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Research Article

Phenolic Profiling of Berries Waste and Determination of Their Antioxidant Potential

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Berries waste is a major issue in Australia's annual food wastage, which can reach 7.3 million tonnes. This study assessed the phenolic content and antioxidant potential of four fruit berry wastes, including blueberries (*Vaccinium corymbosum*), blackberries (*Rubus* spp.), raspberries (*Rubus idaeus*), and strawberries (*Fragaria* spp.), followed by their characterization and quantification. Blueberry wastes were high in phenolic content (total phenolic content: 1.97 ± 0.16 mg GAE/$g_{F.W}$; total flavonoid content: 220.43 ± 13.15 μg QE/$g_{F.W}$; total tannins content: 16.47 ± 0.98 μg CE/$g_{F.W}$), and antioxidant potentials are 2,2′-diphenyl-1-picrylhydrazyl: 2.23 ± 0.17 mg AAE/$g_{F.W}$; 2,2′-azino-bis-(3-ethylbenzothiazoline-6-sulphonic acid): 1.79 ± 0.09 mg AAE/$g_{F.W}$; ferric reducing antioxidant power: 68.71 ± 11.11 μg AAE/$g_{F.W}$ (total antioxidant capacity: 1.22 ± 0.03 mg AAE/$g_{F.W}$). The LC-ESI-QTOF-MS/MS analysis identified 87 compounds from blueberry (57), strawberry (40), raspberry (47), and blackberry wastes (27). Indicated by HPLC quantification, blueberry wastes had higher levels of phenolic acid (syringic acid and coumaric acid) and flavonoid (kaempferol and kaempfero l-3-glucoside). Our study reported that phenolics from berry wastes could be utilized in different food, feed, pharmaceutical, and nutraceutical industries.

1. Introduction

Berries have grown in popularity over the last decade and are still available for consumption in fresh or processed forms (such as juices, jams, and frozen berries) [1]. Blueberries (*Vaccinium corymbosum* L.), strawberries (*Fragaria* spp.), raspberries (*Rubus idaeus* L.), and blackberries (*Rubus* spp.) are the most consumed berries [2]. Consumers desire healthy and nutritious food to help them avoid health risks and enhance their health conditions. As a result, customers are more interested in nutritional and functional foods [3].

The annual harvest of berries in Australia is around 109,000 tons [4], and meanwhile, the annual food waste has reached 7.3 million tonnes [5]. Berries wastage occurs at every level of the food supply chain, including the harvest, transportation, storage, and retail [6]. Berries are likely to get soft or mushy due to inappropriate handling, thus leading to economic loss [7]. Berries contain rich phenolic compounds such as anthocyanins, kaempferol, catechins, myricetin, quercetin, and epicatechins [8].

Phenolic compounds are secondary metabolites that have aromatic rings and hydroxyl groups [9]. Individual or in combination, phenolic compounds have a high antioxidant ability [10]. The structure of dietary phenolic compounds ranges from monomers, oligomers to polymers [11]. Phenolic compounds are classified on the basis of their chemical structure and biological role into phenolic acids, flavonoids, and tannins [12]. The positive benefits of phenolic compounds are their robust antioxidant activity, which has the capability of scavenging oxygen radicals and other harmful substances [13]. Phenolic compounds have anti-inflammatory properties and the ability to prevent

cardiovascular disease, diabetes, and cancer [14] and diminish oxidative stress-induced damage, making them an excellent functional food component for the food industries [15].

Phenolics can be extracted with a variety of organic solvents, and the antioxidant capacity depends on the extraction method, solvent utilized, and conditions [16]. The antioxidant capacity of phenolic profiles and berry waste samples can be assessed by several spectrophotometric methods with different mechanisms, including total phenolic content (TPC), total flavonoids content (TFC), total tannins content (TTC), 2,2′-diphenyl-1-picrylhydrazyl (DPPH), ferric reducing antioxidant potential (FRAP), 2,2′-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) free radical scavenging assays, and total antioxidant capacity (TAC) [17]. Characterization of phenolic compounds by using liquid chromatography integrated with electrospray ionization, triple quadrupole, and two mass spectrometry (LC-ESI-QTOF-MS/MS) and quantification of phenolic compounds using high-performance liquid chromatography combined with photodiode array (HPLC-PDA) [18].

Berry chemical composition and content are determined by variety, growing location, ambient circumstances, maturation stage upon harvest, and storage conditions [19]. The most abundant phenolics characterized in berries are hydroxybenzoic acids derivatives, anthocyanins, quercetin, kaempferol, myricetin, catechins, and epicatechin [8]. Among all of these compounds, anthocyanins are the major one that contributes to berries' color [20]. Although phenolic compounds in different berries have been isolated and identified in different studies, there is still a lack of knowledge on the phenolic profile of berry waste. Only a few studies have focused on Australian-grown berries. This research project focuses on phenolic compounds of berries' wastes, including blueberries, strawberries, raspberries, and blackberries and their antioxidant potential. Furthermore, identification and characterization of specific phenolic components can be achieved through LC-ESI-QTOF-MS/MS and quantification by HPLC-PDA. The results of this study will provide adequate information on the antioxidant properties of Australian-grown berry waste to enable them to be used in a variety of food industries.

2. Materials and Methodology

2.1. Chemicals. All chemicals used in the extraction and characterization were of analytical grade for this study. Milli-Q water (deionized) was from Millipore Milli-Q Gradient Water Purification System (Darmstadt, Germany). The standards for antioxidant assays were purchased from Sigma-Aldrich (St. Louis, MO, USA), including gallic acid, quercetin, catechin, and L-ascorbic acid. In addition, Folin-Ciocalteu's phenol reagent, aluminum chloride hexahydrate, potassium persulfate, vanillin, ferric (III) chloride anhydrous, 2,4,6-tripyridyl-s-triazine (TPTZ), 2,2′-azino-bis-(3-ethylbenzothiazoline-6-sulphonic acid) (ABTS), and 2,2′-diphenyl-1-picrylhydrazyl (DPPH) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Fifty percent acetic acid solution was obtained from Sigma–Aldrich (St. Louis, MO, USA). The HPLC grade methanol was procured from Fisher Chemical (San Jose, CA, USA). Acetonitrile was obtained from LiChrosolv (Darmstadt, Germany). Sodium carbonate anhydrous was obtained from chem-supply (Gillman, SA, Australia), 98% sulfuric acid was purchased from RCI Labscan Limited (Bangkok, Thailand), and sodium acetate hydrated was procured from Ajax Finechem (Scoresby, VIC, Australia). The reference standards used in HPLC include epicatechin, gallic acid, syringic acid, *p*-coumaric acid, protocatechuic acid, chlorogenic acid, catechin, kaempferol, kaempferol 3-*O*-glucoside, and quercetin, obtained from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Sample Preparation. Four different Australian-grown berries including blueberries (Northern highbush var.), strawberries (Albion var.), raspberries (Chilcotin var.), and blackberries (Driscoll's Victoria blackberries var.) were collected from local markets in Melbourne, Victoria, Australia. Samples were blended into a slurry by using a 1.5 L electric blender (Russell Hobbs Classic, model DZ-1613, Melbourne, VIC, Australia) and stored at -20°C for further analysis.

2.3. Extraction of Phenolic Compounds. Phenolic compounds of the berries waste were extracted using 5 g of the sample in 20 mL 80% ethanol by modifying the protocol of Gu et al. [21]. Slurry samples were homogenized by using Ultra-Turrax® T25 Homogenizer (IKA, Staufen, Germany) at 10,000 rpm for 20 s followed by incubation in a shaking incubator (ZWYR-240, Labwit Scientific, Melbourne, Victoria, Australia) at 120 rpm, 4°C for 12 hours. Samples were centrifugated (Hettich ROTINA 380R, Melbourne, Victoria, Australia) at 10,000 rpm for 10 min at 10°C. The extracts were filtered through a 0.45 μm syringe filter (Thermo Fisher Scientific Inc., Waltham, MA, USA) for HPLC-PDA and LC-MS/MS analysis.

