Author/s:
Suleria, HAR;Barrow, CJ;Dunshea, FR

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Screening and Characterization of Phenolic Compounds and Their Antioxidant Capacity in Different Fruit Peels

Hafiz A. R. Suleria [1,2,*], Colin J. Barrow [2] and Frank R. Dunshea [1,3]

1 School of Agriculture and Food, Faculty of Veterinary and Agricultural Sciences, The University of Melbourne, Parkville, VIC 3010, Australia; fdunshea@unimelb.edu.au
2 Centre for Chemistry and Biotechnology, School of Life and Environmental Sciences, Deakin University, Waurn Ponds, VIC 3217, Australia; colin.barrow@deakin.edu.au
3 Faculty of Biological Sciences, The University of Leeds, Leeds LS2 9JT, UK
* Correspondence: hafiz.suleria@unimelb.edu.au; Tel.: +61-4-7043-9670

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Abstract: Fruit peels have a diverse range of phytochemicals including carotenoids, vitamins, dietary fibres, and phenolic compounds, some with remarkable antioxidant properties. Nevertheless, the comprehensive screening and characterization of the complex array of phenolic compounds in different fruit peels is limited. This study aimed to determine the polyphenol content and their antioxidant potential in twenty different fruit peel samples in an ethanolic extraction, including their comprehensive characterization and quantification using the LC-MS/MS and HPLC. The obtained results showed that the mango peel exhibited the highest phenolic content for TPC (27.51 ± 0.63 mg GAE/g) and TFC (1.75 ± 0.08 mg QE/g), while the TTC (9.01 ± 0.20 mg CE/g) was slightly higher in the avocado peel than mango peel (8.99 ± 0.13 mg CE/g). In terms of antioxidant potential, the grapefruit peel had the highest radical scavenging capacities for the DPPH (9.17 ± 0.19 mg AAE/g), ABTS (10.79 ± 0.56 mg AAE/g), ferric reducing capacity in FRAP (9.22 ± 0.25 mg AA/g), and total antioxidant capacity, TAC (8.77 ± 0.34 mg AAE/g) compared to other fruit peel samples. The application of LC-ESI-QTOF-MS/MS tentatively identified and characterized a total of 176 phenolics, including phenolic acids (49), flavonoids (86), lignans (11), stilbene (5) and other polyphenols (25) in all twenty peel samples. From HPLC-PDA quantification, the mango peel sample showed significantly higher phenolic content, particularly for phenolic acids (gallic acid, 14.5 ± 0.4 mg/g) and flavonoids (quercetin, 11.9 ± 0.4 mg/g), as compared to other fruit peel samples. These results highlight the importance of fruit peels as a potential source of polyphenols. This study provides supportive information for the utilization of different phenolic rich fruit peels as ingredients in food, feed, and nutraceutical products.

Keywords: fruit peels; polyphenols; phenolic acids; flavonoids; flavan-3-ols; hydrolysable and condensed tannins; antioxidant activities; LC-MS and HPLC

1. Introduction

Food processing industries discard huge amounts of fruit wastes, particularly peels, seeds, and some other fruit residues [1]. These fruit wastes have different challenges for many countries, including Australia. Inappropriate landfill management results in emissions of gases including methane and carbon dioxide, while incomplete incineration involves the subsequent formation of secondary wastes such as dioxins, furans, acid gases, and releases of other dangerous pollutants that can cause serious environmental and health issues [2]. For these reasons, there is an urgent need to find uses for these food wastes, including fruit peel wastes. Some fruit peels have been recycled into products ranging from agricultural compost, biofuel, and citric acid [3]. However, fruit peels also

provide an excellent source of carbohydrates, fibre, proteins, and phytochemicals, particularly phenolic compounds with high antioxidant capacities [4]. These components are not generally recovered from peels and so provide a future source of valuable antioxidant ingredients. Polyphenols are a large group of secondary metabolites commonly present in fruits and vegetables, which play a prominent role in human health and nutrition [5]. Phenolic compounds consist of aromatic rings with hydroxyl groups, organic acids, and acylated sugars. These phenolic moieties have high antioxidant activity which prevents the formation of free radicals [6]. The most abundant polyphenols in different fruit peels include flavan-3-ols, flavonols, phenolic acids, anthocyanins, and hydroquinones [7].

The fruit juice industries generate substantial quantities of peel residues during juice processing [8]. The major phenolic compounds present in different fruit peels (apple, pomegranates, mango, pineapple, and citrus peels) include hydroxybenzoic and hydroxycinnamic acids (caffeic acid, gallic acid, protocatechuic acid, and chlorogenic acid), hydrolysable tannins (pedunculagin, punicalin, punicalagin, and ellagic and gallic acids) and flavonoids including anthocyanins [9]. The phenolic compounds identified in avocado and custard apple peels include high contents of condensed tannins and flavonoids including procyanidins [10], whereas those in banana peels are mainly gallocatechin, catechin, and epicatechin [11]. *Prunus* cultivars such as nectarine, peaches, and apricot peels are rich in hydroxycinnamates and flavan-3-ols that have potential antioxidant activities [12]. The antioxidant potential of polyphenols can be estimated with different in vitro spectrophotometric-based methods, including (i) the determination of total phenolics, (ii) free radical scavenging methods, (iii) non-radical redox potential-based methods, and (iv) metal-chelating methods [13]. In addition, polyphenols can also inactivate the Fenton reaction by reacting with different metal ions [14]. For this reason, a set of different in vitro spectrophotometric-based assays with different mechanisms, including total phenolic content (TPC), total flavonoid content (TFC), total tannin content (TTC), 2, 2′-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging assay, ferric reducing assay (FRAP), 2, 2′-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) assay and total antioxidant capacity (TAC), were used to estimate overall phenolic contents and map their antioxidant potential [15].

In recent years, there is increasing interest in the extraction of phenolic compounds from different plant materials. Extraction, identification, and characterization of novel phenolics from different plant-based materials are challenging due to their chemical and structural diversity and complexity. The liquid chromatography coupled with electrospray-ionization and quadrupole time-of-flight mass spectrometry (LC-ESI-QTOF-MS/MS) is an innovative tool with high sensitivity and is the most effective method for the characterization of both low and high molecular weight phenolic and non-phenolic compounds [16]. Also, high-performance liquid chromatography (HPLC) coupled with the photodiode array detector (PDA) is a useful tool for quantifying targeted polyphenols. Although several studies have quantified selected phenolic compounds from a range of different fruit by-products using conventional HPLC-UV-based techniques, there is limited literature available on the relative abundance and distribution of numerous phenolic compounds in Australia's grown fruit peels, particularly using advanced LC-MS/MS characterization methods. As far we know, only some selected phenolic compounds have been characterized in fruit peels using LC-MS/MS [17]. Therefore, extraction, identification, and characterization of phenolics from different fruit peels using advanced analytical techniques including the LC-ESI-QTOF-MS/MS will provide further information in developing innovative functional foods, nutraceuticals, and pharmaceuticals on a commercial scale from these food wastes.

The objective of this study is to determine the phenolic content including TPC, TFC, TTC in twenty (20) different fruit peel samples and assess their antioxidant potential by determining DPPH, TAC, FRAP, and ABTS. Moreover, the identification and characterization of untargeted phenolic compounds were achieved through the LC-ESI-QTOF-MS/MS followed by the quantification of twenty targeted phenolics through HPLC-PDA. This study provides supportive information for the use of different phenolic rich fruit peels as ingredients in food, feed, and nutraceutical products.

2. Materials and Methods

2.1. Chemicals

In this study, most of the chemicals, reagents, and standards were analytical grade and purchased from Sigma-Aldrich (Castle Hill, NSW, Australia). Gallic acid, L-ascorbic acid, vanillin, hexahydrate aluminium chloride, Folin-Ciocalteu's phenol reagent, sodium phosphate, iron(III) chloride hexahydrate (Fe[III]$Cl_3.6H_2O$), hydrated sodium acetate, hydrochloric acid, sodium carbonate anhydrous, ammonium molybdate, quercetin, catechin, 2,2′-diphenyl-1-picrylhy-drazyl (DPPH), 2,4,6tripyridyl-s-triazine (TPTZ), and 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) were purchased from the Sigma-Aldrich (Castle Hill, NSW, Australia) for the estimation of polyphenols and antioxidant potential. Sulfuric acid (H_2SO_4) with 98% purity was purchased from RCI Labscan (Rongmuang, Thailand). HPLC standards including gallic acid, *p*-hydroxybenzoic acid, caftaric acid, caffeic acid, protocatechuic acid, sinapinic acid, chlorogenic acid, syringic acid, ferulic acid, coumaric acid, catechin, quercetin, quercetin-3-galactoside, diosmin, quercetin-3-glucuronide, epicatechin gallate, quercetin-3-glucoside, kaempferol and kaempferol-3-glucoside were produced by Sigma-Aldrich (Castle Hill, NSW, Australia) for quantification proposes. HPLC and LC-MS grade reagents including methanol, ethanol, acetonitrile, formic acid, and glacial acetic acid were purchased from Thermo Fisher Scientific Inc. (Scoresby, VIC, Australia). To perform various in vitro bioactivities and antioxidant assays, 96 well-plates were bought from the Thermo Fisher Scientific (VIC, Australia). Additionally, HPLC vials (1 mL) were procured from the Agilent technologies (VIC, Australia).

2.2. Sample Preparation

Twenty different Australian grown fresh and mature fruits varieties (2–3 kg) including apple (Royal gala), apricot (Mystery), avocado (Hass), banana (Cavendish), custard apple (African Pride), dragon fruit (Red-fleshed), grapefruit (Thompson), kiwifruit (Hayward), mango (Kensington Pride), lime (Tahitian), melon (Rock melons), nectarine (Fantasia), orange (Navels), papaya (Sunrise Solo), passionfruit (Misty Gem), peach (Florda gold), pear (Packham's Triumph), pineapple (Aussie Rough), plum (Angeleno), and pomegranate (Griffith) were purchased from a local produce market in Melbourne, Australia. The fruits were manually cleaned, and peels were removed and freeze-dried according to the method of Peng, et al. [18], described in the supplementary material. Figure 1 represents the graphical and schematic layout of our study.

2.3. Extraction of Phenolic Compounds

To extract the phenolic compounds, 2.0 ± 0.5 g of each fruit peel powder was mixed with 20 mL 70% ethanol by modifying the method of Gu, et al. [19], explained in the supplementary material.

2.4. Estimation of Phenolics and Antioxidant Potential

For the phenolic estimation in selected fruit peel samples, TPC, TFC, and TTC assays were performed, while for measuring their antioxidant capacities, four different types of antioxidant assays including FRAP, DPPH, ABTS, and TAC were performed by adopting our previously published methods of Tang, et al. [20], explained in the supplementary material. The data was determined using a Multiskan® Go microplate photometer (Thermo Fisher Scientific, Waltham, MA, USA).

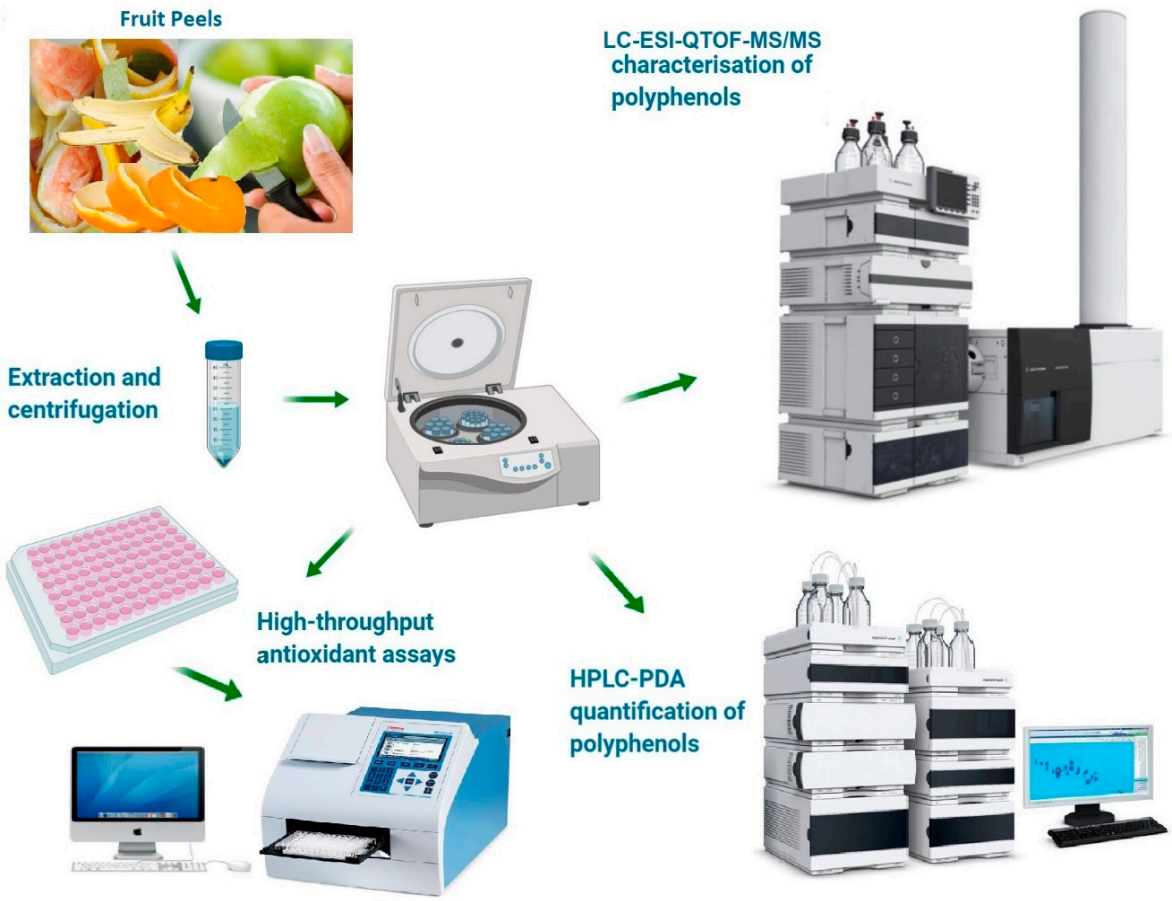


Figure 1. Graphical overview and schematic layout of the proposed research study.

2.5. Characterization and Quantification of Phenolics Using LC-ESI-QTOF-MS/MS and HPLC-PDA

The phenolic compound characterization was performed on an Agilent 1200 HPLC with 6520 Accurate-Mass Q-TOF-MS (Agilent Technologies, Santa Clara, CA, USA). The separation and characterization of phenolics were conducted by adopting our previously published method of Zhong, et al. [21], elaborated in the supplementary material. However, for the quantification of targeted phenolics present in different fruit peel samples was achieved with an Agilent 1200 HPLC coupled with a photodiode array (PDA) detector by following the protocol of Ma, et al. [22], explained in the supplementary material.

2.6. Statistical Analysis

All analyses were performed in triplicate, and the results are presented as mean ± standard deviation (n = 3). The mean differences between different samples were analyzed by one-way analysis of variance (ANOVA) and Tukey's honestly significant differences (HSD) multiple rank test at $p \leq 0.05$. ANOVA was carried out via Minitab 19.0 (Minitab, LLC, State College, PA, USA) and GraphPad Prism 7.05 Software for Windows (GraphPad 7.05 Software, San Diego, CA, USA, www.graphpad.com). For correlations between polyphenol content and antioxidant activities, Pearson's correlation coefficient at $p \leq 0.05$ and multivariate statistical analysis including a principal component analysis (PCA), XLSTAT-2019.1.3 were used by Addinsoft Inc. New York, NY, USA.

3. Results and Discussion

This study involved the screening and characterization of phenolic compounds with antioxidant potential from twenty different fruit peel samples. An untargeted polyphenol identification and

characterization were achieved by the LC-ESI-QTOF-MS/MS, an advanced analytical technique which can provide comprehensive phytochemical screening and MS/MS characterization. For the quantification of phenolic compounds, the twenty most abundant phenolic compounds including (10) phenolic acids and (10) flavonoids present in different fruit peels were targeted and quantified by the HPLC-PDA. A strong correlation between phenolic compound levels and antioxidant activities was observed in all selected fruit peel samples.

3.1. Phenolic Estimation (TPC, TFC and TTC)

Fruit peels contain high concentrations of phenolic compounds including flavonoids, phenolic acids, and tannins. The phenolic contents in different fruit peel samples were determined with TPC, TFC, and TTC assays.

Table 1 summarizes the polyphenol concentrations and antioxidant potentials of twenty selected fruit peel samples. The TPC values of these fruit peel samples varied widely, with mango, grapefruit, and lime peel samples exhibiting the highest TPC values (27.51 ± 0.63, 27.22 ± 1.00 and 23.32 ± 2.07 mg GAE/g, respectively), followed by orange and avocado peel samples. The lowest phenolic contents were detected in dragon fruit, nectarine, and passion fruit peels. Comparing all the peel samples, the mango peel sample had significantly higher phenolic contents ($p < 0.05$) than any other fruit peels. Previously, Nguyen, et al. [23] reported significantly higher phenolic contents in mango peels as compared to other tropical fruits, including passion fruit and dragon fruit, which is consistent with our results. In our study, total phenolic content was measured using the Folin-Ciocalteu reagent that has the ability to react with both phenolics and non-phenolic compounds such as ascorbic acid and other reducing substances [24]. Grape and lime peel were reported to be rich in ascorbic acid, which may be one of the contributors to their high total polyphenol content [25]. However, grapefruit and lime peel were previously found to be abundant in polymethoxylated flavones, phenolic acids, and flavanones including naringin and neohesperidin [26]. Previously, similar trends but with higher TPC values were detected in different fruit juices, including grapefruit (657.65 ± 69.20 mg GAE/g), lime (579.41 ± 91.14 mg GAE/g) and orange (523.44 ± 87.20 mg GAE/g) [27]. Nurliyana, et al. [28] also found that dragon peel has a high phenolic content, most likely due to the abundance of betacyanins (pigments) rather than polyphenols, which increased the TPC values [29]. Considering these facts, polyphenol characterization through advanced analytical techniques including LC-MS/MS can provide more reliable and useful information for their applications in different food, feed, nutraceutical, and pharmaceutical industries.

Table 1. The polyphenol concentrations and antioxidant potentials of twenty different selected fruit peels.

Sample	TPC (mg GAE/g)	TFC (mg QE/g)	TTC (mg CE/g)	DPPH (mg AAE/g)	ABTS (mg AAE/g)	FRAP (mg AAE/g)	TAC (mg AAE/g)
Apple peel	10.82 ± 0.51 ^{e}	1.22 ± 0.10 $^{b–e}$	2.25 ± 0.12 ^{e}	5.20 ± 0.25 ^{b}	4.96 ± 0.17 ^{d}	3.20 ± 0.04 ^{d}	2.97 ± 0.16 ^{d}
Apricot peel	5.60 ± 0.27 ^{f,g}	1.22 ± 0.09 $^{b–e}$	1.07 ± 0.05 ^{f}	3.73 ± 0.55 ^{c}	3.21 ± 0.04 ^{e}	2.27 ± 0.11 ^{e}	2.28 ± 0.04 ^{e,f}
Avocado peel	18.79 ± 1.46 ^{c}	1.24 ± 0.11 $^{b–d}$	9.01 ± 0.20 ^{a}	8.67 ± 0.44 ^{a}	7.19 ± 0.72 ^{c}	3.65 ± 0.07 ^{c}	4.50 ± 0.16 ^{c}
Banana peel	6.13 ± 0.25 ^{f,g}	1.32 ± 0.12 ^{b,c}	1.22 ± 0.08 ^{f}	1.20 ± 0.12 ^{e}	1.31 ± 0.03 ^{g,h}	0.81 ± 0.03 ^{i,j}	2.36 ± 0.22 ^{e,f}
Custard apple peel	15.72 ± 0.74 ^{d}	1.21 ± 0.08 $^{b–e}$	8.32 ± 0.56 $^{a–c}$	2.52 ± 0.52 ^{d}	4.00 ± 0.44 ^{e}	1.51 ± 0.02 ^{f}	2.58 ± 0.04 ^{d,e}
Dragon fruit peel	0.45 ± 0.12 ^{k}	0.03 ± 0.01 ^{h}	0.03 ± 0.01 ^{h}	1.03 ± 0.16 ^{e}	0.56 ± 0.08 ^{h}	0.06 ± 0.01 ^{l}	0.19 ± 0.02 ^{i}
Grapefruit peel	27.22 ± 1.00 ^{a}	0.82 ± 0.14 ^{f}	7.60 ± 0.35 ^{c}	9.17 ± 0.19 ^{a}	10.79 ± 0.56 ^{a}	9.22 ± 0.25 ^{a}	8.77 ± 0.34 ^{a}
kiwi fruit peel	5.30 ± 0.40 ^{g,h}	0.45 ± 0.06 ^{g}	3.51 ± 0.33 ^{d}	5.03 ± 0.39 ^{b}	8.95 ± 0.18 ^{b}	1.13 ± 0.10 $^{g–i}$	0.79 ± 0.05 ^{h}
Lime peel	23.32 ± 2.07 ^{b}	1.14 ± 0.17 $^{c–e}$	8.42 ± 0.63 ^{a,b}	2.73 ± 0.34 ^{d}	1.46 ± 0.14 ^{g}	0.92 ± 0.07 $^{h–j}$	2.27 ± 0.08 ^{e,f}
Mango peel	27.51 ± 0.63 ^{a}	1.75 ± 0.08 ^{a}	8.99 ± 0.13 ^{a}	8.67 ± 0.49 ^{a}	9.32 ± 0.24 ^{b}	6.19 ± 0.26 ^{b}	6.19 ± 0.23 ^{b}
Melon peel	2.39 ± 0.02 $^{i–k}$	0.03 ± 0.01 ^{h}	0.02 ± 0.01 ^{h}	0.48 ± 0.28 ^{e}	1.16 ± 0.20 ^{g,h}	0.08 ± 0.01 ^{l}	0.93 ± 0.23 $^{g–h}$
Nectarine peel	1.53 ± 0.04 ^{j,k}	0.09 ± 0.01 ^{h}	0.23 ± 0.18 ^{h}	1.29 ± 0.09 ^{e}	1.25 ± 0.13 ^{g,h}	0.91 ± 0.07 $^{h–j}$	0.97 ± 0.05 ^{g,h}
Orange peel	21.31 ± 1.37 ^{b}	1.08 ± 0.06 $^{c–f}$	8.12 ± 0.26 ^{b,c}	4.79 ± 0.31 ^{b}	3.36 ± 0.16 ^{e}	2.44 ± 0.12 ^{e}	2.55 ± 0.08 ^{d,e}
Papaya peel	3.13 ± 0.15 $^{h–j}$	1.06 ± 0.07 $^{c–f}$	1.09 ± 0.04 ^{f}	1.13 ± 0.11 ^{e}	3.30 ± 0.17 ^{e}	0.91 ± 0.07 ^{i,j}	1.12 ± 0.13 ^{g,h}
Passion fruit peel	1.55 ± 0.21 ^{j,k}	0.04 ± 0.01 ^{h}	0.19 ± 0.02 ^{h}	0.72 ± 0.13 ^{e}	1.04 ± 0.07 ^{g,h}	0.42 ± 0.04 ^{k}	1.32 ± 0.05 ^{g}
Peach peel	5.84 ± 0.33 ^{f,g}	1.02 ± 0.08 $^{d–f}$	0.16 ± 0.05 ^{h}	1.33 ± 0.11 ^{e}	1.03 ± 0.06 ^{g,h}	0.89 ± 0.07 ^{i,j}	1.13 ± 0.07 ^{g,h}
Pear peel	4.30 ± 0.29 $^{g–i}$	1.07 ± 0.12 $^{c–f}$	0.10 ± 0.03 ^{h}	0.84 ± 0.12 ^{e}	1.21 ± 0.06 ^{g,h}	0.65 ± 0.08 ^{j,k}	1.18 ± 0.03 ^{g,h}
Pineapple peel	7.83 ± 0.35 ^{f}	1.47 ± 0.07 ^{b}	1.23 ± 0.05 ^{f}	1.30 ± 0.07 ^{e}	2.36 ± 0.06 ^{f}	1.30 ± 0.16 ^{f,g}	2.00 ± 0.14 ^{f}
Plum peel	4.81 ± 0.30 ^{g,h}	0.96 ± 0.08 ^{e,f}	0.29 ± 0.05 ^{g,h}	1.01 ± 0.10 ^{e}	1.19 ± 0.08 ^{g,h}	0.71 ± 0.04 ^{j,k}	0.87 ± 0.04 ^{h}
Pomegranate peel	3.89 ± 0.21 $^{g–i}$	0.97 ± 0.10 ^{e,f}	0.99 ± 0.02 $^{f–g}$	4.60 ± 0.08 ^{b,c}	3.34 ± 0.09 ^{e}	1.25 ± 0.13 $^{f–h}$	2.40 ± 0.18 ^{e,f}

All values are expressed as mg/g mean ± standard deviation (n = 3). Alphabetic letters indicate the significant difference ($p < 0.05$) in a row using a one-way analysis of variance (ANOVA) and Tukey's test. TPC, Total phenolic content; TFC, total flavonoid content; TTC, total tannins content; FRAP, ferric reducing antioxidant power assay; DPPH, 2,2′-diphenyl-1-picrylhydrazyl assay; ABTS, 2,2′-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid assay; TAC, total antioxidant capacity; GAE, gallic acid equivalents; CE, catechin equivalents; QE, quercetin equivalents; AAE, ascorbic acid equivalents.

