Supplemental material

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

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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 ± 0.15 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 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. 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]Cl₃·6H₂O), hydrated sodium acetate, hydrochloric acid, ammonium molybdate, quercetin, catechin, 2,2’-diphenyl-1-picrylhydrazyl (DPPH), 2,4,6-tripyridyl-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, Tuttingen, 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 DPPH 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 H₂SO₄, 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 x 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, and iii) 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 ≤ 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 ≤ 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.
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) | MS² Product ions | Fruit Peels |
|-----|------------------------------------|-------------------|----------|----------------------|------------------|-------------------|----------------|-------------|-----------------|-------------|
| 1   | Vanillyl acid 4-sulfate            | C₇H₆O₅S          | 5.068    | [M-H]                | 247.9991         | 246.9912          | 246.9911       | -2.8        | 167             | *MNG, PER, KWF |
| 2   | Gallic acid 4-O-glucoside          | C₇H₆O⁵          | 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                        | C₇H₆O₃          | 6.872    | **[M-H]**            | 170.0215         | 169.0142          | 169.0146       | 2.4         | 125             | *MNG, ORN, PER, POM, KWF, LMN |
| 4   | Ellagic acid arabinoside           | C₇H₆O$_{12}$     | 7.020    | [M-H]                | 434.4850         | 433.0412          | 433.0422       | 2.3         | 300             | ORN         |
| 5   | Protocatechuic acid 4-O-glucoside  | C₈H₈O₅          | 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, POM, AVO, AVO, PAP |
| 6   | 2-Hydroxybenzoic acid              | C₇H₆O₃          | 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, AVO, PAP |
| 7   | 4-Hydroxybenzoic acid 4-O-glucoside| C₇H₆O₅           | 11.171   | [M-H]                | 300.0845         | 299.0772          | 299.0762       | -3.3        | 255, 137        | *GRF, MNG, MEL, PER |
| 8   | 2,3-Dihydroxybenzoic acid          | C₇H₆O₃          | 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              | C₇H₆O₃          | 13.079   | **[M+H]+**           | 184.0372         | 185.0445          | 185.0452       | 3.8         | 170, 142        | *KWF, MNG, AVO, DGF, GRF, PEC |
| 10  | 3,4-Dimethyldiigallic acid         | C₇H₆O₅           | 16.475   | **[M+H]+**           | 198.0528         | 199.0601          | 199.0605       | 2.0         | 153, 139, 125, 111 | *DG, KWF, MNG, ORN, PAP, PEC, AVO, AVO, PAP, CTA |
| 11  | Gallic acid 3-O-gallate             | C₇H₆O₃          | 21.104   | [M-H]                | 322.0325         | 321.0252          | 321.0240       | -3.7        | 169             | *MNG, PER     |
| 12  | Paeoniflorin                       | C₇H₆O$_{11}$     | 58.033   | **[M-H]**            | 480.1632         | 479.1559          | 479.1577       | 3.8         | 449, 357, 327   | *LMN, AVO, DGF |
| 13  | 1,5-Dicaffeoylquinic acid          | C₈H₈O$_{12}$     | 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           | C₇H₆O$_{5}$      | 5.341    | [M-H]                | 274.0147         | 273.0074          | 273.0067       | -2.6        | 193, 178        | PLM          |
| 15  | Caffeoyl glucose                   | C₇H₆O₃          | 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          | C₈H₈O₃          | 8.632    | **[M-H]**            | 296.0532         | 295.0459          | 295.0468       | 3.1         | 115             | *AVO, DGF, PIN, GRF, LMN, ORN, PER |
| 17  | Cinnamic acid                      | C₈H₈O₂           | 9.351    | **[M-H]**            | 148.0524         | 147.0451          | 147.0448       | -2.0        | 103             | *APL, APR, BNA, CTA, LMN, PEC, PAP, PIN, PLM, POM, AVO, DGF, MEL |
| 18  | Feruloyl tartaric acid             | C₇H₆O₃          | 10.419   | [M-H]                | 326.0638         | 325.0565          | 325.0566       | 0.3         | 193, 149        | *MNG, PER, POM |
| 19  | Caffeoyl tartaric acid             | C₇H₆O₃          | 13.765   | **[M-H]**            | 312.0481         | 311.0408          | 311.0418       | 3.2         | 161             | *POM, MNG, ORN, PSN |
| 20  | 3-Sinapoylquinic acid              | C₈H₈O$_{12}$     | 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           | C₈H₈O$_{12}$     | 18.131   | **[M-H]**            | 338.1002         | 337.0929          | 337.0924       | -1.5        | 265, 173, 162   | *APL, APR, CTA, KWF, NEC, PEC, PSN, PLM, AVO, AVO, DFG, MEL |
| No. | Compound                        | Formula | Mass (Da) | Calculated Mass (Da) | P.E. | Retention Time (min) | Ions   |
|-----|---------------------------------|---------|-----------|----------------------|------|----------------------|--------|
| 22  | Ferulic acid 4-O-glucoside     | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.01                 | **(M+H)** |
| 23  | Ferulic acid                   | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |
| 24  | Hydroxycaffeic acid            | C₂₀H₁₈O₈| 328.118   | 328.118              | 0.1  | 6.41                 | **(M+H)** |
| 25  | p-Coumaric acid 4-O-glucoside  | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.02                 | **(M+H)** |
| 26  | Caffeic acid 4-O-glucuronide   | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |
| 27  | Caffeic acid 3-O-glucuronide   | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |
| 28  | Sinapic acid                   | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |
| 29  | 3-Caffeoylquinic acid          | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |
| 30  | p-Coumaroyl tyrosine           | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |
| 31  | 5-S-Dehydrodiferulic acid      | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |
| 32  | Rosmarinic acid                | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |
| 33  | 3-Caffeoylquinic acid          | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |
| 34  | Verbascone                     | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |
| 35  | 1,2,2'-Triferuloylgentiobiose  | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |
| 36  | Chicoric acid                  | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |
| 37  | 1-Sinapoyl-2,2'-diferuloylgentiobiose | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |
| 38  | p-Coumaroyl malic acid         | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |
| 39  | Cinnamoyl glucuronic acid      | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |

**Hydroxyphenylacetic acids**

| No. | Compound                        | Formula | Mass (Da) | Calculated Mass (Da) | P.E. | Retention Time (min) | Ions   |
|-----|---------------------------------|---------|-----------|----------------------|------|----------------------|--------|
| 44  | 3,4-Dihydroxyphenylacetic acid | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |
| 45  | 2-Hydroxy-2-phenylacetic acid  | C₁₀H₁₀O₇| 272.096   | 272.096              | 0.1  | 6.12                 | **(M+H)** |

**Hydroxyphenylpropanoic acids**
| Flavonoids |  |
|---|---|
| **Flavonols** |  |
| 46 | Dihydroferulic acid 4-sulfate | C_{8}H_{12}O_{5} | 4.076 | [M-H]⁻ | 276.0304 | 275.0231 | 275.0229 | -0.7 | 195, 151, 177 | AVO |
| 47 | Dihydroferulic acid 4-O-glucuronide | C_{8}H_{12}O_{9} | 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 | O_{6} | 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_{8}H_{12}O_{9} | 22.536 | [M-H]⁻ | 358.0900 | 357.0827 | 357.0811 | -4.5 | 181 | *GRF, PEC, PER, PIN, POM |
| **Flavones** |  |
| 50 | Prodelphinidin dimer B3 | C_{8}H_{12}O_{4} | 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_{8}H_{12}O_{7} | 22.306 | **[M+H]**⁺ | 442.0900 | 441.0827 | 441.0805 | -5.0 | 289, 169, 125 | *KWF, PER, AVO |
| 52 | (-)-Epigallocatechin | C_{8}H_{12}O_{7} | 24.121 | **[M+H]**⁺ | 306.0740 | 305.0667 | 305.0675 | 2.6 | 261, 219 | AVO |
| 53 | 3'-O-Methylcatechin | C_{8}H_{12}O_{6} | 24.124 | **[M+H]**⁺ | 304.0947 | 303.0874 | 303.0878 | 1.3 | 271, 163 | *PER, AVO, LMN |
| 54 | (+)-Catechin | C_{8}H_{12}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_{8}H_{12}O_{5} | 27.887 | **[M+H]**⁺ | 472.1006 | 471.0933 | 471.0923 | -2.1 | 169, 319 | *GRF, POM, AVO |
| 56 | Procyanidin trimer C1 | C_{8}H_{12}O_{8} | 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_{8}H_{12}O_{5} | 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_{8}H_{12}O_{3} | 31.732 | [M-H]⁻ | 496.1217 | 495.1144 | 495.1123 | -4.2 | 451, 313 | *APL, NEC, PEC, AVO, KWF, PER, PLM |
| 59 | Cinnamantannin A2 | C_{8}H_{12}O_{4} | 35.276 | **[M+H]**⁺ | 1154.269 | 1153.262 | 1153.260 | -1.8 | 739 | *CTA, KWF, PLM, AVO, DGF |
| 60 | Procyanidin dimer B1 | C_{8}H_{12}O_{2} | 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-apyosyl-glucoside) | C_{8}H_{12}O_{7} | 4.416 | [M-H]⁻ | 650.1483 | 649.1410 | 649.1429 | 2.9 | 605 | PEC |
| 62 | Gardenin B | C_{8}H_{12}O_{7} | 10.234 | **[M+H]**⁺ | 358.1053 | 359.1126 | 359.1118 | -2.2 | 344, 329, 311 | *CTA, AVO, BNA |
| 63 | Cirsilineol | C_{8}H_{12}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_{8}H_{12}O_{3} | 18.251 | [M-H]⁻ | 254.0579 | 253.0652 | 253.0643 | -3.5 | 227, 199, 171 | *AVO, PER, PIN |
| 65 | Apigenin 7-O-glucuronide | C_{8}H_{12}O_{3} | 20.967 | **[M+H]**⁺ | 446.0849 | 447.0922 | 447.0910 | -2.7 | 271, 253 | *CTA, DGF, PAP, KWF |
| 66 | Rhofolin | C_{8}H_{12}O_{4} | 27.229 | **[M+H]**⁺ | 578.1636 | 577.1563 | 577.1538 | -4.3 | 413, 269 | PSN, LMN |
| 67 | Apigenin 7-O-apyosylglucoside | C_{8}H_{12}O_{4} | 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_{8}H_{12}O_{5} | 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_{8}H_{12}O_{3} | 46.538 | [M+H]** | 608.1741 | 609.1814 | 609.1788 | -4.3 | 301, 286 | LMN |
| No. | Compound                          | Formula  | Molecular Weight | Retention Time (Minutes) | Fold Change | LC-MS/MS Method | PLM, LMN, PAP | *APL, APR, BNA, DGF, KWF, ORN, PSN, PEC, PER, PLM, POM, AVO, LMN, MEL, PAP |
|-----|----------------------------------|----------|------------------|--------------------------|-------------|-----------------|--------------|--------------------------------------------------|
| 70  | 6-Hydroxyluteolin 7-rhamnoside   | C_{3}H_{12}O_{11} | 467.58           | 448.1006                 | 447.0933    | 447.0928        | -1.1         | 301                                               |
| 71  | Chrysoeriol 7-O-glucoside        | C_{24}H_{36}O_{11} | 542.26           | 462.1162                 | 463.1235    | 463.1255        | 4.3          | 445, 427, 409, 381                                |
| 72  | Apigenin 6-C-glucoside           | C_{25}H_{30}O_{13} | 557.54           | 432.1056                 | 431.0983    | 431.0983        | 0.1          | 413, 341, 311                                     |
|     | **Flavanones**                   |          |                  |                          |             |                 |              |                                                   |