2.4. Estimation of Polyphenols and Antioxidant Assays. The estimation of phenolics (TPC, TFC, and TTC) and the determination of total antioxidant capacity (DPPH, FRAP, ABTS, and TAC) were performed according to previously published papers by Tang et al. [22]. Absorption data was attained using the Multiskan® Go microplate photometer (Thermo Fisher Scientific, Waltham, MA, USA).

2.4.1. Determination of Total Phenolic Content (TPC). Total phenolic content was determined by modifying the spectrophotometric method of Peng et al. [23]. Twenty-five microliters of Folin-Ciocalteu reagent (1 : 3 diluted with water), 25 μL of extracts, and 200 μL water were added to the 96-well plate (Costar, Corning, NY, USA) and performed in triplicate. The reaction mixture was incubated for 5 min at room temperature (~25°C) and was protected from light. Twenty-five microliters of 10% (*w/w*) sodium carbonate was added, and the reaction mixture was protected from light for 1 hour at room temperature. Absorbance was measured at 765 nm using a spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA). The gallic acid standard was used

to calculate the calibration curve, with concentrations ranging from 0 to 200 μg/mL. The TPC of the sample was expressed in mg of gallic acid equivalents per gram of the sample (mg GAE/$g_{F.W}$).

2.4.2. Determination of Total Flavonoid Content (TFC). Total flavonoid content was estimated by modifying the aluminum chloride method of Feng et al. [24]. Eighty microliters of the sample, 120 μL of sodium acetate (50 mg/mL), and 80 μL of 2% (*w/v*) aluminum chloride were added to the 96-well plate. The absorbance of the reaction mixture was measured at 440 nm after incubation for 2.5 hours at room temperature and was protected from light. TFC was expressed in quercetin equivalent (μg QE/$g_{F.W}$), calculated by the quercetin standard curve ranging from 0 to 50 μg/mL.

2.4.3. Determination of Total Tannins Content (TTC). Total tannins content was determined by modifying the method of Haile and Kang [25]. One hundred and fifty microliters of 4% (*w/v*) methanolic vanillin solution was added to 25 μL of sample and 25 μL of 32% methanolic sulfuric acid in the 96-well plate. The absorbance of the mixture was measured at 500 nm after the incubation for 15 min. TTC was estimated using a catechin calibration curve with concentrations ranging from 0 to 1000 g/mL and expressed in mg catechin equivalents (CE) per g of sample weight (μg CE/$g_{F.W}$).

2.4.4. 2,2′ Diphenyl-1-picrylhydrazyl (DPPH) Assay. By adapting the approach of Ouyang et al. [26], the DPPH method was utilized to estimate the berries' free radical scavenging activity. Forty microliters of sample and 260 μL of 0.1 mM DPPH methanolic solution were added to the 96-well plate. The absorbance was measured at 517 nm after vigorously shaking the reaction mixture in the dark for 30 min at room temperature. The DPPH radical scavenging activity was determined using an ascorbic acid standard curve with concentrations ranging from 0 to 50 g/mL and expressed in mg of ascorbic acid equivalent per gram (mg AAE/$g_{F.W}$) of the sample.

2.4.5. Ferric Reducing Antioxidant Power (FRAP) Assay. The FRAP assay determines the antioxidant capacity by reducing Fe^{3+} to Fe^{3+}-TPTZ complex (ferric-2,4,6-tripyridyl-s-triazine) into Fe^{2+}-TPTZ. The ferric reducing power of the samples was estimated by modifying the method of Rajurkar and Hande [27]. Three hundred millimolar sodium acetate solution, 10 mM TPTZ solution, and 20 mM Fe [III] solution (ratio 10 : 1:1) were mixed to prepare the FRAP solution. In a 96-well plate, 20 μL of the extract and 280 μL of prepared dye solution were added and incubated for 10 minutes at 37°C. At 593 nm, the absorbance was measured. The results were expressed as μg ascorbic acid equivalents per g (μg AAE/$g_{F.W}$), based on the ascorbic acid standard curve ranging from 0 to 150 μg/mL.

2.4.6. 2,2′-Azino-bis-(3-ethylbenzothiazoline-6-sulfonic Acid) (ABTS) Assay. Free radical scavenging activity was estimated by the method of [27] with slight modification. The $ABTS^{+}$ stock solution was prepared by adding 5 mL of 7 mM ABTS and 88 μL of 140 mM potassium persulfate and incubated for 16 hours shielded from light. Ten microliters of sample and 290 μL of ABTS dye solution were added to the 96-well plate incubated for 6 min at room temperature and absorbance was measured at 734 nm. The results were presented in mg ascorbic acid equivalent per gram of sample (mg AAE/$g_{F.W}$) with ascorbic acid concentration ranging from 0 to 150 μg/mL for the standard curve.

2.4.7. Determination of Total Antioxidant Capacity (TAC). As reported in Prieto et al. [28], the phosphomolybdate technique was employed to determine total antioxidant capacity. The antioxidant dye was prepared by the addition of sulfuric acid (0.6 M), 0.028 M sodium phosphate, and 4 mM ammonium molybdate at the ratio of 1 : 1:1. After filling the 96-well plate with 40 μL of sample and 260 μL of antioxidant dye, it was incubated at 95°C for 10 mins. The absorbance at 695 nm was measured after the mixture had been cooled to room temperature. TAC was calculated using the ascorbic acid standard curve at concentrations ranging from 0 to 200 g/mL and expressed in mg ascorbic acid equivalents (AAE) per g of fresh sample weight.

2.5. Characterization of Phenolic Compounds by LC-ESI-QTOF-MS/MS Analysis. Phenolic compounds identification and characterization were performed by using Agilent 1200 series HPLC (Agilent Technologies, Santa Clara, CA, USA) equipped with an Agilent 6530 Accurate-Mass Quadrupole Time-of-Flight (Q-TOF) LC/MS (Agilent Technologies, Santa Clara, CA, USA), and the method was followed as described by Suleria, Barrow, and Dunshea [18]. The flow rate was set at 0.8 mL/min, and the injection volume of the sample was 6 μL. The separation of the phenolic compounds was carried out by using an LC column 250 × 4.6 mm, 4 μm (Phenomenex, Torrance, CA, USA) (column temperature at 25°C, sample temperature at 10°C). Mobile phase A: water and acetic acid (98 : 2), mobile phase B: acetonitrile, water, and acetic acid (50 : 49.5 : 0.5). The condition set for the program was as follows: 0 min with 10% B, 20 min with 25% B, 30 min with 35% B, 40 min with 40% B, 70 min with 55% B, 75 min with 80% B, 77 min with 100% B, 79 min with 100% B, and 82–85 min with isocratic 10% B. Positive and negative modes were used for peak identification. Nitrogen gas was employed as a nebulizer and drying gas at 300°C, with a flow rate of 5 L/min at 45 psi. Capillary and nozzle voltage was placed at 3.5 kV and 500 V, respectively, and the mass spectra were obtained at the range of 50–1300 amu. Data analyses were performed using Agilent LC-ESI-QTOF-MS/MS Mass Hunter workstation software (Qualitative Analysis, version B.03.01, Agilent).

2.6. HPLC-PDA Analysis. The Agilent 1200 series HPLC (Agilent Technologies, CA, USA), equipped with a photodiode array (PDA) detector, was used to quantify the

targeted phenolic components in waste from blueberries, strawberries, raspberries, and blackberries. The method is the sightly modification of Feng et al. [29]. The column and conditions were the same as described above in LC-ESI-QTOF-MS/MS procedure, but the sample injected was 20 μL. Phenolic compounds in the samples were evaluated at three different wavelengths (280 nm, 320 nm, and 370 nm). Agilent LC-ESI-QTOF-MS/MS Mass Hunter Data workstation software (Qualitative analysis, version B.03.01, Agilent) was used to gather and analyze data.

