Characterization of Phenolics in Rejected Kiwifruit and Their Antioxidant Potential

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Abstract: Kiwifruit hold significant nutritional value and are a good source of antioxidants due to their diverse range of bioactive compounds. Kiwifruit waste is generated throughout the food supply chain, particularly during transportation and storage. Kiwifruit rejected from the retail market due to unfavorable appearance still possess potential economic value as kiwifruit are abundant in phenolic compounds. The present work studied the phenolic profile and antioxidant potential of rejected kiwifruit, including SunGold (*Actinidia chinensis*), Hayward (*Actinidia deliciosa*), and round organic Hayward (*Actinidia deliciosa*). Regarding phenolics estimation, SunGold possessed the highest TPC (0.72 ± 0.01 mg GAE/g), while Hayward exhibited the highest TFC (0.05 ± 0.09 mg QE/g). In antioxidant assays, SunGold showed the highest antioxidant activities in DPPH (0.31 ± 0.35 mg AAE/g), FRAP (0.48 ± 0.04 mg AAE/g), ABTS (0.69 ± 0.07 mg AAE/g), •OH-RSA (0.07 ± 0.03 mg AAE/g) assays, and FICA (0.19 ± 0.07 mg EDTA/g), whereas Hayward showed the highest RPA (0.09 ± 0.02 mg AAE/g) and TAC (0.57 ± 0.04 mg AAE/g). Separation and characterization of phenolics were conducted using LC-ESI-QTOF-MS/MS. A total of 97 phenolics were tentatively characterized from rejected SunGold (71 phenolics), Hayward (55 phenolics), and round organic Hayward (9 phenolics). Hydroxycinnamic acids and flavonols were the most common phenolics characterized in the three samples. The quantitative analysis was conducted by HPLC-PDA and found that chlorogenic acid (23.98 ± 0.95 mg/g), catechin (23.24 ± 1.16 mg/g), and quercetin (24.59 ± 1.23 mg/g) were the most abundant phenolics present in the rejected kiwifruit samples. The notable presence of phenolic compounds and their corresponding antioxidant capacities indicate the potential value of rescuing rejected kiwifruit for further utilization and commercial exploitation.

Keywords: rejected kiwifruit; food waste; phenolic compounds; polyphenols; antioxidant potential; LC-ESI-QTOF-MS/MS

1. Introduction

Food waste is a growing global issue that has gained increasing attention and discussion due to its adverse impact on the economy, environment, and society [1]. Fruits are susceptible to injuries, mechanical bruising, and over-ripening with the current methods of transportation and storage. This leads to considerable amounts of consumable foods being rejected at the retail level due to inadequate appearance that fails to meet quality standards [2]. Previously, it has been reported that approximately three million tons of kiwifruit are produced every year worldwide [3]. This indicates that there may be a significant amount of kiwifruit being rejected and wasted from the supply chain that could have been rescued to be further utilized up to their nutritional and commercial potential.

Kiwifruit, belonging to the genus *Actinidia*, is a well-known edible fruit, commonly found in central and southern China [4]. Besides fresh consumption, kiwifruit can also be processed into multiple food products, including juice, dried slices, jam, vinegar, wine, yogurt, and jelly [5]. Apart from being a core ingredient in various foodstuffs, kiwifruit have been reported to have several health benefits, including antioxidative, anti-inflammatory, and antimicrobial properties [5,6]. It is suggested that such properties are the actions of the bioactive compounds, including various polyphenols, β-carotene, chlorophylls, quinic acid, and flavanones, which are present abundantly within kiwifruit. Epidemiological evidence shows that regularly consuming polyphenol-rich foods prevents the undesirable effects of aging and improves cardiovascular regularity, brain function, and immune health [7,8].

Kiwifruit is a broad term for a wide range of species; Hayward (*A. deliciosa*), SunGold (*A. chinensis*), and Bidan (*A. eriantha*) are the most commonly grown kiwifruit species. Other species such as Hardy (*A. arguta*) and AnminG2 (*A. kolomikta*) are grown in cooler regions for their frost resistance [9]. The species and cultivars of kiwifruit significantly affect their bioactive compounds content as well as antioxidant activities. For example, different species of kiwifruit contain different levels of anthocyanin, which results in variation in pigmentation among different species or varieties of kiwifruit [10]. Moreover, varying weather and fertilization conditions have also been suggested to influence kiwifruit's phenolic content [11]. For instance, Hayward and Bidan grown under organic conditions appear to contain higher bioactive compounds than those grown conventionally in a past study [12].