Flavonoids are the predominant class of phenolic substances found in almost all plants, which was determined via the aluminium chloride colorimetric method in this study. Aluminium chloride reacts with carbonyl group present in flavonoids, forming a stable complex [30]. The highest amount of flavonoid was found in the mango peel (1.75 ± 0.08 mg QE/g), followed by pineapple and banana peels (1.47 ± 0.07 and 1.32 ± 0.12 mg QE/g, respectively). Marina and Noriham [31] also reported higher flavonoid contents in mango peel than other tropical fruit peels such as papaya and guava peels, which is consistent with our study. Previously, Morais, et al. [32] determined the TFC in different parts of the avocado (*Persea americana*), and found that avocado peels had more flavonoids than seeds and pulp. Ayala-Zavala, et al. [33] also reported that the peels of tropical exotic fruits like avocado, pineapple, banana, papaya, passion fruit, and melon contain more phenolic acids and flavonoids than pulp. Overall, TFC values of our twenty different fruit peels were slightly higher than previously reported values, which may be due to the difference in the growing area, climatic conditions, varietal differences, and extraction. Fruits growing under different climatic regions have different flavonoid content in their peels, the peels being the outer part of fruit bodies exposed to more to sunlight as compared to pulp, leading to the synthesis of the abundant and diverse nature of flavonoids. Nogata, et al. [34] reported that the flavonoid contents in the outer layer of citrus fruits are higher than the inner layers and pulps. The flavonoid profile differs among species and cultivars of the same fruits grown in different regions under different climatic conditions, soil characteristics, and cultivation techniques [35]. Moreover, the efficiency of the extraction of flavonoids also varies under different extraction conditions, such as the type of solvents, solvent concentration, extraction time and temperature, solvent-to-solid ratio, etc. [36,37].

Tannins are also one of the important groups of phenolic compounds which can be classified into hydrolysable tannins and condensed tannins. Avocado peels exhibited the highest TTC values of 9.01 ± 0.20 mg CE/g, followed by mango (8.99 ± 0.13 mg CE/g), lime, and custard apple peels (8.42 ± 0.63 and 8.32 ± 0.56 mg CE/g, respectively), while few tannins were detected in dragon fruit, melon, nectarine, passion fruit, peach and pear peels. Overall, most of our TTC values are in accordance with previously published work, while we also had high values of tannins in mango peel as compared to the previously published literature. Previously, the mango fruit peel has already been reported to be a rich source of hydrolysable tannins, while hydrolysable tannins can decrease significantly during the ripening process [38]. One of the possible reasons might be the difference in sample preparations, storage conditions, and extraction techniques. In our study, all the fruit peels were freeze-dried prior to the extraction of polyphenols; it has been reported that freeze-drying facilitates the overall polyphenol extraction. Freeze-drying can also preserve the highest percentage of condensed tannins as compared to other conventional drying methods. Freeze-drying also helps to accelerate the release of bounded phenolic compound [39], deactivating oxidative and hydrolytic enzymes, improving the extraction and protecting the phenolic compounds [40].

3.2. Antioxidant Potential (DPPH, ABTS, FRAP and TAC)

To further investigate the antioxidant potential of the twenty different fruit peels, different antioxidant assays based on different mechanisms were applied in this study. Antioxidant assays including DPPH and ABTS were used to measure the radical scavenging ability, while FRAP and TAC assays were used to determine the reducing power of samples. The results shown in Table 1 were reported in mg ascorbic acid equivalents (AAE) per g of samples (mg AAE/g).

The DPPH assay is widely used to determine the free radical scavenging activity, which is mainly attributed to polyphenols [15]. Grapefruit, mango, and avocado peels exhibit higher DPPH radical scavenging ability (9.17 ± 0.19, 8.67 ± 0.49 and 8.67 ± 0.44 mg AAE/g, respectively). Previously, different varieties of mango peel extracts have shown concentration-dependent DPPH free radical scavenging activity [41]. Most of our DDPH values are in accordance with the previously published literature. Moreover, the DPPH assay showed significantly higher levels of antioxidant capacity in freeze-dried fruit peels as compared to fresh fruit peels. The freeze-drying process generates

redox-active metabolites that can scavenge and neutralize free radicals [42]. The DPPH assay is one of the non-specific free radical scavenging assays since it measures scavenged free radicals from both phenolic and non-phenolic compounds, including ascorbic acid. Therefore, the antioxidant potential of plant polyphenols cannot be properly assessed only through DPPH assays. For this reason, a set of different in vitro reagent-based assays can be applied to estimate antioxidant potential, while the confirmation of these antioxidant compounds can be achieved through the LC-MS characterization.

The ABTS assay is another widely used method for determining the antiradical scavenging abilities based on the hydrogen atom donating tendency of phenolic compounds. The scavenged ABTS free radicals were measured using a colorimetric assay where antioxidants in samples reduce $ABTS^{+}$ and form a stable free radical [15]. The ABTS assay exhibits high similarity with that of the DPPH assay with the highest ABTS value from the grapefruit peel with 10.79 ± 0.56 mg AAE/g, followed by the mango peel (9.32 ± 0.24 mg AAE/g), kiwi fruit peel (8.95 ± 0.18 mg AAE/g), and avocado peel (7.19 ± 0.72 mg AAE/g) samples. In comparison, banana, dragon fruit, melon, nectarine, passion fruit, peach, pear, and plum peels exhibited relatively low ABTS radical scavenging ability. Previously, a similar $ABTS^{\cdot+}$scavenging tendency was found in white and pink freeze-dried grapefruit peel extracts [42]. Pal, et al. [43] also found the ABTS radical scavenging ability in kiwi fruit at different ripening stages. Tremocoldi, et al. [44] reported slightly higher ABTS radical scavenging activities in different avocado varieties, including Hass and Fuerte peel samples, as compared to our results. Ortega-Arellano, et al. [45] also reported the ABTS antioxidant activity for both Hass and Reed peels, which is consistent with our results.

The FRAP assay evaluates the ability of samples to donate electrons to reduce a Fe^{+3}-TPTZ complex to a blue Fe^{+2}-TPTZ complex. Grapefruit peel exhibited the highest FRAP reducing power with 9.22 ± 0.25 mg AAE/g, followed by mango peel (6.19 ± 0.26 mg AAE/g), avocado peel (3.65 ± 0.07 mg AAE/g) and apple peel samples (3.20 ± 0.04 mg AAE/g), while the FRAP reducing power from dragon fruit, melon, passion fruit, pear, and plum peels were relatively low as compared to other fruit peels. Previously, Oboh and Ademosun [46] also reported high FRAP activity in orange and apple peels that was attributed to their bound phenolics compounds and flavonoids. Furthermore, FRAP activities previously reported in other fruit peels including kiwifruit, lime, pineapple, banana, and mango was also in accordance with our study [47].

The total antioxidant capacity (TAC) assay is based on an electron transfer mechanism. This assay is very similar to FRAP, where molybdenum (VI) will be reduced to molybdenum (V) through antioxidant compounds or phenolic compounds. Similar to the results of FRAP assay, the highest TAC values were reported in the grapefruit peel (8.77 ± 0.34 mg AAE/g), followed by mango, avocado, and apple peels (6.19 ± 0.23, 4.50 ± 0.16 and 2.97 ± 0.16 mg AAE/g, respectively). In comparison, dragon fruit, kiwi fruit, melon, nectarine, papaya, peach, pear, and plum peels had relatively low TAC values. The strong antioxidant activities including DPPH, ABTS, and FRAP of different citrus fruits have already been reported, while grapefruit had the strongest antioxidant potential [48]. Antioxidant assays involved multiple reactions and mechanisms to estimate the antioxidant potential of any plant material, and unfortunately, there is no single method that can accurately reflect the overall antioxidant potential due to the complex nature of phytochemicals. For this reason, the MS/MS characterization is one of the key areas in phytochemical research to used compute overall phenolic compounds and their antioxidant potential.

In general, grapefruit, mango, and avocado peels exhibit distinctive antioxidant activity in four different types of antioxidant assays. Our polyphenolic and antioxidant results indicated that further research is needed to determine the actual contribution of polyphenols toward the antioxidant potential by minimizing other distracting factors of in vitro reagent-based assays, including the contribution of non-phenolic compounds toward the antioxidant potential.

3.3. LC-ESI-QTOF-MS/MS Characterization

LC-MS/MS has been widely used for the identification and characterization of bioactive compounds, including phenolics from different fruits, vegetable, and medicinal plants. An untargeted qualitative analysis of phenolics from twenty different fruit peel samples was achieved via LC-ESI-QTOF-MS/MS analysis in both negative and positive modes of ionization (Table S1, Figures S1 and S2—Supplementary Data). Phenolics present in different fruit peel samples were tentatively identified and characterized from their *m/z* value and MS spectra in both negative and positive modes of ionization ($[M - H]^-$/$[M + H]^+$) using Agilent LC-MS Qualitative Software and Personal Compound Database and Library (PCDL). Compounds with mass error < ± 5 ppm and PCDL library score more than 80 were selected for further MS/MS identification and *m/z* characterization and verification purposes. In our study, LC-MS/MS enabled the tentative identification and characterization of 176 phenolics in twenty different fruit peel samples, including phenolic acids (49), flavonoids (86), lignans (11), stilbene (5) and other polyphenols (25) listed in Table S1 (Supplementary data).

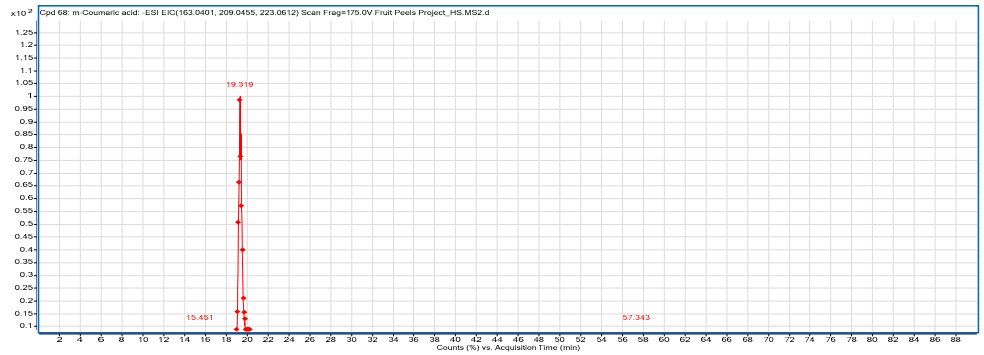
3.3.1. Phenolic Acids

Phenolic acids are the most abundant bioactive compounds present in different fruits [5]. In our study, a total of 49 phenolic acids were tentatively characterized, including hydroxybenzoic acids (12), hydroxycinnamic acids (31), hydroxyphenylacetic acids (2), and hydroxyphenylpropanoic acids (4).

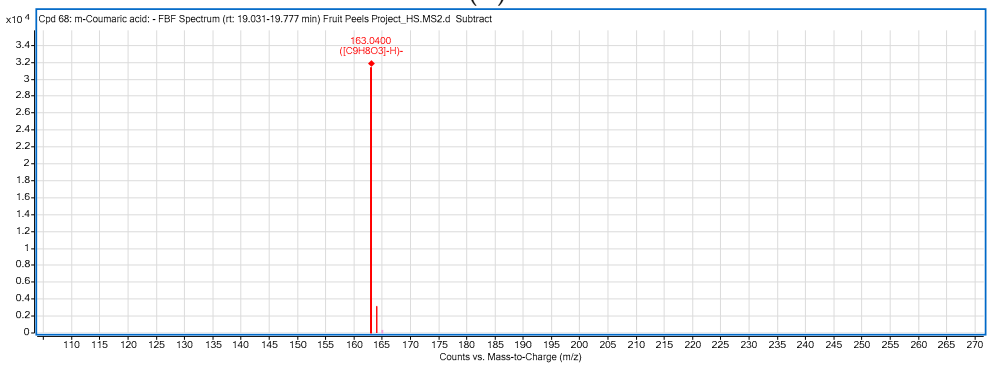
Hydroxybenzoic acids are widely present in different fruits such as mango, apple, custard apple, citrus, strawberries, and raspberries with significant antioxidant potential. Compound **1** presenting in mango, pear and kiwifruit was proposed as vanillic acid 4-sulfate based on the observed *m/z* at 246.9911 in negative ionization mode and further confirmed by the MS/MS experiment which displayed a characteristic loss of SO_3 (80 Da) at *m/z* 167 [49]. Most of the phenolic acids showed the loss of CO_2 (44 Da) and hexosyl moiety (162 Da) [50]. Compound **3** (*m/z* 169.0146), compound **6** (*m/z* 137.0244) and compound **8** (*m/z* 153.0193) were identified as gallic acid, 2-hydroxybenzoic acid and 2,3-dihydroxybenzoic acid, showing product ions at *m/z* 125, at *m/z* 93 and at *m/z* 109, represented the loss of CO_2 from the precursor ions [50,51]. Previously, Kim, et al. [52] had also tentatively identified gallic acid from white and red dragon fruit peel and pulp samples.

Hydroxycinnamic acids contained collectively a larger number of detected compounds than in any other subclass in this study. In our study, a total of 31 hydroxycinnamic acids were identified with remarkable antioxidant potential. Six caffeic acid derivatives were successfully identified in our work. Compound **15** (*m/z* 341.0861) and compound **26** (*m/z* 355.0686) exhibited a product ion at *m/z* 179 (caffeic acid ion) by losing glucoside (162 Da) and glucuronide (176 Da) in negative mode and identified as caffeoyl glucose and caffeic acid 3-*O*-glucuronide [53].

Ferulic acid (Compound **23**) was also observed in eight different peel samples. In an MS^2 experiment, ferulic acid displayed the product ions at *m/z* 178, *m/z* 149, and *m/z* 134, indicating the loss of CH_3, CO_2, and CH_3 with CO_2 from the precursor, respectively [54]. Compound **25** (RT = 19.319 min) was tentatively identified as *m*-coumaric acid with the precursor $[M - H]^-$ *m/z* at 163.0406 and confirmed by the MS/MS spectra (Figure 2), which exhibited the fragments at *m/z* 119 due to the loss of CO_2 [54]. Compound **47** (dihydroferulic acid 4-*O*-glucuronide, *m/z* at 371.0986) and compound **49** (dihydrocaffeic acid 3-*O*-glucuronide, *m/z* at 357.0811) were both detected only in the negative ionization mode, and the characteristic loss of the glucuronide (176 Da) moiety was observed in both compounds, which produced the fragment ions at *m/z* 195 and at *m/z* 181, respectively [55].



(**A**)



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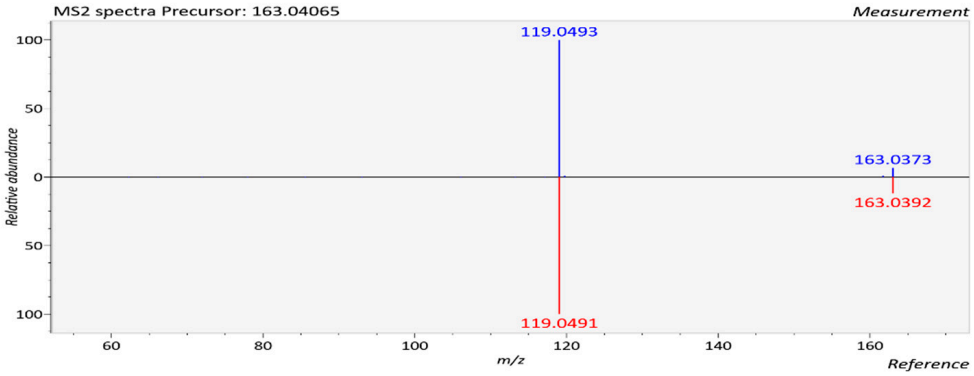

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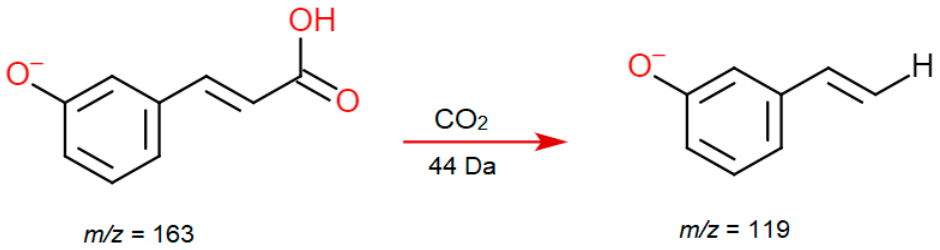

(**D**)

Figure 2. The LC-ESI-QTOF-MS/MS characterization of *m*-coumaric acid. (**A**) A chromatograph of *m*-coumaric acid (Compound 25, Table S1—Supplementary Data) in the negative mode $[M - H]^-$ which was tentatively identified and characterized in fifteen different fruit peel samples; (**B**) a mass spectrum of *m*-coumaric acid with a precursor of *m*/*z* 163.0406 in the apple peel; (**C**) MS/MS spectrum of *m*-coumaric acid with the product ion of *m*/*z* 119 (confirmed from online LC-MS library and database); (**D**) a fragmentation pattern of the *m*-coumaric acid in negative mode $[M - H]^-$, with precursor of *m*/*z* 163 and a product ion of *m*/*z* 119 due to the loss of CO_2.

3.3.2. Flavonoids

Flavonoids (in total 86) are the most abundant class with antioxidant potential found in the fruit peels. Flavonoids were divided into eight subclasses, including flavanols (11), flavones (12), flavanones (8), flavonols (19), dihydrochalcones (3), dihydroflavonols (2), anthocyanins (12) and Isoflavonoids (19).

A total of eight flavanones was discovered in the peels. Quercetin 3′-*O*-glucuronide (Compound **82**) and myricetin 3-*O*-arabinoside (Compound **83**) were found in both modes and tentatively identified by the precursor ions $[M - H]^-$ *m/z* at 477.067 and $[M - H]^-$ *m/z* at 449.0716. The product ion at *m/z* 301 in the MS^2 spectrum of quercetin 3′-*O*-glucuronide was produced by the loss of glucuronide (176 Da) from the precursor [56], and the peaks at *m/z* 317 (loss of pentose moiety, 132 Da) confirmed the identity of myricetin 3-*O*-arabinoside [57].

3.3.3. Other Polyphenols

A total of 25 other polyphenols were identified from the peels, which were further divided into hydroxycoumarins (5), hydroxybenzaldehydes (2), hydroxybenzoketones (2), hydroxyphenylpropenes (1), curcuminoids (3), furanocoumarins (1), phenolic terpenes (2), tyrosols (5) and other polyphenols (4).

Coumarin (Compound **138**) and scopoletin (Compound **139**) were found in both negative and positive modes and tentatively identified according to the precursors $[M + H]^+$ at *m/z* 147.0448 and $[M - H]^-$ at *m/z* 191.0345. In the MS^2 experiment of 147.0448, peaks at *m/z* 103 $[M + H - CO_2]$ and *m/z* 91 [M + H − 2CO] achieved the identification of coumarin, and in the MS/MS spectra of *m/z* 191.0345, peaks at 176 [M − H − 15, loss of CH_3] are characteristic for scopoletin [58,59].

3.3.4. Lignans

A total of eleven lignans were identified in most of the fruit peels. Compounds **161** and **163** presenting in the positive mode were identified as enterolactone and schisandrin C according to the *m/z* 299.1283 and *m/z* 385.1652, respectively. The MS/MS experiment achieved the identification of these lignans. Enterolactone exhibited the fragment ions at *m/z* 281, 187, and 165, representing the loss of H_2O, $C_6H_8O_2$ and $C_9H_8O_2$, respectively [60]. The presence of schisantherin C was verified by the product ions at *m/z* 370 (loss of CH_3, 15 Da), *m/z* 315 (loss of C_5H_{10}, 70 Da) and *m/z* 300 (loss of CH_3 and C_5H_{10}, 85 Da) [61].

3.3.5. Stilbenes

A total of five stilbenes were identified in different fruit peel samples. Resveratrol (Compound **173,** $[M - H]^-$ *m/z* at 227.0709 presenting in custard apple and avocado peels) and resveratrol 5-*O*-glucoside (Compound **174**, $[M - H]^-$ *m/z* at 389.1245 appearing in passion fruit, pomegranate, and kiwi fruit peels) were detected in both ionization modes. In the MS^2 spectra, Resveratrol showed the characteristic *m/z* at 212 (loss of CH_3), 185 (loss of CHCOH), 157 (loss of CHCOH and CO), and 143 (loss of CHCOH and C_2H_2O) [62]. The excepted loss of glucoside (162 Da) was observed in the MS^2 fragmentation of resveratrol 5-*O*-glucoside, which allowed the identification of this compound [63].