2.7. Statistical Analysis. The trials were carried out in triplicate, and the data were provided as the mean ± standard deviation ($n = 3$). To test for differences in mean values across samples, a one-way analysis of variance (ANOVA) was employed, followed by Tukey's honestly significant differences (HSD) multiple rank test at $p < 0.05$. Minitab Program (Windows version 18.0; Minitab, LLC, State College, PA, USA) was used to do ANOVA. The significant difference was set at $p < 0.05$, followed by Pearson's correlation coefficients.

3. Results and Discussion

3.1. Phenolic Compound Estimation (TPC, TFC, and TTC). Berries are famous as nutrient-rich fruits with high antioxidant potential [30]. The berries' waste extracts were used to analyze and estimate the phenolic compounds by TPC, TFC, and TTC assays.

In our study, the blueberry waste possessed statistically ($p < 0.05$) higher phenolic content (1.97 ± 0.16 mg GAE/g $_{F.W}$) than strawberry, blackberry, and raspberry waste. Previously, Castrica et al.'s [31] study showed 1253.6 mg TAE/100 g in strawberry waste. Upon comparing with the fresh berries, the blueberries had 2.93 mg GAE/g [32], strawberries had 649.3 to 2123.8 μg GAE/g [33], blackberries had from 22.1 (fresh) to 126.3 mg GAE/g (dehydrated) [34], and raspberry juice ranged between 1879 and 2465 μg GAE/g $_{F.W}$ [35]. The fresh berries have higher TPC than the waste berries. Considering that phenolic compounds can be further characterized by an analytical methodology, the information can be used for various food, nutraceutical, and pharmaceutical industries.

The highest concentration of TFC was observed in blueberry waste with a concentration of 220.43 ± 13.15 μg QE/g, which was a similar result to TPC, followed by raspberry, blackberry, and strawberry waste. Bunea et al. [36] reported that TFC values of different varieties of fresh blueberries extracted by acidified methanol ranged between 84.33 and 112.50 mg QE/100g$_{F.W}$ whereas Okan et al. [37] reported that TFC values ranged between 0.40 and 0.50 mg QE/g in fresh blueberries among several cultivars such as Berkeley, Blueray, Darrow, and Misty. The results are also consistent with Basu and Maier [38], in which the TFC value of blueberries was higher than red raspberries, blackberries, and strawberries with 90% ethanol. The waste blueberries have a higher value than the fresh berries; this might be due to the chemical composition and content of the berries, which differ depending on variety, growing area, ambient circumstances, maturation stage at harvest, and storage conditions. [19].

In the TTC assay, the blueberry waste had the highest value, 16.47 ± 0.98 μg CE/g, which is a significantly higher value than the other three samples. Diaconeasa et al. [39] reported that blueberry and raspberry contain significantly higher ($p < 0.05$) TTC content compared to strawberry and blackberry, which is inconsistent with the results of this study. According to Subbiah et al.'s [32] study, Australian-grown fresh blueberries were 7.41 mg CE/g. The fresh berries exhibited higher values than waste berries which might be attributed to the extraction using various organic solvents. Depending on the type of extraction, solvent selection, and conditions, the antioxidant capacity may also be different. [16].

3.2. Antioxidant Activities (DPPH, FRAP, ABTS, and TAC). As a consequence of the complexity of bioactive compounds in food, it is common to utilize a mix of analytical procedures to measure the antioxidant capacity of food samples utilizing multiple processes [40]. This study determined the antioxidant capacity of four different berries' waste by DPPH, FRAP, ABTS, and TAC assays.

DPPH assay is commonly used to determine antioxidant capacity. Blueberry waste has the highest radical scavenging activity with 2.23 ± 0.17 mg AAE/g, followed by raspberry, strawberry, and blackberry waste. Previously, fresh berries results indicated that blueberry and raspberry had the highest antioxidant activity, followed by blackberry and strawberry with a reasonable degree of antioxidant activity [41]. Subbiah et al. [32] again showed that blueberries followed by raspberries had the highest radical scavenging capacity whereas the blackberry leaves indicated the presence of 111.5 mg AAE/g $_{d.w.}$ [42]. The difference in the antioxidant potential might be due to the fact that the chemical composition and content of the berries are based on their variety, growing location, environmental conditions, maturity stage at the time of harvest, and storage conditions [19].

In FRAP assay, our study reported that blueberry waste had the highest FRAP content with 68.71 ± 11.11 μg AAE/g, followed by blackberry, raspberry, and strawberry waste. Previously, the processing waste of blueberry peel of fat-soluble fraction was 62.56 μmol Fe (II)/g and the water-soluble fraction was 41.99 μmol Fe (II)/g [43]. Another study showed that fresh blueberries (30.0 μmol of Fe^{2+}/g) had higher antioxidant activity than raspberries (27.7 μmol of Fe^{2+}/g) [44]. A study by Subbiah et al. [32] of Australian-grown berries showed that the blueberries had the highest antioxidant capacity followed by blackberries.

In the ABTS assay, the antioxidant capacity is estimated by the reaction of the extracts with $ABTS^{+}$ radical cation generated in the system [36]. All berries were found with the ABTS radical scavenging activity: blueberry waste possesses the highest value with 1.79 ± 0.09 mg AAE/g $_{F.W}$, followed by blackberry waste which is significantly higher ($p < 0.05$) than strawberry and raspberry waste. The antioxidant ability of

fresh raspberries was higher than blackberry, strawberry, and blueberry [38]. Blueberries grown in Korea had higher antioxidant activity than strawberries [45]. According to Subbiah et al. [32], strawberries had a higher antioxidant capacity than blueberries. The difference in results may be due to the method of extraction, solvent selection, and conditions [16].

In the TAC assay, the results obtained in our study showed that blueberry waste has a significantly higher ($p < 0.05$) TAC value than the other three berries waste samples, which had no significant difference among them. Shan et al. [46] reported that the fresh raspberry extract with acetone contains a lower TAC level. In a previous study led by Huang et al. [47], the total antioxidant capacity in the methanolic extract of blueberries was 14.98 mmol Trolox/100 g; that of blackberries was 11.48 mmol Trolox/100 g, and that of strawberries was 4.44 ± 0.45 mmol Trolox/100 g $_{D.W}$. The fresh blackberry and blueberry TAC were recorded as 6125.7 and 4814.6 mg AAE/100 g $_{D.W}$, respectively, by Lee et al. [48]. In Subbiah et al.'s [32] study, fresh blueberries followed by raspberries had higher antioxidant activity. Antioxidant potential can be estimated using various mechanisms since no single method has been developed to estimate overall antioxidant potential accurately due to the complex nature of phenolic compounds. Hence, the characterization of phenolic compounds utilizing the analytical approach can compute total phenolic compounds and their antioxidant potential. Blueberry waste had significantly ($p < 0.05$) higher phenolic concentration and antioxidant activity than other berries waste. Table 1 shows the estimation of phenolic content and antioxidant activity present in berries waste.

3.3. Correlation of Phenolics and Antioxidant Activities. Pearson's correlation test used Graphpad Prism 8 to determine the correlation between TPC, TFC, TTC, and antioxidant assays (DPPH, FRAP, ABTS, and TAC). TAC was significantly correlated with TTC ($r = 0.987$, $p < 0.05$), indicating that tannins significantly contributed to the total antioxidant capacity. The positive correlation suggests that tannins are the primary antioxidants in blueberries, strawberries, raspberries, and blackberries. Because tannins include a variety of phenolic hydroxyl groups, phenolic compounds indicate a strong antioxidant potential and free radical scavenging activity [47].

FRAP had reducing capability measured by the ferric ions, also appeared to have a significant correlation with TTC ($r = 0.965$, $p < 0.05$), indicating that tannins content in the waste berries samples had an outstanding contribution to ferric reducing ability. The TTC value of blueberries was highly correlated with FRAP [49]. Previous studies reported that the expression of antioxidant activity was due to the synergistic effect between different phenolic compounds and could not be explicitly attributed to one component. Thus, antioxidant activity is determined not only by concentration but also by the structure and interaction between the antioxidants [50].