Hayward is considered the most prevalent cultivar of kiwifruit sold in markets. It is an oval-shaped fruit with dull brown hairy skin and bright translucent green flesh that has a sweet and sour flavor [6]. Despite having the largest market share, the Hayward variety has considerably lower phenolic content compared with other varieties of kiwifruit, including Bidan and Hardy [13]. Golden kiwifruit varieties differ from Hayward in their smooth, hairless, bronze-colored skin and their sweet bright yellow flesh [14]. Moreover, golden kiwifruit have been suggested to contain higher content of bioactive compounds, mainly phenolic compounds and dietary fiber, than Hayward [15].

Polyphenols are secondary metabolites found ubiquitously in plants and are abundant in kiwifruit [3,16]. Polyphenols act as excellent antioxidants because their chemical structure makes them good hydrogen or electron donors, capable of stabilizing unpaired electrons (radicals) and chelating transition metal ions [17]. The antioxidant activity of polyphenols in kiwifruit can be evaluated by in vitro approaches based on scavenging free radicals. Previously, Tingting, et al. [18] found that kiwifruit and their products, including kiwifruit wine, juice, and vinegar, have high antioxidant activities. Furthermore, Bursal and Gülçin [19] reported intense radical scavenging activity from the aqueous extracts of kiwifruit. Recent studies have mentioned the influence of different cultivars on the phenolic profiles of different kiwifruit varieties. For instance, Bidan varieties were recorded to have a higher level of polyphenols and to have shown more potent antioxidant activity than Hayward [15].

Liquid chromatography-electrospray ionization-quadrupole-time of flight/mass spectrometry (LC-ESI-QTOF-MS/MS) can be used to characterize numerous biological compounds. High-performance liquid chromatography with a photodiode array detector (HPLC-PDA) is also widely used to quantify complex molecules, including polyphenols. Several phenolic classes were characterized in previous studies, including flavanol, flavonol, hydroxybenzoic acid, and hydroxycinnamic acid. Epicatechin, catechin, quinic acid, caffeic acid, kaempferol, and gallic acid were commonly found phenolic compounds in different varieties of kiwifruit [13,15,20]. Many scientists have previously studied the composition of phenolic compounds and antioxidant activities of kiwifruit, but only a few studies have emphasized rejected kiwifruit.

Therefore, this study aimed to elucidate the phenolic profile and antioxidant potential of rejected kiwifruit. The main objectives of this study were to extract phenolic compounds from rejected Hayward, SunGold, and round organic Hayward kiwifruit; estimate the

total phenolic profile by determining total phenolic content (TPC), total flavonoids content (TFC), and total tannins content (TTC); evaluate antioxidant activities by 2,2′-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging assay, ferric reducing antioxidant power (FRAP) assay, 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) assay, reducing power (RPA) assay, hydroxyl radical scavenging activity (•OH-RSA) assay, ferrous ion chelating activity (FICA), and total antioxidant capacity (TAC); and identify, characterize, and quantify phenolics using LC-ESI-QTOF-MS/MS and HPLC-PDA. The results provide crucial information on the nutritional value of rejected kiwifruit and promote the effective utilization of fruit in the supply chain to minimize wastage.

2. Materials and Methods

2.1. Chemicals and Reagents

Most of the chemicals used for extraction and characterization were analytically graded and purchased from Sigma-Aldrich (Castle Hill, NSW, Australia). Gallic acid, quercetin, catechin, and ascorbic acid purchased from Sigma-Aldrich (St. Louis, MO, USA) were used as standards in antioxidant assays. Folin–Ciocalteu's phenol reagent, hydrochloric acid, aluminum chloride hexahydrate, vanillin, 2,2′-diphenyl-1-picrylhydrazyl (DPPH), 2,4,6-tripyridyl-s-triazine (TPTZ), potassium persulfate, and 2,2′-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Ferric chloride (Fe[III]Cl$_3$·6H$_2$O), sodium carbonate anhydrous, sodium acetate hydrated, potassium ferricyanide K$_3$[Fe(CN)$_6$], trichloroacetic acid (TCA), ferric chloride (FeCl$_3$), 0.2 M sodium phosphate buffer, hydrogen peroxide (H$_2$O$_2$), 3-hydroxybenzoic acid, ferrous chloride, ferrozine, ethylenediaminetetraacetic acid (EDTA), ethanol, and sulfuric acid were acquired from Thermo Fisher (Scoresby, Melbourne, VIC, Australia) and were utilized in the antioxidant assays.