The LC-MS/MS characterizations of phenolic compounds presented in different fruit peels have remarkable antioxidant capacities. Most of the hydroxycinnamic hydroxybenzoic acids and their derivatives and flavonoid and their derivatives have strong free radical scavenging ability. The presence of these phenolics in different fruit peel samples indicates that these food wastes could be valuable sources of natural antioxidant compounds. In short, these fruit peels could be utilized in different food, feed, nutraceutical, and pharmaceutical industries.

3.4. Distribution of Phenolic Compounds—Venn Diagram

To further investigate the distribution of phenolic compounds in different fruit peels, Venn diagrams were generated among fruits grown in different climate zones including tropical, sub-tropical, and temperate (Figure 3). Although the aim of this study was not to explore the relationship between

growing regions and phenolic contents in different fruit peel samples, we tentatively characterized their phenolic profiling through Venn diagrams. This preliminary analysis indicates that it is worth further exploring the relationship between growing regions and phenolic contents in different fruit peel samples. The comparison showed that there are differences in the phenolic compositions of fruits grown in different climate zones, and so it may be possible to optimize phenolic levels in these fruits and their peels through the targeted selection of the growing location.

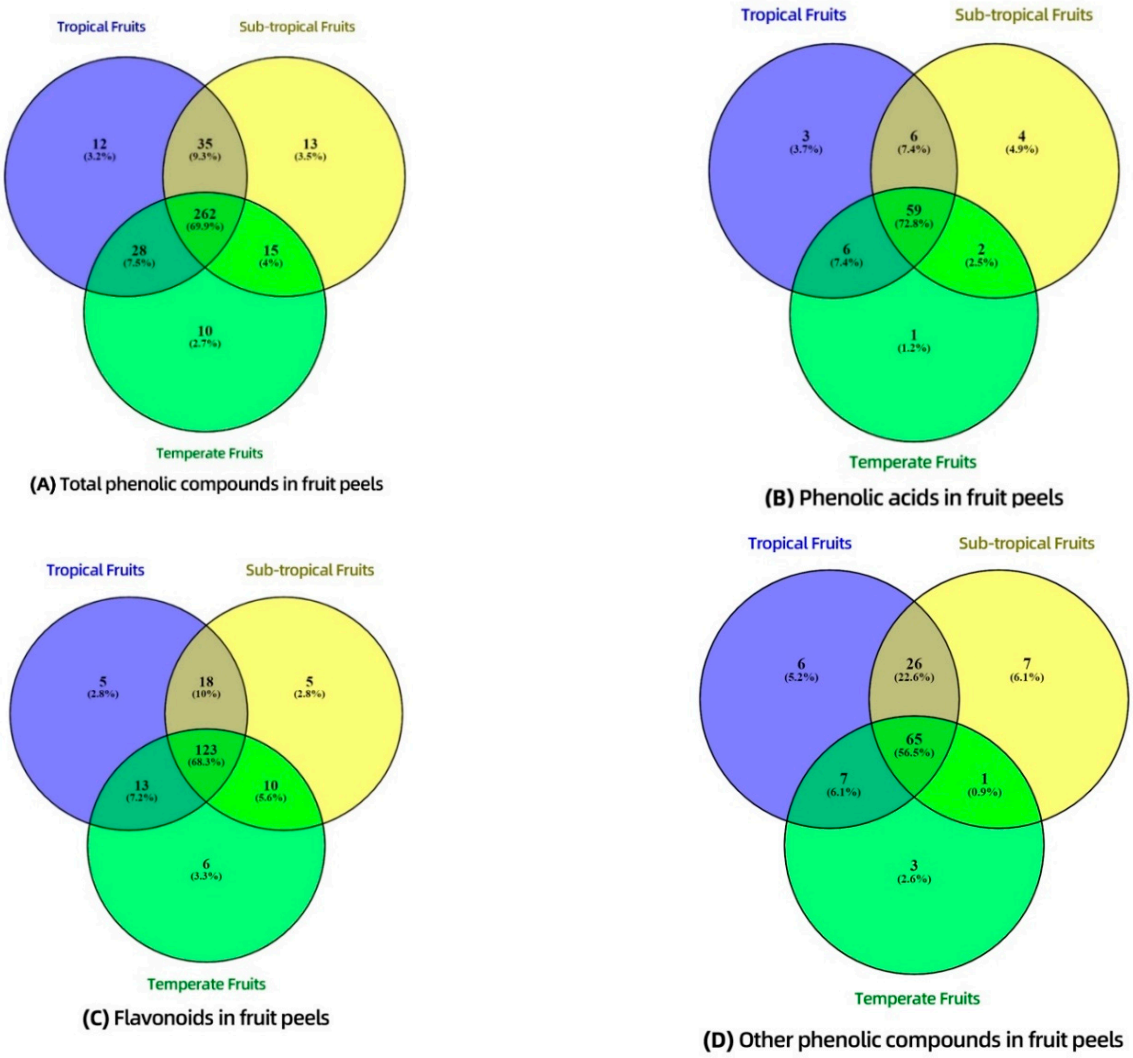

Figure 3. Venn diagram of phenolic compounds presented in different fruit peel samples grown in different regions. (**A**) shows the relations of total phenolic compounds present in different fruit peel samples grown in three different zones. (**B**) shows the relations of phenolic acids present in different fruit peel samples. (**C**) shows the relations of flavonoids present in different fruit peel samples. (**D**) shows the relations of other phenolic compounds present in different fruit peel samples.

Fruit peel samples were divided into three groups according to their growing regions, which were tropical (banana, custard apple, dragon fruit, mango, papaya, and pineapple peels), sub-tropical (pomegranate, passion fruit, orange, grapefruit, avocado, lime peels), and temperate (apple, apricot, kiwi fruit, peach, pear, melon, plum, nectarine peels).

From Figure 3A, a total of 375 phenolics were tentatively identified in all twenty selected fruit peels. Among "*total phenolic compounds*", 69.9% of them were commonly identified in all three zones, including tropical, sub-tropical, and temperate regions. From Figure 3B,C, a total of 72.8% of the "*phenolic acids*" and 68.3% of the "*flavonoids*" were commonly identified in all three zones. The proportions of common phenolic acids and flavonoids shared by all the fruit peels were almost similar to that of total phenolic compounds, which indicated the compositions of these compounds were similar in tropical, sub-tropical, and temperate fruits, despite different growing regions. However, Figure 3D shows that "*other phenolic compounds*" had only 56.5% of commonly identified compounds in the three groups, the proportions of which were much lower than those in the total phenolic compounds. The lower proportion of shared compounds of *"other phenolic compound"* indicated that they might be the main contributors responsible for the differences in overall phenolic concentrations and antioxidant activities of different fruit peels collected from three different climatic zones. Additionally, tropical and sub-tropical fruits were more similar in the compositions of other phenolic compounds, while temperate fruits had a quite different composition. The difference may be explained by a previous study, which indicated that tropical fruits often had richer phenolic contents and stronger antioxidant capabilities than temperate fruits due to the presence of some phenolic compounds in tropical fruits that functioned as lipid peroxidation inhibitors and decreased deleterious effects in plants caused by the strong ultraviolet radiation in tropical regions [64]. For example, stilbenes possess an antioxidant ability that can decrease oxidative stress caused by UV irradiation, as well as for the defense system of plants against fungi and bacteria [65]. Also, other phenolic compounds with anti-insect functions might exist exclusively in tropical fruits, as a warmer climate usually favors pest threats [66,67].

In this work we found that there is a strong relationship between growing regions and phenolic contents in different fruit peel samples, and we elucidate the differences in the compositions of phenolic compounds, particularly "*other phenolic compounds*". Further work is required to explore the impacts of individual phenolics.

3.5. HPLC-PDA Quantitative Analysis

HPLC has been widely used as an effective tool for the identification and quantification of phenolic compounds in different fruit and vegetable samples. The twenty most abundant phenolic compounds present in the different fruit peels, including 10 phenolic acids and 10 flavonoids, were selected for quantification. Tables 2 and 3 show the quantified phenolic acids and flavonoids by comparing retention time with reference standards, and results were calculated using standard curves.

3.5.1. Phenolic Acids

In our study, ten targeted phenolic acids were quantified in the twenty fruit peels. Table 2 showed that the mango peel was most abundant in terms of the overall phenolic acids (72.2 ± 4.5 mg/g) and most of the individual phenolic acid, while melon peels significantly had the lowest overall phenolic acid content. Mango peels significantly had the highest phenolic content for seven out of ten targeted phenolic acids, including gallic acid (14.5 ± 0.4 mg/g), chlorogenic acid (13.8 ± 0.9 mg/g), caffeic acid (4.5 ± 0.4 mg/g), *p*-hydroxybenzoic acid (10.5 ± 0.4 mg/g), syringic acid (11.5 ± 0.7 mg/g), ferulic acid (6.3 ± 0.4 mg/g), and coumaric acid (5.1 ± 0.2 mg/g), respectively. Previously, Palafox-Carlos, et al. [68] detected gallic acid, chlorogenic acid, and protocatechuic acids in different mango varieties, including in both pulp and peels. Chlorogenic acid was the most abundant in their study, while gallic acid was the most abundant in our study. However, Kim, et al. [69] reported that gallic acid was the predominant phenolic acid in mango peels, which is in agreement with our results. In another study, Hu, et al. [70], reported a gallic acid concentration of 0.08–0.59 mg/g among mango peel samples, which is much

lower than our results. These variations can be explained by the variability of phenolic content with cultivar type and maturity, growing regions, and climatic conditions.

Another study of Marina and Noriham [31] indicated that mango peels had higher phenolic content than papaya peels, which also agrees with our quantification results for the ten targeted phenolic acids. Moreover, Gorinstein, et al. [71] also reported a similar trend that mango had significantly higher phenolic contents than avocado peel samples. However, they also reported a higher phenolic content in kiwifruit than in mango, which is in contrast with our results. The difference might be caused by the difference in varieties and growing conditions as they, used grown fruits from Singapore, while our study was conducted on grown fruits from Australia. Apart from mango, other tropical fruits, including banana, custard apple, dragon fruit, papaya, passion fruit, and pineapple peels, did not show significantly higher phenolic contents than other temperate or subtropical fruits, although some of these fruits, such as the banana, were reported to have high phenolic contents and antioxidant ability [72].

Pomegranate was another fruit other than mango which had a significantly higher content for most of the phenolic acids. Previously, Li, et al. [73] detected 249.4 ± 17.2 mg/g phenolic contents in pomegranate peels, which indicated that this fruit was an excellent source of phenolics. Moreover, the study of Marina and Noriham [31] also indicated that pomegranates possessed high phenolic contents. From our results, similar conclusions can be postulated, as pomegranate has a significantly higher phenolic acid content compared with other fruit peels. Additionally, Pal, et al. [74] reported approximately a three-fold higher phenolic content in the pomegranate peel than in the orange peel, which is consistent with our study. Apart from pomegranate, grapefruit and lime peels were also quantified in our study and significantly showed the highest contents for several phenolic acids. Previously, Sir Elkhatim, et al. [75] compared the phenolic contents between peels of citrus fruits including orange, grapefruit, and lime, and reported that grapefruit peels had the highest phenolic content, followed by lime and orange peels, which showed a similar pattern with our results for the targeted phenolic acids. Li, et al. [76] also reported similar results that the grapefruit peel had the highest phenolic contents compared with other citrus fruit peels.

As for temperate fruits, apple peels had significantly higher contents of protocatechuic acid (7.4 ± 0.4 mg/g) than all other fruits. While the apple peel did not have higher overall phenolic acid contents among all the 20 fruits, it is one of the most widely consumed fruits known for its antioxidant ability [77], and importantly, the peel is often consumed. Previously, Russell, et al. [78] reported a higher content of phenolic acids, including gallic acid, protocatechuic acid, *p*-hydroxybenzoic acid, syringic acid, and sinapinic acid, in apple peels than in the peel of pears of Scottish varieties, which is consistent with our results. The study of Mihailović, et al. [79] indicated that chlorogenic acid was the most dominant phenolic acid presented in the apple peel, which is in agreement with our study, which detected the highest chlorogenic acid content of 11.2 ± 0.1 mg/g for apple peels. Moreover, Veberic, et al. [80] also reported that chlorogenic acid was the most abundant phenolic acid in the apple peel with the content range of 4.1–79.5 mg/100 g. The variation can be attributed to a difference in apple varieties. Previous studies have suggested that most tropical fruits have higher phenolic contents than temperate fruits, as phenolic compounds are essential for inhibiting lipid peroxidation and deleterious effects in plant tissues caused by strong ultraviolet radiation in tropical areas [64]. It can also be concluded from previous studies that, although some temperate fruits were already potential phenolic sources, topical fruits had richer phenolic contents, which makes them better sources of phenolic acids [64]. In our study, the tropical fruit mango showed significantly higher phenolic acid content in the peel than all the sub-tropical and temperate fruits, which is consistent with previous studies.

Table 2. Phenolic acids quantified in different fruit peel samples using HPLC-PDA.

Fruit Peels	Gallic Acid	Protocatechuic Acid	Caftaric Acid	Chlorogenic Acid	*p*-hydroxybenzoic Acid	Caffeic Acid	Syringic Acid	Coumaric Acid	Ferulic Acid	Sinapinic Acid	Sum of Phenolic Acids
APL-P	4.2 ± 0.9^{d}	7.4 ± 0.4^{a}	-	11.2 ± 0.1^{b}	6.5 ± 0.8^{c}	2.1 ± 0.9^{c}	1.1 ± 0.7^{g}	-	1.2 ± 0.3^{h}	-	33.7 ± 1.5^{C}
APR-P	2.1 ± 0.6^{g}	-	2.4 ± 0.4^{e}	5.9 ± 0.2^{e}	3.1 ± 0.3^{f}	3.5 ± 0.1^{b}	-	-	4.5 ± 0.1^{c}	1.3 ± 0.1^{e}	22.8 ± 1.7^{D}
AVO-P	3.2 ± 0.5^{e}	4.2 ± 0.2^{b}	1.2 ± 0.1^{g}	9.5 ± 0.1^{c}	4.5 ± 0.6^{d}	-	3.5 ± 0.3^{d}	4.1 ± 0.1^{b}	-	2.7 ± 0.6^{c}	32.9 ± 2.5^{C}
BNA-P	1.2 ± 0.2^{i}	-	-	4.5 ± 0.5^{f}	2.8 ± 0.1^{g}	-	4.1 ± 0.5^{c}	-	3.7 ± 0.2^{d}	-	16.3 ± 1.9^{G}
CTA-P	1.4 ± 0.2^{h}	-	4.7 ± 0.9^{c}	7.5 ± 0.3^{d}	4.5 ± 0.9^{d}	-	-	1.8 ± 0.4^{f}	1.8 ± 0.3^{g}	3.9 ± 0.8^{b}	25.6 ± 1.6^{D}
DGF-P	1.1 ± 0.5^{i}	-	3.5 ± 0.5^{d}	4.1 ± 0.9^{g}	1.2 ± 0.7^{i}	-	3.1 ± 0.9^{d}	2.8 ± 0.1^{d}	2.7 ± 0.8^{e}	-	18.5 ± 2.1^{F}
GRF-P	5.4 ± 0.9^{c}	3.4 ± 0.4^{c}	7.8 ± 0.5^{a}	-	3.5 ± 0.9^{e}	4.2 ± 0.5^{a}	-	3.1 ± 0.8^{c}	2.1 ± 0.4^{f}	1.7 ± 0.7^{d}	31.2 ± 1.9^{C}
KWF-P	1.1 ± 0.9^{i}	-	4.2 ± 0.4^{c}	3.2 ± 0.5^{i}	2.8 ± 0.1^{g}	-	2.1 ± 0.1^{e}	4.1 ± 0.8^{b}	1.2 ± 0.7^{h}	-	18.7 ± 1.7^{F}
LMN-P	-	1.2 ± 0.8^{e}	2.4 ± 0.5^{e}	-	4.2 ± 0.4^{d}	1.2 ± 0.6^{e}	-	2.1 ± 0.4^{e}	4.5 ± 0.9^{c}	4.9 ± 0.7^{a}	20.5 ± 2.1^{E}
MNG-P	14.5 ± 0.4^{a}	-	2.1 ± 0.1^{f}	13.8 ± 0.9^{a}	10.5 ± 0.4^{a}	4.5 ± 0.4^{a}	11.5 ± 0.7^{a}	5.1 ± 0.2^{a}	6.3 ± 0.4^{a}	3.9 ± 0.9^{b}	72.2 ± 4.5^{A}
MEL-P	-	1.1 ± 0.7^{e}	-	1.6 ± 0.3^{j}	-	-	2.3 ± 0.1^{e}	-	1.2 ± 0.2^{h}	-	6.2 ± 1.2^{M}
NEC-P	1.5 ± 0.7^{h}	1.2 ± 0.2^{e}	-	4.5 ± 0.4^{f}	2.8 ± 0.1^{g}	1.7 ± 0.9^{d}	-	-	1.1 ± 0.1^{h}	-	12.8 ± 1.9^{I}
ORN-P	5.4 ± 0.9^{c}	-	3.1 ± 0.4^{d}	5.6 ± 0.3^{e}	3.6 ± 0.1^{e}	-	1.8 ± 0.2^{f}	-	2.1 ± 0.7^{f}	1.8 ± 0.2^{d}	23.4 ± 2.3^{D}
PAP-P	2.4 ± 0.7^{f}	-	5.6 ± 0.1^{b}	-	2.9 ± 0.2^{g}	-	2.4 ± 0.9^{e}	-	1.8 ± 0.4^{g}	-	15.1 ± 1.1^{H}
PSN-P	-	-	5.2 ± 0.8^{b}	-	2.1 ± 0.4^{h}	-	3.5 ± 0.3^{d}	-	1.1 ± 0.1^{h}	-	11.9 ± 1.9^{J}
PEC-P	1.5 ± 0.4^{h}	1.2 ± 0.1^{e}	-	3.7 ± 0.9^{h}	-	1.8 ± 0.2^{d}	-	-	2.7 ± 0.1^{e}	1.4 ± 0.9^{e}	12.3 ± 1.3^{I}
PER-P	1.1 ± 0.7^{i}	-	2.1 ± 0.8^{f}	-	3.2 ± 0.3^{f}	-	1.5 ± 0.4^{f}	-	1.2 ± 0.1^{h}	-	9.1 ± 1.7^{L}
PIN-P	1.5 ± 0.9^{h}	2.1 ± 0.2^{d}	-	-	1.2 ± 0.1^{i}	1.1 ± 0.5^{e}	-	2.8 ± 0.3^{d}	-	1.9 ± 0.7^{d}	10.6 ± 1.9^{K}
PLM-P	1.4 ± 0.3^{h}	-	-	-	3.8 ± 0.1^{e}	-	1.7 ± 0.7^{f}	-	4.2 ± 0.4^{c}	-	11.1 ± 2.1^{J}
POM-P	6.7 ± 0.1^{b}	7.4 ± 0.6^{a}	-	11.8 ± 0.7^{b}	9.8 ± 0.1^{b}	4.5 ± 0.7^{a}	6.7 ± 0.9^{b}	-	5.8 ± 0.2^{b}	-	52.7 ± 3.9^{B}

All values are expressed as "mg/g", mean ± standard deviation ($n = 3$). Alphabetic letters indicate significant difference ($p < 0.05$) in a row using a one-way analysis of variance (ANOVA) and Tukey's test. Fruit peel samples were mentioned in abbreviations. Apple peel "APL-P", Apricot peel "APR-P", Avocado peel "AVO-P", Banana peel "BNA-P", Custard apple peel "CTA-P", Dragon fruit peel "DGF-P", Grapefruit peel "GRF-P", Kiwifruit peel "KWF-P", Lime peel "LMN-P", Mango peel "MNG-P", Melon peel "MEL-P", Nectarine peel "NEC-P", Orange peel "ORN-P", Papaya peel "PAP-P", Passionfruit peel "PSN-P", Peach peel "PEC-P", Pear peel "PER-P", Pineapple peel "PIN-P", Plum peel "PLM-P", and Pomegranate peel "POM-P".

3.5.2. Flavonoids

Flavonoids are the largest group of phenolics and are present in most of the fruits. Among the fruit peels investigated, the mango peel has the highest content for overall flavonoids (57.1 ± 2.4 mg/g), while passion fruit had the lowest (10.4 ± 1.4 mg/g) listed in Table 3.

Mango peels showed similarly high contents for flavonoids as for phenolic acids, significantly with the highest contents of epicatechin gallate (3.2 ± 0.9 mg/g), quercetin-3-galactoside (10.9 ± 0.1 mg/g), quercetin-3-glucuronide (11.5 ± 0.7 mg/g), quercetin (11.9 ± 0.4 mg/g), and kaempferol (9.8 ± 0.7 mg/g). Previously, catechin and quercetin-3-galactoside were quantified by López-Cobo, et al. [81] in different mango peel samples. Compared with other fruits, Marina and Noriham [31] reported higher catechin and epicatechin contents in mango peels than other tropical fruit peels, such as papaya peel and guava peel, which is consistent with our study. However, a few studies reported lower flavonoids in mango pulp as compared to kiwifruit and avocado pulp, which did not agree with our fruit peel extracts [71]. The contradictory results might be explained by previous literature indicating that peels contained more flavonoids as compared to pulp [68].

Apart from mango peel, dragon fruit peel was also found to be abundant with flavonoids while catechin was dominantly detected in it with a concentration of 7.5 ± 0.9 mg/g. Previously, flavonoids including kaempferol and quercetin derivatives were detected and quantified in dragon fruit peels [82]. The pineapple peel sample had a relatively low flavonoid content among all the twenty fruits which showed a different pattern from mango and dragon fruit peels, but these results agree with the previous study of Silva, et al. [83], who reported significantly higher flavonoid contents in mango, papaya, and passion fruit than in pineapple, in which only a few flavonoids were detected in the pineapple peel sample. The pomegranate peel sample also had higher flavonoids (35.7 ± 4.7 mg/g) similar to phenolic contents. For individual flavonoids, pomegranate peel had the highest epicatechin content (4.1 ± 0.3 mg/g). Previously, Li, Guo, Yang, Wei, Xu and Cheng [73] reported higher flavonoids in pomegranate peel than our results, which may be because we only quantified the ten most abundant flavonoids across the fruit samples observed, and there is a chance that individual fruits may have high concentrations of a flavonoid outside this group. Another study showed that flavonoid contents in pomegranate and mango juices were significantly lower than the phenolic acid contents, which is consistent with our results [68]. Our results indicated that both mango and pomegranate peels are excellent sources of phenolic compounds.