This research's correlation coefficient revealed a non-significant relationship between TFC and TPC. Previous research has found that TFC and TPC in berries were unrelated as well, considering that total flavonoid content accounts for only 2.4–4.0% of total soluble phenol content in berry fruits [51]. Pearson's correlation coefficients for the relationship between antioxidant determination assays are shown in Table 2.

3.4. LC-ESI-QTOF-MS/MS Analysis of Phenolic Compounds in Berry Waste. LC-ESI-QTOF-MS/MS is an effective tool for preliminary identification and characterization of phenolic compounds in plants by positive (ESI^+) and negative (ESI^-) ionization modes. Based on their m/z and MS spectra, the phenolic compounds were tentatively identified using Agilent LC-MS mass hunter qualitative software and the Personal Compounds Database and Library (PCDL). The mass error <5 ppm and a PCDL score of more than 80 were used to select compounds for further analysis, and compounds were identified using MS/MS identification and m/z characterization (Table 3). In this study, a total of 87 phenolic compounds were characterized in berries waste samples, including phenolic acids (30), flavonoids (50), other polyphenols (5), and lignans (3).

3.4.1. Phenolic Acids. A total of 30 phenolic acids were identified and characterized including hydroxybenzoic acids (12), hydroxycinnamic acids (14), hydroxyphenyl acetic acids (2), and hydroxyphenyl pentanoic acids (2) compounds in four berries samples.

Hydroxybenzoic Acid Derivatives. Gallic acid (compound **1**, $[M–H]^-$ m/z 169.0138) was identified based on the product ion at m/z 125 due to the loss of CO_2 (44 Da) [52]. In our study, gallic acid was detected in raspberry, blueberry, and blackberry waste. Previously, gallic acid was identified in green tea [53] and found in various maturity stages in strawberries [54]. The presence of gallic acid was also observed in grapes and possessed dual antioxidant and prooxidant properties [55]. Compound gallic acid was also reported in date [56], blackberry [57], raw banana [58], apple juice [59], pomegranate [60], cloves [61], raw eggplant [62], and raw cauliflower [63].

4-Hydroxybenzoic acid 4-*O*-glucoside (compound **5**, m/z 299.0767) and protocatechuic acid 4-*O*-glucoside (compound **6**, m/z 315.0723) were tentatively characterized, and the fragmentation peaks at m/z 137 and m/z 153, respectively, confirmed the compounds due to the corresponding loss of hexosyl moiety (162 Da) from the parent ions [52]. In our study, compound **5** was detected in strawberry and raspberry waste, whereas compound **6** was identified in strawberry, raspberry, and blueberry waste. Compound **5** was previously detected in spices and herbs including anise, caraway, coriander, fennel, and star anise [64]. Fruits and vegetables have a low percentage of 4-hydroxybenzoic acid 4-*O*-glucoside, according to Lafay and Gil-Izquierdo [65]. Other studies detected the presence of compound **5** in blackberries, red raspberries, strawberries

Table 1: Estimation of phenolic content and antioxidant activity present in berries waste.

Antioxidant assays	Blueberries waste	Strawberries waste	Blackberries waste	Raspberries waste
TPC (mg GAE/g)	1.97 ± 0.16^{a}	1.13 ± 0.04^{a}	0.85 ± 0.05^{b}	0.73 ± 0.01^{b}
TFC (μg QE/g)	220.43 ± 13.15^{a}	7.13 ± 0.36^{b}	9.38 ± 0.19^{b}	16.93 ± 1.20^{b}
TTC (μg CE/g)	16.47 ± 0.98^{a}	9.87 ± 0.29^{b}	6.59 ± 0.02^{c}	5.95 ± 0.51^{c}
DPPH (mg AAE/g)	2.23 ± 0.17^{a}	1.56 ± 0.11^{b}	0.76 ± 0.02^{c}	2.01 ± 0.04^{a}
FRAP (μg AAE/g)	68.71 ± 11.11^{a}	4.15 ± 0.17^{d}	43.56 ± 5.08^{b}	30.13 ± 1.83^{c}
ABTS (mg AAE/g)	1.79 ± 0.09^{a}	0.63 ± 0.02^{b}	1.12 ± 0.08^{a}	0.70 ± 0.05^{b}
TAC (mg AAE/g)	1.22 ± 0.03^{a}	0.62 ± 0.01^{b}	0.50 ± 0.02^{b}	0.33 ± 0.02^{c}

The data shown in the table as mean ± standard deviation ($n = 3$); lettering (^{a,b,c,d}) indicated the significant difference in the means ($p < 0.05$) using a one-way analysis of variance (ANOVA) and Tukey's HSD test. GAE: gallic acid equivalents; QE: quercetin equivalents; CE: catechin equivalents; AAE: ascorbic acid equivalents; TPC: Total phenolic content; TFC: total fl usingd content; TTC: total tannin content; DPPH: 2,2′-diphenyl-1-picrylhydrazyl; FRAP: ferric reducing antioxidant power, ABTS: 2,2′-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid; TAC: total antioxidant content.

Table 2: Pearson's correlation coefficients for relationship between antioxidant determination assays.

Variables	TPC	TFC	TTC	DPPH	FRAP	ABTS
TFC	0.82					
TTC	0.92	0.92				
DPPH	0.79	0.63	0.56			
FRAP	0.93	0.97	0.96*	0.72		
ABTS	0.60	0.06	0.40	0.37	0.29	
TAC	0.85	0.93	0.98*	0.46	0.94	0.27

*Significant correlation with $p < 0.05$.

[64], blackcurrant, gooseberry, and blueberries [66]. Compound **6** was previously detected in blackberry, blackcurrant, gooseberry, highbush blueberry, and redcurrant [66].

Hydroxycinnamic Acids and Other Phenolic Acid Derivatives. Sinapic acid (Compound **24,** $[M–H]^{-}$ *m/z* 223.0612) was detected in raspberry and blueberry waste samples, and the compound was confirmed by the fragments at *m/z* 205, *m/z* 179, and *m/z* 163, due to the corresponding loss of H_2O, CO_2, and two CH_2O units from the precursor ion, respectively [67]. Sinapic acid has been previously reported to have pharmacological properties, including antimicrobial, anti-inflammatory, antidiabetes, antimutagenicity, and antioxidant activity, prevents neurodegeneration [68], and increases hair growth [69]. Previously, this compound was detected in strawberries, raspberries, lemon, broccoli, orange, cabbage, and radish [70]. The compound was reported in spices and herbs as well such as anise, basil, nutmeg, and thyme [71].

m-Coumaric acid (compound **23** at *m/z* 163.0407) was detected in all four samples, and the compound was confirmed by the fragmentation peaks at *m/z* 119, due to the consecutive loss of CO_2 [72]. Previously, this compound was detected in blueberries, strawberries, red raspberries [73], and extra virgin olive oil [74]. A previous study showed that coumaric acid had significant potential to exhibit anti-inflammatory and antioxidant properties [75].

3.4.2. Flavonoids. Flavonoids (29) were characterized in four berries waste including flavanols (6), flavones (6), flavanones (3), flavonols (13), isoflavonoids (9), anthocyanins (8), dihydroflavonols (3), and dihydrochalcones (2).

Flavanols. Compound **33** ($[M–H]^{-}$ at *m/z* 577.1352) was tentatively identified as procyanidin dimer B1 and present in strawberry and raspberries waste. This compound was confirmed in MS/MS analysis by losing phloroglucinol from the precursor molecule [76]. Previously, this compound was detected in cocoa powder [77], blackberry, strawberry, apricot, peach, plum, pomegranate [78], and apple [79]. Compound 36 ($[M+H]^{+}$ *m/z* 611.1418) was identified as Prodelphinidin dimer B3 upon MS/MS analysis with the product ions at *m/z* 469, due to the heterocyclic ring fission followed by removal of phloroglucinol. The product ions at *m/z* 311 were attributed to the reduction into monomers through quinone methide fission cleavage [80]. The product ions at *m/z* 291 were due to the loss of the –OH group from gallocatechin [80]. The compound was detected in raspberry and blueberry waste samples in our study. Previously, this compound was identified in whole-grain barley flour [81], blackberry, grape, banana, and broad bean pod [78].