HPLC grade methanol, acetic acid, and acetonitrile for the conduction of the HPLC-PDA analysis were purchased from Sigma-Aldrich (St. Louis, MO, USA). Protocatechuic acid, catechin, *p*-hydroxybenzoic acid, chlorogenic acid, caffeic acid, epicatechin gallate, gallic acid, epicatechin, kaempferol, and quercetin were used as reference standards and were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Sample Preparation

Rejected kiwifruit samples used in the intended research project were mainly consumer rejects, based on low-grade quality of the fruit, especially in terms of shape, color, size, freshness, injuries, and ripeness. Rejected Hayward, SunGold, and round organic Hayward kiwifruit were used as samples for this study and were purchased from a local market in Melbourne, Victoria, Australia. Approximately 2 to 3 kg of each variety of fresh kiwifruit were collected and weighed; peel and seeds were discarded. Furthermore, each sample's pulp was blended into a slurry with a 1.5 L blender (Russell Hobbs Classic, model DZ-1613, Melbourne, VIC, Australia). Samples were kept at −20 °C until required for further analysis.

2.3. Extraction of Phenolic Compounds

The slurry (1 g) was homogenized in (10 mL) of 70% (*v/v*) ethanol with an Ultra-Turrax T25 Homogenizer (IKA, Staufen, Germany) at room temperature, 10,000 rpm for 30 s. After homogenization, samples were put in an incubator shaker (ZWYR-240, Labwit, Ashwood, VIC, Australia) at 120 rpm at 4 °C overnight. Then samples were centrifuged (ROTINA 380R centrifuge, Hettich, VIC, Australia) at 5000 rpm for 15 min. Next, the collected supernatant was filtered through 0.45 μm syringe filter (Titan, SMI-Lab Hut Co. Ltd., Maisemore, UK) and stored at −20 °C for further analysis.

2.4. Estimation of Polyphenols and Antioxidant Assays

TPC, TFC, and TTC were assessed for polyphenol content, while DPPH, FRAP, ABTS, RPA, OH-RSA, FICA, and TAC assays were conducted to estimate the antioxidant potential

of the extracts. All the assays were performed in triplicates using previously modified method of Tang, et al. [21] and Subbiah, et al. [22]. The data were obtained from the Multiskan® Go microplate reader (Thermo Fisher Scientific, Waltham, MA, USA).

2.4.1. Determination of Total Phenolic Content (TPC)

The modified method of Severo, et al. [23] was used to determine the TPC in kiwifruit samples. An amount of 25 μL of the extract was added in triplicate on 96-well plates, followed by 25 μL Folin reagent and 200 μL Milli-Q water. Next, the mixed solution was incubated for 5 min at room temperature. After incubation, 25 μL of 10% sodium carbonate (*w/w*) was added to the mixture and kept away from light for 60 min at room temperature. Gallic acid solution was prepared from 0–200 μg/mL to construct the standard curve. Absorbance was measured at 764 nm, and data are reported in mg gallic acid equivalents per gram fresh weight (mg GAE/g fw).

2.4.2. Determination of Total Flavonoids Content (TFC)

The modified aluminum chloride approach was used to evaluate the TFC of kiwifruit [24]. In total, 80 μL of 2% aluminum chloride was mixed with the same volume of diluted extract and then 120 μL of sodium acetate (50 mg/mL) was added to the mixture. Incubation was carried out in a dark place for 150 min. Then, the absorbance was measured at a wavelength of 440 nm. Quercetin standard curve was calculated (0–50 μg/mL), and data are expressed as mg quercetin equivalents (mg QE/g fw).

2.4.3. Determination of Total Tannins Content (TTC)

Modified approach of Zou, et al. [25] was used to determine the TTC. In a 96-well plate, 25 μL sample was added, followed by 150 μL methanolic vanillin reagent (4%, *w/v*) and 5 μL of sulfuric acid (32%, *v/v*). The absorbance was measured at 500 nm after 15 min of incubation at 25 °C. The tannins content was quantified by linear regression using catechin standard (0–1000 μg/mL). TTC is expressed as mg catechin equivalents (mg CE/g fw) of fresh weight.

2.4.4. 2,2′-Diphenyl-1-Picrylhydrazyl (DPPH) Free Radical Scavenging Assay

The approach of Alvarez-Jubete, et al. [26] was modified for this study's DPPH assay. A portion of 0.1 mM DPPH methanol solution was mixed with extract in a 96-well plate in a 1:1 volume ratio. The mixed reagent was incubated for 30 min and then the absorbance was measured at 517 nm. The ascorbic acid solution was prepared from 0–50 μg/mL to obtain the standard curve. The radical scavenging capacity of DPPH was calculated as mg of ascorbic acid equivalent (mg AAE/g fw) per fresh weight.

2.4.5. Ferric Reducing Antioxidant Power (FRAP) Assay

The FRAP approach can estimate the ability of a compound to reduce Fe^{3+} complex into Fe^{2+} complex. The method of Chen, et al. [27], with some modification, was applied to measure the reducing antioxidant power of samples. Firstly, the same volume of 20 mM $FeCl_3$, TPTZ solution, and 300 mM sodium acetate solution were mixed to prepare the FRAP reagent. Then, 420 μL of FRAP reagent was mixed with 30 μL of sample solution. The mixed solution's absorbance was measured at 593 nm after incubation for 10 min at 37 °C. Ascorbic acid ranging from 0 to 50 μg/mL was used to obtain the standard curve. Results are presented as mg AAE/g fw.

