) MS^3 [529 → 431]: 270 (22.7), 269 (100), 268 (13.7), 225 (18.5) MS^4 [529 → 431 → 269]: 241 (16.9), 226 (20.3), 225 (100), 149 (62.9)	Apigenin-*O*-hexoside derivative	Strawberries
14	4.1	–	609	MS^2 [609]: 489 (100), 371 (33.6), 491 (22.8), 490 (21.8) MS^3 [609 → 489]: 369 (100), 399 (50.8), 370 (26.2), 371 (20.1) MS^4 [600 → 489 → 369]: 313 (100), 341 (29.9), 343 (22.8), 133 (26.4)	Luteolin-6,8-di-C-hexoside (lucenin-2)	Lemons
15	4.1	–	405	MS^2 [405]: 197 (15.0), 193 (17.4), 191 (100) MS^3 [405 → 191]: 111 (100)	Citric acid derivative	Papayas
16	4.2	–	353	MS^2 [353]: 173 (100), 111 (56.0) MS^3 [353 → 173]: 111 (100)	4-*O*-caffeoylquinic acid	Cherimoyas[1]
17	4.2	–	565	MS^2 [565]: 519 (45.4), 403 (100), 385 (25.2), 223 (45.9) MS^3 [565 → 403]: 223 (65.6), 179 (100)	Caffeic acid-*O*-(sinapoyl-*O*-hexoside)	Strawberries[1]
18	4.3	–	519	MS^2 [519]: 259 (100) MS^3 [519 → 259]: 241 (14.5), 199 (42.2), 169 (14.3), 97 (100)	Unknown	Papayas
19	4.5	–	341	MS^2 [341]: 179 (100), 161 (59.3), 135 (11.6) MS^3 [341 → 179]: 135 (100), 161 (31.0)	Caffeic acid-*O*-hexoside	Cherimoyas[1] Papayas Strawberries
20	4.6	273	577	MS^2 [577]: 426 (28.3), 425 (100), 407 (76.3), 289 (28.4) MS^3 [577 → 425]: 408 (24.1), 407 (100) MS^4 [577 → 425 → 407]: 289 (100), 285 (73.3), 245 (36.7), 205 (28.5)	Proanthocyanidin B dimer	Strawberries
21	4.7	215, 272, 334	593	MS^2 [593]: 473 (100), 353 (51.2), 383 (22.5), 503 (20.8), 474 (18.0) MS^3 [593 → 473]: 353 (100), 383 (20.1), MS^4 [593 → 473 → 353]: 325 (100), 297 (57.4)	Apigenin-6,8-di-*C*-glycoside (vicenin-2)	Lemons Passion fruits
22	4.7	–	411	MS^2 [411]: 250 (16.7), 249 (100), 161 (50.8) MS^3 [411 → 249]: 161 (100), 159 (32.5), 143 (34.2), 129 (28.5), 113 (58.3), 101 (36.3)	(Iso)pentyl dihexoside	Cherimoyas[1]
23	4.8	–	783	MS^2 [783]: 481 (18.1), 302 (44.1), 301 (100), 275 (16.2) MS^3 [783 → 301]: 301 (33.6), 257 (11.0), 229 (79.5), 185 (100)	bis-HHDP-*O*-hexoside	Strawberries
24	4.8	–	429	MS^2 [429]: 368 (11.6) 323 (13.0), 283 (100), 267 (14.7), 207 (22.4) MS^3 [429 → 283]: 152 (27.9), 151 (100), 149 (15.7)	Biochanin A-*O*-rhamnoside	Passion Fruits[1]

Table 1 (*continued*)

N°	t_R (min)	λ_{max} (nm)	$[M-H]^-$ (*m*/*z*)	HPLC-DAD–ESI/MS^n *m*/*z* (% base peak)	Identification	Fruit
25	4.8	267	315	MS^2 [315]: 269 (60.9), 223 (20.6), 161 (47.3), 153 (100) MS^3 [315 → 153]: 135 (31.6), 109 (100), 108 (42.1)	Protocatechuic acid-*O*-hexoside	Papayas
26	4.9	–	461	MS^2 [461]: 416 (12.1), 415 (100) MS^3 [461 → 415]: 270 (18.4), 269 (100), 163 (19.0) MS^4 [461 → 415 → 269]: 227 (25.4), 225 (100), 201 (16.9), 149 (62.9)	Apigenin-*O*-rhamnoside	Passion Fruits
27	5.0	209, 271, 346	623	MS^2 [623]: 503 (100), 383 (64.3), 413 (31.2), 504 (20.9) MS^3 [623 → 503]: 383 (64.3), 384 (21.4), 413 (13.1) MS^4 [623 → 503 → 383]: 368 (11.0), 356 (17.9), 340 (10.8), 313 (27.7), 312 (100)	Lucenin-2,4-methyl ether (diosmetin 6,8-di-*C*-hexoside)	Lemons
28	5.2	–	447	MS^2 [447]: 411 (100) MS^3 [447 → 411]: 250 (16.7), 249 (100), 161 (50.8) MS^4 [447 → 411 → 249]: 161 (97.9), 113 (100), 101 (67.5)	(Iso)pentyl-hexoside derivative	Cherimoyas
29	5.2	–	447	MS^2 [447]: 402 (21.1), 401 (100) MS^3 [447 → 401]: 270 (45.6), 269 (100), 161 (23.2) MS^4 [447 → 401 → 269]: 227 (17.8), 225 (100), 201 (36.9), 151 (42.5),149 (62.9)	Apigenin-*O*-pentoside	Papayas[1] Passion Fruits
30	5.3	315	865	MS^2 [865]: 695 (100), 577 (90.2), 407 (38.8) MS^3 [865 → 695]: 544 (98.2), 543 (100), 452 (89.0), 451 (65.0) MS^4 [865 → 695 → 543]: 525 (100), 407 (70.0), 289 (54.5)	Proanthocyanidin B trimer	Strawberries
31	5.3	–	502	MS^2 [502]: 457 (22.3), 456 (100) MS^3 [502 → 456]: 323 (100), 179 (18.1), 221 (12.4) MS^3 [502 → 456 → 323]: 221 (100), 179 (50.2), 161 (63.6), 125 (55.9), 119 (47.2)	Amygdalin	Passion Fruits
32	5.4	–	757	MS^2 [757]: 505 (37.9), 450 (30.5), 449 (100), 287 (79.2) MS^3 [757 → 449]: 288 (11.4), 287 (100), 286 (11.8) MS^4 [757 → 449 → 287]: 152 (54.3), 151 (100), 107 (82.6)	Eriodictoyl-7-*O*-rutinoside-4-*O*-hexoside	Lemons[1]
33	5.4	–	431	MS^2 [431]: 385 (100), 223 (60.2), 186 (15.0) MS^3 [431 → 385]: 223 (79.7), 153 (100) MS^4 [431 → 385 → 153]: 109 (100)	Roseoside	Passion Fruits[1]
34	5.4	–	385	MS^2 [385]: 348 (36.4), 209 (40.6), 191 (100) MS^3 [385 → 191]: 147 (100), 85 (30.6)	Feruloylglucaric acid	Papayas[1]
35	5.4	–	417	MS^2 [417]: 381 (100) MS^3 [417 → 381]: 249 (100), 161 (23.6)	Saccharide	Papayas
20	5.5	–	577	MS^2 [577]: 426 (26.8), 425 (100), 408 (20.7), 407 (86.2) MS^3 [577 → 425]: 408 (28.0),407 (100), 273 (11.3) MS^4 [577 → 425 → 407]: 289 (100), 285 (71.0), 281 (27.2), 205 (49.1)	Proanthocyanidin B dimer	Cherimoyas Strawberries
36	5.5	–	755	MS^2 [755]: 591 (37.2), 573 (27.4), 489 (25.3), 300 (71.2), 301 (100) MS^3 [755 → 301]: 299 (26.0), 273 (59.0), 255 (25.4), 213 (21.2), 179 (100) MS^3 [755 → 300 → 179]: 151 (100)	Quercetin-3-*O*-(2′ rhamnosyl)-rutinoside (Manghaslin)	Papayas[1]
37	5.6	–	325	MS^2 [325]: 265 (12.2), 187 (43.1), 163 (100), 145 (95.9), 119 (19.2) MS^3 [325 → 163]: 146 (19.8), 119 (100), 118 (10.5)	*p*-Coumaric acid-*O*-hexoside	Strawberries Lemons
38	5.7	219, 328	355	MS^2 [355]: 193 (100), 217 (50.6), 175 (47.5), 191 (18.3) MS^3 [355 → 193]: 135 (100), 149 (28.6), 178 (74.1), 163 (10.8)	Ferulic acid-*O*-hexoside	Lemons Strawberries
39	5.7	–	391	MS^2 [391]: 217 (100), 216 (20.5), 191 (45.7), 111 (27.9) MS^3 [391 → 217]: 191 (61.8), 111 (100)	Citric acid derivative	Cherimoyas Passion fruits
40	5.8	–	385	MS2 [385]: 248 (33.2), 247 (19.4), 223 (100), 205 (31.8), 190 (18.8) MS^3 [385 → 223]: 208 (43.8), 205 (33.4), 179 (19.4), 164 (100)	Sinapic acid-*O*-hexoside	Lemons, Papayas[1] Strawberries
41	5.9	–	289	MS^2 [289]: 246 (20.6), 245 (100), 179 (20.7), 105 (32.6) MS^3 [289 → 245]: 227 (27.8), 203 (100), 188 (22.3), 161 (22.4) MS^4 [289 → 245 → 203]:187 (64.4), 185 (100), 175 (95.0), 161 (43.5), 157 (40.5)	Catechin	Cherimoyas Strawberries
42	6.0	–	313	MS^2 [313]: 295 (24.2), 191 (100), 147 (34.8) MS^3 [313 → 191]: 111 (100), 67 (33.3)	Citric acid derivative	Lemons
43	6.3	–	355	MS^2 [355]: 191 (100), 209 (33.3) MS^3 [355 → 191]: 147 (100), 85 (61.1)	Coumarylglucaric acid	Papayas[1]
44	6.3	–	431	MS^2 [431]: 270 (16.5), 269 (100) MS^3 [431 → 269]: 241 (46.3), 225 (100), 224 (16.8), 201 (41.3), 149 (19.0)	Apigenin-*O*-hexoside	Strawberries
45	6.4	–	449	MS^2 [449]: 431 (26.8), 355 (100), 329 (23.5), 269 (36.2), 193 (41.1) MS^3 [449 → 355]: 193 (100), 192 (12.8), 165 (10.7) MS^4 [449 → 355 → 193]: 178 (100), 165 (11.7), 135 (69.1), 149 (68.4)	Ferulic acid-*O*-hexoside derivative	Strawberries
46	6.4	–	447	MS^2 [447]: 429 843.7), 357 (79.0), 328 (19.8), 327 (100) MS^3 [447 → 327]: 327 (35.6), 299 (100), 285 (63.1), 255 (17.5)	Luteolin 8-C-hexoside (orientin)	Lemons[1] Passion Fruits