Flavonols, Isoflavonoids, and Anthocyanins. Compound **51** ($[M–H]^{-}$ at *m/z* 463.0888) was tentatively identified as Myricetin 3-*O*-rhamnoside and detected in all four samples. In MS/MS analysis, further confirmation was achieved by the fragment peak at 317 due to the loss of rhamnoside [82]. Previously, it was found in highbush blueberry [83], white myrtle berries [84], and lentils [85]. 3′-Hydroxygenistein (compound **62,** precursor ion $[M + H]^{+}$ *m/z* 285.0538) was identified by the product ions at *m/z* 269 (loss of H_2O) and *m/z* 259 (loss of CO) [86]. This compound was detected in all four berry waste samples.

Table 3: Characterization of phenolic compounds in different Berry wastes by LC-ESI-QTOF-MS/MS.

No.	Compound Name	Molecular formula	RT (min)	Mode (ESI+/ ESI-)	Molecular Weight	Theoretical Weight	Observed Weight	Mass error	MS/MS Product ion	Berries waste
Phenolic acids										
Hydroxybenzoic acid										
1	Gallic acid	$C_7H_6O_5$	9.7	**[M-H]-	170.0215	169.0142	169.0138	−2.4	125	*RAB, BLB, BKB
2	Galloyl glucose	$C_{13}H_{16}O_{10}$	10.186	[M-H]-	332.0743	331.067	331.0681	3.3	169, 125	*BLB, STB, RAB
3	2-Hydroxybenzoic acid	$C_7H_6O_3$	11.108	**[M-H]-	138.0317	137.0244	137.0241	−2.2	93	RAB
4	4-*O*-Methylgallic acid	$C_8H_8O_5$	14.479	**[M+H]+	184.0372	185.0445	185.0448	1.6	170, 142	*BKB, BLB
5	4-Hydroxybenzoic acid 4-*O*-glucoside	$C_{13}H_{16}O_8$	20.429	[M-H]-	300.0845	299.0772	299.0767	−1.7	255, 137	*STB, RAB
6	Protocatechuic acid 4-*O*-glucoside	$C_{13}H_{16}O_9$	20.777	**[M-H]-	316.0794	315.0721	315.0723	0.6	153	*STB, RAB, BLB
7	3,4-*O*-Dimethylgallic acid	$C_9H_{10}O_5$	22.848	**[M+H]+	198.0528	199.0601	199.0597	−2.0	153, 139, 125, 111	*BLB, STB, RAB, BKB
8	Ellagic acid glucoside	$C_{20}H_{16}O_{13}$	35.505	[M-H]-	464.0591	463.0518	463.0504	−3.0	301	*STB, RAB
9	2,3-Dihydroxybenzoic acid	$C_7H_6O_4$	38.316	**[M-H]-	154.0266	153.0193	153.019	−2.0	109	*BLB, STB, RAB,
10	Ellagic acid arabinoside	$C_{19}H_{14}O_{12}$	40.862	**[M-H]-	434.0485	433.0412	433.0399	−3.0	300	RAB, STB, BKB, BLB
11	Ellagic acid	$C_{14}H_6O_8$	44.556	**[M-H]-	302.0063	300.999	300.9987	−1.0	284, 229, 201	*RAB, BKB, STB
12	Ellagic acid acetyl-xyloside	$C_{21}H_{16}O_{13}$	54.198	[M-H]-	476.0591	475.0518	475.0525	1.5	301	RAB
Hydroxycinnamic acids										
13	Ferulic acid 4-*O*-glucuronide	$C_{16}H_{18}O_{10}$	4.272	[M-H]-	370.09	369.0827	369.0808	−5.1	193	BLB
14	3-Sinapoylquinic acid	$C_{18}H_{22}O_{10}$	14.245	[M-H]-	398.1213	397.114	397.1136	−1.0	233, 179	BLB
15	Caffeoyl glucose	$C_{15}H_{18}O_9$	18.994	[M-H]-	342.0951	341.0878	341.0881	0.9	179, 161	*RAB, BLB, STB
16	1-Sinapoyl-2,2′-diferuloylgentiobiose	$C_{43}H_{48}O_{21}$	19.728	[M-H]-	900.2688	899.2615	899.2623	0.9	613, 201	BKB
17	Caffeic acid 3-*O*-glucuronide	$C_{15}H_{16}O_{10}$	20.518	[M-H]-	356.0743	355.067	355.0671	0.3	179	*RAB, BLB, STB
18	3-Feruloylquinic acid	$C_{17}H_{20}O_9$	23.036	[M-H]-	368.1107	367.1034	367.1049	4.1	298, 288, 192, 191	RAB
19	Isoferulic acid	$C_{10}H_{10}O_4$	23.158	[M-H]-	194.0579	193.0506	193.0511	2.6	178, 149, 134	*BLB, RAB
20	Ferulic acid 4-*O*-glucoside	$C_{16}H_{20}O_9$	23.158	[M-H]-	356.1107	355.1034	355.1028	−1.7	193, 178, 149, 134	BLB
21	3-Caffeoylquinic acid	$C_{16}H_{18}O_9$	24.764	**[M-H]-	354.0951	353.0878	353.0876	−0.6	253, 190, 144	*BLB, BKB
22	p-Coumaric acid 4-*O*-glucoside	$C_{15}H_{18}O_8$	25.068	**[M-H]-	326.1002	325.0929	325.0921	−2.5	163	*STB, BLB, BKB
23	m-Coumaric acid	$C_9H_8O_3$	25.068	**[M-H]-	164.0473	163.04	163.0407	4.3	119	*STB, RAB, BLB, BKB

Table 3: Continued.