| 73  | Hesperetin 3'-sulfate            | C_{16}H_{10}O_{5}S | 6.681            | 382.0359                 | 381.0286    | 381.0293        | 1.8          | 301, 286, 257                                    |
| 74  | Hesperetin 3',7-O-diglucuronide  | C_{40}H_{36}O_{18}S | 21.163           | 654.1432                 | 653.1359    | 653.1361        | 0.3          | 477, 301, 286, 242                               |
| 75  | 6-Prenylnaringenin               | C_{28}H_{24}O_{6} | 35.742           | 340.1311                 | 341.1384    | 341.1375        | -2.6         | 323, 137                                          |
| 76  | Narirutin                        | C_{28}H_{24}O_{6} | 38.326           | 580.1792                 | 579.1719    | 579.1710        | -1.6         | 271                                               |
| 77  | Neoeocirticrin                    | C_{31}H_{24}O_{6} | 39.899           | 596.1741                 | 595.1668    | 595.1684        | 2.7          | 431, 287                                          |
| 78  | Hesperidin                       | C_{40}H_{36}O_{18} | 42.745           | 610.1898                 | 611.1971    | 611.1956        | -2.5         | 593, 465, 449, 303                               |
| 79  | Hesperetin 3'-O-glucuronide      | C_{28}H_{24}O_{6} | 47.521           | 478.1111                 | 477.1038    | 477.1033        | -1.0         | 301, 175, 113                                    |
| 80  | Naringin 4'-O-glucoside          | C_{20}H_{16}O_{5} | 53.036           | 742.2320                 | 741.2247    | 741.2249        | 0.3          | 433, 271                                          |
|     | **Flavonols**                     |          |                  |                          |             |                 |              |                                                   |
| 81  | Myricetin 3-O-rutinoside         | C_{24}H_{26}O_{7} | 8.156            | 626.1483                 | 625.1410    | 625.1423        | 2.1          | 301                                               |
| 82  | Quercetin 3-O-glucoronide        | C_{24}H_{26}O_{7} | 12.511           | 478.0747                 | 477.0674    | 477.0670        | -0.8         | 301                                               |
| 83  | Myricetin 3-O-arabinoside        | C_{26}H_{26}O_{7} | 16.496           | 450.0798                 | 449.0725    | 449.0716        | -2.0         | 317                                               |
| 84  | 3-Methoxyisorinsetin             | C_{16}H_{16}O_{5} | 16.328           | 402.1315                 | 403.1388    | 403.1395        | 1.7          | 388, 373, 355, 327                               |
| 85  | 3-Methoxynobiletin               | C_{24}H_{26}O_{7} | 17.999           | 432.1420                 | 433.1493    | 433.1488        | -1.2         | 403, 385, 373, 345                               |
| 86  | Myricetin 3-O-galactoside        | C_{24}H_{26}O_{7} | 19.288           | 480.0904                 | 479.0831    | 479.0810        | -4.4         | 317                                               |
| 87  | Patuletin 3-O-glucosyl-(1->6)- [apiosyl(1->2)]-glucoside | C_{26}H_{26}O_{7} | 26.768           | 788.2011                 | 787.1938    | 787.1960        | 2.8          | 625, 463, 301, 271                               |
| 88  | Isorhamnetin                     | C_{24}H_{26}O_{7} | 27.076           | 316.0583                 | 315.0510    | 315.0504        | -1.9         | 300, 271                                          |
| 89  | Spinacetin 3-O-(2                | C_{24}H_{26}O_{7} | 33.242           | 948.2536                 | 947.2463    | 947.2456        | -0.7         | 741, 609, 301                                    |
| 90  | Isorhamnetin 3-O-glucuronide     | C_{24}H_{26}O_{7} | 34.082           | 492.0904                 | 491.0831    | 491.0875        | 3.9          | 315, 300, 272, 255                               |
| 91  | Quercetin 3-O-glucosyl-xyloside  | C_{24}H_{26}O_{7} | 36.319           | 596.1377                 | 595.1304    | 595.1311        | 1.2          | 265, 138, 116                                    |
| 92  | Kaempferol 3,7-O-diglcuoside     | C_{27}H_{26}O_{7} | 37.879           | 610.1534                 | 609.1461    | 609.1451        | -1.6         | 447, 285                                          |