(*continued on next page*)

Table 1 (*continued*)

N°	t_R (min)	λ_{max} (nm)	$[M-H]^-$ (*m/z*)	HPLC-DAD–ESI/MS^n *m/z* (% base peak)	Identification	Fruit
47	6.4	–	403	MS^2 [403]: 241 (100), 197 (24.2), 179 (34.8) MS^3 [403 → 241]: 198 (22.5), 197 (100) MS^4 [403 → 241 → 197]: 153 (100), 135 (10.3), 123 (28.2)	Syringic acid derivative	Lemons
48	6.4	–	486	MS^2 [486]: 441 (15.2), 440 (100), 307 (45.0) MS^3 [486 → 440]: 307 (100), 163 (28.0) MS^4 [486 → 440 → 307]: 163 (100), 119 (76.7)	Coumaric acid derivative	Passion Fruits
49	6.7	–	561	MS^2 [561]: 543 (35.1), 435 (29.3), 329 (36.6), 289 (100), 245 (46.7) MS^3 [561 → 289]: 247 (53.9), 245 (100), 245 (48.3), 227 (43.1), 164 (13.6) MS^4 [561 → 289 → 245]: 212 (32.3), 203 (100),187 (32.4)	Propelargonidin B dimer	Strawberries
50	6.8	–	849	MS^2 [849]: 577 (100), 559 (27.9), 407 (37.1), 287 (33.0) MS^3 [849 → 577]: 425 (100), 408 (73.4), 407 (69.9), 289 (56.5) MS^4 [849 → 577 → 425]: 408 (31.8), 407 (100), 289 (99.3)	Propelargonidin B trimer	Strawberries
51	6.8	202, 232, 280	653	MS^2 [653]: 555 (100), 411 (14.3), 556 (11.9) MS^3 [653 → 555]: 453 (16.8), 411 (100), 249 (65.9) MS^4 [653 → 555 → 411]: 250 (33.8), 249 (100), 161 (74.6), 113 (50.2)	(Iso)pentyl dihexoside derivative	Cherimoyas
52	6.9	–	533	MS^2 [533]: 371 (100), 353 (40.0), 515 (76.0), 488 (23.8) MS^3 [533 → 371]: 353 (87.2), 191 (100), 190 (44.7), 179 (13.8)	Caffeic acid-*O*-hexoside derivative	Lemons
53	7.0	–	531	MS^2 [531]: 387 (100), 388 (11.5) MS^3 [531 → 387]: 207 (100), 164 (25.4), 163 (59.3), 119 (10.5) MS^4 [531 → 387 → 207]: 163 (100), 119 (32.6)	Coumaric acid derivative	Cherimoyas[1]
54	7.0	–	335	MS^2 [335]: 161 (100), 135 (38.9), 113 (54.1) MS^3 [335 → 161]: 113 (100), 135 (61.8), 101 (31.0)	Caffeoylshikimic acid	Passion Fruits[1]
55	7.2	–	479	MS^2 [479]: 389 (11.1), 359 (100), 167 (19.8) MS^3 [479 → 359]: 167 (100) MS^4 [479 → 359 → 167]: 123 (100), 95 (13.9)	Vanillic acid derivative	Lemons
56	7.2	–	468	MS^2 [468]: 306 (100), 272 (39.6), 254 (20.5), 253 (19.4) MS^3 [468 → 306]: 255 (30.2), 254 (100), 179 (49.3), 128 (15.4) MS^4 [468 → 306 → 254]: 179 (100), 161 (40.3), 135 (34.1), 119 (11.3)	Caffeic acid derivative	Passion Fruits
20	7.4	–	577	MS^2 [577]: 559 (40.3), 425 (100), 451 (49.8), 407 (90.8), 289 (57.4) MS^3 [577 → 425]: 407 (100) MS^4 [577 → 407 → 425]: 289 (100), 205 (37.0), 187 (45.6)	Proanthocyanidin B dimer	Cherimoyas Strawberries
57	7.5	–	461	MS^2 [461]: 443 (20.4), 371 (44.2), 341 (100), 311 (60.2) MS^3 [461 → 341]: 313 (24.8), 326 (23.2), 299 (100) MS^4 [461 → 341 → 299]: 298 (88.6), 271 (100), 161 (54.7), 89 (55.5)	Diosmetin-6-*C*-hexoside	Lemons
58	7.7	–	447	MS^2 [447]: 301 (100) MS^3 [447 → 301]: 258 (45.4), 257 (56.1), 229 (52.1), 185 (82.7)	Ellagic acid-*O*-deoxyhexoside	Strawberries
59	7.7		309	MS^2 [309]: 193 (100), 291 (45.3), 133 (10.3) MS^3 [309 → 193]: 149 (61.9), 134 (100), 115 (27.6)	Feruloylmalic acid	Papayas[1]
60	7.8	–	699	MS^2 [699]: 539 (34.8), 537 (100), 395 (17.7), 393 (80.7), 138 (16.8) MS^3 [699 → 537]: 477 (11.3), 437 (21.1), 395 (100), 393 (36.4) MS^4 [699 → 537 → 393]: 249 (100), 161 (65.5), 113 (52.9)	Saccharide	Cherimoyas
61	7.9	200, 228, 285	595	MS^2 [595]: 287 (100), 288 (17.2) MS^3 [595 → 287]: 152 (28.4), 151 (100) MS^4 [595 → 287 → 151]: 107 (100)	Eriodictoyl-7-*O*-rutinoside (Eriocitrin)	Lemons
62	7.9	223, 277	934	MS^2 [934]: 915 (53.9), 897 (77.7), 783 (46.9) 633 (71.1), 301 (100) MS^3 [934 → 301]: 301 (100), 257 (77.7), 229 (63.1), 185 (54.1)	Galloyl-bis-HHDP-*O*-hexoside	Strawberries
63	8.0	–	517	MS^2 [517]: 472 (26.9), 471 (100), 323 (42.2) MS^3 [517 → 471]: 323 (100), 222 (14.1), 179 (19.4), 161 (18.0) MS^4 [517 → 471 → 323]: 221 (100), 179 (75.8), 143 (70.2), 125 (68.5), 132 (49.0), 119 (50.9)	Methyl-amygdalin	Passion Fruits
64	8.3	–	609	MS^2 [609]: 255 (100), 539 (39.5), 301 (22.3), 301 (11.3), 255 (24.5) MS^3 [609 → 301]: 273 (35.1), 179 (100), 151 (77.7), 107 (19.0)	Quercetin-3-*O*-rutinoside (Rutin)	Strawberries Lemons Cherimoyas[1] Papayas Passion fruits
65	8.5	–	351	MS^2 [351]: 213 (19.6), 191 (10.4), 190 (64.5), 189 (100), 171 (28.0) MS^3 [351 → 189]: 148 (27.7), 147 (100)	Cinnamic acid-3-*O*-acetylhexoside	Strawberries
66	8.7	–	431	MS^2 [431]: 341 (20.8), 312 (16.3), 311(100) MS^3 [431 → 311]: 283 (100) MS^4 [431 → 311 → 283]: 240 (100), 183 (39.7), 164 (80.8), 119 (37.6)	Apigen-8-*C*-hexoside (Vitexin)	Lemons Passion fruits
67	8.7		397	MS^2 [397]: 134 (25.3), 175 (21.9), 193 (100), 217 (44.4), 337 (32.6) MS^3 [397 → 193]: 134 (100), 149 (38.3)	Ferulic acid derivative	Strawberries
68	8.8	–	295	MS^2 [295]: 277 (10.0), 179 (76.5), 133 (100), 115 (21.9)	Caffeoylmalic acid	Papayas[1]

Table 1 (*continued*)