No.	Compound Name	Molecular formula	RT (min)	Mode (ESI+/ ESI-)	Molecular Weight	Theoretical Weight	Observed Weight	Mass error	MS/MS Product ion	Berries waste
24	Sinapic acid	$C_{11}H_{12}O_5$	25.985	[M-H]-	224.0685	223.0612	223.0613	0.4	205, 163	*RAB, BLB
25	Caffeic acid	$C_9H_8O_4$	29.254	[M-H]-	180.0423	179.035	179.0353	1.7	143, 133	BLB
26	1,5-Dicaffeoylquinic acid	$C_{25}H_{24}O_{12}$	54.005	[M-H]-	516.1268	515.1195	515.1167	−5.4	353, 335, 191, 179	BLB
Hydroxyphenylacetic acids										
27	2-Hydroxy-2-phenylacetic acid	$C_8H_8O_3$	14.156	[M-H]-	152.0473	151.04	151.0393	−4.6	136, 92	RAB
28	3,4-Dihydroxyphenylacetic acid	$C_8H_8O_4$	24.599	[M-H]-	168.0423	167.035	167.0355	3.0	149, 123	*BLB, RAB
Hydroxyphenylpropanoic acids										
29	Dihydroferulic acid 4-sulfate	$C_{10}H_{12}O_7S$	4.073	[M-H]-	276.0304	275.0231	275.0229	−0.7	195, 151, 177	*BLB, STB
30	3-Hydroxy-3-(3-hydroxyphenyl) propionic acid	$C_9H_{10}O_4$	14.156	[M-H]-	182.0579	181.0506	181.0501	−2.8	163, 135, 119	*RAB, BLB
Flavonoids										
Flavanols										
31	(-)-Epigallocatechin	$C_{15}H_{14}O_7$	14.129	**[M-H]-	306.074	305.0667	305.0651	−5.2	261, 219	*BLB,
32	(-)-Epicatechin	$C_{15}H_{14}O_6$	23.875	**[M-H]-	290.079	289.0717	289.073	4.5	245, 205, 179	*STB, BLB, RAB
33	Procyanidin dimer B1	$C_{30}H_{26}O_{12}$	27.851	**[M-H]-	578.1424	577.1351	577.1352	0.2	451	*STB, RAB,
34	Procyanidin trimer C1	$C_{45}H_{38}O_{18}$	33.638	**[M-H]-	866.2058	865.1985	865.1967	−2.1	739, 713, 695	*RAB, BKB
35	4′-*O*-Methylepigallocatechin	$C_{16}H_{16}O_7$	35.718	[M+H]+	320.0896	321.0969	321.096	−2.8	302	BLB
36	Prodelphinidin dimer B3	$C_{30}H_{26}O_{14}$	42.89	[M+H]+	610.1323	611.1396	611.1418	3.6	469, 311, 291	*BLB, RAB
Flavones										
37	Apigenin 7-*O*-(6″-malonyl-apiosyl-glucoside)	$C_{29}H_{30}O_{17}$	28.105	[M-H]-	650.1483	649.141	649.1391	−2.9	605	RAB
38	Apigenin 6,8-di-C-glucoside	$C_{27}H_{30}O_{15}$	29.928	**[M-H]-	594.1585	593.1512	593.1521	1.5	503, 473	*RAB, STB, BLB, BKB
39	Chrysoeriol 7-*O*-glucoside	$C_{22}H_{22}O_{11}$	34.774	[M+H]+	462.1162	463.1235	463.1229	−1.3	445, 427, 409, 381	BLB
40	Diosmin	$C_{28}H_{32}O_{15}$	39.307	**[M+H]+	608.1741	609.1814	609.1808	−1.0	301, 286	BKB
41	Apigenin 6-C-glucoside	$C_{21}H_{20}O_{10}$	40.889	**[M-H]-	432.1056	431.0983	431.0995	2.8	413, 341, 311	*STB, RAB, BLB
42	6-Hydroxyluteolin 7-*O*-rhamnoside	$C_{21}H_{20}O_{11}$	51.707	**[M-H]-	448.1006	447.0933	447.0913	−4.5	301	*STB, RAB, BKB, BLB
Flavanones										
43	Naringin	$C_{27}H_{32}O_{14}$	41.701	[M-H]-	580.1792	579.1719	579.1713	−1.0	271	STB
44	Hesperetin 3′-*O*-glucuronide	$C_{22}H_{22}O_{12}$	51.387	**[M-H]-	478.1111	477.1038	477.1021	−3.6	301, 175, 113, 85	BLB
45	Hesperetin 3′-sulfate	$C_{16}H_{14}O_9S$	87.181	[M-H]-	382.0359	381.0286	381.0287	0.3	301, 286, 257, 242	BKB
Flavonols										

Table 3: Continued.

No.	Compound Name	Molecular formula	RT (min)	Mode (ESI+/ ESI-)	Molecular Weight	Theoretical Weight	Observed Weight	Mass error	MS/MS Product ion	Berries waste
46	Kaempferol 3-*O*-xylosyl-glucoside	$C_{26}H_{28}O_{15}$	21.074	**[M+H]+	580.1428	581.1501	581.1523	3.8	419, 401, 383	*STB, RAB
47	Quercetin 3-*O*-xylosyl-glucuronide	$C_{26}H_{26}O_{17}$	26.47	**[M+H]+	610.117	611.1243	611.1254	1.8	479, 303, 285, 239	*RAB, STB
48	Kaempferol 3-*O*-glucosyl-rhamnosyl-galactoside	$C_{33}H_{40}O_{20}$	27.211	[M-H]-	756.2113	755.204	755.2051	1.5	285	RAB
49	Kaempferol 3-*O*-(2″-rhamnosyl-galactoside) 7-*O*-rhamnoside	$C_{33}H_{40}O_{19}$	30.01	**[M-H]-	740.2164	739.2091	739.2087	−0.5	593, 447, 285	RAB
50	Myricetin 3-*O*-rutinoside	$C_{27}H_{30}O_{17}$	36.902	[M-H]-	626.1483	625.141	625.1393	−2.7	301	RAB
51	Myricetin 3-*O*-rhamnoside	$C_{21}H_{20}O_{12}$	37.824	**[M-H]-	464.0955	463.0882	463.0888	1.3	317	*STB, RAB, BLB, BKB
52	Myricetin 3-*O*-glucoside	$C_{21}H_{20}O_{13}$	38.564	**[M-H]-	480.0904	479.0831	479.0808	−4.8	317	BLB
53	Quercetin 3′-sulfate	$C_{15}H_{10}O_{10}S$	42.143	[M-H]-	381.9995	380.9922	380.9932	2.6	301	BLB
54	Kaempferol 3,7-*O*-diglucoside	$C_{27}H_{30}O_{16}$	43.021	**[M-H]-	610.1534	609.1461	609.1443	−3.0	447, 285	*BLB, RAB, BKB, STB
55	Quercetin 3′-*O*-glucuronide	$C_{21}H_{18}O_{13}$	45.113	[M-H]-	478.0747	477.0674	477.0671	−0.6	301	*STB, BLB, RAB
56	Quercetin 3-*O*-(6	$C_{24}H_{22}O_{15}$	49.085	[M+H]+	550.0959	551.1032	551.1023	−1.6	303	BLB
57	Quercetin 3-*O*-arabinoside	$C_{20}H_{18}O_{11}$	49.416	**[M-H]-	434.0849	433.0776	433.0758	−4.2	301	*BLB, RAB
58	Isorhamnetin 3-*O*-glucuronide	$C_{22}H_{20}O_{13}$	53.828	**[M-H]-	492.0904	491.0831	491.0824	−1.4	315, 300, 272, 255	*STB, BLB
Isoflavonoids										
59	2′-Hydroxyformononetin	$C_{16}H_{12}O_5$	12.326	[M+H]+	284.0685	285.0758	285.0762	1.4	270, 229	BKB
60	Formononetin 7-*O*-glucuronide	$C_{22}H_{20}O_{10}$	21.782	[M-H]-	444.1056	443.0983	443.0977	−1.4	267, 252	BKB
61	5,6,7,3′,4′-Pentahydroxyisoflavone	$C_{15}H_{10}O_7$	23.461	**[M+H]+	302.0427	303.05	303.05	0.0	285, 257	*BLB, RAB, STB
62	3′-Hydroxygenistein	$C_{15}H_{10}O_6$	29.534	**[M+H]+	286.0477	287.055	287.0538	−4.2	269, 259	*RAB, BKB, STB, BLB
63	3′-Hydroxydaidzein	$C_{15}H_{10}O_5$	31.989	[M+H]+	270.0528	271.0601	271.0612	4.1	253, 241, 225	STB
64	6”-*O*-Malonylglycitin	$C_{25}H_{24}O_{13}$	32.472	[M+H]+	532.1217	533.129	533.1308	3.4	285, 270, 253	BLB
65	3′,4′,7-Trihydroxyisoflavanone	$C_{15}H_{12}O_5$	36.267	[M-H]-	272.0685	271.0612	271.0618	2.2	177, 151, 119, 107	STB
66	6″-*O*-Malonyldaidzin	$C_{24}H_{22}O_{12}$	39.379	[M+H]+	502.1111	503.1184	503.1181	−0.6	255	BLB
67	6″-*O*-Malonylgenistin	$C_{24}H_{22}O_{13}$	39.807	[M+H]+	518.106	519.1133	519.1146	2.5	271	*STB, BLB
Anthocyanins										
68	Delphinidin 3-*O*-glucoside	$C_{21}H_{21}O_{12}$	23.693	[M+H]+	465.1033	466.1106	466.1122	3.4	303	BLB
69	Peonidin 3-*O*-sambubioside-5-*O*-glucoside	$C_{33}H_{41}O_{20}$	26.503	**[M+H]+	757.2191	758.2264	758.2227	−4.9	595, 449, 287	RAB
70	Delphinidin 3-*O*-arabinoside	$C_{20}H_{19}O_{11}$	27.403	[M+H]+	435.0927	436.1	436.1002	0.5	303	BLB
71	4-*O*-Methyldelphinidin 3-*O*-D-glucoside	$C_{22}H_{23}O_{12}$	28.579	[M+H]+	479.119	480.1263	480.1275	2.5	317, 303, 285, 271	BLB

Table 3: Continued.