For more detailed information on the compounds and their properties, please refer to the original article in *Foods* 2020, 9, x FOR PEER REVIEW.
|   | Quercetin 3-O-xylosyl-rutinoside | Kaempferol 3-O-glucosyl-rhamnosyl-galactoside | Kaempferol 3-O-(2''-rhamnosyl-galactoside) 7-O-rhamnoside | Quercetin 3-O-xylosyl-glucuronide | Myricetin 3-O-rhamnoside | Quercetin 3-O-arabinoside | Quercetin 3-O-(6''-malonyl-glucoside) |   |
|---|------------------------------|-----------------------------------------------|------------------------------------------------|-----------------|------------------|-------------------|---------------------|---|
| 93 | C_{17}H_{20}O_{11} | 39.018 | **[M+H]^+** | 742.1956 | 743.2029 | 743.2060 | 4.2 | 479, 317 | *DGF, AVO, CTA, PAP |
| 94 | C_{17}H_{20}O_{10} | 40.181 | **[M+H]^+** | 756.2113 | 755.204 | 755.2004 | -4.8 | 285 | *APL, AVO, MEL, ORN, PSN, PEC, PIN, PLM, POM, LMN |
| 95 | C_{17}H_{20}O_{11} | 41.953 | **[M+H]^+** | 740.2164 | 739.2091 | 739.2088 | -0.4 | 593, 447, 285 | *APR, AVO, LMN, ORN, PAP, PIN, PLM, POM |
| 96 | C_{17}H_{20}O_{11} | 43.207 | **[M+H]^+** | 610.1170 | 611.1243 | 611.1255 | 2.0 | 479, 303, 285, 239 | *KWF, GFR, AVO |
| 97 | C_{17}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 | C_{17}H_{20}O_{12} | 46.344 | **[M+H]^+** | 434.0849 | 433.0776 | 433.0776 | 0.1 | 301 | *APL, GFE, MNG, ORN, PEC, PLM, CTA, DGF, PAP |
| 99 | C_{17}H_{20}O_{13} | 48.691 | [M+H]^+ | 550.0959 | 551.1032 | 551.1074 | 4.62 | 303 | *CTA, APL, ORN |