N°	t_R (min)	λ_{max} (nm)	$[M-H]^-$ (*m*/*z*)	HPLC-DAD–ESI/MS^n *m*/*z* (% base peak)	Identification	Fruit
				MS^3 [295 → 133]: 115 (100), 87 (80.1), 71 (33.4)		
69	9.1	–	487	MS^2 [487]: 442 (54.0), 441 (100), 293 (57.3) MS^3 [487 → 441]: 294 (20.7), 293 (100), 131 (21.8), 149 (49.3) MS^4 [487 → 441 → 293]: 147 (100), 132 (47.0), 113 (82.0), 89 (71.0)	Cinnamic acid-*O*-xylosylhexoside	Strawberries Passion Fruits[1]
70	9.5	–	425	MS^2 [425]: 327 (100), 209 (21.9) MS^3 [425 → 327]: 209 (84.8), 191 (100) MS^4 [425 → 327 → 191]: 147 (100), 85(17.3)	Glucaric acid derivative	Papayas
20	9.6	–	577	MS^2 [577]: 451 (31.7), 425 (100), 408 (28.1), 407 (30.1), 287 (27.2) MS^3 [577 → 425]: 408 (21.5), 407 (100), 299 (21.3), 273 (50.6) MS^4 [577 → 425 → 407]: 389 (46.7), 289 (100), 245 (51.0), 205 (36.9)	Proanthocyanidin B dimer	Cherimoyas
71	9.7	–	595	MS^2 [595]: 459 (38.5), 288 (50.3), 287 (100) MS^3 [595 → 287]: 151 (18.4), 152 (50.2), 125 (100), 107 (64.7)	Eriodictoyl-7-*O*-neohesperidoside	Lemons
72	9.7	–	639	MS^2 [639]: 517 (10.6), 316 (23.2), 315 (100), 301 (61.5) MS^3 [639 → 315]: 301 (13.9), 300 (100) MS^4 [639 → 315 → 300]: 272 (75.4), 255 (100)	Isorhamnetin-*O*-dihexoside	Passion Fruits[1]
73	9.7	–	455	MS^2 [455]: 306 (100), 288 (34.8), 272 (11.6), 160 (16.4) MS^3 [455 → 306 → 254]: 210 (40.6), 179 (100), 161 (43.7), 135 (28.8)	Caffeic acid derivative	Papayas
74	9.9	–	463	MS^2 [463]: 302 (15.3), 301 (100), 179 (21.3, 151 (28.6) MS^3 [463 → 301]: 258 (51.6), 179 (100), 151 (66.8) MS^4 [463 → 301 → 179]: 151 (100)	Quercetin-3-*O*-hexoside	Cherimoyas[1] Strawberries
75	9.8		561	MS^2 [561]: 326 (40.8), 324 (38.9), 307 (78.6), 163 (100) MS^4 [561 → 163]: 145 (45.8), 119 (100)	Coumaric acid derivative	Passion Fruits
76	9.8	–	501	MS^2 [502]: 466 (10.2), 455 (100) MS^3 [502 → 455]: 307 (100), 163 (69.6) MS^4 [502 → 455 → 307]: 163 (100), 145 (86.7), 125 (29.2)	Coumaric acid derivative	Passion Fruits
77	10.3	–	653	MS^2 [653]: 345 (88.8), 330 (100), 302 (45.7), 287 (21.3) MS^3 [653 → 345]: 330 (100) MS^4 [653 → 345 → 330]: 302 (40.6), 301 (83.1), 287 (100), 285 (41.3)	Dimethoxyquercetin-*O*-(*p*-coumaroyl) hexoside	Lemons[1]
78	10.4	–	415	MS^2 [415]: 285 (59.6), 179 (100), 161 (58.6), 143 (22.4) MS^3 [415 → 179]: 161 (100), 135 (41.8), 119 (59.5)	Caffeic acid derivative	Passion Fruits
79	10.6	–	699	MS^2 [699]: 555 (100), 535 (54.3), 478 (26.9), 411 (39.3) MS^3 [699 → 555]: 454 (39.4), 453 (29.2), 412 (33.1), 411 (100) MS^4 [699 → 555 → 411]: 249 (100), 161 (47.8), 125 (32.5)	(Iso)pentyl dihexoside derivative	Cherimoyas
80	10.6	–	649	MS^2 [649]: 563 (41.4), 518 (11.4), 517 (100), 431 (27.0), 269 (44.5) MS^3 [649 → 517]: 431 (33.4), 285 (24.1), 270 (54.9), 269 (100)	Apigenin-7-*O*-(malonyl-apyosil)-hexoside	Lemons
81	10.6	–	771	MS^2 [771]: 610 (26.3), 609 (100) MS^3 [771 → 609]: 302 (13.7), 301 (100) MS^4 [771 → 609 → 301]: 257 (39.4), 179 (84.9), 151 (100)	Quercetin-3-*O*-rutinoside-7-*O*-hexoside (Rutin-7-*O*-hexoside)	Lemons
82	10.9	228, 284, 341	579	MS^2 [579]: 272 (19.0), 271 (100), 269 (58.6) MS^3 [579 → 270]: 269 (34.0), 177 (16.9), 165 (13.1), 151 (100) MS^4 [579 → 270 → 151]: 177 (15.4), 169 (100), 109 (92.3), 107 (33.4)	Naringenin-7-*O*-rutinoside (narirutin)	Lemons
83	11.0	–	643	MS^2 [643]: 322 (14.0), 321 (100) MS^3 [643 → 321]: 179 (100), 143 (30.8), 133 (31.7) MS^4 [643 → 321 → 179]: 161 (100), 143 (83.6), 135 (48.2)	Caffeic acid derivative	Passion Fruits
84	11.1	230, 352	477	MS^2 [477]: 301 (100), MS^3 [477 → 301]: 272 (10.8), 257 (13.0), 179 (100), 151 (90.0), 107 (18.9) MS^4 [477 → 301 → 179]: 169 (17.8), 151 (100)	Quercetin-3-*O*-glucuronide	Cherimoyas[1] Papayas Strawberries
85	11.1	–	553	MS^2 [553]: 307 (10.3), 306 (100), 177 (15.4) MS^3 [553 → 306]: 288 (60.7), 272 (48.4), 254 (100), 128 (23.6) MS^4 [553 → 306 → 254]: 179 (100), 161 (80.3), 135 (61.7)	Caffeic acid derivative	Passion fruits
86	11.3	–	607	MS^2 [607]: 300 (14.7), 299 (100), 284 (51.9) MS^3 [607 → 299]: 285 (23.2), 284 (100) MS^4 [607 → 299 → 284]: 284 (62.0), 256 (100)	Diosmetin 7-*O*-rutinoside (Diosmin)	Lemons
87	11.5	–	417	MS^2 [417]: 372 (11.4), 371 (100), 209 (97.5), 161 (17.9) MS^3 [417 → 371]: 209 (100), 191 (68.9), 135 (31.7) MS^4 [417 → 371 → 209]: 147 (100)	Caffeoylglucaric acid	Passion Fruits[1]
88	11.8	–	223	MS^2 [223]: 208 (100), 179 (52.5), 180 (26.7), 179 (100) MS^3 [223 → 208]: 164 (100), 149 (29.8), 135 (18.7)	Sinapic acid	Cherimoyas[1]
89	11.9	224, 283	355	MS^2 [355]: 310 (19.2), 309 (100), 207 (66.2), 147 (90.8) MS^3 [355 → 309]: 147 (100)	Cinnamic acid-*O*-hexoside	Strawberries
90	12.0	–	163	MS^2 [163]: 119 (100)	*p*-coumaric acid	Papayas Passion fruits
91	12.2	–	699	MS^2 [699]: 537 (100), 393 (57.7), 538 (31.0) MS^3 [699 → 537]: 435 (15.8), 394 (24.9), 393 (100), 291 (12.5)	Saccharide	Cherimoyas

(*continued on next page*)

Table 1 (*continued*)