For citrus fruit peels, the kaempferol-3-glucoside content was highest in lime peel (3.7 ± 0.4 mg/g), which is higher than those in orange, grapefruit, and pomegranate. Previously, Singh and Immanuel [84] reported similar results that lime peel had a higher total flavonoid content compared with other citrus species, such as orange. However, a more recent study of Sir Elkhatim, Elagib, and Hassan [75] showed that orange peel contained higher amounts of flavonoids than lime and grapefruit peels, which is in contrast with our results. The variation can be attributed to the difference in fruit varieties and extraction methods. In temperate fruits, quercetin-3-glucoside was the most abundant in apple peel, with a concentration of 4.5 ± 0.9 mg/g. Previously, Schieber, et al. [85] also reported quercetin-3-glucoside was present in apple pomace at a low concentration. Another study of Mihailović, Mihailovic, Kreft, Ciric, Joksović and Djurdjevic [79] reported flavonoids including catechin (0.187 ± 0.007 mg/g) and quercitrin (0.256 ± 0.002 mg/g) from peels of wild apple varieties, which were also detected in our study. In summary, all twenty fruit peel samples have a considerable quantity of phenolic compounds, including both phenolic acids & flavonoids, and these fruit peels are potential commercial sources of these phenolics.

Table 3. Flavonoids quantified in different fruit peel samples using HPLC-PDA.

Fruit Peels	Catechin	Epicatechin	Epicatechin Gallate	Quercetin-3-Galactoside	Quercetin-3-Glucuronide	Quercetin-3-Glucoside	Kaempferol-3-Glucoside	Diosmin	Quercetin	Kaempferol	Sum of Flavonoids
APL-P	3.2 ± 0.8 ^{b}	-	1.5 ± 0.1 ^{d}	5.7 ± 0.6 ^{b}	-	4.5 ± 0.9 ^{a}	-	2.1 ± 0.4 ^{b}	9.6 ± 0.9 ^{b}	-	26.6 ± 1.9 ^{C}
APR-P	-	2.1 ± 0.8 ^{b}	2.3 ± 0.1 ^{b}	-	3.8 ± 0.7 ^{d}	3.5 ± 0.2 ^{b}	3.2 ± 0.4 ^{b}	-	6.9 ± 0.7 ^{c}	4.5 ± 0.1 ^{d}	26.3 ± 2.1 ^{C}
AVO-P	2.1 ± 0.9 ^{d}	1.8 ± 0.4 ^{c}	-	4.9 ± 0.7 ^{c}	1.7 ± 0.8 ^{f}	2.8 ± 0.1 ^{c}	1.9 ± 0.5 ^{e}	1.7 ± 0.1 ^{c}	3.9 ± 0.9 ^{g}	2.9 ± 0.4 ^{f}	23.7 ± 2.7 ^{D}
BNA-P	1.5 ± 0.7 ^{e}	-	-	3.8 ± 0.9 ^{d}	-	1.7 ± 0.1 ^{e}	-	-	4.8 ± 0.8 ^{e}	-	11.8 ± 2.1 ^{H}
CTA-P	2.1 ± 0.4 ^{d}	-	1.9 ± 0.7 ^{c}	-	1.4 ± 0.1 ^{f}	-	1.7 ± 0.5 ^{e}	-	3.2 ± 0.9 ^{h}	3.9 ± 0.4 ^{d}	14.2 ± 1.9 ^{G}
DGF-P	7.5 ± 0.9 ^{a}	-	1.5 ± 0.1 ^{d}	4.5 ± 0.7 ^{c}	1.7 ± 0.4 ^{f}	-	2.4 ± 0.7 ^{d}	-	4.9 ± 0.3 ^{e}	3.5 ± 0.7 ^{e}	26.0 ± 1.1 ^{C}
GRF-P	-	-	2.1 ± 0.7 ^{b}	2.9 ± 0.1 ^{e}	-	1.7 ± 0.7 ^{e}	1.9 ± 0.3 ^{e}	1.1 ± 0.7 ^{d}	5.9 ± 0.1 ^{d}	4.2 ± 0.9 ^{d}	19.8 ± 1.9 ^{E}
KWF-P	1.5 ± 0.2 ^{e}	-	1.1 ± 0.9 ^{e}	-	4.5 ± 0.3 ^{c}	-	1.2 ± 0.8 ^{f}	1.7 ± 0.1 ^{c}	5.4 ± 0.2 ^{d}	7.1 ± 0.7 ^{b}	22.5 ± 2.7 ^{D}
LMN-P	2.7 ± 0.1 ^{c}	-	-	4.8 ± 0.7 ^{c}	8.7 ± 0.2 ^{b}	-	3.7 ± 0.4 ^{a}	1.9 ± 0.6 ^{b}	-	1.2 ± 0.1 ^{h}	23.0 ± 1.3 ^{D}
MNG-P	7.1 ± 0.3 ^{a}	-	3.2 ± 0.9 ^{a}	10.9 ± 0.1 ^{a}	11.5 ± 0.7 ^{a}	-	2.7 ± 0.4 ^{c}	-	11.9 ± 0.4 ^{a}	9.8 ± 0.7 ^{a}	57.1 ± 2.4 ^{A}
MEL-P	-	1.9 ± 0.3 ^{c}	-	2.8 ± 0.9 ^{e}	-	1.7 ± 0.1 ^{e}	-	-	4.5 ± 0.3 ^{f}	-	10.9 ± 1.2 ^{I}
NEC-P	2.1 ± 0.8 ^{d}	-	1.7 ± 0.1 ^{d}	1.8 ± 0.7 ^{g}	-	-	2.9 ± 0.7 ^{c}	-	2.9 ± 0.9 ^{i}	3.1 ± 0.1 ^{e}	14.5 ± 2.1 ^{G}
ORN-P	3.5 ± 0.1 ^{b}	2.4 ± 0.4 ^{b}	-	3.8 ± 0.2 ^{d}	-	-	3.9 ± 0.1 ^{a}	-	-	1.9 ± 0.8 ^{g}	15.5 ± 1.7 ^{F}
PAP-P	-	1.7 ± 0.3 ^{c}	1.9 ± 0.9 ^{c}	-	4.7 ± 0.1 ^{c}	-	1.7 ± 0.9 ^{e}	-	4.9 ± 0.4 ^{e}	2.9 ± 0.2 ^{f}	17.8 ± 2.1 ^{F}
PSN-P	1.8 ± 0.7 ^{e}	-	-	1.7 ± 0.1 ^{f}	-	2.1 ± 0.9 ^{d}	-	1.7 ± 0.1 ^{c}	-	3.1 ± 0.8 ^{e}	10.4 ± 1.4 ^{I}
PEC-P	1.2 ± 0.5 ^{f}	-	1.9 ± 0.3 ^{c}	2.1 ± 0.4 ^{f}	-	1.8 ± 0.2 ^{e}	-	1.1 ± 0.1 ^{d}	-	4.1 ± 0.7 ^{d}	12.2 ± 1.7 ^{H}
PER-P	1.8 ± 0.7 ^{e}	1.9 ± 0.9 ^{c}	-	-	1.7 ± 0.4 ^{f}	-	1.1 ± 0.1 ^{f}	-	-	7.4 ± 0.7 ^{b}	13.9 ± 2.1 ^{G}
PIN-P	-	-	1.5 ± 0.1 ^{d}	-	-	3.7 ± 0.1 ^{b}	-	3.1 ± 0.6 ^{a}	-	6.5 ± 0.7 ^{c}	14.8 ± 1.9 ^{G}
PLM-P	3.1 ± 0.1 ^{b}	-	1.4 ± 0.9 ^{d}	2.7 ± 0.3 ^{e}	-	3.1 ± 0.5 ^{c}	-	1.9 ± 0.7 ^{b}	-	4.1 ± 0.2 ^{d}	16.3 ± 2.1 ^{F}
POM-P	2.1 ± 0.1 ^{d}	4.1 ± 0.3 ^{a}	-	5.7 ± 0.1 ^{b}	2.1 ± 0.7 ^{e}	-	3.6 ± 0.2 ^{a}	1.1 ± 0.3 ^{d}	9.4 ± 0.9 ^{b}	7.6 ± 0.7 ^{b}	35.7 ± 4.7 ^{B}

All values are expressed as "mg/g", mean ± standard deviation (n = 3). Alphabetic letters indicate the significant difference ($p < 0.05$) in a row using ANOVA and Tukey's test. Fruit peel samples were mentioned in abbreviations. Apple peel "APL-P", Apricot peel "APR-P", Avocado peel "AVO-P", Banana peel "BNA-P", Custard apple peel "CTA-P", Dragon fruit peel "DGF-P", Grapefruit peel "GRF-P", Kiwifruit peel "KWF-P", Lime peel "LMN-P", Mango peel "MNG-P", Melon peel "MEL-P", Nectarine peel "NEC-P", Orange peel "ORN-P", Papaya peel "PAP-P", Passionfruit peel "PSN-P", Peach peel "PEC-P", Pear peel "PER-P", Pineapple peel "PIN-P", Plum peel "PLM-P" and Pomegranate peel "POM-P".

3.6. Heat Map and Hierarchical Clustering Phenolic Compound Analysis

For further analyzing the hierarchical clustering of targeted phenolic compounds in the twenty selected fruit peels, a heat map was constructed (Figure 4). The distance measure used for determining the similarity between fruits and compounds was the correlation, while the clustering method used for rows and columns was based on average concentration. For tree ordering, the tightest clusters were clustered first.

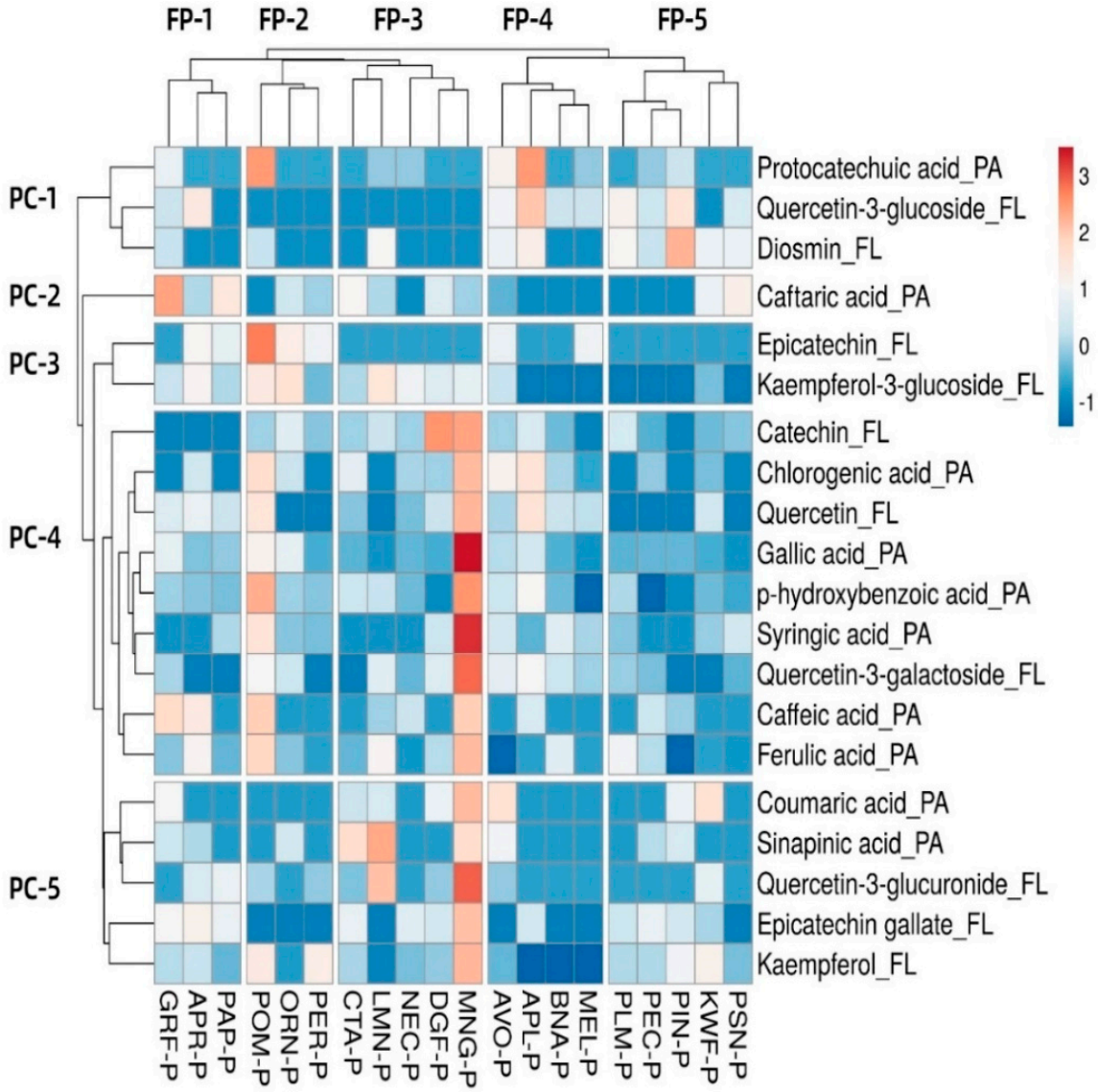

Figure 4. Heatmap showing phenolic compounds' distribution and concentration among twenty fruit peel samples. Red boxes mean concentrations are higher among different fruit peel samples. Blue boxes mean lower concentrations. PA: phenolic acids; FL: flavonoids; FP 1-5: fruit peel clusters 1; PC 1-5: phenolic compound clusters. Fruit peel samples were mentioned in abbreviations. Apple peel "APL-P", Apricot peel "APR-P", Avocado peel "AVO-P", Banana peel "BNA-P", Custard apple peel "CTA-P", Dragon fruit peel "DGF-P", Grapefruit peel "GRF-P", kiwifruit peel "KWF-P", Lime peel "LMN-P", Mango peel "MNG-P", Melon peel "MEL-P", Nectarine peel "NEC-P", Orange peel xORN-P", Papaya peel "PAP-P", Passionfruit peel "PSN-P", Peach peel "PEC-P", Pear peel "PER-P", Pineapple peel "PIN-P", Plum peel "PLM-P" and Pomegranate peel "POM-P".

In the heat map, five clusters in rows and columns were generated and highlighted by the hierarchical clustering; different clusters of samples indicate significant differences in phenolic profiles. The color difference showed the abundance of phenolic acids and flavonoids in different fruit peels. From the results, it can be observed that MGN-P, DGF-P, NEC-P, LMN-P, and CTA-P were clustered together in the group (FP-3), which shared similar patterns of phenolic contents. Within this cluster, MGN-P had red color areas for gallic acid and syringic acid, representing higher contents. Previously, Pereira-Netto [64] reported that tropical fruits shared similarly higher contents of phenolics than temperate fruits, which agrees with the clustering, where tropical fruits MGN-P, DGF-P, LMN-P, and CTA-P were grouped together.

Phenolic compounds were also grouped into five main clusters (PC-1, PC-2, PC-3, PC-4, and PC-5) in the dendrogram and were further grouped into different sub-clusters according to the similarity of their concentration patterns in the twenty fruit peel samples. Overall, PC-1 to PC-5 clusters indicated that several phenolic acids (caffeic acid, ferulic acid, coumaric acid, sinapinic acid) and flavonoids (quercectin-3-glucournoide, epicatechin gallate and kaempferol) had greater similarity in terms of the concentration among different fruit peel samples. However, some phenolic acids (caftaric acid, protocatechuic acid) and flavonoids (epicatechin and kaempferol-3-glucoside) showed variability with respect to other phenolic compound clusters.

3.7. Correlation between Phenolic Compounds, Targeted Phenolics Quantified through HPLC-PDA and Antioxidant Assays

The correlation between phenolic content (TPC, TFC, TTC, phenolic acids and flavonoids—quantified through HPLC-PDA) and antioxidant activities (DPPH, FRAP, ABTS, and TAC) was performed with a Pearson's correlation test (Table 4). In addition, principal components analysis (PCA, Figure 5) was performed to investigate the overall similarities and differences between the phenolic content, targeted phenolic acid, and flavonoids quantified through HPLC in different peels of fruit samples, and the relationship between the various methods used in the evaluation of the antioxidant potential. The targeted (10) phenolic acids and (10) flavonoids were calculated by summarizing the content of the proposed compounds in the HPLC-PDA table to investigate the correlations between overall phenolics and their antioxidant activities.

Table 4. Pearson's correlation coefficients (r) between phenolic content (TPC, TFC, TTC, phenolic acids, and flavonoids) and antioxidant activities (DPPH, FRAP, ABTS, and TAC).

Variables	TPC	TFC	TTC	DPPH	ABTS	FRAP	TAC	Phenolic Acids
TFC	0.488 *							
TTC	0.932 **	0.457 *						
DPPH	0.718 **	0.396	0.720 **					
ABTS	0.591 **	0.270	0.622 **	0.904 **				
FRAP	0.722 **	0.314	0.603 **	0.868 **	0.835 **			
TAC	0.780 **	0.397	0.668 **	0.850 **	0.779 **	0.967 **		
Phenolic acids	0.496 *	0.343	0.515 *	0.761 **	0.628 *	0.614 **	0.640 **	
Flavonoids	0.349	0.232	0.355	0.633 *	0.535 *	0.473 *	0.452 *	0.911 **

* Significant correlation with $p \leq 0.05$; ** Significant correlation with $p \leq 0.01$. Phenolic acids and flavonoids are quantified through HPLC-PDA.

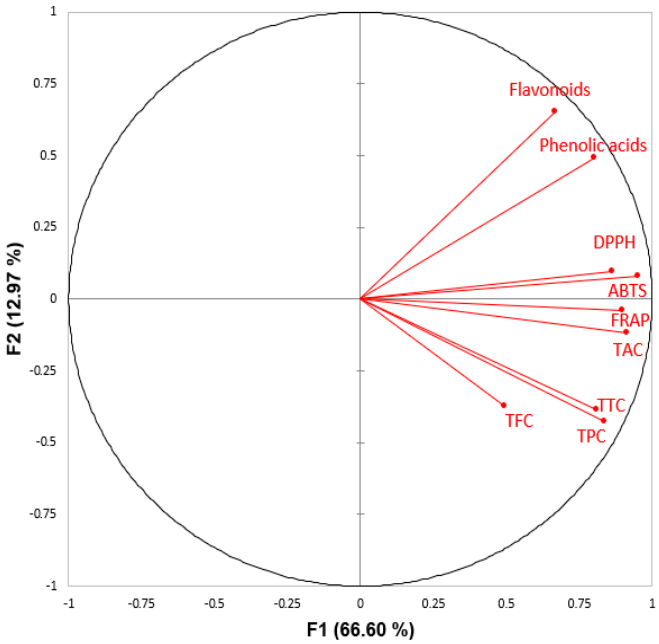

Figure 5. Principal component analysis (PCA) of the phenolic content (TPC, TFC, TTC, phenolic acids and flavonoids—quantified through HPLC-PDA) and antioxidant activities (DPPH, ABTS, FRAP, and TAC) of twenty different fruit peel samples.

A total of 79.57% variability of the initial data can be explained by the first two factors (F1 and F2) in Figure 5. Regarding antioxidant assays, DPPH, FRAP, ABTS, and TAC were strongly correlated with each other ($p \leq 0.01$). This significantly positive correlation was previously reported by Floegel, et al. [86]. They found that both DPPH and ABTS assays evaluate the free radical scavenging ability, and the ABTS assay can better reflect the hydrophilic, lipophilic, and high-pigmented antioxidants in fruits compared to the DPPH assay. The high correlation between DPPH, ABTS, FRAP, and TAC indicated that phenolic compounds present in twenty different fruit peel extracts exhibit the strong scavenging ability of DPPH, ABTS-reducing ability, and ferric ion- and phosphomolybdate ion-reducing abilities, respectively. The significantly positive correlations between FRAP and other antioxidant assays were in agreement with a previous study [87].

The TPC was highly significantly correlated with four antioxidant assays (DPPH, ABTS, FRAP, and TAC), which suggested that phenolic compounds are primary contributors to the antioxidant activities of the twenty different fruit peel samples. These results are in agreement with our previously published studies on phenolic compounds in different fruits and vegetable pulp samples and their antioxidant potential [19]. In addition, TPC were strongly correlated with TTC with $r = 0.932$, $p \leq 0.01$. However, a non-significant correlation between TFC and antioxidant assays was found, indicating that the contribution from flavonoids to the antioxidant potential of some peel samples was limited. The TFC method used in this study only targeted specific flavonoids, because the aluminum chloride selectively reacts with flavonols and the flavone luteolin [88], which may explain the non-significant correlations. In addition, strong correlations between TTC and four antioxidant assays were found, indicating that tannin present in selected fruit peel samples had a significant contribution to the antioxidant activities.

The phenolic acids content detected in HPLC was highly significantly correlated with most of the antioxidant assays (DPPH, ABTS, FRAP, and TAC) with $r = 0.761$, 0.628, 0.614, 0.640, respectively ($p \leq 0.05$), indicating that phenolic acids were one of the significant contributors to the antioxidant activities. Flavonoids detected by HPLC were also significantly correlated with most of the antioxidant assays, which was not consistent with the correlation results between the TFC value and antioxidant assays discussed before. One of the reasons might be that we selected only 10 of the most abundant

flavonoids across all the fruit peels for quantification purposes, while TFC assays specifically react with all types of flavonoids. In addition, the overall flavonoids detected by HPLC were not correlated with the TFC value (r = 0.232), which might be due to the high proportion of other subclasses of flavonoids rather than our targeted (10) flavonoids. Overall, both phenolic acids and flavonoids were strongly correlated with antioxidant assays, which indicated that both phenolic classes have strong antioxidant activities.

4. Conclusions

In conclusion, most of the selected fruit peels were found to have considerable amounts of phenolic content with very high in vitro antioxidant potential. The TPC, TFC, DPPH, FRAP, TAC and ABTS scavenging activity was higher in mango peel as compared to other fruit peels. The mango peel sample also showed significantly higher phenolic compounds, including gallic acid and quercetin, as compared to other fruit peel samples. The LC-ESI-QTOF-MS/MS technique was successfully applied for characterization of the phenolic compounds in different fruit peels; a total of 176 phenolic compounds were tentatively characterized. Quantification by HPLC-PDA also verified that fruit peels are rich in phenolic compounds. The obtained results supported the idea that fruit peels are a potential food waste source of phenolic compounds, with high antioxidant potential that has potential utility in food, feed, and nutritional supplements. In the future, in vitro digestibility, bioavailability, bioaccessibility, toxicological, and animal studies are required for developing these different fruit peels as commercial ingredients.

Supplementary Materials: The following are available online at http://www.mdpi.com/2304-8158/9/9/1206/s1, Table S1: Characterization of phenolic compounds in different fruit peel samples by LC-ESI-QTOF-MS/MS, Figure S1: Characterization of phenolic compounds in different fruit peels in the negative mode of ionization by LC-ESI-QTOF-MS/MS, Figure S2: Characterization of phenolic compounds in different fruit peels in the positive mode of ionization by LC-ESI-QTOF-MS/MS.