**Dihydrochalones**

|   | 3-Hydroxyphloretin 2'-O-xylosyl-glucoside | 3-Hydroxyphloretin 2'-O-glucoside | Phloridzin |   |
|---|---------------------------------|----------------------------------|------------|---|
| 100 | C_{17}H_{20}O_{10} | 37.564 | [M-H]^- | 584.1741 | 583.1668 | 583.1665 | -0.5 | 289 | *APL, MNG, PER, PIN |
| 101 | C_{17}H_{20}O_{10} | 43.048 | **[M+H]^+** | 452.1319 | 451.1246 | 451.1258 | 2.7 | 289, 273 | *APL, AVO, CTA, DGF, GFR, KWF, MNG, PAP, PER |
| 102 | C_{17}H_{20}O_{10} | 51.613 | **[M+H]^+** | 436.1369 | 435.1296 | 435.1284 | -2.8 | 273 | *APL, CTA, KWF, ORN, PEC, PLM, POM, AVO, DGF, PAP |

**Dihydroflavonols**

|   | Dihydromyricetin 3-O-rhamnoside | Dihydroquercetin |   |
|---|---------------------------------|-----------------|---|
| 103 | C_{17}H_{20}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 | C_{17}H_{20}O_{10} | 31.135 | **[M+H]^+** | 304.0583 | 303.0510 | 303.0504 | -2.0 | 285, 275, 151 | *CTA, KWF, MNG, PEC, PER, PAP |

**Anthocyanins**

|   | Cyanidin 3-O-diglucoside-5-O-glucoside | Cyanidin 3-O-(6''-p-coumaroyl-glucoside) | Delphinidin 3-O-xyloside | Petunidin 3-O-(6'-acetyl-glucoside) | Isopenidin 3-O-arabinoside | Delphinidin 3-O-glucosyl-galactoside | Peonidin 3-O-sambubioside-5-O-glucoside | Cynidin 3-O-(2-O-(6''-E)-caffeoyl-D-glucoside)-D-glucoside-5-O-D-glucoside | Cynidin 3,5-O-diglucoside | Delphinidin 3-O-glucoside |   |
|---|----------------------------------|----------------|-----------------|-----------------|----------------|----------------|---------------------|-------------------|-------------------|-----------------|-----------------|---|
| 105 | C_{17}H_{20}O_{10} | 21.567 | **[M+H]^+** | 773.2140 | 774.2213 | 774.2216 | 0.4 | 610, 464 | *PAP, LMN, DGF |
| 106 | C_{17}H_{20}O_{10} | 22.205 | **[M+H]^+** | 595.1452 | 596.1525 | 596.1553 | 4.7 | 287 | *KWF, APL, MNG, NEC, PEC, PER, PLM, POM, DGF, CTA, AVO, PAP |
| 107 | C_{17}H_{20}O_{11} | 25.983 | **[M+H]^+** | 435.0927 | 434.0854 | 434.0860 | 1.4 | 303 | *MEL, CTA, KWF |
| 108 | C_{17}H_{20}O_{11} | 27.386 | [M+H]^+ | 521.1295 | 522.1368 | 522.1358 | -1.9 | 317 | MEL |
| 109 | C_{17}H_{20}O_{11} | 29.965 | [M+H]^+ | 433.1135 | 434.1208 | 434.1213 | 1.1 | 271, 253, 243 | *MNG, DGF |
| 110 | C_{17}H_{20}O_{11} | 36.884 | **[M+H]^+** | 627.1561 | 628.1634 | 628.1636 | 0.3 | 465, 3030 | AVO |
| 111 | C_{17}H_{20}O_{11} | 37.050 | **[M+H]^+** | 757.2191 | 758.2264 | 758.2263 | -0.1 | 595, 449, 287 | *AVO, LMN, PAP |
| 112 | C_{17}H_{20}O_{14} | 39.696 | [M+H]^+ | 949.2614 | 950.2687 | 950.2690 | 0.3 | 787, 463, 301 | *APL, MNG, ORN, PEC, PER, POM |
| 113 | C_{17}H_{20}O_{12} | 42.367 | **[M+H]^+** | 611.1612 | 612.1685 | 612.1664 | -3.4 | 449, 287 | *AVO, CTA, KWF, LMN, PAP, PEC, DGF |
| 114 | C_{17}H_{20}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$_{6}$H$_{10}$O$_{2}$ | 48.482 | [M+H]$^+$ | 479.1190 | 480.1263 | 480.1257 | -1.2 | 317, 303, 285, 271 | *DGF, AVO