N°	t_R (min)	λ_{max} (nm)	$[M-H]^-$ (*m/z*)	HPLC-DAD–ESI/MS^n *m/z* (% base peak)	Identification	Fruit
				MS^4 [699 → 537 → 393]: 331 (79.4), 249 (100), 161 (73.6), 89 (34.2)		
92	12.3	200, 228, 284	609	MS^2 [609]: 302 (18.6), 301 (100) MS^3 [609 → 301]: 286 (100), 283 (52.4), 242 (71.2), 125 (53.4) MS^4 [609 → 301 → 286]: 199 (100), 258 (76.9), 244 (86.4), 201 (52.7)	Hesperetin-7-*O*-rutinoside (Hesperidin)	Lemons Passion Fruits[1]
93	12.3	–	487	MS^2 [487]: 441 (14.5), 307 (100), 163 (97.5) MS^3 [487 → 163]: 145 (100), 119 (41.7)	Coumaric acid derivative	Passion Fruits
94	15.6	–	447	MS^2 [447]: 446 (22.5), 425 (22.5), 315 (100), 300 (57.4) MS^3 [463 → 315]: 300 (19.5), 300 (100), 257 (64.5) MS^4 [461 → 315 → 301]: 258 (20.6), 257 (100), 242 (13.9), 229 (37.8), 185 (34.7)	Methyl-ellagic acid-*O*-pentoside	Strawberries
95	12.5	–	193	MS^2 [193]: 178 (17.8), 149 (100) MS^3 [193 → 149]: 134 (100)	Ferulic acid	Cherimoyas[1] Papayas Passion fruits
96	15.9	–	435	MS^2 [435]: 274 (13.1), 273 (100) MS^3 [435 → 273]: 167 (100), 123 (34.5)	Phloretin-*O*-hexoside (Phloridzin)	Strawberries
97	13.1	–	407	MS^2 [407]: 372 (10.7), 239 (100), 149 (10.1), 137 (14.2), 125 (94.0) MS^3 [407 → 239]: 180 (52.1), 179 (100), 137 (26.2) MS^4 [407 → 239 → 179]: 135 (100)	Caffeic acid derivative	Lemons
86	13.1	–	371	MS^2 [371]: 210 (32.9), 209 (100), 191 (36.1) MS^3 [371 → 209]: 147 (100), 179 (16.5)	Caffeoylglucaric acid	Strawberries[1]
98	13.3	–	517	MS^2 [517]: 387 (15.1), 307 (100), 163 (46.3) MS^3 [517 → 307]: 205 (26.4), 163 (100), 119 (65.0), 125 (28.0)	Coumaric acid derivative	Passion Fruits
99	13.3	–	563	MS^2 [563]: 553 (46.2), 372 (22.2), 371 (100) MS^3 [563 → 371]: 403 (17.6), 209 (100), 210 (21.3) MS^4 [563 → 371 → 209]: 147 (100)	Caffeoylglucaric acid derivative	Passion Fruits
100	13.6	–	681	MS^2 [681]: 619 (13.2), 579 (33.3), 537 (100), 375 (20.5) MS^3 [681 → 537]: 376 (27.7), 375 (100), 360 (80.0), 345 (78.3) MS^4 [681 → 537 → 375]: 360 (100), 359 (27.9), 345 (97.3)	Limocitrol-3-*O*-hexoside-7-*O*-rutinoside	Lemons
101	13.7	–	461	MS^2 [461]: 316 (17.7), 315 (100) MS^3 [461 → 315]: 301 (100), 257 (31.5) MS^4 [461 → 315 → 301]: 258 (13.6), 257 (100), 242 (11.7), 229 (29.8)	Methyl-ellagic acid-*O*-deoxyhexoside	Strawberries
102	13.7	–	513	MS^2 [513]: 313 (47.1), 311 (100), 179 (44.4), 161 (37.3), 149 (31.3) MS^3 [513 → 311]: 293 (23.1), 179 (76.1), 161 (47.4), 149 (100), 135 (12.0)	Caffeoyltartaric acid derivative	Cherimoyas[1]
103	14.0	–	609	MS^2 [609]: 560 (56.5), 523 (74.4), 301 (100), 339 (87.4) MS^3 [609 → 301]: 286 (100), 283 (62.4), 242 (16.9) MS^4 [609 → 301 → 286]: 199 (100), 258 (66.7), 244 (74.3), 201 (37.9)	Hesperetin-7-*O*-neohesperidoside (neohesperidin)	Lemons Passion fruits
104	14.7	–	461	MS^2 [461]: 447 (62.0), 446 (30.9), 299 (100), 255 (43.0) MS^3 [461 → 299]: 284 (100), 297 (36.3)	Hispidulin-7-*O*-hexoside	Lemons
105	14.9	–	184	MS^2 [184]: 169 (100), 125 (18.2)	Methyl-gallic acid	Papayas
106	15.2	–	537	MS^2 [537]: 435 (13.0), 393 (100), 291 (13.2), MS^3 [537 → 393]: 331 (21.6), 291 (55.5), 249 (100), 161 (67.7)	Saccharide	Cherimoyas
107	15.6	–	593	MS^2 [593]: 666 (15.2), 327 (42.0), 286 (13.9), 285 (100), 258 (15.8) MS^3 [593 → 285]: 257 (100), 255 (19.4), 241 (17.1), 213 (21.7), 151 (35.6)	Kaempferol-3-*O*-rutinoside	Strawberries
108	15.6	–	785	MS^2 [785]: 742 (28.8), 741 (93.7), 597 (87.7), 453 (100) MS^3 [785 → 453]: 411 (100), 394 (41.9), 393 (66.1), 161 (53.2) MS^4 [785 → 453 → 411]: 393 (66.1), 249 (41.9) 161 (100)	(Iso)pentyl dihexoside derivative	Cherimoyas
109	15.7	–	591	MS^2 [591]: 529 (64.6), 530 (36.2), 489 (96.4), 447 (100) MS^3 [591 → 447]: 285 (100), 284 (48.1)	Kaempferol-3-*O*-(hydroxy-3-methylglutari*C*-hexoside)	Lemons[1]
110	16.0	–	447	MS^2 [447]: 285 (100), 284 (75.5), 257(60.2), 255 (61.4) MS^3 [447 → 285]: 257 (100), 256 (18.3), 255 (14.4)	Kaempferol-3-*O*-hexoside	Strawberries
111	16.0	–	699	MS^2 [699]: 526 (17.6), 525 (92.9), 423 (29.3), 381 (100) MS^3 [699 → 381]: 249 (100), 248 (78.1), 125 (79.8) MS^4 [699 → 381 → 249]: 161 (100), 143 (61.3), 101 (87.4), 83 (40.5)	Saccharide	Cherimoyas
112	16.0	–	363	MS^2 [363]: 249 (77.4), 161 (100), 113 (48.2) MS^3 [363 → 161]: 143 (43.5), 113 (100), 101 (18.1), 89 (52.1)	Saccharide	Passion Fruits
113	16.5	–	623	MS^2 [623]: 315 (100), 300 (30.7), 273 (25.5) MS^3 [623 → 315]: 301 (18.8), 300 (100), 272 (59.3), 255 (29.8)	Isorhamnetin-*O*-rutinoside	Lemons[1]
114	16.5	–	537	MS^2 [537]: 394 (24.5), 393 (100), 291 (13.5) MS^3 [537 → 393]: 349 (40.0), 291 (81.7), 249 (100), 125 (78.5) MS^4 [537 → 393 → 249]: 161 (100), 101 (26.1), 83 (48.5)	Saccharide	Cherimoyas
115	16.5	–	499	MS^2 [499]: 453 (100), 307 (81.1), 163 (31.9) MS^3 [499 → 453]: 384 (11.0), 307 (100), 163 (42.8)	Coumaric acid derivative	Passion Fruits

Table 1 (*continued*)

N°	t_R (min)	λ_{max} (nm)	$[M-H]^-$ (*m/z*)	HPLC-DAD–ESI/MS^n *m/z* (% base peak)	Identification	Fruit
				MS^4 [499 → 453 → 307]: 163 (100), 145 (42.8)		
116	17.4	–	517	MS^2 [517]: 458 (18.2), 355 (50.0), 337 (100), 275 (15.3) MS^3 [517 → 337]: 309 (20.1), 191 (100), 173 (75.3), 163 (30.4)	Coumarylquinic acid derivative	Lemons[1]
117	17.8	–	527	MS^2 [527]: 311 (100), 293 (60.4), 221 (47.6), 191 (51.6), 161 (48.7), MS^3 [527 → 311]: 293 (21.3), 179 (84.2), 149 (100), 161 (27.6)	Caffeoyl tartaric acid derivative	Cherimoyas[1]
118	17.8	–	413	MS^2 [413]: 354 (23.9), 353 (100) MS^3 [413 → 353]: 229 (100)	Unknown	Passion Fruits
119	17.8	–	537	MS^2 [537]: 491 (100), 323 (57.0) MS^3 [537 → 491]: 473 (93.1), 446 (14.2) 323 (100) MS^4 [537 → 491 → 323]: 160 (100), 263 (75.3), 89 (11.0)	Unknown	Papayas
120	18.3	–	461	MS^2 [461]: 285 (100) MS^3 [461 → 285]: 257 (100), 255 (60.3), 241 (32.7), 229 (39.4), 169 (34.1) MS^4 [461 → 285 → 257]: 241 (100), 229 (54.7), 163 (23.3)	Kaempferol-3-*O*-glucuronide	Strawberries
121	18.5	–	625	MS^2 [625]: 474(11.1), 473 (100), 341 (25.7), 293 (11.7) MS^3 [625 → 473]: 342 (36.2), 341 (100), 326 (21.7), 293 (36.5), 233 (33.7), 191 (31.4) MS^4 [625 → 473 → 341]: 179 (100), 161 (56.8), 135 (27.1)	Caffeic acid derivative	Cherimoyas
122	18.7	–	489	MS^2 [489]: 285 (20.3), 284 (100), 273 (18.4), 255 (18.0), 210 (14.9) MS^3 [489 → 285]: 257 (100), 255 (21.2), 229 (62.4), 195 (39.7)	Kaempferol-3-*O*-acetyllhexoside	Strawberries
123	18.9	–	499	MS^2 [499]: 458 (18.2), 353 (50.0), 337 (100), 191 (25.8) MS^3 [499 → 337]: 191 (100), 173 (75.3), 163 (50.4), 129 (30.9) MS^4 [499 → 337 → 191]: 173 (100), 127 (66.1)	4-*O*-caffeoyl-5-*O*-*p*-coumaroylquinic acid	Lemons[1]
124	19.3	–	593	MS^2 [593]: 447 (24.9), 307(19.4), 286 (18.4), 285 (100) MS^3 [593 → 285]: 267 (52.2), 257 (100), 255 (23.7), 229 (34.1)	Kaempferol-3-*O*-coumarylhexoside	Strawberries
125	19.8	–	529	MS^2 [529]: 367 (100), 353 (17.3), 337 (32.3), 191 (19.8) MS^3 [529 → 367]: 191 (100), 173 (28.3) MS^4 [529 → 367 → 191]: 173 (91.3), 134 (31.2), 127 (100), 109 (17.4)	1-*O*-Caffeoyl-5-*O*-feruloylquinic acid	Lemons[1]
126	20.5	–	493	MS^2 [493]: 448 (27.7), 447 (100), 379 (12.4), 286 (32.0) MS^3 [493 → 447]: 315 (100), 300 (67.9), 195 (47.5) MS^3 [493 → 447 → 315]: 301 (100), 300 (23.7), 271 (19.1), 255 (56.6)	Isorhamnetin-*O*-pentoside	Papayas Passion fruits
127	21.3	–	507	MS^2 [507]: 462 (14.6), 461 (100) MS^3 [507 → 461]: 316 (12.3), 315 (100), 308 (29.1), 143 (19.1) MS^4 [507 → 461 → 315]: 300(100), 283 (22.9), 272 (25.3), 255(21.2)	Isorhamnetin-*O*-rhamnoside	Passion Fruits[1]
128	21.4	–	555	MS^2 [555]: 193 (100), 361 (93.2), 379 (74.1) MS^3 [555 → 193]: 134 (100), 149 (31.9), 178 (15.1)	Ferulic acid derivative	Lemons
129	21.9	–	491	MS^2 [491]: 316 (27.3), 315 (100), 300 (30.2) MS^3 [491 → 315]: 301 (14.9), 300 (100), 271 (19.3) MS^4 [491 → 315 → 300]: 283 (22.9), 272 (44.3), 255 (100)	Isorhamnetin-*O*-glucuronide	Strawberries
130	22.6	–	327	MS^2 [327]: 291 (100), 247 (87.7), 185 (34.3), 171 (15.0) MS^3 [327 → 291]: 247 (100), 203 (44.5)	Brevifolin carboxylic acid derivative	Papayas[1]
131	23.0	–	597	MS^2 [597]: 477 (100), 417 (41.5), 387 (10.2), 357 (86.6) MS^3 [597 → 477]: 357 (100), 417 (76.3), 387 (39.4), 209 (27.7)	Phloretin-3,5-di-*C*-hexoside	Lemons[1]
132	24.4	–	469	MS^2 [469]: 425 (19.2), 424 (37.3), 423 (100), MS^3 [469 → 423]: 291 (100), 233 (31.3), 159 (48.1) MS^4 [469 → 423 → 291]: 161 (100), 113 (69.0), 101 (19.4), 85 (91.2)	Unknown	Passion Fruits
133	25.9	–	459	MS^2 [459]: 337 (100), 295 (50.9), 173 (35.7), 163 (52.6) MS^2 [459]: 337 (61.4), 296 (29.3), 295 (100), 163 (50.8) MS^3 [459 → 337]: 147 (72.4), 173 (100), 129 (58.3) MS^3 [459 → 295]: 173 (100), 129 (82.5), 85 (48.6)	Coumaroylquinic acid derivative	Lemons
134	26.1	–	541	MS^2 [541]: 325 (81.2), 205 (56.1), 163 (100) MS^3 [541 → 163]: 145 (100), 85 (65.8)	Coumaric acid derivative	Passion Fruits
135	26.5	–	463	MS^2 [463]: 444 (33.1), 444 (51.1), 417 (28.3), 254 (100) MS^3 [463 → 254]: 210 (18.0), 179 (100) MS^4 [463 → 254 → 179]: 136 (25.5), 135 (100)	Caffeic acid derivative	Passion Fruits
136	26.6	–	397	MS^2 [397]: 235 (23.8), 179 (100), 149 (11.5), 131 (23.5) MS^3 [397 → 179]: 149 (84.5), 135 (100)	Caffeic acid derivative	Lemons
137	26.7	–	507	MS^2 [507]: 462 (27.8), 461 (100), 460 (37.5), 293 (76.6), 289 (42.2) MS^3 [507 → 461]: 293 (100) MS^4 [507 → 461 → 293]: 191 (73.6), 149 (100), 131 (33.3), 113 (56.2)	Quinic acid derivative	Papayas
138	26.8	–	483	MS^2 [483]: 437 (100), 437 (90.1), 291 (21.6) MS^3 [483 → 438]: 293 (98.1), 291 (100), 147 (26.6) MS^4 [483 → 438 → 291]: 159 (100), 101 (81.7)	Unknown	Passion Fruits
139	27.2	–	593	MS^2 [593]: 286 (44.5), 285 (100) MS^3 [593 → 285]: 285 (25.9), 270 (81.0), 243 (100), 226 (10.1),177 (16.9), 164 (53.7)	Isosakuranetin-7-*O*-rutinoside (didymin)	Lemons