No.	Compound Name	Molecular formula	RT (min)	Mode (ESI+/ ESI-)	Molecular Weight	Theoretical Weight	Observed Weight	Mass error	MS/MS Product ion	Berries waste
72	Cyanidin 3-*O*-galactoside	$C_{21}H_{21}O_{11}$	31.975	**[M+H]+	449.1084	450.1157	450.1165	1.8	287	*BLB, RAB, STB, BKB
73	Isopeonidin 3-*O*-arabinoside	$C_{21}H_{21}O_{10}$	34.642	[M+H]+	433.1135	434.1208	434.1216	1.8	271, 253, 243	*BLB, BKB, STB
74	Cyanidin 3,5-*O*-diglucoside	$C_{27}H_{31}O_{16}$	42.874	**[M+H]+	611.1612	612.1685	612.171	4.1	449, 287	* BLB, BKB, STB, RAB
75	Cyanidin 3-*O*-(6″-p-coumaroyl-glucoside)	$C_{30}H_{27}O_{13}$	48.704	**[M+H]+	595.1452	594.1379	594.1374	−0.8	287	*BLB, BKB, STB,
Dihydroflavonols										
76	Dihydroquercetin 3-*O*-rhamnoside	$C_{21}H_{22}O_{11}$	32.876	**[M-H]-	450.1162	449.1089	449.1087	−0.4	303	*RAB, BKB
77	Dihydromyricetin 3-*O*-rhamnoside	$C_{21}H_{22}O_{12}$	35.511	[M-H]-	466.1111	465.1038	465.1036	−0.4	301	*RAB, STB, BKB
78	Dihydroquercetin	$C_{15}H_{12}O_7$	36.405	**[M-H]-	304.0583	303.051	303.0506	−1.3	285, 275, 151	*RAB, BLB, BKB
Dihydrochalcones										
79	3-Hydroxyphloretin 2′-*O*-glucoside	$C_{21}H_{24}O_{11}$	19.176	**[M-H]-	452.1319	451.1246	451.1231	−3.3	289, 273	RAB
80	Phloridzin	$C_{21}H_{24}O_{10}$	55.965	[M-H]-	436.1369	435.1296	435.1289	−1.6	273	*STB, BLB
Other Polyphenols Hydroxybenzaldehydes										
81	p-Anisaldehyde	$C_8H_8O_2$	13.734	**[M+H]+	136.0524	137.0597	137.0595	−1.5	122, 109	*BKB, STB, BLB
82	4-Hydroxybenzaldehyde	$C_7H_6O_2$	30.518	**[M-H]-	122.0368	121.0295	121.0301	5.0	77	*STB, BKB
Tyrosols										
83	3,4-DHPEA-AC	$C_{10}H_{12}O_4$	45.776	[M-H]-	196.0736	195.0663	195.0657	−3.1	135	STB
Other polyphenols										
84	Arbutin	$C_{12}H_{16}O_7$	7.436	[M-H]-	272.0896	271.0823	271.0831	3.0	109	*BLB, RAB
Lignans										
85	Episesamin	$C_{20}H_{18}O_6$	4.305	[M-H]-	354.1103	353.103	353.1014	−4.5	338, 163	BLB
86	Schisantherin A	$C_{30}H_{32}O_9$	34.04	**[M+H]+	536.2046	537.2119	537.2123	0.7	519, 415, 385, 371	*RAB, BKB, STB
87	Secoisolariciresinol-sesquilignan	$C_{30}H_{38}O_{10}$	38.134	[M-H]-	558.2465	557.2392	557.2393	0.2	539, 521, 509, 361	BLB

**Compounds were detected in both negative $[M-H]^-$ and positive $[M+H]^+$ mode of ionization while only single mode data was presented. Berry waste samples mentioned in abbreviations are strawberry waste "STB", raspberry waste "RAB", blueberry waste "BLB", and blackberry waste "BKB".

Anthocyanins are powerful natural antioxidants, and anthocyanidins are abundant in berries [87]. The presence of a significant concentration of anthocyanidins in the skin of the berries has been reported by Olas [55]. Anthocyanins are responsible for colors including blue, purple, and red and are used as natural pigments in the food industries [48].

Dihydrochalcones and Dihydroflavonols. Phloridzin (compound **80,** $[M–H]^-$ *m/z* 435.1289) was detected in strawberry and blueberry waste with peak fragmentation at *m/z* 273 corresponding to the loss of glucoside [88]. Previously, this compound was identified in apple [89], plum [90], pomegranate [91], and dried Mexican oregano [92]. Dihydroquercetin (compound **78**, $[M–H]^-$ *m/z* 303.0506) was identified based on the fragment peaks at *m/z* 275, *m/z* 285, and *m/z* 151 due to the loss of CO (28 Da), H_2O (18 Da), and RDA-cleavage, respectively [93]. In our study, this compound was detected in raspberry, blueberry, and blackberry waste and was previously detected in dried Mexican oregano [92].

3.4.3. Lignans. Schisantherin A (compound **86**) was identified in positive ionization mode at *m/z* 537.2123 and the compound had product ions at *m/z* 519, *m/z* 415, *m/z* 385, and *m/z* 371 and was characterized as schisantherin A due to the loss of H_2O, C_6H_5COOH, $C_6H_5COOH—CH_2O$, and $C_6H_5COOH—C_2H_4O$ [94]. In our study, this compound was detected in raspberry, blackberry, and strawberry waste. Previously, this compound was detected in *Schisandra rubriflora* [95] and *Schisandra chinensis* [96].

The LC-ESI-QTOF-MS/MS characterization of the phenolic compounds present in four waste berries has remarkable antioxidant potential. Phenolic acids and flavonoids have vigorous radical scavenging activity, and thus, waste berries can be a valuable source of natural antioxidants in various industries, including food, nutraceuticals, and pharmaceuticals.

3.5. Venn Diagram Analysis of Phenolic Compounds Distribution. Berry wastes have a wide range of phenolic compounds and researchers have shown a keen interest. Venn diagrams have been generated for total phenolic compounds, phenolic acids, flavonoids, and other polyphenols according to the berries waste samples in blueberries (blue), strawberries (red), raspberries (yellow), and blackberries waste (green) in Figure 1.

In the total phenolic Venn diagram, the unique compounds present were 37 in blueberry, 21 in raspberry, 27 in blackberry, and 16 in strawberry waste. 36 compounds were overlapping in all four samples and 30 compounds overlapped in strawberry, raspberry, and blueberry waste. Four compounds were the lowest overlapped in strawberry and blackberry waste. According to Rodrigues et al. [97], fresh blueberries have higher total phenolic compounds than raspberries, strawberries, and blackberries.

In the phenolic acids' Venn diagram, the unique compounds present in blueberry, raspberry, blackberry, and strawberry waste were 6, 3, 3, and 3, respectively. The maximum compound overlapped was 12 in strawberry, blueberry, and raspberry waste. The lowest overlapped compound was 1 in strawberry and raspberry waste. Blueberries have high phenolic acid higher phenolic acids than red raspberries [98].

In the flavonoids' Venn diagram, the maximum unique compounds were in blueberry (20) followed by blackberry waste (17). 17 compounds overlapped among all four samples and the lowest overlapped were 2 in strawberry and raspberry waste. Flavonoids were higher in blueberries and blackberries than in raspberries and strawberries [8]. In other polyphenols, the unique compounds were 12, 9, 8, and 6 in blueberry, raspberry, blackberry, and strawberry waste, respectively. The maximum overlapped compounds were 8 in blueberry, strawberry, and raspberry waste. The lowest overlapped compound was in strawberry and blackberry waste.