| 116 | Pelargonidin 3-O-rutinoside | C$_{6}$H$_{14}$O$_{4}$ | 50.950 | [M+H]$^+$ | 579.1714 | 580.1787 | 580.1814 | 4.6 | 271, 433 | LMN

| **Isoflavonoids** |
|-------------------|

| 117 | 6''-O-Malonylglycitin | C$_{6}$H$_{12}$O$_{3}$ | 7.256 | **[M+H]$^+$** | 532.1217 | 533.1290 | 533.1286 | -0.8 | 285, 270, 253 | *PAP, POM

| 118 | Sativanone | C$_{6}$H$_{12}$O | 9.333 | [M-H]$^-$ | 300.0998 | 299.0925 | 299.0932 | 2.3 | 284, 269, 225 | CTA

| 119 | 2',7-Dihydroxy-4',5'-dimethoxyisoflavone | C$_{6}$H$_{12}$O | 10.651 | **[M+H]$^+$** | 314.0790 | 315.0863 | 315.0868 | 1.5 | 300, 282 | MNG

| 120 | Dihydrobiochanin A | C$_{6}$H$_{12}$O | 15.236 | [M+H]$^+$ | 286.0841 | 287.0914 | 287.0911 | -1.0 | 269, 203, 201, 175 | *AVO, CTA, KWF

| 121 | 6''-O-Malonyldaidzin | C$_{6}$H$_{12}$O$_{2}$ | 16.246 | **[M+H]$^+$** | 502.1111 | 503.1184 | 503.1200 | 3.2 | 255 | *AVO, PSN

| 122 | Glycitin | C$_{6}$H$_{12}$O$_{2}$ | 20.950 | **[M+H]$^+$** | 446.1213 | 447.1286 | 447.1294 | 1.8 | 285 | *CTA, PER

| 123 | Equal | C$_{6}$H$_{12}$O | 21.803 | [M+H]$^+$ | 242.0943 | 243.1016 | 243.1019 | 1.2 | 255, 211, 197 | LMN

| 124 | Violanone | C$_{6}$H$_{16}$O | 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$_{6}$H$_{16}$O$_{2}$ | 28.896 | **[M+H]$^+$** | 284.0685 | 285.0758 | 285.0760 | 0.7 | 270, 229 | LMN

| 126 | 6''-O-Acetyldaidzin | C$_{6}$H$_{16}$O$_{2}$ | 29.504 | **[M+H]$^+$** | 458.1213 | 457.1140 | 457.1121 | -4.2 | 221 | *MNG, PLM, DGF, PAP

| 127 | Dalbergin | C$_{6}$H$_{16}$O$_{2}$ | 30.324 | [M-H]$^-$ | 268.0736 | 267.0663 | 267.0664 | -4.1 | 252, 224, 180 | *DGF, AVO

| 128 | 3',4',7-Trihydroxyisofavanone | C$_{6}$H$_{16}$O$_{3}$ | 31.267 | **[M-H]$^-$** | 272.0685 | 271.0612 | 271.0605 | -2.6 | 177, 151, 119, 107 | *CTA, GFR, PSN, PER, DGF, KWF, LMN

| 129 | Formononetin 7-O-glucuronide | C$_{6}$H$_{16}$O$_{3}$ | 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$_{6}$H$_{16}$O$_{3}$ | 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-Acetylglucitinin | C$_{6}$H$_{16}$O$_{3}$ | 43.656 | **[M+H]$^+$** | 488.1319 | 489.1392 | 489.1413 | 4.3 | 285, 270 | *DGF, PAP, LMN

| 132 | 3'-Hydroxygenistein | C$_{6}$H$_{16}$O$_{3}$ | 51.410 | **[M+H]$^+$** | 286.0477 | 287.0550 | 287.0557 | 2.4 | 269, 259 | *AVO, CTA, LMN, PAP, GFR, PLM, POM