(*continued on next page*)

Table 1 (*continued*)

N°	t_R (min)	λ_{max} (nm)	$[M-H]^-$ (*m*/*z*)	HPLC-DAD–ESI/MS^n *m*/*z* (% base peak)	Identification	Fruit
140	27.7	–	507	MS^2 [507]: 464 (49.5), 461 (100), 163 (21.0) MS^3 [507 → 461]: 205 (14.7), 307 (100), 163 (64.9) MS^4 [507 → 461 → 307]: 163 (100), 145 (47.1), 119 (90.6), 101 (10.5), 89 (22.1)	Coumaric acid derivative	Passion fruits
141	27.9	–	486	MS^2 [486]: 294 (87.2), 272 (76.7), 254 (100), 210 (96.8) MS^3 [486 → 254]: 179 (100), 171 (54.9) MS^4 [486 → 254 → 179]: 135 (100)	Caffeic acid derivative	Passion fruits
142	28.2	–	643	MS^2 [643]: 499 (100), 599 (34.5), 576 (12.5), 500 (10.5) MS^3 [643 → 499]: 247 (45.1), 193 (100), 178 (43.5), 149 (27.3) MS^4 [643 → 499 → 193]: 178 (100)	Ferulic acid derivative	Lemons
143	28.7	–	533	MS^2 [533]: 488 (19.7), 487 (100), 325 (16.9), 163 (60.0), MS^3 [533 → 487]: 325 (100), 163 (33.8) MS^4 [533 → 487 → 325]: 163 (100), 145 (39.8), 119 (88.8)	Coumaric acid-*O*-dihexoside	Passion Fruits[1]
144	29.0	–	417	MS^2 [417]: 337 (87.2), 295 (100), 251 (25.7) MS^3 [417 → 295]: 189 (42.7), 173 (100), 163 (37.1), 129 (64.1) MS^4 [417 → 295 → 173]: 129 (100), 111 (48.6), 85 (30.9)	Coumarylquinic acid derivative	Lemons

Their UV spectra have not been properly observed due to low intensity.
[1] Reported for the first time in this fruit.

Table 2
Characterisation of phenolic components from papayas and strawberries by HPLC-DAD–ESI$^+$/MS^n.

N°	t_R (min)	λ_{max} (nm)	$[M-H]^+$ (*m*/*z*)	HPLC-DAD–ESI/MS^n *m*/*z* (% base peak)	Identification	Fruit
A1	3.4	515, 282	449	MS^2 [449]: 288 (12.4), 287 (100) MS^3 [449 → 287]: 231 (11.9), 213 (100), 165 (17.2), 137 (59.3)	Cyanidin-3-*O*-hexoside	Strawberries
A2	3.8	501	433	MS^2 [433]: 272 (20.4), 271 (100) MS^3 [433 → 271]: 215 (42.7), 197 (88.4), 145 (23.9), 129 (20.6), 121 (100), 117 (29.1)	Pelargonidin-3-*O*-hexoside	
A3	3.8	502, 278	579	MS^2 [579]: 271 (100), 272 (15.9), 433 (15.6) MS^3 [579 → 271]: 197 (100), 159 (20.9), 143 (94.4), 141 (29.6), 121 (72.8),	Pelargonidin-3-*O*-rutinoside	
F1	5.5	–	611	MS^2 [611]: 465 (42.9), 303 (100) MS^3 [611 → 303]: 285 (20.0), 259 (44.9), 257 (64.3), 229 (35.2), 213 (15.3), 165 (10.3), 137 (100)	Quercetin-*O*-rhamnosylhexoside	Papayas[1]
A4	5.8	503, 278	475	MS^2 [475]: 272 (12.5), 271 (100), MS^3 [475 → 271]: 215 (24.4), 197 (100), 181 (23.2), 121 (63.1)	Pelargonidin-3-*O*-acetylhexoside	Strawberries
A2	6.0	–	433	MS^2 [431]: 271 (100), 225 (74.8), 188 (89.3), 147 (59.3), 141 (35.2) MS^3 [433 → 271]: 197 (100), 121 (71.3)	Pelargonidin-3-*O*-hexoside	
A2	7.3	–	433	MS^2 [431]: 271 (100), 225 (81.4), 188 (91.2), 147 (58.9), 141 (36.9) MS^3 [433 → 271]: 215 (10.2), 197 (100), 121 (67.9)	Pelargonidin-3-*O*-hexoside	

Their UV spectra have not been properly observed due to low intensity.
[1] Reported for the first time in this fruit.

characterised as ellagic acid deoxyhexoside, previously detected in strawberries. Furthermore, compounds **94** and **101** were identified based on other reports (Aaby et al., 2012) as methyl-ellagic acid-*O*-pentoside and methyl-ellagic acid-*O*-deoxyhexoside, respectively.

Compound **47** (t_R = 6.4 min) presented a $[M-H]^-$ at *m*/*z* 403, yielding fragments at *m*/*z* 241 and 197 (by loss of 162 and 44 Da, respectively), suggesting that it could be a syringic acid derivative according to Barros et al. (2012).

Compound **55** (t_R = 7.2 min) with $[M-H]^-$ at *m*/*z* 479 with fragment ion at *m*/*z* 167 was classified as a vanillic acid derivative (Ornelas-Paz et al., 2013).

Compound **104** (t_R = 14.9 min) with $[M-H]^-$ at *m*/*z* 184, showed a 15 Da elimination giving a gallic acid ion as base peak (*m*/*z* 169). Thus, by comparison with other works (Rivera-Pastrana et al., 2010), this compound was classified as methyl-gallic acid.

3.1.3. Identification of flavonoids

Flavonoid conjugates were the main class of compounds characterised in our target fruits, belonging to 6 subtypes: flavones, flavonols, flavan-3-ols, flavanones, dihydrochalcones and tannins. For better organisation, we divided flavonoids into three groups: *O*-glycosides, *C*-glycosides and tannins.

3.1.3.1. O-glycosides. Compound **24** (t_R = 4.8 min) with $[M-H]^-$ at *m*/*z* 429 was characterised as biochanin A-*O*-rhamnoside, showing characteristic fragment ions at *m*/*z* 283 (by loss of 146 Da) and 151 (Klejdus et al., 2007). This isoflavone was characterised for the first time in passion fruits juice.

Compounds **13** and **44** were characterised as an apigenin-*O*-hexoside derivative and apigenin-*O*-hexoside, respectively, showing typical aglycone at *m*/*z* 269, after sequential loss of different residues (Ornelas-Paz et al., 2013).

Apigenin-*O*-rhamnoside and apigenin-*O*-pentoside (compounds **26** and **29**) exhibited $[M-H]^-$ ions at *m*/*z* 477 and 461, respectively, both showing sequential loss of formate adduct and glycoside moieties. To our best knowledge, **29** was detected for the first time in papayas.