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Supplemental material

Screening and characterization of phenolic compounds and their antioxidant capacity in different fruit peels

Hafiz A. R. Suleria[1,2*], Colin J. Barrow[2] and Frank R. Dunshea[1,3]

[1] School of Agriculture and Food, Faculty of Veterinary and Agricultural Sciences, The University of Melbourne, Parkville 3010, VIC, Australia; hafiz.suleria@unimelb.edu.au (H.A.R.S.); fdunshea@unimelb.edu.au (F.R.D.)

[2] Centre for Chemistry and Biotechnology, School of Life and Environmental Sciences, Deakin University, Waurn Ponds, VIC 3217, Australia; colin.barrow@deakin.edu.au (C.J.B)

[3] Faculty of Biological Sciences, The University of Leeds, Leeds LS2 9JT, United Kingdom.

* Correspondence: hafiz.suleria@unimelb.edu.au; Tel: +61 470 439 670

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Abstract: Fruit peels have a diverse range of phytochemicals including carotenoids, vitamins, dietary fibres and phenolic compounds, some with remarkable antioxidant properties. Nevertheless, the comprehensive screening and characterization of the complex array of phenolic compounds in different fruit peels is limited. This study aimed to determine the polyphenol content and their antioxidant potential in twenty different fruit peel samples in ethanolic extraction, including their comprehensive characterization and quantification by the LC-MS/MS and HPLC. The obtained results showed that mango peel exhibited the highest phenolic content for TPC (27.51 ± 0.63 mg GAE/g), TFC (1.75 ± 0.08 mg QE/g) while the TTC (9.01 ± 0.20 mg CE/g) was slightly higher in avocado peel than mango peel (8.99 ± 0.13 mg CE/g). In terms of antioxidant potential, grapefruit peel had the highest radical scavenging capacities for the DPPH (9.17 ± 0.19 mg AAE/g), ABTS (10.79 ± 0.56 mg AAE/g), ferric reducing capacity in FRAB (9.22 ± 0.25 mg AA/g) and total antioxidant capacity, TAC (8.77 ± 0.34 mg AAE/g) compared to other fruit peel samples. Application of LC-ESI-QTOF-MS/MS tentatively identified and characterized a total of 176 phenolics including phenolic acids (49), flavonoids (86), lignans (11), stilbene (5) and other polyphenols (25) in all twenty peel samples. From HPLC-PDA quantification, mango peel sample showed significantly higher phenolic content, particularly for phenolic acids (gallic acid, 14.5 ± 0.4 mg/g) and flavonoids (quercetin, 11.9 ± 0.4 mg/g), as compared to other fruit peel samples. These results highlight the importance of fruit peels as a potential source of polyphenols. This study provides supportive information for utilization of different phenolic rich fruit peels as ingredients in the food, feed and nutraceutical.

Keywords: Fruit peels; polyphenols; phenolic acids; flavonoids; flavan-3-ols; hydrolysable and condensed tannins; antioxidant activities; LC-MS and HPLC.

Materials and Methods (Supplementary material)

2.1. Chemicals and Reagents

Most of the chemicals used for extraction and characterization were analytical grade and purchased from Sigma-Aldrich (Castle Hill, NSW, Australia). Folin-Ciocalteu's phenol reagent, gallic acid, L-ascorbic acid, vanillin, hexahydrate aluminium chloride, sodium phosphate, iron(III) chloride hexahydrate (Fe[III]Cl_3.6H_2O), hydrated sodium acetate, hydrochloric acid, ammonium molybdate, quercetin, catechin, 2,2'-diphenyl-1-picrylhy-drazyl (DPPH), 2,4,6tripyridyl-s-triazine (TPTZ), and 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) were purchased from the Sigma-Aldrich (Castle Hill, NSW, Australia) for the estimation of polyphenols and antioxidant potential. Reference standards for the HPLC including gallic acid, protocatechuic acid, caftaric acid, *p*-hydroxybenzoic acid, chlorogenic acid, caffeic acid, syringic acid, coumaric acid, ferulic acid, sinapinic acid, catechin, epicatechin gallate, quercetin-3-galactoside, quercetin-3-glucuronide, quercetin-3-glucoside, quercetin, diosmin, kaempferol and kaempferol-3-glucoside were produced by Sigma-Aldrich (Castle Hill, NSW, Australia) for quantification proposes. Sodium carbonate anhydrous were purchased from Chem-Supply Pty Ltd. (Adelaide, SA, Australia) and 98% sulfuric acid were bought from RCI Labscan (Rongmuang, Thailand). HPLC and LC-MS grade reagents include methanol, ethanol, acetonitrile, formic acid and glacial acetic acid were purchased from Thermo Fisher Scientific Inc (Scoresby, VIC, AU). To perform various *in vitro* bioactivities and antioxidant assays, 96 well-plates were purchased from Thermo Fisher Scientific (VIC, Australia). Additionally, HPLC vials (1 mL) were purchased from Agilent technologies (VIC, Australia).

2.2. Sample Preparation

Twenty different Australian grown fresh and mature fruits varieties (2-3 kg) including apple (Royal gala), apricot (Mystery), avocado (Hass), banana (Cavendish), custard apple (African Pride), dragon fruit (Red-fleshed), grapefruit (Thompson), kiwifruit (Hayward), mango (Kensington Pride), lime (Tahitian), melon (Rock melons), nectarine (Fantasia), orange (Navels), papaya (Sunrise Solo), passionfruit (Misty Gem), peach (Florda gold), pear (Packham's Triumph), pineapple (Aussie Rough), plum (Angeleno), and pomegranate (Griffith) were purchased from a local produce market in Melbourne, Australia. The fruits were manually cleaned, peels were removed and cut into desirable slices (0.5 x 1 cm) and frozen at − 20 °C for overnight followed by lyophilization at − 45 °C/50 MPa using the Dynavac engineering FD3 Freeze Drier (Belmont, W.A., Australia) and Edwards RV12 oil sealed rotary vane pump (Bolton, England). The freeze-dried fruit peels were grounded into a refined powder by electric grinder (Sunbeam Multi Grinder - EM0405, Melbourne, VIC, AU), packed into silver flat Ziplock aluminum foil - vacuum sealing bags (Best supply, NSW, AU) and stored at – 20 °C.

2.3. Extraction of Phenolic Compounds

To extract the phenolic compounds, 2.0 ± 0.5 g of each fruit peel powder was mixed with 20 mL 70% ethanol. The samples were homogenized at 10, 000 rpm for 30 s using the IKA Ultra-Turrax T25 homogenizer (Rawang, Selangor, Malaysia) and subjected to shaking incubator (ZWYR-240, Labwit, Ashwood, VIC, Australia) at 120 rpm for 12 h (4 °C). After incubation, the extracts were centrifuged with Hettich Refrigerated Centrifuge (ROTINA380R, Tuttlingen, Baden-Württemberg, Germany) at 5, 000 rpm for 15 min. The supernatants were collected and stored at − 20 °C for 2 weeks for antioxidant analysis. For HPLC and LC-MS analysis, the extracts were filtrated through a 0.45 μm syringe filter (Thermo Fisher Scientific Inc., Waltham, MA, USA).

2.4. Estimation of Polyphenols and Antioxidant Potential

For polyphenol estimation in selected fruit peel samples, TPC, TFC, and TTC assays were performed while for measuring their antioxidant potential, four different types of antioxidant assays including DPPH, ABTS, FRAP and TAC were performed by adopting our previously published

methods of Tang, *et al.* [18]. The data was determined using a Multiskan® Go microplate photometer (Thermo Fisher Scientific, Waltham, MA, USA).

2.4.1. Determination of Total Phenolic Content (TPC)

For the TPC, 25 μL extracts of each peel extract, 200 μL of water and 25 μL of Folin–Ciocalteu reagent solution (1:3 v/v), diluted with water was added to 96 well plate (Corning Inc., Midland, NC, USA) followed by incubation at 25 °C for 5 minutes. After that, 25 μL 10% (w:w) sodium carbonate was added and incubated for 1 h at 25 °C followed by the measurement of absorbance at 765 nm by a spectrophotometer plate reader (Thermo Fisher Scientific, Waltham, MA, USA). The quantification of total phenolic content was based on a standard curve generated from gallic acid with the concentrations from 0 – 200 μg/mL and results were expressed as mass (mg) of gallic acid equivalents (GAE) per weight of sample.

2.4.2. Determination of Total Flavonoids Content (TFC)

For the TFC, 80 μL of each peel extract, 80 μL of 2% (w/v) aluminum chloride solution and 120 μL of 50 g/L sodium acetate solution were added in a 96-well plate followed by incubation at 25 °C for 2.5 h and absorbance was measured at 440 nm. For quantification, a standard curve was made with quercetin (0 – 50 μg/mL) and results were expressed as mass (mg) of quercetin equivalents (QE) per weight of sample.

2.4.3. Determination of Total Tannins Content (TTC)

For the TTC, 25 μL of extract, 150 μL 4% (w/v) vanillin solution and 25 μL of 32% (v/v) sulphuric acid were incubated at 25 °C for 15 min, absorbance was measured at 500 nm. For quantification, a standard curve was generated from catechin using the concentrations of 0 - 1000 μg/mL and results were expressed as mass (mg) of catechin equivalents (CE) per weight of sample.

2.4.4. Determination of 2,2′-Diphenyl-2-picryl-hydrazyl (DPPH) Antioxidant Assay

For the DDH assays, 40 μL of each fruit peel extract and 260 μL of 0.1 M DPPH radical methanol solution was added into 96-well plate and incubated at 25 °C for 30 min. The absorbance was measured at 517 nm using a microplate reader. A standard curve was generated using 0 - 50 μg/mL ascorbic acid aqueous solution. The results were expressed as mass (mg) of ascorbic acid equivalents (AAE) per weight of sample.

2.4.5. Determination of Ferric Reducing Antioxidant Power (FRAP) Assay

To prepare the FRAP reagent, 300 mM sodium acetate buffer (pH 3.6), 10 mM TPTZ solution, and 20 mM ferric chloride in a ratio of 10:1:1 (v/v/v) was prepared freshly. A 20 μL of peel extracts and 280 μL of freshly prepared FRAP reagent were mixed in a 96 well plate followed by incubation at 37 °C for 10 min, absorbance was measured at 593 nm. A standard curve was achieved using concentrations of 0 - 50 μg/mL ascorbic acid and results were expressed as mass (mg) of AAE per weight of sample.

2.4.6. Determination of 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) Assay

The $ABTS^+$ dye was prepared with 5 mL of 7 mM of ABTS solution mixed with 88 μL of 140 mM potassium persulfate solution, incubated in the dark at room temperature for 16 h to generate an $ABTS^+$ free radical solution. Further, $ABTS^+$ stock solution was prepared by diluted with ethanol to gain absorbance of 0.70 at 734 nm. For the ABTS assay, 10 μL fruit peel extract and 290 μL of freshly prepared $ABTS^+$ solution were added in 96 well plate and incubated at 25 °C for 6 min. Subsequently, the absorbance was measured at 734 nm. A standard curve was achieved using concentrations of 0 - 150 μg/mL ascorbic acid and the results were expressed as mass (mg) of AAE per weight of sample.

2.4.7. Determination of Total Antioxidant Capacity (TAC)

For the TAC, 40 μL of each fruit peel extract was added to 260 μL of phosphomolybdate reagent (0.6 M H_2SO_4, 0.028 M sodium phosphate and 0.004 M ammonium molybdate). The mixture was incubated at 95 °C for 10 min, cooled at room temperature and absorbance was measured at 695 nm. A standard curve was generated using concentrations of 0 - 200 μg/mL ascorbic acid and the results were expressed as mass (mg) of AAE per weight of sample.

2.5. Characterization of Phenolic compounds using LC-ESI-QTOF-MS/MS Analysis

The phenolic compound characterization was performed on an Agilent 1200 HPLC with an Agilent 6520 Accurate- Mass Q-TOF LC/MS (Agilent Technologies, Santa Clara, CA, USA). The separation was conducted using a Synergi Hydro-RP 80 Å, reverse phase column (250 mm x 4.6 mm, 4 μm particle size) with protected C18 ODS (4.0 × 2.0 mm) guard column (Phenomenex, Lane Cove, NSW, Australia) by adopting our previously published method of Zhong, *et al.* [19]. In brief, the mobile phase consisted of water/acetic acid (98:2, v/v; eluent A) and acetonitrile/acetic acid/ water (50:0.5:49.5, v/v/v; eluent B). The gradient profile was described as follows: 10–25% B (0–25 min), 25–35% B (25–35 min), 35–40% B (35–45 min), 40–55% B (45–75 min), 55–80% B (75–79 min), 80–90% B (79–82 min), 90–100% B (82–84 min), 100–10% B (84–87 min), isocratic 10% B (87–90 min). A 6 μL of each peel extract was injected and the flow rate was set at 0.8 mL/min. Peaks were identified in both positive and negative ion modes with the capillary and nozzle voltage set to 3.5 kV and 500 V, respectively. Additionally, following conditions were maintained; i) nitrogen gas temperature at 300 °C, ii) sheath gas flow rate of 11 L/min at 250 °C, ii) nitrogen gas nebulisation at 45 psi. A complete mass scan ranging from *m*/*z* 50 to 1300 was used, MS/MS analyses were carried out in automatic mode with collision energy (10, 15 and 30 eV) for fragmentation. Peak identification was performed in both positive and negative modes while the instrument control, data acquisition and processing were performed using LC-ESI-QTOF-MS/MS MassHunter workstation software (Qualitative Analysis, version B.03.01, Agilent Technologies, Santa Clara, CA, USA).

2.6. Quantification of Phenolic compounds using HPLC-PDA

The quantitative measurement of targeted phenolic compounds present in different fruit peels samples was performed with an Agilent 1200 HPLC equipped with a photodiode array (PDA) detector by adopting our previously published protocol of Ma, *et al.* [20]. In brief, the same column and conditions were maintained as described above in LC-ESI-QTOF-MS/MS, except for a sample injection volume of 20 μL. The twenty most abundant phenolic compounds present in the different fruit peels including 10 phenolic acids and 10 flavonoids, were selected for quantification purposes. The phenolic compounds were determined at three different wavelengths, including 280 nm, 320 nm, and 370 nm. The quantification of targeted polyphenols was based on the calibration standard curve and the result was expressed as mg/g of sample. Data collection and processing was performed using Agilent MassHunter workstation software (Agilent Technologies, Santa Clara, CA, USA).

2.7. Statistical Analysis

All analyses were performed in triplicates and the results are presented as mean ± standard deviation (n = 3). The mean differences between different samples were analyzed by one-way analysis of variance (ANOVA) and Tukey's honestly significant differences (HSD) multiple rank test at $p \leq 0.05$. ANOVA was carried out by Minitab for Windows version 19.0 (Minitab, LLC, State College, PA, USA) and GraphPad Prism 7.05 Software for Windows (GraphPad 7.05 Software, San Diego, CA, USA, www.graphpad.com). For correlations between polyphenol content and antioxidant activities by Pearson's correlation coefficient at $p \leq 0.05$ and multivariate statistical analysis including principal component analysis (PCA), XLSTAT – 2019.1.3 were used by Addinsoft Inc. New York, N.Y USA.

174 **Table S1.** Characterization of phenolic compounds in different fruit peel samples by LC-ESI-QTOF-MS/MS.

No.	Proposed compounds	Molecular Formula	RT (min)	Ionization (ESI^+/ESI^-)	Molecular Weight	Theoretical (*m*/*z*)	Observed (*m*/*z*)	Error (ppm)	MS^2 Product ions	Fruit Peels
Phenolic acid										
	Hydroxybenzoic acids									
1	Vanillic acid 4-sulfate	$C_8H_8O_7S$	5.068	$[M-H]^-$	247.9991	246.9918	246.9911	-2.8	167	*MNG, PER, KWF
2	Gallic acid 4-*O*-glucoside	$C_{13}H_{16}O_{10}$	6.866	$[M-H]^-$	332.0743	331.0670	331.0674	1.2	169, 125	*APL, APR, GRF, MNG, ORN, PSN, PER, PIN, PLM, POM
3	Gallic acid	$C_7H_6O_5$	6.873	**$[M-H]^-$	170.0215	169.0142	169.0146	2.4	125	*MNG, ORN, PER, POM, KWF, LMN
4	Ellagic acid arabinoside	$C_{19}H_{14}O_{12}$	7.020	$[M-H]^-$	434.0485	433.0412	433.0422	2.3	300	ORN
5	Protocatechuic acid 4-*O*-glucoside	$C_{13}H_{16}O_9$	7.379	**$[M-H]^-$	316.0794	315.0721	315.0718	-1.0	153	*APL, APR, BNA, GRF, KWF, MNG, ORN, PSN, PEC, PER, PIN, PLM, POM, AVO, PAP
6	2-Hydroxybenzoic acid	$C_7H_6O_3$	7.628	**$[M-H]^-$	138.0317	137.0244	137.0244	0.1	93	*APL, APR, BNA, GRF, KWF, MNG, NEC, PEC, PSN, PER, PIN, AVO, PAP
7	4-Hydroxybenzoic acid 4-*O*-glucoside	$C_{13}H_{16}O_8$	11.171	$[M-H]^-$	300.0845	299.0772	299.0762	-3.3	255, 137	*GRF, MNG, MEL, PER
8	2,3-Dihydroxybenzoic acid	$C_7H_6O_4$	12.714	$[M-H]^-$	154.0266	153.0193	153.0193	0.1	109	*APL, GRF, KWF, NEC, PEC, ORN, PSN, PIN, PLM
9	3-*O*-Methylgallic acid	$C_8H_8O_5$	13.079	**$[M+H]^+$	184.0372	185.0445	185.0452	3.8	170, 142	*KWF, MNG, AVO, DGF, GRF, PEC
10	3,4-*O*-Dimethylgallic acid	$C_9H_{10}O_5$	16.475	**$[M+H]^+$	198.0528	199.0601	199.0605	2.0	153, 139, 125, 111	*DGF, KWF, MNG, ORN, PAP, PEC, AVO, CTA
11	Gallic acid 3-*O*-gallate	$C_{14}H_{10}O_9$	21.104	$[M-H]^-$	322.0325	321.0252	321.0240	-3.7	169	*MNG, PER
12	Paeoniflorin	$C_{23}H_{28}O_{11}$	58.033	**$[M-H]^-$	480.1632	479.1559	479.1577	3.8	449, 357, 327	*LMN, AVO, DGF
	Hydroxycinnamic acids									
13	1,5-Dicaffeoylquinic acid	$C_{25}H_{24}O_{12}$	4.134	**$[M-H]^-$	516.1268	515.1195	515.1198	0.6	353, 335, 191, 179	*NEC, ORN, PSN, AVO, CTA
14	Isoferulic acid 3-sulfate	$C_{10}H_{10}O_7S$	5.341	$[M-H]^-$	274.0147	273.0074	273.0067	-2.6	193, 178	PLM
15	Caffeoyl glucose	$C_{15}H_{18}O_9$	7.012	$[M-H]^-$	342.0951	341.0878	341.0861	-5.0	179, 161	*BNA, DGF, GRF, KWF, NEC, ORN, PSN, PLM, POM
16	*p*-Coumaroyl tartaric acid	$C_{13}H_{12}O_8$	8.632	**$[M-H]^-$	296.0532	295.0459	295.0468	3.1	115	*AVO, DGF, PIN, GRF, LMN, ORN, PER
17	Cinnamic acid	$C_9H_8O_2$	9.351	**$[M-H]^-$	148.0524	147.0451	147.0448	-2.0	103	*APL, APR, BNA, CTA, LMN, PEC, PER, PIN, PLM, POM, AVO, DGF, MEL
18	Feruloyl tartaric acid	$C_{14}H_{14}O_9$	10.419	$[M-H]^-$	326.0638	325.0565	325.0566	0.3	193, 149	*MNG, PER, POM
19	Caffeoyl tartaric acid	$C_{13}H_{12}O_9$	13.756	**$[M-H]^-$	312.0481	311.0408	311.0418	3.2	161	*POM, MNG, ORN, PSN
20	3-Sinapoylquinic acid	$C_{18}H_{22}O_{10}$	14.154	**$[M-H]^-$	398.1213	397.1140	397.1144	1.0	233, 179	*CTA, NEC, ORN, AVO, DGF, PAP
21	3-*p*-Coumaroylquinic acid	$C_{16}H_{18}O_8$	18.131	**$[M-H]^-$	338.1002	337.0929	337.0924	-1.5	265, 173, 162	*APL, APR, CTA, KWF, NEC, PEC, PSN, PLM, AVO, DRF, MEL