3.6. Heat Map Analysis of Phenolic Compounds. A heat map and hierarchical clustering diagram were constructed for the quantitative analysis of phenolic compounds in fruit berries by HPLC-PDA. Ten phenolic compounds, including 5 phenolic acids and 5 flavonoids, were identified.

The phenolic components of waste or discarded berries such as blackberries, raspberries, blueberries, and strawberries were created in a hierarchically clustered heat map. The samples and the phenolic compounds were present at the axis of the map. The branching pattern showed their similarity, and each branch point showed a divergence. The lighter green color had higher content, while the blue color included less. Hence, the color distinction indicated the difference between the berries.

The phenolic compounds were divided into four groups including PC-1, PC-2, PC-3, and PC4, whereas the berries waste groups into BW-1, BW-2, BW-3, and BW-4. The phenolic acids (chlorogenic acid and protocatechuic acid) and flavonoids (quercetin and kaempferol) showed great similarity. The dissimilarity between phenolic acids (gallic acid, syringic acid) and flavonoids (kaempferol-3-glucoside, quercetin) is striking.

Blueberry waste has shown high phenolic acids (syringic acid, *p*-coumaric acid, protocatechuic acid) and flavonoids (kaempferol, kaempferol-3-glucoside, catechin, quercetin) in the heat map followed by the strawberries. Raspberry waste was noted for its high gallic acid content, followed by strawberry waste. A similar result was observed in Subbiah, Zhong, Nawaz, Barrow, Dunshea, and Suleria [32] where gallic acid was high in raspberries. Huang et al. [99] recorded the presence of gallic acid in strawberries. *p*-coumaric acid and catechin were present in the blueberry processing waste [100]. Figure 2 shows that the blueberry and blackberry waste were rich in protocatechuic acid, quercetin, and

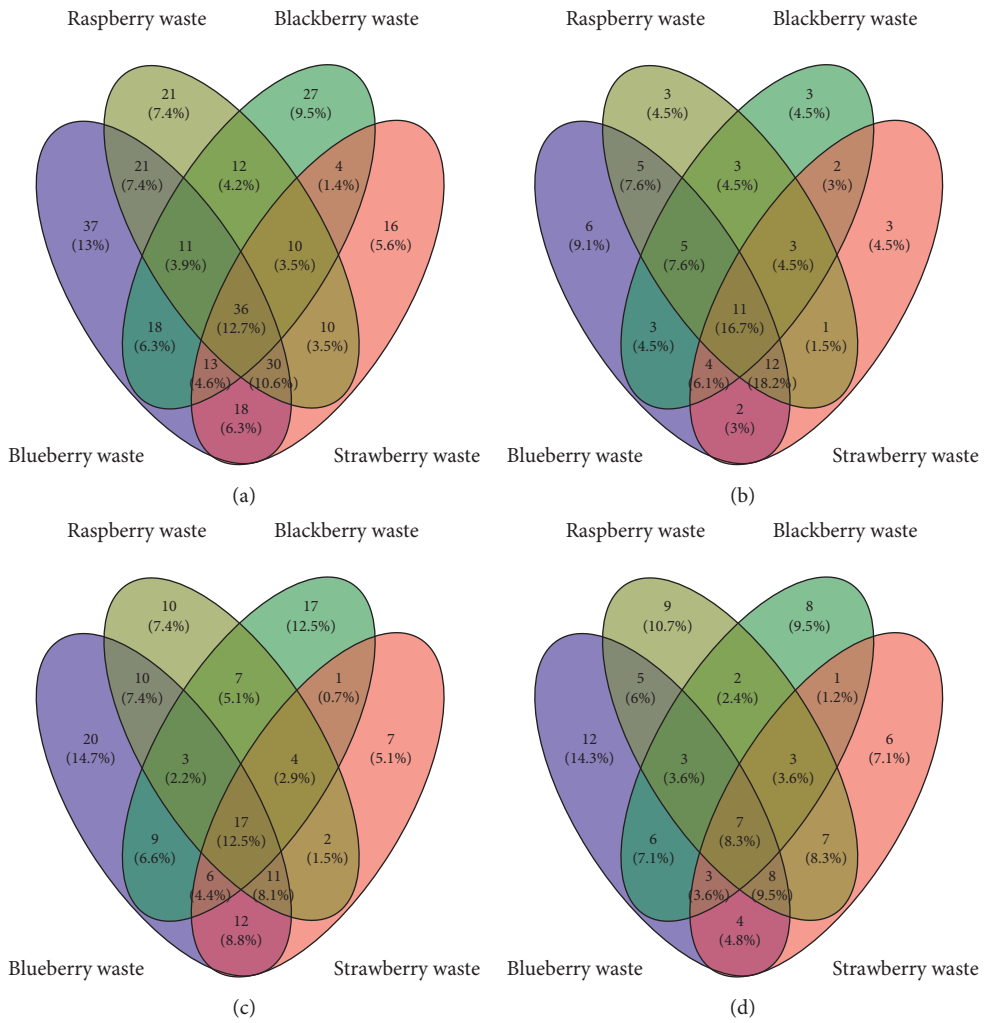

Figure 1: Venn diagram of phenolic compounds present in four waste berries. (a) shows the relations of total phenolic compounds among the four berry waste samples. (b) shows the relations of phenolic acids present in berry samples. (c) shows the relations of flavonoids among the berries. (d) shows the relations between other phenolic compounds in different waste berry samples.

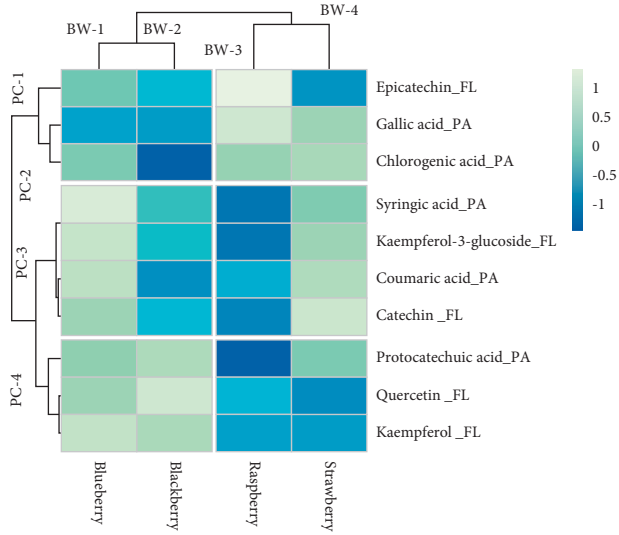

Figure 2: Heatmap showing phenolic compounds' distribution and concentration among four samples of berries waste. Lighter green boxes mean concentrations are higher among different berries samples. Blue boxes mean lower concentrations. PA: phenolic acids; FL: flavonoids; BW 1–4: fruit berries waste; PC 1–4: phenolic compound clusters.

kaempferol, which agrees with Aaby et al. [101]. Previously, strawberries (gallic acid and catechin), blueberries (gallic acid, chlorogenic acid, quercetin, and catechin), and blackberries were rich in gallic acid [102].

4. Conclusion

In conclusion, four waste berries were Australian grown with higher phenolic contents and antioxidant potential. Blueberry waste had the highest phenolic acids and antioxidant content. Eighty-seven phenolic compounds in the four berries were identified by LC-ESI-QTOF-MS/MS. Phenolic compounds present in the berry waste were quantified using HPLC. The produced outcomes of berry waste can be beneficial and employed in the food and nutraceutical industries. Further research on bioavailability, bioaccessibility, and toxicology can be conducted to commercialize the components.

Data Availability

The data used to support the findings of this study are available from the corresponding authors upon request.

Conflicts of Interest

The authors have no relevant affiliations or financial involvement with any organization or entity with a financial interest in or financial conflict with the subject matter or materials discussed in the manuscript. This includes employment, consultancies, honoraria, stock ownership or options, expert testimony, grants or patents received or pending, or royalties.

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