Compound **36** (t_R = 5.5 min) with $[M-H]^-$ at *m*/*z* 755 gave origin to a fragment ion at *m*/*z* 301 (aglycone) by loss of 146 + 308 Da. Based on literature comparison (Simirgiotis et al., 2009), this compound was characterised for the first time in *Carica papaya* as quercetin-3-*O*-(2-rhamnosyl)-rutinoside, contradicting previous reports, stating that this compound could be useful in differentiation between both papayas species.

Identification of dimethoxyquercetin-*O*-(coumaryl)hexoside (compound **77**), here described in lemons for the first time, was

achieved by comparison of its MS^n data with literature (Zanutto et al., 2013).

Quercetin-3-*O*-rutinoside, quercetin-3-*O*-hexoside and quercetin-3-*O*-glucuronide (compounds **64**, **74** and **84**) with $[M-H]^-$ ion at *m*/*z* 609, 463 and 477, respectively, all gave origin to quercetin aglycone, by loss of different glycosides moieties (Aaby et al., 2012; Simirgiotis et al., 2009).

Limocitrol-3-*O*-hexoside-7-*O*-rutinoside (compound **100**) was detected at 13.6 min in lemons and showed loss of a rutinoside unit from $[M-H]^-$ at *m*/*z* 681. Further MS^n fragmentation was similar to that observed for limocitrol-3-*O*-hexoside (Dugo et al., 2005).

Kaempferol-3-*O*-rutinoside (**107**), kaempferol-3-*O*-hexoside (**110**), kaempferol-3-*O*-glucuronide (**120**), kaempferol-3-*O*-acetylhexoside (**122**) and kaempferol-3-*O*-coumarylhexoside (**124**) showed loss of different glycosides but had in common a characteristic aglycone fragment (*m*/*z* at 285) attributed to kaempferol (Aaby et al., 2012; Ornelas-Paz et al., 2013).

Compound **109** (t_R = 15.7 min), also reported for the first time in lemons, showed the same fragmentation pattern as previously reported for kaempferol-3-*O*-(hydroxy-3-methylglutaric-hexoside) in *Rosa* (Porter, van den Bos, Kite, Veitch, & Simmonds, 2012).

Compound **72**, **113**, **126**, **127** and **129** showed $[M-H]^-$ ions at *m*/*z* 639, 493, 407, 493 and 491, respectively, and losses of different glycoside moieties resulting into isorhamnetin aglycone (*m*/*z* 315) (Rivera-Pastrana et al., 2010). Thus, were characterised as isorhamnetin-3-*O*-dihexoside (**72**), isorhamnetin-*O*-rutinoside (**113**), isorhamnetin-*O*-pentoside (**126**), isorhamntin-*O*-rhamnoside (**127**) and isorhamnetin-*O*-glucuronide (**129**). To our best knowledge, this is the first report of isorhamnetin conjugates presence in passion fruits and strawberries.

Compound **80** (t_R = 10.6 min) was detected in lemons with $[M-H]^-$ ion at *m*/*z* 649 was tentatively assigned as apigenin-7-*O*-(malonly-apyosil)-hexoside according to its fragmentation pattern and literature data (Dugo et al., 2005).

Flavanones were the most abundant *Citrus* flavonoids (compounds **32**, **61**, **80**, **85**, **87** and **136**) and usually occur as *O*-glycosyl derivatives, the interglycosidic linkage in rhamnose–hexose disaccharides generally being rutinoside or neohesperidoside (Gonzalez-Molina et al., 2010).

Compound **32** exhibited $[M-H]^-$ ions at *m*/*z* 757 showing base peak at *m*/*z* 287 (eriodictyol aglycone), by successive loss of glycoside residues (308 + 162 Da). Hence, this compound was identified as eriodictyol-7-*O*-rutinoside-4-*O*-hexoside, found in lemons for the first time.

Eriodictyol-7-*O*-rutinoside (**61**), naringenin-7-*O*-rutinoside (**82**), diosmetin-7-*O*-rutinoside (**86**), hesperetin-7-*O*-rutinoside (**92**) and isosakuranetin-7-*O*-rutinoside (**139**) were plausibly identified according to literature data (Dugo et al., 2005; Gonzalez-Molina et al., 2010). With higher retention times, compounds **71** (t_R = 9.7 min) and **103** (t_R = 14.0 min) were tentatively characterised as hesperetin-7-*O*-neohesperidoside and eriodictyol-7-*O*-neohesperidoside, respectively, since neohesperidosides moieties tend to elute later than rutinosides (Dugo et al., 2005). Moreover, rutinosides fragment more easily than the neohesperidosides, such that all rutinosides produce only the fragment ion $[M-H-308]$ in their MS^n spectra.

Based on literature reports (Gouveia & Castilho, 2010), compound **104** (t_R = 14.7 min) was identified as hispidulin-7-*O*-hexoside, being described here for the first time in lemons.

Compound **96** (t_R = 15.9 min) with molecular ion at *m*/*z* 435 was characterised as phloridzin (phloretin-*O*-hexoside) (Roowi & Crozier, 2011).

3.1.3.2. C-glycosides. For luteolin-8-*C*-hexoside (orientin) at 6.4 min (compound **46**) its MS^n spectra showed $[M-H]^-$ at *m*/*z* 447 and typical fragment ions of *C*-glycosides at *m*/*z* 327 $[M-H-120]^-$ and 357 $[M-H-90]^-$ along with luteolin aglycone (*m*/*z* 285). This compound was identified as a *C*-8 flavonoid, since the fragmentation did not reveal $[M-H-18]$, representative of *C*-6 isomers. This compound is abundant in passion fruits (Zeraik & Yariwake, 2010; Zucolotto et al., 2012) and, as far as we know, it is reported for the first time in lemon juice.

Compound **66** (t_R = 8.7 min) exhibited a $[M-H]^-$ ion at *m*/*z* 431 and its characteristic fragment ions $[M-H-90]^-$ and $[M-H-120]^-$, being characterised as apigenin-8-*C*-hexoside (vitexin) based on the literature data (Zucolotto et al., 2012).

Compound **57** (t_R = 7.5 min) with $[M-H]^-$ at m/z 461 was identified as diosmetin-6-*C*-hexoside, which has been previously found in lemons (Gonzalez-Molina et al., 2010).

Compounds **14**, **21** and **27** showed successive neutral losses of 120 Da and were identified as luteolin-6,8-di-*C*-glycoside (lucenin-2), apigenin-6,8-di-*C*-glycoside (vicenin-2) and diosmetin-6,8-di-*C*-glucoside (lucenin-2,4-methyl ether), respectively, according to previous reports in lemons and passion fruits (Dugo et al., 2005; Gonzalez-Molina et al., 2010; Zucolotto et al., 2012).

Compound **131** (t_R = 23.0 min) was identified as phloretin-3,5-di-*C*-hexoside, since its fragment ions matches the ones reported in literature (Roowi & Crozier, 2011). This compound has been found in tropical *Citrus* species, including *Citrus microcarpa*, *Citrus hystrix*, *Citrus medica* and *Citrus suhuiensis*, but never in *C. limon*'s juice.

3.1.3.3. Tannins. Tannins present in foodstuffs are classified into condensed (proanthocyanidins: oligomers and polymers of flavan 3-ol monomer units) and hydrolysable compounds (gallic and ellagic acid or HHDP-based compounds). In the present study, this class of polyphenols was only found in cherimoyas and strawberries juice.

Compounds **20** had $[M-H]^-$ at *m*/*z* 577 and was identified as type B dimer of proanthocyanidin ((epi)catechin-(epi)catechin) by comparison of its fragmentation behaviour with previous works (Aaby et al., 2012; Barreca et al., 2011). With an additional (epi)catechin unit, compound **30** (t_R = 5.3 min) showing $[M-H]^-$ ion at *m*/*z* 865 was classified as a proanthocyanidin B type trimer.

Compounds **49** (t_R = 6.7 min) and **50** (t_R = 6.8 min) with $[M-H]^-$ at *m*/*z* 561 and 849 were characterised, respectively, as type B dimers and trimers of propelargonidin, i.e., proanthocyanidins with (epi)catechin-(epi)afzelechin sequence (Aaby et al., 2012).

Catechin monomer (compound **41**) occurred at 5.9 min and displayed $[M-H]^-$ at *m*/*z* 289 along with characteristic fragment ions at *m*/*z* 245, 203 and 187 (Barreca et al., 2011).

Two ellagitannins were detected in strawberries: compounds **23** (t_R = 4.8 min) and **62** (t_R = 7.9 min) with $[M-H]^-$ at *m*/*z* 783 and 934 were classified as bis-HHDP-*O*-hexoside and galloyl-bis-HHDP-*O*-hexoside, respectively, based on comparison of their fragmentation pattern with previously data on strawberries (Aaby et al., 2012; Ornelas-Paz et al., 2013).

3.1.4. Other compounds

The MS/MS data for brevifolin carboxylic acid derivative (compound **130**) with $[M-H]^-$ ion at *m*/*z* 327 was in agreement with previous reports for brevifolin carboxylic acid in pomegranate fruits and leaves (Fischer, Carle, & Kammerer, 2011). To the best of our knowledge, brevifolin carboxylic acid has not been yet reported in papayas.

Additionally, some other non-phenolic compounds were also detected in this analysis, such as organic acids and saccharide derivatives.

The presence of quinic, L-ascorbic, malic and citric acids (compounds **5**, **7**, **10**, and **12**, respectively) was confirmed by their MS^n data (Flores, Hellín, & Fenoll, 2012). Moreover, quinic acid

derivatives (compounds **6** and **137**) and citric acid conjugates (compounds **15**, **39** and **42**) were also found, exhibiting identical fragmentation behaviours.

Compound **11** (t_R = 3.7 min) with $[M-H]^-$ at 209 was glucaric acid, identified based on its characteristic fragment ions 191, 147 and 85 (Simirgiotis et al., 2009). An additional glucaric acid derivative was also detected at 9.5 min in papayas (compound **70**).