22	Ferulic acid 4-*O*-glucoside	$C_{16}H_{20}O_9$	18.495	**[M-H]$^-$	356.1107	355.1034	355.1024	-2.8	193, 178, 149, 134	*APR, KWF, MNG, NEC, PIN, PLM, POM, AVO, CTA, PAP
23	Ferulic acid	$C_{10}H_{10}O_4$	18.512	**[M-H]$^-$	194.0579	193.0506	193.0500	-3.1	178, 149, 134	*APR, KWF, NEC, PSN, PLM, AVO, DGF, PAP
24	Hydroxycaffeic acid	$C_9H_8O_5$	19.279	[M-H]$^-$	196.0372	195.0299	195.0294	-2.6	151	*ORN, PEC, PLM
25	*m*-coumaric acid	$C_9H_8O_3$	19.319	**[M-H]$^-$	164.0473	163.0400	163.0406	3.7	119	*APL, APR, BNA, CTA, GRF, KWF, NEC, PEC, PSN, PIN, PLM, POM, AVO, DGF, PAP
26	Caffeic acid 3-*O*-glucuronide	$C_{15}H_{16}O_{10}$	19.588	**[M-H]$^-$	356.0743	355.0670	355.0686	4.5	179	*CTA. GRF, KWF, ORN, PIN, DGF
27	Ferulic acid 4-*O*-glucuronide	$C_{16}H_{18}O_{10}$	19.704	**[M-H]$^-$	370.0900	369.0827	369.0834	1.9	193	*APR, AVO, CTA, GRF, KWF, ORN, PSN, PLM, LMN, MNG, POM
28	Caffeic acid 4-sulfate	$C_9H_8O_7S$	20.240	[M-H]$^-$	259.9991	258.9918	258.9916	-0.8	179, 135	ORN
29	3-Caffeoylquinic acid	$C_{16}H_{18}O_9$	20.815	**[M-H]$^-$	354.0951	353.0878	353.0877	-0.3	253, 190, 144	*APL, APR, CTA, DGF, KWF, PEC, ORN, PSN, PLM, AVO, LMN, PAP
30	*p*-Coumaric acid 4-*O*-glucoside	$C_{15}H_{18}O_8$	20.881	[M-H]$^-$	326.1002	325.0929	325.0925	-1.2	163	*APL, AVO, GRF, KWF, MNG, PEC, PLM, POM
31	*p*-Coumaroyl tyrosine	$C_{18}H_{17}NO_5$	25.148	[M-H]$^-$	327.1107	326.1034	326.1035	0.3	282	DGF
32	1-Sinapoyl-2,2'-diferuloylgentiobiose	$C_{43}H_{48}O_{21}$	26.763	[M-H]$^-$	900.2688	899.2615	899.2579	-4.0	613, 201	KWF
33	Sinapic acid	$C_{11}H_{12}O_5$	30.185	**[M-H]$^-$	224.0685	223.0612	223.0603	-4.0	205, 163	*AVO, CTA, APL, KWF, PAP. LMN, PIN
34	Caffeic acid	$C_9H_8O_4$	31.284	**[M-H]$^-$	180.0423	179.0350	179.0349	-0.6	143, 133	*CTA, GRF, NEC, ORN, PSN, PLM, PAP, PER, PIN
35	Verbascoside	$C_{29}H_{36}O_{15}$	31.531	[M-H]$^-$	624.2054	623.1981	623.1984	0.4	477, 461, 315, 135	*CTA, DGF, LMN
36	5-5'-Dehydrodiferulic acid	$C_{20}H_{18}O_8$	32.124	[M+H]$^+$	386.1002	387.1075	387.1064	-2.8	369	*DGF, KWF
37	Rosmarinic acid	$C_{18}H_{16}O_8$	32.802	[M-H]$^-$	360.0845	359.0772	359.0787	4.2	179	*AVO, CTA, DGF, KWF, PER
38	3-Feruloylquinic acid	$C_{17}H_{20}O_9$	33.605	**[M-H]$^-$	368.1107	367.1034	367.1019	-4.1	298, 288, 192, 191	*APL, APR, CTA, MNG, NEC, PEC, ORN, PSN, PER, PLM, AVO, DGF, MEL
39	1,2,2'-Triferuloylgentiobiose	$C_{42}H_{46}O_{20}$	34.101	[M-H]$^-$	870.2582	869.2509	869.2498	-1.3	693, 517	PAP
40	Chicoric acid	$C_{22}H_{18}O_{12}$	35.138	[M−H]$^-$	474.0798	473.0725	473.0754	3.1	293, 311	*DGF, KWF
41	1-Sinapoyl-2-feruloylgentiobiose	$C_{33}H_{40}O_{18}$	36.370	[M-H]$^-$	724.2215	723.2142	723.2124	-2.5	529, 499	APR
42	*p*-Coumaroyl malic acid	$C_{13}H_{12}O_7$	41.506	[M-H]$^-$	280.0583	279.0510	279.0524	5.0	163, 119	PAP
43	Cinnamoyl glucose	$C_{15}H_{18}O_7$	60.985	**[M-H]$^-$	310.1053	309.0980	309.0965	-4.9	147, 131, 103	*PER, DGF
Hydroxyphenylacetic acids										
44	3,4-Dihydroxyphenylacetic acid	$C_8H_8O_4$	20.749	**[M-H]$^-$	168.0423	167.035	167.0343	-4.2	149, 123	*APL, APR, CTA, GRF, MNG, MEL, NEC, PEC, ORN, PSN, PER, PIN, PLM, POM, AVO, DGF
45	2-Hydroxy-2-phenylacetic acid	$C_8H_8O_3$	36.121	**[M-H]$^-$	152.0473	151.0400	151.0407	4.6	136, 92	*CTA, KWF, MNG, ORN, PER, DGF
Hydroxyphenylpropanoic acids										

46	Dihydroferulic acid 4-sulfate	$C_{10}H_{12}O_7S$	4.076	$[M-H]^-$	276.0304	275.0231	275.0229	-0.7	195, 151, 177	AVO
47	Dihydroferulic acid 4-*O*-glucuronide	$C_{16}H_{20}O_{10}$	6.866	$[M-H]^-$	372.1056	371.0983	371.0986	0.8	195	*APL, APR, CTA, KWF, NEC, ORN, PSN, PLM
48	3-Hydroxy-3-(3-hydroxyphenyl) propionic acid	$C_9H_{10}O_4$	10.956	$[M-H]^-$	182.0579	181.0506	181.0500	-3.3	163, 135, 119	*GRF, MNG, ORN, PEC, PER
49	Dihydrocaffeic acid 3-*O*-glucuronide	$C_{15}H_{18}O_{10}$	22.536	$[M-H]^-$	358.090	357.0827	357.0811	-4.5	181	*GRF, PEC, PER, PIN, POM
Flavonoids										
	Flavanols									
50	Prodelphinidin dimer B3	$C_{30}H_{26}O_{14}$	16.428	$^{**}[M+H]^+$	610.1323	611.1396	611.1367	-4.7	469, 311, 291	*CTA, KWF, PEC, POM, AVO, DGF
51	(+)-Catechin 3-*O*-gallate	$C_{22}H_{18}O_{10}$	22.306	$^{**}[M-H]^-$	442.090	441.0827	441.0805	-5.0	289, 169, 125	*KWF, PER, AVO
52	(-)-Epigallocatechin	$C_{15}H_{14}O_7$	24.121	$^{**}[M-H]^-$	306.0740	305.0667	305.0675	2.6	261, 219	AVO
53	3'-*O*-Methylcatechin	$C_{16}H_{16}O_6$	24.124	$^{**}[M-H]^-$	304.0947	303.0874	303.0878	1.3	271, 163	*PER, AVO, LMN
54	(+)-Catechin	$C_{15}H_{14}O_6$	26.597	$^{**}[M-H]^-$	290.0790	289.0717	289.0706	-3.8	245, 205, 179	*APL, APR, CTA, GRF, KWF, MNG, PSN, PEC, PER, PLM, POM, AVO, DGF, PAP
55	4''-*O*-Methylepigallocatechin 3-*O*-gallate	$C_{23}H_{20}O_{11}$	27.887	$^{**}[M-H]^-$	472.1006	471.0933	471.0923	-2.1	169, 319	*GRF, POM, AVO
56	Procyanidin trimer C1	$C_{45}H_{38}O_{18}$	28.966	$^{**}[M-H]^-$	866.2058	865.1985	865.1961	-2.8	739, 713, 695	*APL, CTA, KWF, MNG, PAP, PEC, PLM, POM, AVO, DGF
57	(+)-Gallocatechin 3-*O*-gallate	$C_{22}H_{18}O_{11}$	29.655	$[M-H]^-$	458.0849	457.0776	457.0777	0.2	305, 169	*AVO, PAP
58	4'-*O*-Methyl-(-)-epigallocatechin 7-*O*-glucuronide	$C_{22}H_{24}O_{13}$	31.732	$[M-H]^-$	496.1217	495.1144	495.1123	-4.2	451, 313	*APL, NEC, PEC, AVO, KWF, PER, PLM
59	Cinnamtannin A2	$C_{60}H_{50}O_{24}$	35.276	$^{**}[M-H]^-$	1154.269	1153.262	1153.2600	-1.8	739	*CTA, KWF, PLM, AVO, DGF
60	Procyanidin dimer B1	$C_{30}H_{26}O_{12}$	37.978	$^{**}[M-H]^-$	578.1424	577.1351	577.1348	-0.5	451	*APL, AVO, CTA, GRF, KWF, NEC, PEC, ORN, PLM, POM, DGF, PAP
	Flavones									
61	Apigenin 7-*O*-(6''-malonyl-apiosyl-glucoside)	$C_{29}H_{30}O_{17}$	4.416	$[M-H]^-$	650.1483	649.1410	649.1429	2.9	605	PEC
62	Gardenin B	$C_{19}H_{18}O_7$	10.234	$^{**}[M+H]^+$	358.1053	359.1126	359.1118	-2.2	344, 329, 311	*CTA, AVO, BNA
63	Cirsilineol	$C_{18}H_{16}O_7$	10.827	$^{**}[M+H]^+$	344.0896	345.0969	345.0970	0.3	330, 312, 297, 284	*DGF, BNA, KWF, LMN
64	7,4'-Dihydroxyflavone	$C_{15}H_{10}O_4$	18.251	$[M+H]^+$	254.0579	255.0652	255.0643	-3.5	227, 199, 171	*AVO, PER, PIN
65	Apigenin 7-*O*-glucuronide	$C_{21}H_{18}O_{11}$	20.967	$^{**}[M+H]^+$	446.0849	447.0922	447.0910	-2.7	271, 253	*CTA, DGF, PAP, KWF
66	Rhoifolin	$C_{27}H_{30}O_{14}$	27.229	$^{**}[M-H]^-$	578.1636	577.1563	577.1538	-4.3	413, 269	PSN, LMN
67	Apigenin 7-*O*-apiosylglucoside	$C_{26}H_{28}O_{14}$	35.572	$^{**}[M+H]^+$	564.1479	565.1552	565.1529	-4.1	296	*LMN, KWF, MNG, PAP
68	Apigenin 6,8-di-C-glucoside	$C_{27}H_{30}O_{15}$	43.578	$^{**}[M-H]^-$	594.1585	593.1512	593.1527	2.5	503, 473	*APL, APR, GRF, KWF, ORN, PAP, PSN, PEC, PLM, LMN, MEL, PAP
69	Diosmin	$C_{28}H_{32}O_{15}$	46.538	$[M+H]^+$	608.1741	609.1814	609.1788	-4.3	301, 286	LMN

70	6-Hydroxyluteolin 7-rhamnoside	$C_{21}H_{20}O_{11}$	46.758	**[M-H]$^-$	448.1006	447.0933	447.0928	-1.1	301	*APL, APR, BNA, DGF, KWF, ORN, PSN, PEC, PER, PLM, POM, AVO, LMN, MEL, PAP
71	Chrysoeriol 7-*O*-glucoside	$C_{22}H_{22}O_{11}$	54.226	**[M+H]$^+$	462.1162	463.1235	463.1255	4.3	445, 427, 409, 381	*AVO, APL, KWF, POM, LMN
72	Apigenin 6-C-glucoside	$C_{21}H_{20}O_{10}$	55.754	**[M-H]$^-$	432.1056	431.0983	431.0983	0.1	413, 341, 311	*APL, DGF, LMN, MNG, PLM
	Flavanones									
73	Hesperetin 3'-sulfate	$C_{16}H_{14}O_9S$	6.681	**[M-H]$^-$	382.0359	381.0286	381.0293	1.8	301, 286, 257, 242	*GRF, CTA
74	Hesperetin 3',7-*O*-diglucuronide	$C_{28}H_{30}O_{18}$	21.163	**[M-H]$^-$	654.1432	653.1359	653.1361	0.3	477, 301, 286, 242	*KWF, PIN, PAP
75	6-Prenylnaringenin	$C_{20}H_{20}O_5$	35.742	[M+H]$^+$	340.1311	341.1384	341.1375	-2.6	323, 137	AVO
76	Narirutin	$C_{27}H_{32}O_{14}$	38.326	**[M-H]$^-$	580.1792	579.1719	579.1710	-1.6	271	*APL, NEC, DGF, LMN
77	Neoeriocitrin	$C_{27}H_{32}O_{15}$	39.899	**[M-H]$^-$	596.1741	595.1668	595.1684	2.7	431, 287	*CTA, LMN, NEC, AVO, DGF
78	Hesperidin	$C_{28}H_{34}O_{15}$	42.745	[M+H]$^+$	610.1898	611.1971	611.1956	-2.5	593, 465, 449, 303	LMN
79	Hesperetin 3'-*O*-glucuronide	$C_{22}H_{22}O_{12}$	47.521	**[M-H]$^-$	478.1111	477.1038	477.1033	-1.0	301, 175, 113, 85	*APL, BNA, KWF, MNG, ORN, NEC, PEC, POM, AVO, LMN
80	Naringin 4'-*O*-glucoside	$C_{33}H_{42}O_{19}$	53.036	[M-H]$^-$	742.2320	741.2247	741.2249	0.3	433, 271	CTA
	Flavonols									
81	Myricetin 3-*O*-rutinoside	$C_{27}H_{30}O_{17}$	8.156	**[M-H]$^-$	626.1483	625.1410	625.1423	2.1	301	*LMN, MNG, NEC, PEC, PSN, POM, AVO
82	Quercetin 3'-*O*-glucuronide	$C_{21}H_{18}O_{13}$	12.512	**[M-H]$^-$	478.0747	477.0674	477.0670	-0.8	301	*LMN, ORN, POM, KWF
83	Myricetin 3-*O*-arabinoside	$C_{20}H_{18}O_{12}$	16.496	**[M-H]$^-$	450.0798	449.0725	449.0716	-2.0	317	*ORN, LMN
84	3-Methoxysinensetin	$C_{21}H_{22}O_8$	16.528	**[M+H]$^+$	402.1315	403.1388	403.1395	1.7	388, 373, 355, 327	*AVO, BNA, MNG, NEC, PLM, CTA
85	3-Methoxynobiletin	$C_{22}H_{24}O_9$	17.999	**[M+H]$^+$	432.1420	433.1493	433.1488	-1.2	403, 385, 373, 345	*DGF, PAP, PER
86	Myricetin 3-*O*-galactoside	$C_{21}H_{20}O_{13}$	19.288	[M-H]$^-$	480.0904	479.0831	479.0810	-4.4	317	*BNA, ORN, POM
87	Patuletin 3-*O*-glucosyl-(1->6)-[apiosyl(1->2)]-glucoside	$C_{33}H_{40}O_{22}$	26.768	[M-H]$^-$	788.2011	787.1938	787.1960	2.8	625, 463, 301, 271	ORN
88	Isorhamnetin	$C_{16}H_{12}O_7$	27.076	**[M-H]$^-$	316.0583	315.0510	315.0504	-1.9	300, 271	*PLM, AVO, LMN, PAP
89	Spinacetin 3-*O*-(2	$C_{43}H_{48}O_{24}$	33.242	[M-H]$^-$	948.2536	947.2463	947.2456	-0.7	741, 609, 301	PSN
90	Isorhamnetin 3-*O*-glucuronide	$C_{22}H_{20}O_{13}$	34.082	[M-H]$^-$	492.0904	491.0831	491.0875	3.9	315, 300, 272, 255	*AVO, KWF
91	Quercetin 3-*O*-glucosyl-xyloside	$C_{26}H_{28}O_{16}$	36.319	[M-H]$^-$	596.1377	595.1304	595.1311	1.2	265, 138, 116	*GRF, KWF, LMN, NEC, ORN, PLM
92	Kaempferol 3,7-*O*-diglucoside	$C_{27}H_{30}O_{16}$	37.879	**[M-H]$^-$	610.1534	609.1461	609.1451	-1.6	447, 285	*APL, APR, NEC, PEC, ORN, PSN, PIN, PLM, LMN, PAP

93	Quercetin 3-*O*-xylosyl-rutinoside	$C_{32}H_{38}O_{20}$	39.018	**[M+H]$^+$	742.1956	743.2029	743.2060	4.2	479, 317	*DGF, AVO, CTA, PAP
94	Kaempferol 3-*O*-glucosyl-rhamnosyl-galactoside	$C_{33}H_{40}O_{20}$	40.181	**[M-H]$^-$	756.2113	755.204	755.2004	-4.8	285	*APL, AVO, MEL, ORN, PSN, PEC, PIN, PLM, POM, LMN
95	Kaempferol 3-*O*-(2''-rhamnosyl-galactoside) 7-*O*-rhamnoside	$C_{33}H_{40}O_{19}$	41.953	**[M-H]$^-$	740.2164	739.2091	739.2088	-0.4	593, 447, 285	*APR, AVO, LMN, ORN, PAP, PIN, PLM, POM
96	Quercetin 3-*O*-xylosyl-glucuronide	$C_{26}H_{26}O_{17}$	43.207	**[M+H]$^+$	610.1170	611.1243	611.1255	2.0	479, 303, 285, 239	*KWF, GRF, AVO
97	Myricetin 3-*O*-rhamnoside	$C_{21}H_{20}O_{12}$	44.025	**[M-H]$^-$	464.0955	463.0882	463.0881	-0.2	317	*APL, BNA, NEC, PEC, ORN, PSN, PEC, PLM, POM, LMN, PAP
98	Quercetin 3-*O*-arabinoside	$C_{20}H_{18}O_{11}$	46.344	**[M-H]$^-$	434.0849	433.0776	433.0776	0.1	301	*APL, GRF, MNG, ORN, PEC, PLM, CTA, DGF, PAP
99	Quercetin 3-*O*-(6''-malonyl-glucoside)	$C_{24}H_{22}O_{15}$	48.691	[M+H]$^+$	550.0959	551.1032	551.1074	4.62	303	*CTA, APL, ORN
	Dihydrochalcones									
100	3-Hydroxyphloretin 2'-*O*-xylosyl-glucoside	$C_{26}H_{32}O_{15}$	37.564	[M-H]$^-$	584.1741	583.1668	583.1665	-0.5	289	*APL, MNG, PER, PIN
101	3-Hydroxyphloretin 2'-*O*-glucoside	$C_{21}H_{24}O_{11}$	43.048	**[M-H]$^-$	452.1319	451.1246	451.1258	2.7	289, 273	*APL, AVO, CTA, DGF, GRF, KWF, MNG, PAP, PER
102	Phloridzin	$C_{21}H_{24}O_{10}$	51.613	**[M-H]$^-$	436.1369	435.1296	435.1284	-2.8	273	*APL, CTA, KWF, ORN, PEC, POM, AVO, DGF, PAP
	Dihydroflavonols									
103	Dihydromyricetin 3-*O*-rhamnoside	$C_{21}H_{22}O_{12}$	21.710	**[M-H]$^-$	466.1111	465.1038	465.1021	-3.7	301	*APL, AVO, CTA, KWF, NEC, PEC, PSN, PLM, POM, DGF
104	Dihydroquercetin	$C_{15}H_{12}O_7$	31.135	**[M-H]$^-$	304.0583	303.0510	303.0504	-2.0	285, 275, 151	*CTA, KWF, MNG, PEC, PER, PAP
	Anthocyanins									
105	Cyanidin 3-*O*-diglucoside-5-*O*-glucoside	$C_{33}H_{41}O_{21}$	21.567	**[M+H]$^+$	773.2140	774.2213	774.2216	0.4	610, 464	*PAP, LMN, DGF
106	Cyanidin 3-*O*-(6''-*p*-coumaroyl-glucoside)	$C_{30}H_{27}O_{13}$	22.205	**[M+H]$^+$	595.1452	596.1525	596.1553	4.7	287	*KWF, APL, MNG, PEC, PER, PLM, POM, DGF, CTA, AVO, PAP
107	Delphinidin 3-*O*-xyloside	$C_{20}H_{19}O_{11}$	25.983	**[M-H]$^-$	435.0927	434.0854	434.0860	1.4	303	*MEL, CTA, KWF
108	Petunidin 3-*O*-(6''-acetyl-glucoside)	$C_{24}H_{25}O_{13}$	27.386	[M+H]$^+$	521.1295	522.1368	522.1358	-1.9	317	MEL
109	Isopeonidin 3-*O*-arabinoside	$C_{21}H_{21}O_{10}$	29.965	[M+H]$^+$	433.1135	434.1208	434.1213	1.1	271, 253, 243	*MNG, DGF
110	Delphinidin 3-*O*-glucosyl-glucoside	$C_{27}H_{31}O_{17}$	36.884	**[M+H]$^+$	627.1561	628.1634	628.1636	0.3	465, 3030	AVO
111	Peonidin 3-*O*-sambubioside-5-*O*-glucoside	$C_{33}H_{41}O_{20}$	37.050	**[M+H]$^+$	757.2191	758.2264	758.2263	-0.1	595, 449, 287	*AVO, LMN, PAP
112	Cyanidin 3-*O*-(2-*O*-(6-*O*-(E)-caffeoyl-D glucoside)-D-glucoside)-5-*O*-D-glucoside	$C_{43}H_{49}O_{24}$	39.696	[M+H]$^+$	949.2614	950.2687	950.2690	0.3	787, 463, 301	*APL, MNG, ORN, PEC, PER, POM
113	Cyanidin 3,5-*O*-diglucoside	$C_{27}H_{31}O_{16}$	42.367	**[M+H]$^+$	611.1612	612.1685	612.1664	-3.4	449, 287	*AVO, CTA, KWF, LMN, PAP, PEC, DGF
114	Delphinidin 3-*O*-glucoside	$C_{21}H_{21}O_{12}$	45.066	**[M+H]$^+$	465.1033	466.1106	466.1114	1.7	303	*CTA, AVO, DGF, KWF, PAP, POM