| 133 | 6''-O-Malonygenistein | C$_{6}$H$_{16}$O$_{3}$ | 64.297 | [M-H]$^-$ | 518.1060 | 519.1133 | 519.1157 | 4.6 | 271 | AVO

| 134 | 2-Dehydro-O-desmethylangolensin | C$_{6}$H$_{16}$O$_{3}$ | 77.381 | [M-H]$^-$ | 256.0736 | 255.0663 | 255.0656 | -2.7 | 135, 119 | MNG

| 135 | 3'-Hydroxydaidzein | C$_{6}$H$_{16}$O$_{3}$ | 82.152 | [M-H]$^-$ | 270.0528 | 271.0601 | 271.0588 | -4.8 | 253, 241, 225 | *APR, CTA, PIN

| **Other polyphenols** |
|------------------------|

| 136 | Esculin | C$_{6}$H$_{10}$O$_{5}$ | 13.406 | [M+H]$^+$ | 340.0794 | 341.0867 | 341.0862 | -1.4 | 179, 151 | APR

| 137 | Esculetin | C$_{6}$H$_{10}$O$_{5}$ | 27.821 | [M-H]$^-$ | 178.0266 | 177.0193 | 177.0199 | 3.4 | 149, 133, 89 | CTA

| 138 | Coumarin | C$_{6}$H$_{10}$O$_{5}$ | 32.744 | **[M+H]$^+$** | 146.0368 | 147.0441 | 147.0448 | 4.8 | 103, 91 | *AVO, PLM

| 139 | Scoopoletin | C$_{6}$H$_{10}$O$_{5}$ | 36.851 | **[M+H]$^+$** | 192.0423 | 191.0350 | 191.0345 | -2.6 | 176 | *APR, DGF, LMN

| 140 | Urolithin A | C$_{6}$H$_{10}$O$_{5}$ | 75.771 | [M-H]$^-$ | 228.0423 | 227.0350 | 227.0341 | -3.9 | 198, 182 | *PSN, GFR, PLM

| **Hydroxybenzaldehydes** |
| No | Compound                                    | Formula | MW  | Purity (%) | RT  | Peak Area (μm²) | Characteristics |
|----|---------------------------------------------|---------|------|------------|-----|----------------|----------------|
| 141| p-Anisaldehyde                              | C₆H₈O₂  | 135  | 122.0124   | 137.0197 | 137.0197       | 0.1            |
| 142| 4-Hydroxybenzaldehyde                       | C₆H₆O₆  | 158  | 121.0295   | 121.0301 | 121.0301       | 5.0            |
| 143| Hydroxybenzoketones                          |         |      |            |       |                |                |
| 144| 2-Hydroxy-4-methoxyacetophenone 5-sulfate   | C₁₅H₁₄O₅| 246  | 263.0147   | 261.0074 | 261.0074       | -2.7           |
| 145| 2-Hydroxy-5-prop-1-enylphenol               | C₁₅H₁₄O₅| 265  | 164.0837   | 165.0910 | 165.0902       | -4.8           |
| 146| Curcumin                                    | C₂₁H₁₂O₆| 368  | 367.1187   | 367.1207 | 367.1207       | 4.4            |
| 147| Bisdemethoxycurcumin                        | C₂₁H₁₂O₆| 308.1049| 309.1122  | 309.1137 |             | 4.9            |
| 148| Demethoxycurcumin                           | C₂₁H₁₂O₆| 338.1154| 337.1081  | 337.1080 |             | -0.3           |
| 149| Isopimpinellin                              | C₁₉H₁₂O₆| 287  | 246.0528   | 247.0601 | 247.0613       | 4.9            |
| 150| Rosmanol                                    | C₁₅H₁₀O₆| 225  | 247.1853   | 347.1844 |             | -2.6           |
| 151| Carnosic acid                               | C₁₅H₁₀O₆| 332.1988| 331.1915  | 331.1905 |             | -3.0           |
| 152| Tyrosols                                    |         |      |            |       |                |                |
| 153| Hydroxytyrosol 4-O-glucoside                | C₁₃H₁₂O₇| 316  | 315.1085   | 315.1092 | 315.1092       | 2.2            |
| 154| Oleoside 11-methylester                     | C₁₇H₁₄O₇| 404.1319| 403.1269  | 403.1269 |             | 4.7            |
| 155| 3,4-DHPEA-EDA                                | C₁₅H₁₂O₆| 320.126 | 319.1187  | 319.1189 |             | 0.6            |
| 156| Other polyphenols                           |         |      |            |       |                |                |
| 157| Lithospermic acid                           | C₁₇H₁₄O₆| 505  | 538.1111   | 537.1038 | 537.1048       | 1.9            |
| 158| Arbutin                                     | C₁₃H₁₀O₇| 512  | 272.0896   | 271.0823 | 271.0828       | 1.8            |
| 159| Salvianolic acid B                          | C₁₃H₁₀O₆| 285.98 | 718.1534  | 717.1461 | 717.1436       | -3.5           |
| 160| Salvianolic acid C                          | C₁₃H₁₀O₆| 32.51 | 492.1056   | 491.0983 | 491.0993       | 2.0            |
| 161| Lignans                                     |         |      |            |       |                |                |
| 162| Enterolactone                               | C₁₃H₁₀O₆| 425  | 298.1205   | 299.1278 | 299.1283       | 1.7            |