Cinnamic acid-3-*O*-acetylhexoside, cinnamic acid-xylosylhexoside and cinnamic acid-*O*-hexoside (compounds **65**, **69** and **89**, respectively) were plausibly identified according to Aaby et al. (2012), being detected in passion fruits for the first time.

Compound **22** (t_R = 4.7 min) displayed a $[M-H]^-$ ion at *m*/*z* 411 and showed a similar pattern to that reported for (iso)pentyl-dihexoside in tomato samples (Barros et al., 2012). Five more (iso)pentyl-dihexoside derivatives (compounds **28**, **51**, **79** and **108**) were found in cherimoya juice for the first time. They showed different deprotonated molecular ions but all had in common 411 → 249 fragmentation pattern. However, based only on the data available it was not possible to completely characterise these molecules. Other compounds (**35**, **60**, **91**, **106**, **111**, **112** and **114**) were identified as other saccharide residues based on fragment ions 249, 161 and 113. It is worth noting the high content of saccharides detected in cherimoyas, as expected, being the sweetest of all the tested fruits.

Compound **31** (t_R = 5.3 min) and **33** (t_R = 5.4 min) were detected in passion fruits and characterised as amygdalin and roseoside (vomifoliol hexoside) based on comparison of their MS^n spectra with literature (Wang et al., 2012). Additionally, compound **63** (t_R = 8.0 min) was tentatively identified as methyl-amygdalin, showing loss of 15 Da from amygdalin molecule. The presence of cyanogenic glycosides and terpenoids in passion fruits is in accordance with literature reports (Zeraik & Yariwake, 2010; Zucolotto et al., 2012). To our best knowledge, roseoside was characterised for the first time in this fruit juice.

The identity of some compounds (**18**, **118**, **119**, **132** and **138**) could not be established since their UV and MS^n data did not provide enough information concerning their chemical structure.

3.2. Positive mode ionisation

The pigments in strawberries are mainly attributed to anthocyanins which are more easily characterised with electrospray ionisation operating in the positive mode (ESI^+) (Aaby et al., 2012). The MS/MS and UV data used to identify anthocyanins in strawberries juice is summarized in Table 2.

Based on literature (Aaby et al., 2012; Ornelas-Paz et al., 2013), four anthocyanins were plausibly characterised in strawberries: cyanidin-3-*O*-hexoside (**A1**), pelargonidin-3-*O*-hexoside (**A2**), pelargonidin-3-*O*-rutinoside (**A3**) and pelarginidin-3-*O*-acetylhexoside (**A4**). The different retention times of compound **A2** could be associated to the identity/geometry of the sugar moieties.

Moreover, we also detected quercetin-*O*-rhamnosylhexoside (compound **F1**) in papayas, which gave $[M-H]^+$ at *m*/*z* 611 and showed MS^2 fragment ions $[M-H-146]^+$ and $[M-H-146-162]^+$ at *m*/*z* 465 and 303 (base peak), respectively.

3.3. Quantitative analysis

The individual contents of selected phenolic compounds and the TIPC, determined separately on locally produced and imported fruits are shown in Table 3. It was not possible to quantify all identified compounds because of their low UV-absorption and because some of them were present in trace amounts. In total, 28 main polyphenols, distributed by all fruit juices, were quantified by HPLC-DAD using the corresponding standards for calibration for each group and its concentrations were calculated as reported in Section 2.4. L-AA contents determined previously (Spínola et al., 2013) were also included in Table 3.

According to the HPLC-DAD–ESI/MS^n screening, flavonoids were the group with the higher diversity of compounds. The quantitative data followed the same pattern, however, the high HCAs content of all samples (superior to each flavonoid group alone) is highlighted. Anthocyanins content was very high in strawberries, representing the dominant class of compounds in this fruit. In general, pelargonidin-3-*O*-hexoside was the major polyphenol, followed by cyanidin-3-*O*-hexoside, kaempferol-*O*-acetylhexoside and caffeic acid-*O*-hexoside.

HCAs were present in all samples, its concentration being higher in lemons, followed by passion fruits, papayas and strawberries. Caffeic acid-*O*-hexoside was the most abundant phenolic acid, in a concentration range from 4.94 to 31.60 mg/100 mL juice. Protocatechuic acid-*O*-hexoside was the only hydroxybenzoic acid determined, present only in papayas.

About flavanols, strawberries were a rich source of this group of phenolic compounds (8.55–51.73 mg/100 mL juice). Bis-HHDP-*O*-hexoside was the major compound of this group. (+) Catechin and a proanthocyanidin B dimer, were also detected in a lower amount in cherimoyas (30.91 mg/100 mL juice), and flavanols were absent in lemons, papayas and passion fruits.

Regarding flavones content, lemons showed a significantly higher value than passion fruits (44.77 and 2.90 mg/100 mL juice, respectively). Lucenin-2, diosmetin-6,8-di-*C*-hexoside and apigenin-6,8-di-*C*-glycoside were the flavones with higher concentration. In a very small amount, apigenin-*O*-pentoside was determined in passion fruits. This phenolic group was not detected in other samples.

Flavanones were only detected in lemons. The major quantified flavanones were eriodictoyl-7-*O*-rutinoside, naringenin-7-*O*-rutinoside, eriodictoyl-7-*O*-neohesperidoside and hesperetin-7-*O*-rutinoside, with concentrations ranging between 8.43 and 36.17 mg/100 mL juice.

Concerning flavonols, kaempferol-3-*O*-acetyl was the only, abundant, flavonol in lemons (represent the dominant compounds in this fruit), also present in strawberries. Quercetin derivatives were found in strawberries and cherimoyas.

3.4. TPC and TFC assays and antioxidant capacities

The results obtained for total phenolic and flavonoid contents and antioxidant activity determinations (ORAC and ABTS assays) of five local fruits are presented in Table 4.

A similar trend amongst the performed tests can be observed (lemons ≈ strawberries > papayas ≈ cherimoyas > passion fruits) with exception for TFC assay (lemons ≈ strawberries > cherimoyas > passion fruits > papayas). It means that amongst all fruits lemons and strawberries had the highest antioxidant activities and polyphenol contents whereas passion fruits have the lowest.

The TPC results of tested fruits show different trends towards those in the literature (Table 4). Cherimoyas presented lower content, while, lemons, papayas and passion fruits showed a higher value than those reported. Previous studies (Isabelle et al., 2010; Wolfe et al., 2008) also showed that strawberries have higher TPC than passion fruits.

There is a weak correlation between TIPC content of juices and TPC estimated using Folin–Ciocalteu colorimetric method (R^2 = 0.248), and, in general, average TIPC values were lower than TPC (except for strawberries). However, if anthocyanins content is not considered in TIPC, this correlation goes up to R^2 = 0.870.

TFC was found higher than in all existing reports that present values for cherimoyas, lemons and strawberries. For papayas and passion-fruits, there is no available literature information about TFC.

Table 3
Quantification of individual polyphenols from different fruit juices. TIPC: total individual phenolic content.

Compound	Polyphenol content (mg/100 mL of fruit juice)								
	Cherimoyas	Lemons		Papayas		Passion-fruits		Strawberries	
	Local	Local	Imported	Local	Imported	Local	Imported	Local	Imported
L-Ascorbic acid	21.00	52.07	56.00	118.86	95.90	31.76	27.83	53.35	70.80
Hydroxycinnamic acids									
Caffeic acid-*O*-hexoside-*O*-rhamnoside		2.42	2.09	14.09	11.45	13.4	8.37	1.55	2.88
Caffeic acid hexoside-*O*-pentoside	1.74			20.72	21.63				
Caffeic acid-*O*-hexoside	8.05	10.20	8.57	4.94	2.24	32.10	26.89	24.47	31.60
4-*O*-Caffeyolquinic acid	9.28								
3,5-*O*-Dicaffeoylquinic acid						13.79	12.03		
4,5-*O*-Dicaffeoylquinic acid		2.88	1.74						
Ferulic acid-*O*-hexoside		4.25	3.71					3.79	4.48
Feruloylglucaric acid				0.36					
Total	19.08	19.77	16.11	40.12	35.32	59.29	47.29	29.81	38.98
Hydroxybenzoic acids									
Protocatechuic acid-*O*-hexoside				10.01	3.33				
Flavanols									
Proanthocyanidin B dimer	13.87							11.17	26.49
Catechin	17.03							10.73	24.91
bis-HHDP-*O*-hexoside								51.73	
Proanthocyanidin B trimer								31.22	23.34
Propelargonidin B trimer								16.75	10.27
Ellagic acid-*O*-deoxyhexoside								13.83	8.55
Galloyl-bis-HHDP-*O*-hexoside								9.91	9.58
Total	30.91							145.31	103.70
Flavones									
Apigenin-6,8-di-*C*-glycoside		7.68	9.88			2.14	3.53		
Diosmetin 6,8-di-*C*-hexoside		12.07	12.19						
Lucenin 2		25.011	32.98						
Apigenin-*O*-pentoside				1.44		0.75	3.3		
Total		44.77	55.04	1.44		2.89	6.83		
Flavanones									
Eriodictoyl-7-*O*-rutinoside		36.17	30.11						
Eriodictoyl-7-*O*- neohesperidoside		9.75	10.96						
Naringenin-7-*O*-rutinoside		12.39	9.78						
Hesperetin-7-*O*-rutinoside		8.43	6.43						
Total		66.76	57.28						
Flavonols									
Quercetin-3-*O*-glucuronide	10.10			3.01				34.56	32.96
Quercetin-3-*O*-(2′ rhamnosyl)-rutinoside				14.04					
Kaempferol-3-*O*-acetyllhexoside		65.26	55.34					9.36	
Total	10.10	65.26	55.34	17.05				43.92	32.96
Anthocyanins									
Cyanidin-3-*O*-hexoside								12.85	21.29
Pelargonidin-3-*O*-hexoside								324.03	307.63
Pelargonidin-3-*O*-rutinoside								17.29	9.17
Total								354.17	338.09
TIPC	60.11	196.57	183.77	68.63	38.65	62.18	54.12	524.97	595.50

Again there is a lot of variation amongst the results obtained in the ABTS assay that were higher compared to those from other authors in case of lemons, papayas and passion fruits. However, in the present study were reported lower values for cherimoyas and strawberries compared with those from literature. In their investigation, Chun et al. (2005) obtained a different trend values in the ABTS assay (VCEAC), strawberries showing higher antioxidant capacity than lemons. No VCEAC data was found for the other fruits.