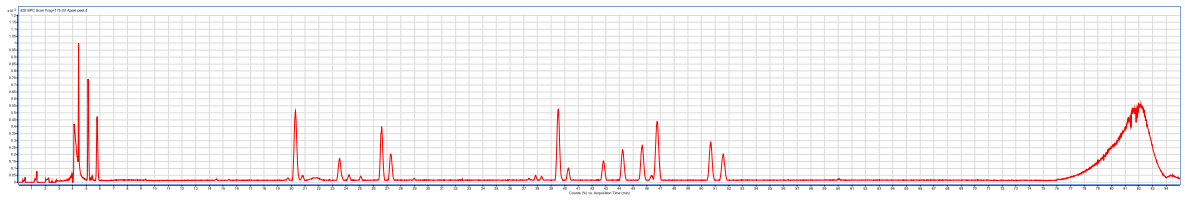
115	4-*O*-Methyldelphinidin 3-*O*-D-glucoside	$C_{22}H_{23}O_{12}$	48.482	$[M+H]^+$	479.1190	480.1263	480.1257	-1.2	317, 303, 285, 271	*DGF, AVO
116	Pelargonidin 3-*O*-rutinoside	$C_{27}H_{31}O_{14}$	50.950	$[M+H]^+$	579.1714	580.1787	580.1814	4.6	271, 433	LMN
Isoflavonoids										
117	6''-*O*-Malonylglycitin	$C_{25}H_{24}O_{13}$	7.256	$^{**}[M+H]^+$	532.1217	533.1290	533.1286	-0.8	285, 270, 253	*PAP, POM
118	Sativanone	$C_{17}H_{16}O_5$	9.333	$[M-H]^-$	300.0998	299.0925	299.0932	2.3	284, 269, 225	CTA
119	2',7-Dihydroxy-4',5'-dimethoxyisoflavone	$C_{17}H_{14}O_6$	10.651	$^{**}[M+H]^+$	314.0790	315.0863	315.0868	1.5	300, 282	MNG
120	Dihydrobiochanin A	$C_{16}H_{14}O_5$	15.236	$[M+H]^+$	286.0841	287.0914	287.0911	-1.0	269, 203, 201, 175	*AVO, CTA, KWF
121	6''-*O*-Malonyldaidzin	$C_{24}H_{22}O_{12}$	16.246	$^{**}[M+H]^+$	502.1111	503.1184	503.1200	3.2	255	*AVO, PSN
122	Glycitin	$C_{22}H_{22}O_{10}$	20.950	$^{**}[M+H]^+$	446.1213	447.1286	447.1294	1.8	285	*CTA, PER
123	Equol	$C_{15}H_{14}O_3$	21.803	$[M+H]^+$	242.0943	243.1016	243.1019	1.2	255, 211, 197	LMN
124	Violanone	$C_{17}H_{16}O_6$	25.419	$^{**}[M-H]^-$	316.0947	315.0874	315.0875	0.3	300, 285, 135	*CTA, ORN, PLM, AVO, DGF, LMN
125	2'-Hydroxyformononetin	$C_{16}H_{12}O_5$	28.896	$[M+H]^+$	284.0685	285.0758	285.0760	0.7	270, 229	LMN
126	6''-*O*-Acetyldaidzin	$C_{23}H_{22}O_{10}$	29.504	$^{**}[M-H]^-$	458.1213	457.1140	457.1121	-4.2	221	*MNG, PLM, DGF, PAP
127	Dalbergin	$C_{16}H_{12}O_4$	30.324	$[M-H]^-$	268.0736	267.0663	267.0644	-4.1	252, 224, 180	*DGF, AVO
128	3',4',7-Trihydroxyisoflavanone	$C_{15}H_{12}O_5$	31.267	$^{**}[M-H]^-$	272.0685	271.0612	271.0605	-2.6	177, 151, 119, 107,	*CTA, GRF, PSN, PER, DGF, KWF, LMN
129	Formononetin 7-*O*-glucuronide	$C_{22}H_{20}O_{10}$	42.450	$^{**}[M-H]^-$	444.1056	443.0983	443.0973	-2.3	267, 252	*PAP, AVO, DGF, LMN
130	5,6,7,3',4'-Pentahydroxyisoflavone	$C_{15}H_{10}O_7$	42.893	$^{**}[M+H]^+$	302.0427	303.0500	303.0487	-4.3	285, 257	*KWF, MNG, NEC, PEC, ORN, PAP, PLM, AVO, DGF, LMN, PAP, APL, BNA, CTA
131	6''-*O*-Acetylglycitin	$C_{24}H_{24}O_{11}$	43.656	$^{**}[M+H]^+$	488.1319	489.1392	489.1413	4.3	285, 270	*DGF, PAP, LMN
132	3'-Hydroxygenistein	$C_{15}H_{10}O_6$	51.410	$^{**}[M+H]^+$	286.0477	287.0550	287.0557	2.4	269, 259	*AVO, CTA, LMN, PAP, GRF, PLM, POM
133	6''-*O*-Malonylgenistin	$C_{24}H_{22}O_{13}$	64.297	$[M+H]^+$	518.1060	519.1133	519.1157	4.6	271	AVO
134	2-Dehydro-*O*-desmethylangolensin	$C_{15}H_{12}O_4$	77.381	$[M-H]^-$	256.0736	255.0663	255.0656	-2.7	135, 119	MNG
135	3'-Hydroxydaidzein	$C_{15}H_{10}O_5$	82.152	$[M+H]^+$	270.0528	271.0601	271.0588	-4.8	253, 241, 225	*APR, CTA, PIN
Other polyphenols										
Hydroxycoumarins										
136	Esculin	$C_{15}H_{16}O_9$	13.406	$[M+H]^+$	340.0794	341.0867	341.0862	-1.4	179, 151	APR
137	Esculetin	$C_9H_6O_4$	27.821	$[M-H]^-$	178.0266	177.0193	177.0199	3.4	149, 133, 89	CTA
138	Coumarin	$C_9H_6O_2$	32.744	$^{**}[M+H]^+$	146.0368	147.0441	147.0448	4.8	103, 91	*AVO, PLM
139	Scopoletin	$C_{10}H_8O_4$	36.851	$^{**}[M-H]^-$	192.0423	191.0350	191.0345	-2.6	176	*APR, DGF, LMN
140	Urolithin A	$C_{13}H_8O_4$	75.771	$[M-H]^-$	228.0423	227.0350	227.0341	-3.9	198, 182	*PSN, GRF, PLM
Hydroxybenzaldehydes										

141	*p*-Anisaldehyde	$C_8H_8O_2$	13.53	**[M+H]$^+$	136.0524	137.0597	137.0597	0.1	122, 109	*AVO, APR, DGF, KWF, ORN, PAP, PSN, PLM, CTA, NEC, PEC, PER
142	4-Hydroxybenzaldehyde	$C_7H_6O_2$	44.568	**[M-H]$^-$	122.0368	121.0295	121.0301	5.0	77	*BNA, GRF, PSN, PEC, PER, PIN, PLM, POM, AVO, PAP
Hydroxybenzoketones										
143	2-Hydroxy-4-methoxyacetophenone 5-sulfate	$C_9H_{10}O_7S$	9.446	[M-H]$^-$	262.0147	261.0074	261.0067	-2.7	181, 97	PER
144	2,3-Dihydroxy-1-guaiacylpropanone	$C_{10}H_{12}O_5$	33.57	**[M-H]$^-$	212.0685	211.0612	211.0605	-3.3	167, 123, 105, 93	*CTA, PIN, APR, AVO, DGF, MNG, PAP, PSN
Hydroxyphenylpropenes										
145	2-Methoxy-5-prop-1-enylphenol	$C_{10}H_{12}O_2$	26.251	[M+H]$^+$	164.0837	165.0910	165.0902	-4.8	149, 137, 133, 124	AVO
Curcuminoids										
146	Curcumin	$C_{21}H_{20}O_6$	22.918	[M-H]$^-$	368.126	367.1187	367.1207	4.4	217	*KWF, DGF
147	Bisdemethoxycurcumin	$C_{19}H_{16}O_4$	77.677	[M+H]$^+$	308.1049	309.1122	309.1137	4.9	291, 263	DGF
148	Demethoxycurcumin	$C_{20}H_{18}O_5$	81.976	[M-H]$^-$	338.1154	337.1081	337.1080	-0.3	217	BNA
Furanocoumarins										
149	Isopimpinellin	$C_{13}H_{10}O_5$	28.172	[M+H]$^+$	246.0528	247.0601	247.0613	4.9	232, 217, 205, 203	*AVO, BNA, CTA
Phenolic terpenes										
150	Rosmanol	$C_{20}H_{26}O_5$	22.230	[M+H]$^+$	346.1780	347.1853	347.1844	-2.6	301, 241, 231	PAP
151	Carnosic acid	$C_{20}H_{28}O_4$	80.419	**[M-H]$^-$	332.1988	331.1915	331.1905	-3.0	287, 269	*BNA, LMN, AVO
Tyrosols										
152	3,4-DHPEA-AC	$C_{10}H_{12}O_4$	11.802	**[M-H]$^-$	196.0736	195.0663	195.0657	-3.1	135	*APR, AVO, KWF, MEL, PIN, DGF, LMN, MNG, PAP
153	Hydroxytyrosol 4-*O*-glucoside	$C_{14}H_{20}O_8$	12.805	**[M-H]$^-$	316.1158	315.1085	315.1092	2.2	153, 123	*DGF, KWF, MNG, ORN, PER, POM, AVO
154	Oleoside 11-methylester	$C_{17}H_{24}O_{11}$	17.600	[M-H]$^-$	404.1319	403.1246	403.1269	4.7	223, 165	*CTA, AVO, DGF, KWF
155	3,4-DHPEA-EDA	$C_{17}H_{20}O_6$	23.564	[M-H]$^-$	320.126	319.1187	319.1189	0.6	275, 195	*AVO, DGF
156	Demethyloleuropein	$C_{24}H_{30}O_{13}$	51.646	**[M-H]$^-$	526.1686	525.1613	525.1599	-2.7	495	*APL, CTA, AVO, MEL
Other polyphenols										
157	Lithospermic acid	$C_{27}H_{22}O_{12}$	5.051	[M-H]$^-$	538.1111	537.1038	537.1048	1.9	493, 339, 295	*MNG, PER, KWF
158	Arbutin	$C_{12}H_{16}O_7$	5.129	**[M-H]$^-$	272.0896	271.0823	271.0828	1.8	109	*PSN, AVO
159	Salvianolic acid B	$C_{36}H_{30}O_{16}$	28.598	[M-H]$^-$	718.1534	717.1461	717.1436	-3.5	519, 339, 321, 295	BNA
160	Salvianolic acid C	$C_{26}H_{20}O_{10}$	32.51	[M-H]$^-$	492.1056	491.0983	491.0993	2.0	311, 267, 249	*CTA, PAP
Lignans										
161	Enterolactone	$C_{18}H_{18}O_4$	4.254	[M+H]$^+$	298.1205	299.1278	299.1283	1.7	281, 187, 165	*CTA, DGF, KWF

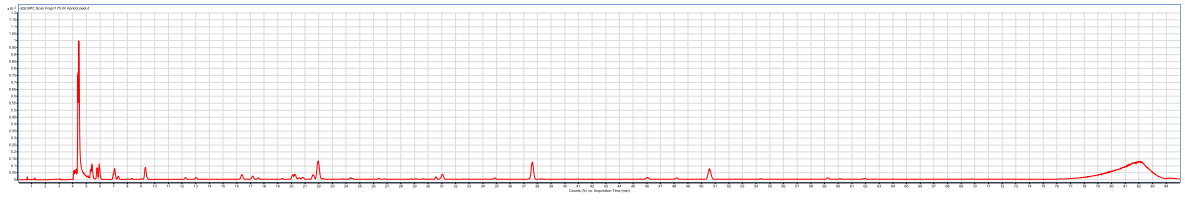
162	Sesamin	$C_{20}H_{18}O_6$	7.759	$[M-H]^-$	354.1103	353.103	353.1020	-2.8	338, 163	*CTA, DGF
163	Schisandrin C	$C_{22}H_{24}O_6$	10.167	$[M+H]^+$	384.1573	385.1646	385.1652	1.6	370, 315, 300	*CTA, LMN, AVO, PAP
164	Arctigenin	$C_{21}H_{24}O_6$	29.065	**$[M-H]^-$	372.1573	371.15	371.1509	2.4	356, 312, 295	AVO
165	7-Oxomatairesinol	$C_{20}H_{20}O_7$	30.089	**$[M+H]^+$	372.1209	373.1282	373.1297	4.0	358, 343, 328, 325	*LMN, ORN
166	Schisantherin A	$C_{30}H_{32}O_9$	37.579	$[M+H]^+$	536.2046	537.2119	537.2115	-0.7	519, 415, 385, 371	*KWF, BNA, CTA, PER
167	Pinoresinol	$C_{20}H_{22}O_6$	40.958	**$[M-H]^-$	358.1416	357.1343	357.1336	-2.0	342, 327, 313, 221	*GRF, AVO
168	7-Hydroxymatairesinol	$C_{20}H_{22}O_7$	47.587	$[M-H]^-$	374.1366	373.1293	373.1283	-2.7	343, 313, 298, 285	*APL, NEC
169	Secoisolariciresinol-sesquilignan	$C_{30}H_{38}O_{10}$	59.607	$[M-H]^-$	558.2465	557.2392	557.2387	-0.9	539, 521, 509, 361	*AVO, CTA
170	Schisandrol B	$C_{23}H_{28}O_7$	63.253	$[M+H]^+$	416.1835	417.1908	417.1929	5.0	224, 193, 165	AVO
171	Schisandrin B	$C_{23}H_{28}O_6$	81.572	$[M+H]^+$	400.1886	401.1959	401.1949	-2.5	386	CTA
Stilbenes										
172	Piceatannol 3-*O*-glucoside	$C_{20}H_{22}O_9$	8.335	$[M-H]^-$	406.1264	405.1191	405.1172	-4.6	243	*CTA, AVO
173	Resveratrol	$C_{14}H_{12}O_3$	31.317	**$[M-H]^-$	228.0786	227.0713	227.0709	-1.8	212, 185, 157, 143	*CTA, AVO, DGF
174	Resveratrol 5-*O*-glucoside	$C_{20}H_{22}O_8$	38.063	**$[M-H]^-$	390.1315	389.1242	389.1245	0.8	227	*PSN, POM, KWF
175	3'-Hydroxy-3,4,5,4'-tetramethoxystilbene	$C_{17}H_{18}O_5$	43.904	$[M+H]^+$	302.1154	303.1227	303.1221	-2.0	229, 201, 187, 175	DGF
176	4-Hydroxy-3,5,4'-trimethoxystilbene	$C_{17}H_{18}O_4$	63.286	$[M+H]^+$	286.1205	287.1278	287.1280	0.7	271, 241, 225	*CTA, DGF

175 *Compound was detected in more than one fruit peel samples, data presented in this table are from asterisk sample. **Compounds were detected in both negative [M-H]- and positive [M+H]+ mode of ionization while only single mode data was presented. Fruit
176 peel samples were mentioned in abbreviations. Apple peel "APL", Apricot peel "APR", Avocado peel "AVO", Banana peel "BNA", Custard apple peel "CTA", Dragon fruit peel "DGF", Grapefruit peel "GRF", kiwifruit peel "KWF", Lime peel "LMN", Mango
177 peel "MNG", Melon peel "MEL", Nectarine peel "NEC", Orange peel "ORN", Papaya peel "PAP", Passionfruit peel "PSN", Peach peel "PEC", Pear peel "PER", Pineapple peel "PIN", Plum peel "PLM" and Pomegranate peel "POM"

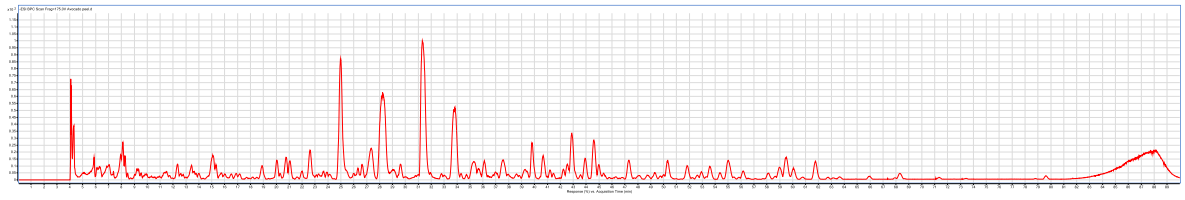
(Apple Peel)



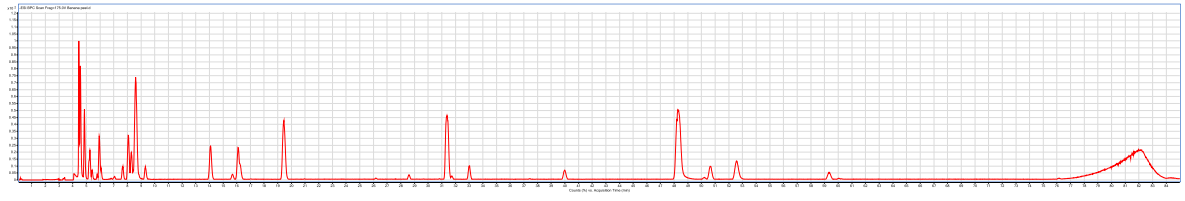
(Apricot peel)



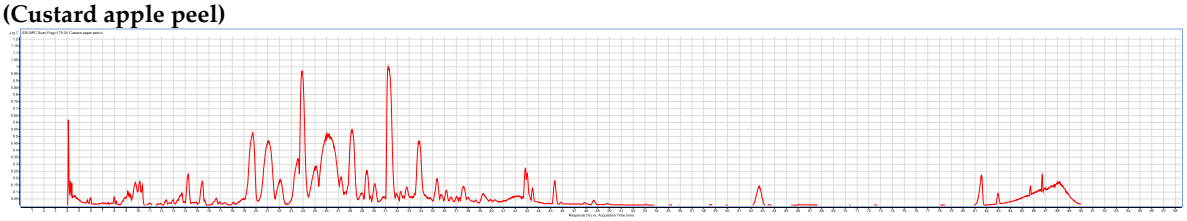
(Avocado peel)



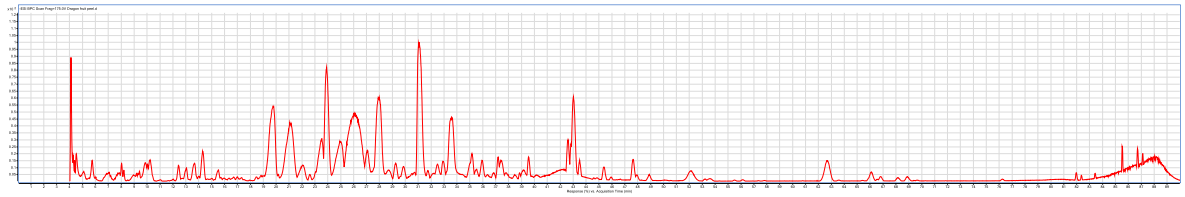
(Banana peel)



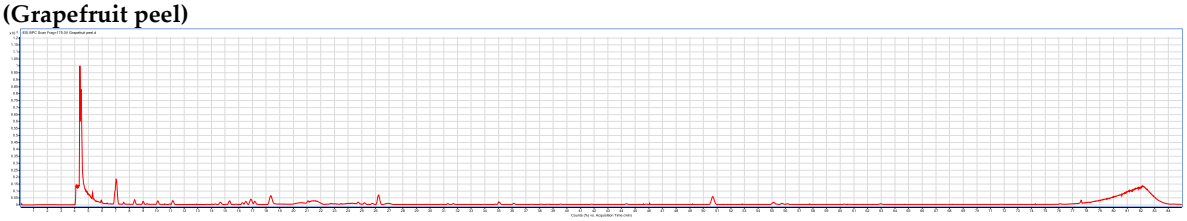
(Custard apple peel)



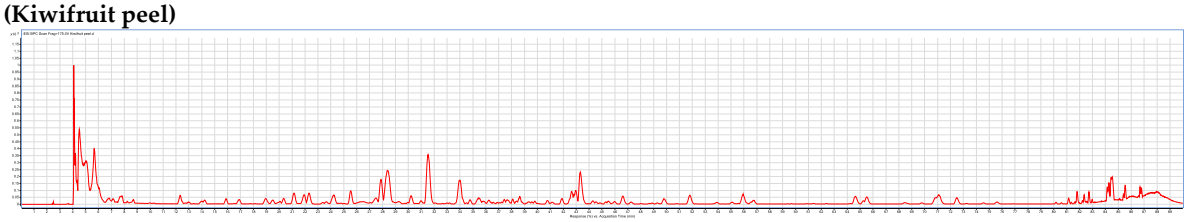
(Dragon fruit peel)



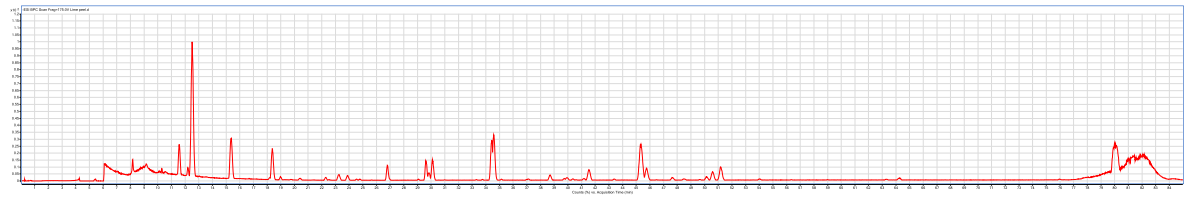
(Grapefruit peel)



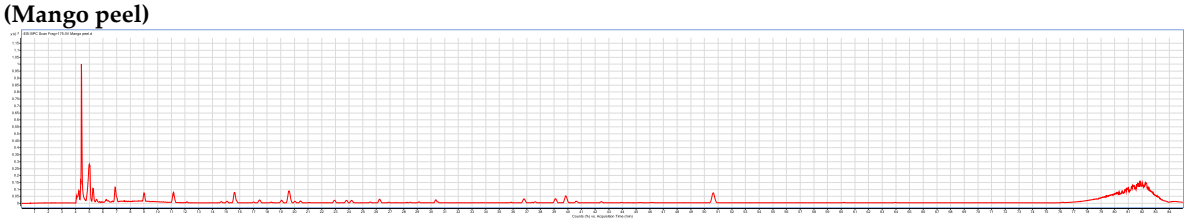
(Kiwifruit peel)



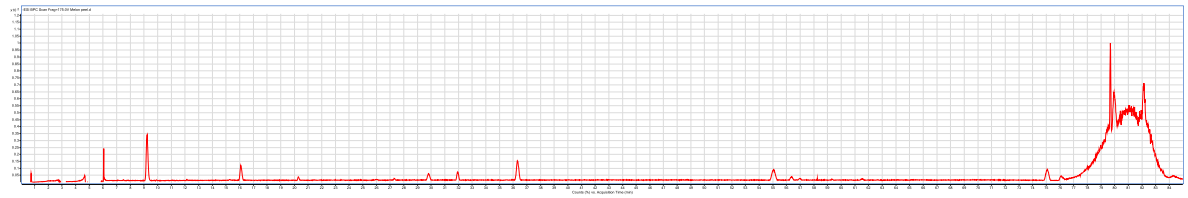
(Lime peel)



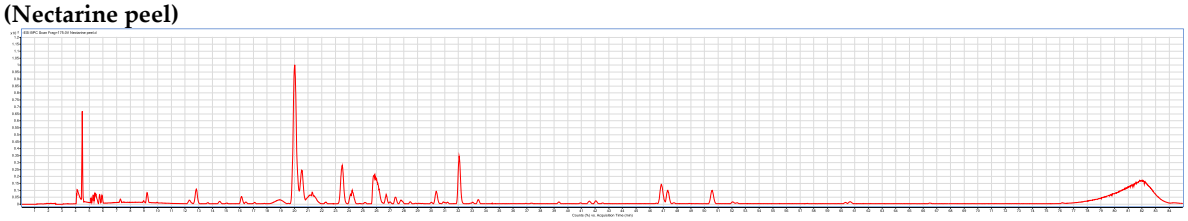
(Mango peel)



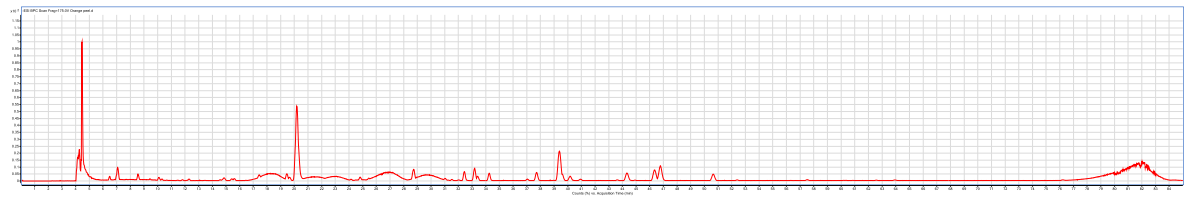
(Melon peel)



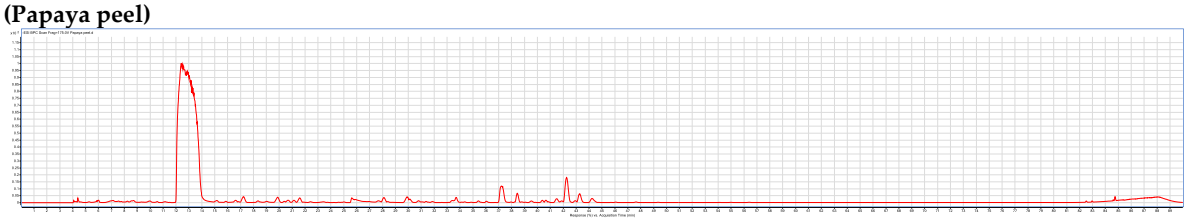
(Nectarine peel)