* CTA, DGF, KWF, ORN, PAP, PSN, PLM, CTA, NEC, PEC, PER
* BNA, GFR, PSN, PEC, PER, PIN, PLM, POM, AVO, PAP
* CTA, PIN, APR, DGF, KWF, MNG, PAP, PSN
* AVO, BNA, CTA
* APR, AVO, KWF, MEL, PIN, DGF, LMN, MNG, PAP
* DGF, KWF, MNG, ORN, PER, POM, AVO
* CTA, AVO, DGF, KWF
* AVO, BNA, CTA
* APL, CTA, AVO, MEL

**[M+H]⁺**
| Entry | Compound                  | Molecular Formula | [M-H] | [M+H] | Retention Time (min) | Mass Difference (Da) | Mass Error (ppm) | Abbreviation(s) |
|-------|---------------------------|-------------------|-------|-------|---------------------|----------------------|------------------|-----------------|
| 162   | Sesamin                   | C_{16}H_{16}O_{6} | 354.1103 | 353.103 | 353.1020            | -2.8                 | 338, 163         | *CTA, DGF       |
| 163   | Schisandrin C             | C_{19}H_{18}O_{6} | 384.1573 | 385.1646 | 385.1652            | 1.6                  | 370, 315, 300    | *CTA, LMN, AVO, PAP |
| 164   | Arctigenin                | C_{16}H_{16}O_{6} | 372.1573 | 371.15  | 371.1509            | 2.4                  | 356, 312, 295    | AVO             |
| 165   | 7-Oxomatairesinol         | C_{16}H_{16}O_{6} | 372.1209 | 373.1282 | 373.1297            | 4.0                  | 358, 343, 328, 325 | *LMN, ORN   |
| 166   | Schisantherin A           | C_{20}H_{20}O_{7} | 536.2046 | 537.2115 | 537.2115            | -0.7                 | 519, 415, 385, 371 | *KWF, BNA, CTA, PER |
| 167   | Pinoresinol               | C_{19}H_{18}O_{6} | 358.1416 | 357.1343 | 357.1336            | -2.0                 | 342, 327, 313, 221 | *GRF, AVO   |
| 168   | 7-Hydroxymatairesinol     | C_{22}H_{24}O_{6} | 374.1366 | 373.1293 | 373.1283            | -2.7                 | 343, 313, 298, 285 | *APL, NEC |
| 169   | Secoisolaricresinol-sesquilignan | C_{30}H_{38}O_{10} | 558.2465 | 557.2392 | 557.2387            | -0.9                 | 539, 521, 509, 356 | *CTA, LMN |
| 170   | Schisandrol B             | C_{20}H_{20}O_{6} | 416.1835 | 417.1908 | 417.1929            | 5.0                  | 224, 193, 165    | AVO             |
| 171   | Schisandrin B             | C_{20}H_{20}O_{6} | 400.1886 | 401.1959 | 401.1949            | -2.5                 | 386              | CTA             |
|       | **Stilbenes**             |                   |       |       |                     |                      |                  |                 |
| 172   | Piceatannol 3-O-glucoside | C_{20}H_{22}O_{9} | 406.1264 | 405.1191 | 405.1172            | -4.6                 | 243              | *CTA, AVO       |
| 173   | Resveratrol               | C_{14}H_{12}O_{3} | 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_{9} | 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} | 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_{5} | 286.1205 | 287.1278 | 287.1280            | 0.7                  | 271, 241, 225    | *CTA, DGF       |

*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 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 peel “MNG”, 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)
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)
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.