The ORAC values found for lemons and papayas in the present work were slightly lower than those reported in literature data. Discrepancies were found for cherimoyas, passion fruits and strawberries. This could be related to the fact that most authors (Aaby et al., 2012; Barreca et al., 2011; Chun et al., 2005; Fu et al., 2013; Gayosso-Garcia Sancho et al., 2011; Isabelle et al., 2010; Kevers et al., 2007; Loizzo et al., 2012; Ornelas-Paz et al., 2013; Rivera-Pastrana et al., 2010; Vasco et al., 2008; Wolfe et al., 2008) perform extraction with organic solvents prior to analysis, which can be seen as a purification procedure, thus concentrating phenolic compounds and consequently higher antioxidant activities. In the present study, fruit juice was used, since the resulting samples are closer to the consumption form.

In parallel, we performed a comparative study with imported fruits processed in the same experimental conditions as the local ones (Table 4), and concluded that, in general, local fruits present

Table 4
Overview of total phenolic and flavonoid contents and antioxidant capacity assays (ABTS, ORAC) of fruit juices.

Fruits	TPC mg GAE/100 g juice	TFC mg QCE/100 g juice	ABTS µmol TE/100 g juice	 mg VCE/100 g juice	ORAC µmol TE/100 g juice
L-Cherimoyas	131.35 ± 4.49	94.76 ± 2.66	879.09 ± 30.34	158.23 ± 3.14	867.27 ± 32.18
Reported	323–683[abc]	3.8[ab]	2300–4400[bc]	N/A	6004[l]
L-Lemons	236.35 ± 5.75	189.20 ± 2.96	1761.27 ± 31.75	316.15 ± 2.38	1323.29 ± 34.16
I-Lemons	221.96 ± 8.09	170.14 ± 3.89	1557,82 ± 50.13	243.70 ± 2.74	1263.41 ± 30.99
Reported	51–109[def]	32[j]	254[e]	347[d]	1848[f]
L-Papayas	159.71 ± 4.67	20.47 ± 4.09	946.78 ± 35.26	169.81 ± 4.01	988.43 ± 26.09
I-Papayas	127.85 ± 4.75	15.30 ± 2.63	906.50 ± 44.87	159.22 ± 3.79	935.50 ± 25.32
Reported	45–54[egh]	N/A	160–292[eg]	N/A	270–1714[fgh]
L-Passion Fruits	138.82 ± 6.49	64.51 ± 2.99	675.14 ± 39.09	121.20 ± 4.88	608.65 ± 44.93
I-Passion Fruits	119.20 ± 7.54	59.53 ± 3.56	623.61 ± 27.44	111.54 ± 3.55	549.68 ± 49.01
Reported	38–134[ceh]	N/A	50–183[ce]	N/A	1582[f]
L-Strawberries	215.56 ± 9.34	176.12 ± 10.02	1455.50 ± 26.73	161.61 ± 2.52	1283.24 ± 32.63
I-Strawberries[*]	218.41 ± 8.95	190.19 ± 9.17	1671.96 ± 27.32	300.13 ± 3.95	1316.09 ± 31.39
Reported	173–385[cdfhi]	15–67[jk]	1100–1326[c]	229[d]	3079–8348[fh]

All measurements are expressed as mean ± SD ($n = 3$).
[*] Higher values than local counterpart. L: local; I: imported. N/A: no available information.
[a] Barreca et al. (2011).
[b] Loizzo et al. (2012).
[c] Vasco et al. (2008).
[d] Chun et al. (2005).
[e] Fu et al. (2013).
[f] Wolfe et al. (2008).
[g] Gayosso-Garcia Sancho et al. (2011).
[h] Isabelle et al. (2010).
[i] Ornelas-Paz et al. (2013).
[j] Kevers et al. (2007).
[k] Lin and Tang (2007).
[l] Gupta-Elera, Garrett, Martinez, Robison, and O'Neill (2011).

higher phenolic contents and antioxidant activities, with the exception of strawberries. Moreover, there were statistically significant differences ($p < 0.05$) between local and imported fruits for all assays. This comparative study was conducted in order to exclude variations due to procedures used in the preparation of the sample. Persistent variations are mainly related with post harvest handling: the local fruits were collected went ready to consume, with control over time and temperature between collection and analysis; imported specimens were collected at unknown date, transported to location under refrigerated conditions. There were some quantitative differences between local and imported fruit juices composition (Table 3) which can partially justify the results obtained in the ABTS and ORAC assays. In general, local juices had higher TIPC than imported counterparts, with the exception of strawberries. In such complex samples as fruits' juice synergistic or antagonistic effects may have occurred, therefore, some discrepancies between polyphenol content and antioxidant properties could be expected within the same fruit species. Cultivar variations and post-harvest conditions seem to play an important role on the obtained results. However, the relevance of these parameters can vary according to species. For example, in the work of Roussos, Paziodimou, and Kafkaletou (2013), lemon fruits from seven cultivars were assessed for fruit quality characteristics and juice phytochemicals. In the principal component analysis (PCA), lemon varieties were grouped together, which did not happen with other citrus species, indicating that cultivar variations are not relevant. Accepting these results as valid, it can be assumed that the variations found in the present work are due mainly to climate and/or post-harvest handling.

Scalzo, Politi, Pellegrini, Mezzetti, and Battino (2005) compared 6 cultivars of strawberry and found significant variation in TPC and antioxidant activity. The variety Camarosa, the one studied in our work, both locally grown and imported from the mainland Portugal, presents a TPC value (201,5 ± 27,9) very similar to our findings (215,6 ± 9,3 for local and 218,4 ± 8,9 for imported fruits) showing that for this particular species cultivar variation is a key issue. Aaby et al. (2012) analysed 27 different strawberries cultivars and reported similar conclusions.

Özkan, Gubbuk, Gunes, and Erdogan (2011) assessed the antioxidant potential of the juices of 3 papaya cultivars: Sunrise Solo, Red Lady, and Tainung. The PCJ antioxidant activities were significantly different from each other ($p < 0.05$). Sunrise Solo had a higher TPC (65 ± 1.9) than Red Lady (53 ± 1.6) and Tainung (41 ± 2.1). This study demonstrated that different papaya cultivars have different antioxidant capacities and TPC amounts.

Devi Ramaiya, Bujang, Zakaria, King, and Shaffiq Sahrir (2013) determined the levels of sugars, ascorbic acid, TPC and total antioxidant activity (TAA) in fruit juices from seven passion fruit (*Passiflora* spp.) cultivars and reported large variations due to the difference in cultivars and ripeness of fruit. Curiously, the vitamin C contents of their *P. edulis* (purple) is coincident with that of Madeira grown fruits; however, TPC and antioxidant data are not comparable since they were performed on methanol–water extract and not on the juice itself.

Both radical scavenging methods (ABTS and ORAC) showed a good correlation with TPC ($R^2 = 0.94$ and $R^2 = 0.84$, respectively), which is in agreement with previous reports (Gayosso-Garcia Sancho et al., 2011; Kevers et al., 2007; Wolfe et al., 2008). A highly positive correlation between the TPC and antioxidant capacity indicated that phenolic compounds are the major responsible for free radicals scavenging ability of these fruits. However, some authors have reported lower correlations ($R^2 < 0.57$) between TPC and antioxidant values (TEAC and ORAC) of fruits, implying that other compounds besides phenolics contribute to their antioxidant capacities (Fu et al., 2013; Isabelle et al., 2010; Vasco et al., 2008).

Antioxidants activity showed good correlation with hydroxycinnamic acids (HCAs) contents ($R^2 = 0.90$ for ABTS and $R^2 = 0.96$ for ORAC) if strawberries were not considered, since this fruit is poor in HCAs. Apparently this is compensated by their high contents of flavanols: when plotting antioxidant activity against TIPC

(anthocyanins excluded) correlations of $R^2 = 0.90$ for ABTS and $R^2 = 0.87$ for ORAC were obtained. Indeed very poor correlations are found whenever anthocyanins are considered as it was previously described by Guerrero et al. (2010).

Previously (Spínola et al., 2013), our group has reported vitamin C contents of these fruits and, in the present study, a poor correlations with antioxidant activity assays ($R^2 < 0.05$) was found, confirming that L-AA provides minor contribution on the antioxidants in fruits. These findings are in agreement with that reported by Isabelle et al. (2010) for Singapore fruits.

4. Conclusions

The HPLC-DAD–ESI/MS^n analysis was successfully applied to identify the main compounds from five different fruit species, all exhibiting a complex composition, mostly flavonoids (*O*- and *C*-glycosylated), phenolic acids, tannins and anthocyanins. 128 different metabolites were characterised (114 phenolics and 24 other phytochemicals), 39 of which are here reported for the first time. The quantification of several individual phenolics was achieved using standards representative of each family of components and TIPC was computed as the sum of those individual phenolics. Antioxidant capacity was significantly correlated with phenolics but not with anthocyanins. The results also showed that antioxidant varied largely across different species, which is in agreement with the presented HPLC composition and could be explained by the high variability of substances with antioxidant characteristics present in the analysed fruits. Variations within species show that the benefits from fruit consumption can be increased by choosing locally grown and ready to eat specimens whenever possible.

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