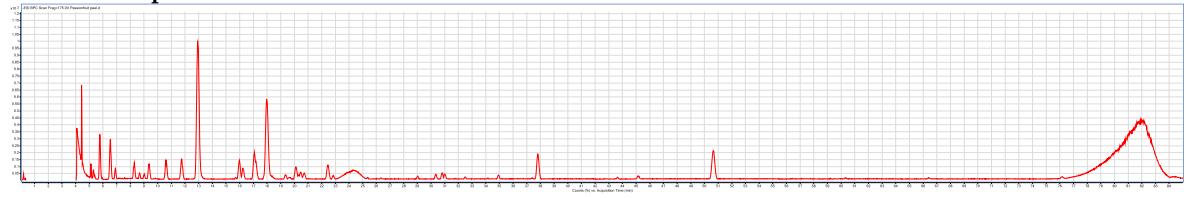
(Orange peel)



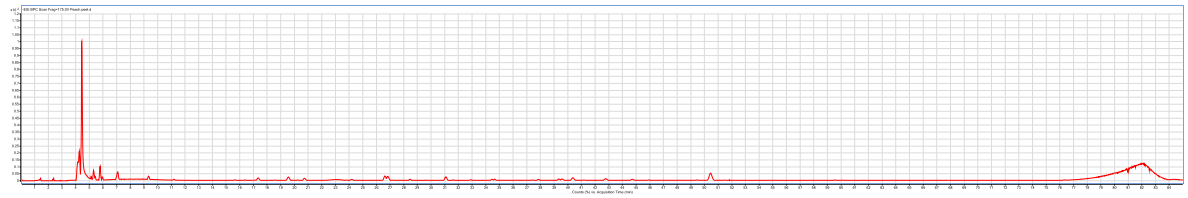
(Papaya peel)



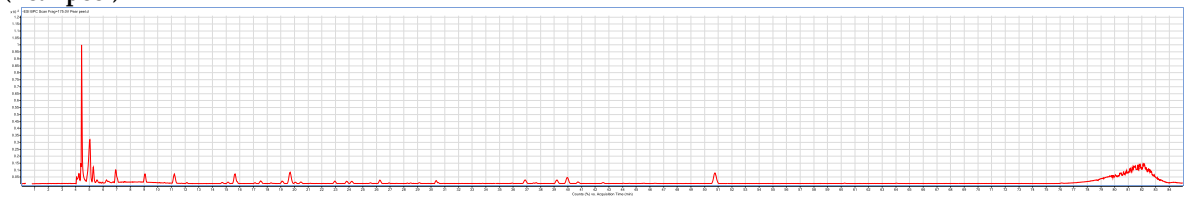
(Passionfruit peel)



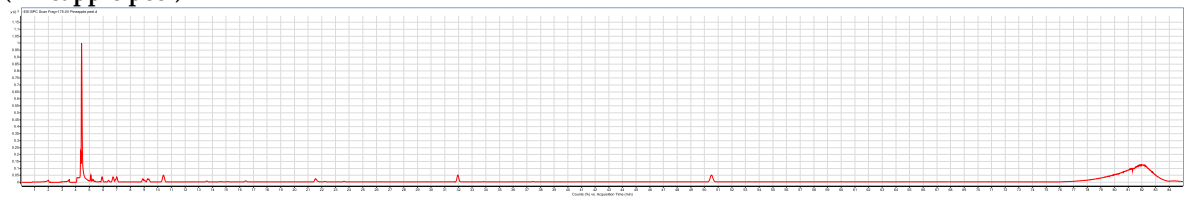
(Peach peel)



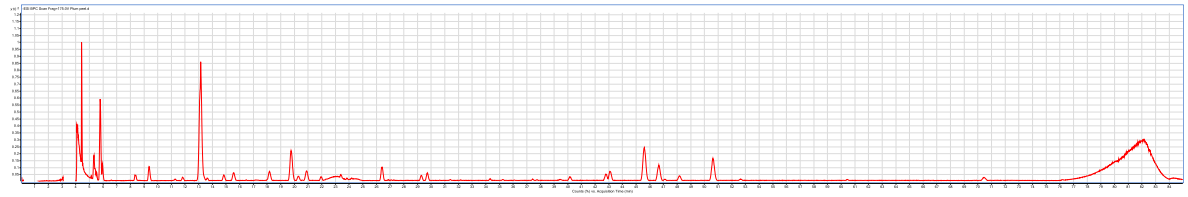
(Pear peel)



(Pineapple peel)



(Plum peel)



(Pomegranate peel)

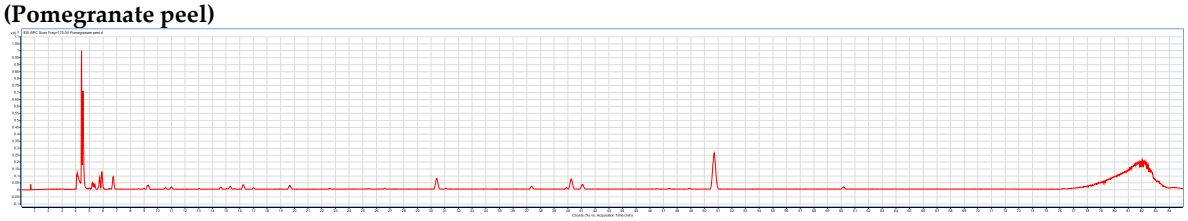
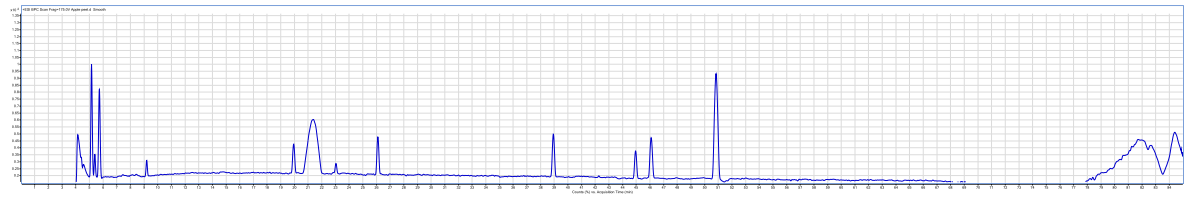
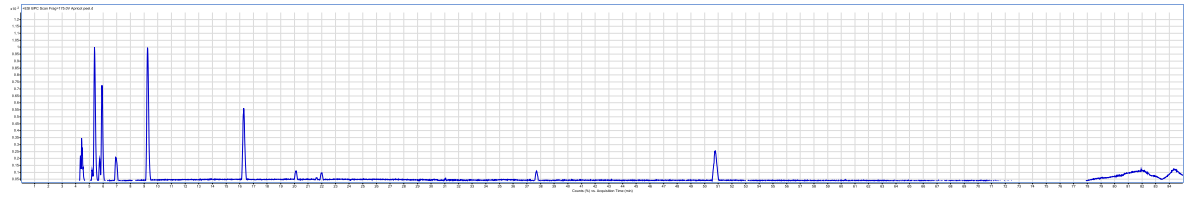


Figure S1: Characterization of phenolic compounds in different fruit peels by LC-ESI-QTOF-MS/MS. Base peak chromatogram (BPC) of twenty fruit peel samples in negative mode of ionization.

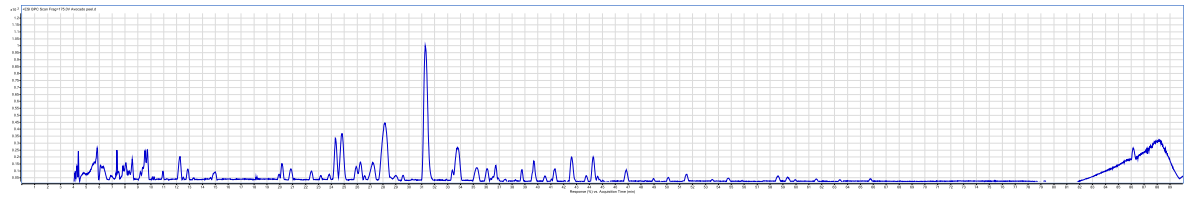
(Apple Peel)



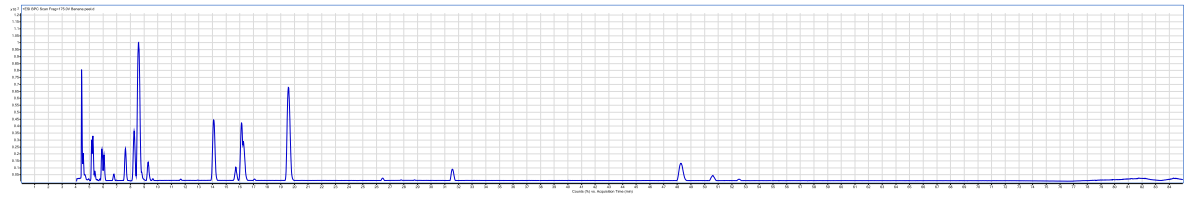
(Apricot peel)



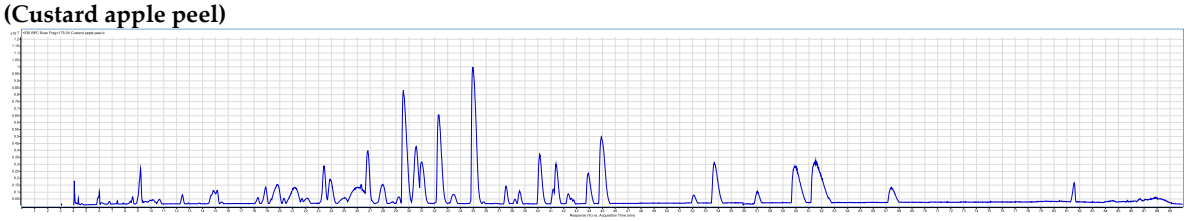
(Avocado peel)



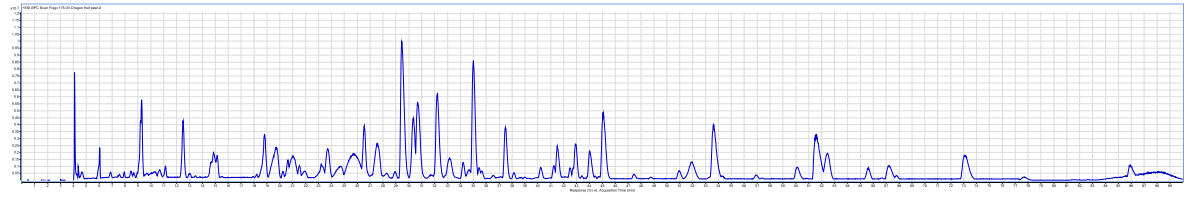
(Banana peel)



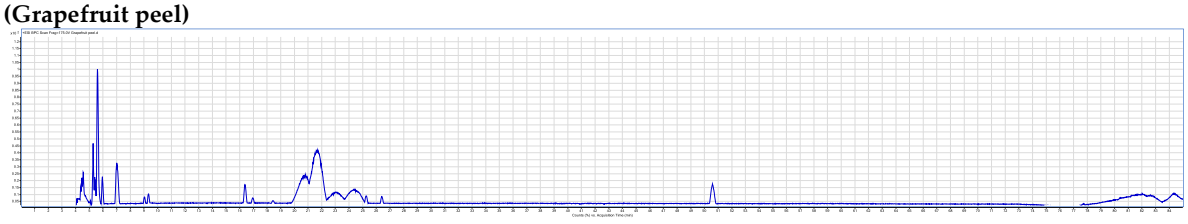
(Custard apple peel)



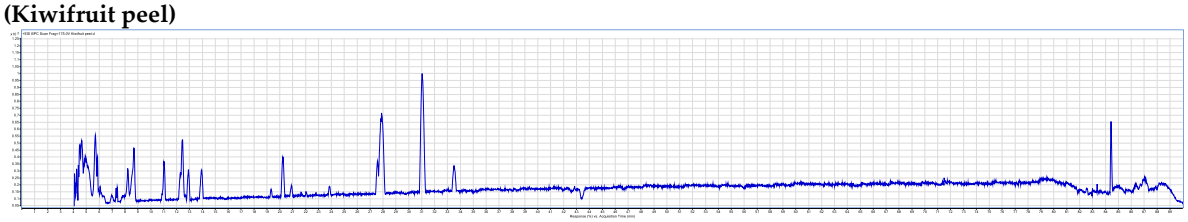
(Dragon fruit peel)



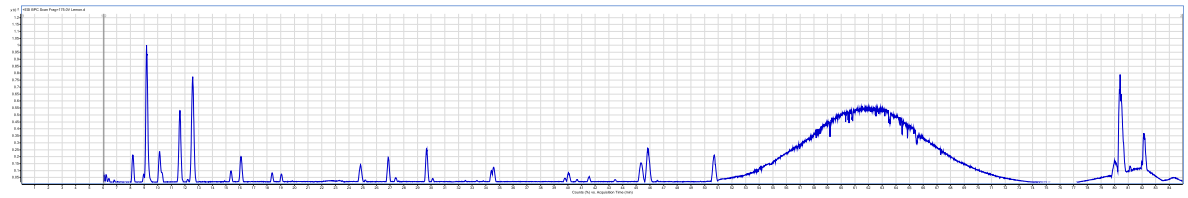
(Grapefruit peel)



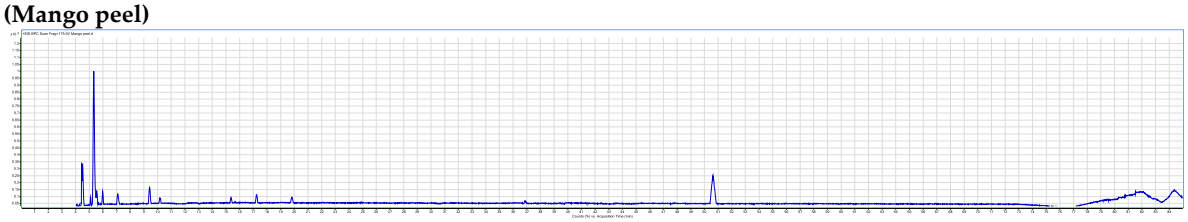
(Kiwifruit peel)



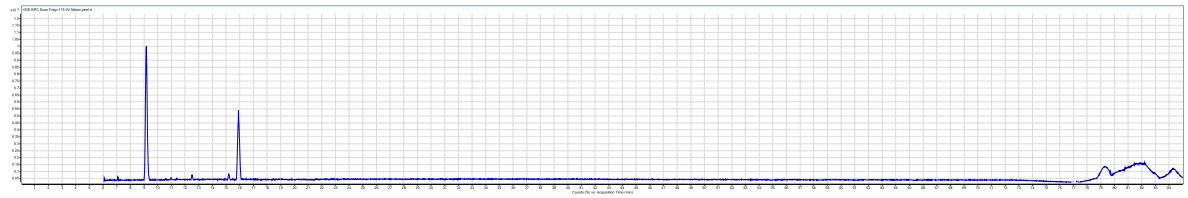
(Lime peel)



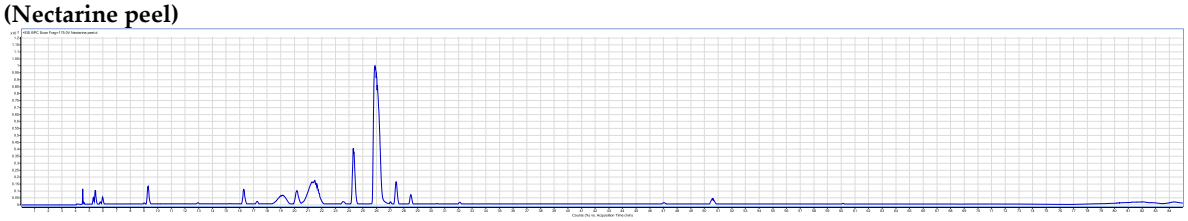
(Mango peel)



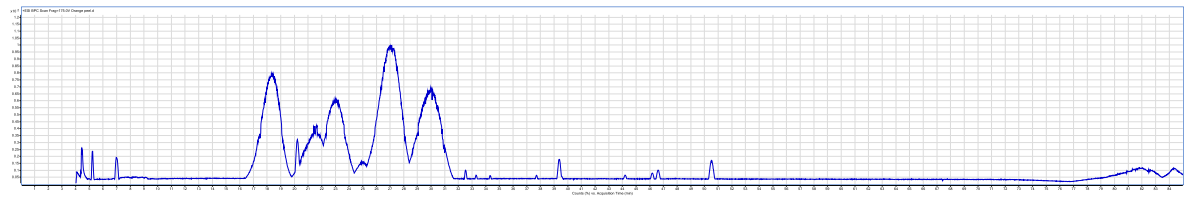
(Melon peel)



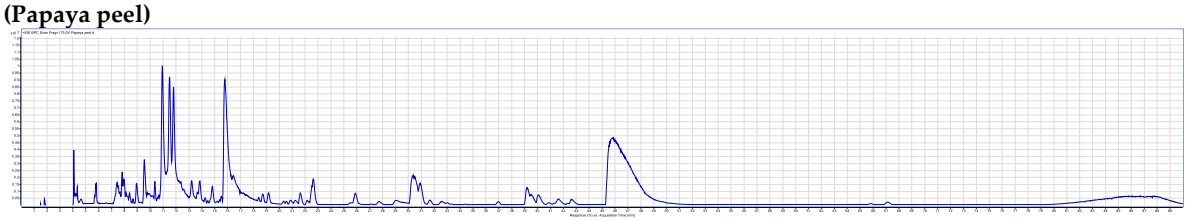
(Nectarine peel)



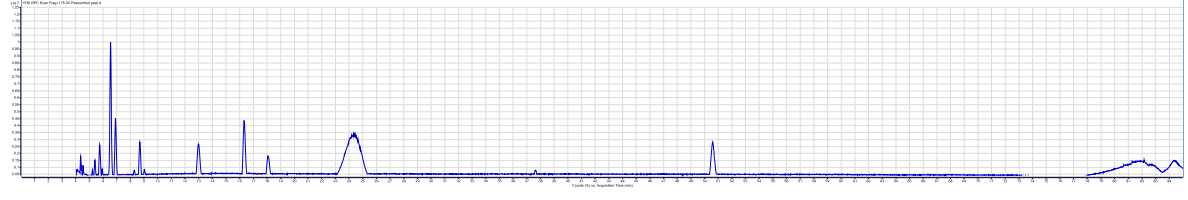
(Orange peel)



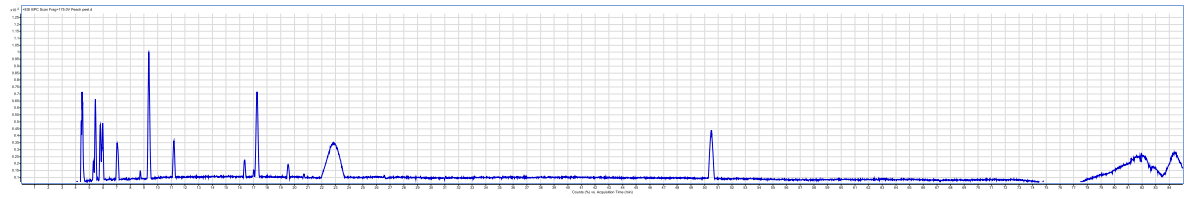
(Papaya peel)



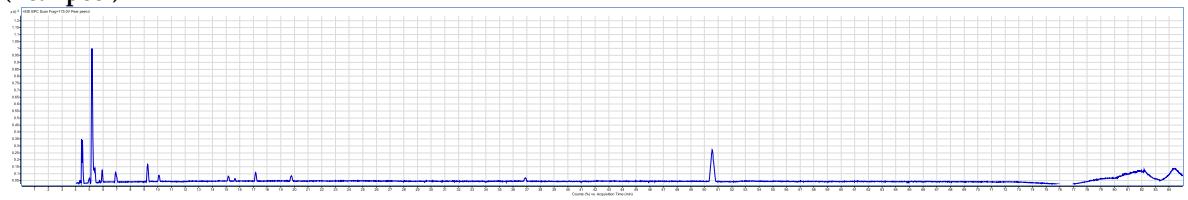
(Passionfruit peel)



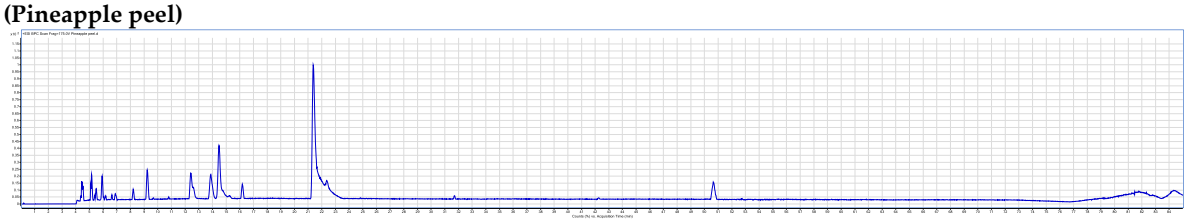
(Peach peel)



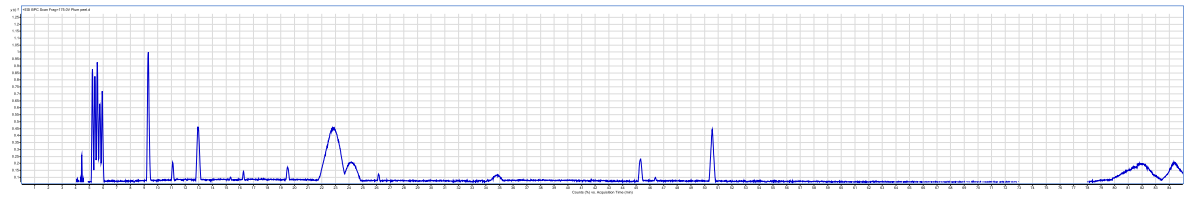
(Pear peel)



(Pineapple peel)



(Plum peel)



(Pomegranate peel)

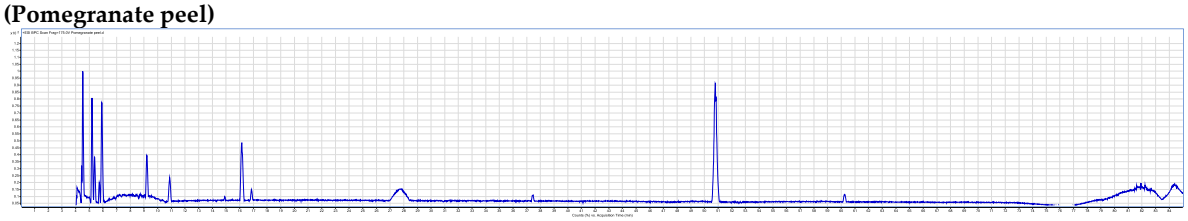


Figure S2: Characterization of phenolic compounds in different fruit peels by LC-ESI-QTOF-MS/MS. Base peak chromatogram of twenty fruit peel samples in positive mode of ionization.