2.4.6. 2,2′-Azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) Assay

The modified approach of Severo, et al. [23] was used to evaluate the sample's capacity to scavenge free radicals. First, 7 mM ABTS and 140 mM potassium persulfate were mixed in a 625:11 volume ratio and then incubated in a dark place for one day. The solution was diluted with ethanol after incubation to acquire an ABTS cation solution with absorbance of 0.70 ± 0.02 at 734 nm. A portion of 290 μL of diluted ABTS solution was mixed with

10 μL of sample. Next, the absorbance was measured at a wavelength of 734 nm after incubation for 6 min at 25 °C. Ascorbic acid from 0 to 150 μg/mL was used to create a standard curve, and results are shown as mg AAE/g fw.

2.4.7. Reducing Power Assay (RPA)

The reducing power activity was determined by modifying the method of Ferreira, et al. [28]. First, 10 μL of extract, 25 μL of 0.2 M sodium phosphate buffer (pH 6.6), and 25 μL of $K_3[Fe(CN)_6]$ were added sequentially, followed by incubation at 25 °C for 20 min. Then, 25 μL of 10% TCA solution was added to stop the reaction, followed by the addition of 85 μL of water and 8.5 μL of $FeCl_3$. The solution was further incubated for 15 more minutes at 25 °C. Then the absorbance was measured at 750 nm. Ascorbic acid from 0 to 500 μg/mL was used to obtain a standard curve, and data are presented as mg AAE/g fw.

2.4.8. Hydroxyl Radical Scavenging Activity (•OH-RSA)

The Fenton-type reaction method of Smirnoff and Cumbes [29] was used to determine •OH-RSA with some modifications. An amount of 50 μL extract was mixed with 50 μL of 6 mM $FeSO_4·7H_2O$ and 50 μL of 6 mM H_2O_2 (30%), followed by incubation at 25 °C for 10 min. After incubation, 50 μL of 6 mM 3-hydroxybenzoic acid was added and absorbance was measured at a wavelength of 510 nm. Ascorbic acid from 0 to 300 μg/mL was used to obtain a standard curve, and data are presented as mg AAE/g fw.

2.4.9. Ferrous Ion Chelating Activity (FICA)

The Fe^{2+} chelating activity of the sample was measured according to Dinis, et al. [30], with modifications. A portion of 15 μL extract was mixed with 85 μL of water, 50 μL of 2 mM ferrous chloride (with additional 1:15 dilution in water), and 50 μL of 5 mM ferrozine (with additional 1:6 dilution in water), followed by incubation at 25 °C for 10 min. Then the absorbance was measured at a wavelength of 562 nm. Ethylenediaminetetraacetic acid (EDTA) from concentrations of 0 to 30 μg/mL was used to obtain a standard curve, and data are presented as mg EDTA/g fw.

2.4.10. Total Antioxidant Capacity (TAC)

The phosphomolybdate method of Prieto, et al. [31] with some modification was used to determine TAC. In total, 40 μL extract was mixed with 260 μL phosphomolybdate reagent (0.6 M H_2SO_4, and 28 mM sodium phosphate, 4 mM ammonium molybdate), followed by incubation at 95 °C for 10 min. Next, the absorbance was measured at a wavelength of 695 nm after dropping to room temperature. Ascorbic acid from 0 to 200 μg/mL was used to obtain a standard curve, and data are presented as mg AAE/g fw.

2.5. LC-ESI-QTOF-MS/MS Analysis

The identification of polyphenol was carried out by Agilent 1200 series HPLC (Agilent Technologies, CA, USA) equipped with Agilent 6520 Accurate-Mass Q-TOF LC-MS/MS (Agilent Technologies, CA, USA). Synergi Hydro-RP 80Å, LC column 250 × 4.6 mm, 4 mm (Phenomenex, Torrance, CA, USA), was used to separate each compound [32]. Mobile phase A (water:acetic acid = 98:2, *v/v*) and mobile phase B (acetonitrile:water:acetic acid = 50:49.5:0.5, *v/v/v*) were degassed at 21 °C for 15 min. The flow rate was set at 0.8 mL/min, and 6 μL of each sample was injected. Gradient elution was achieved by changing the ratio of mobile phases A and B: 10% phase B from 0 to 20 min, 25% phase B from 20 to 30 min, 35% phase B from 30 to 40 min, 40% phase B from 40 to 70 min, 55% phase B from 70 to 75 min, 80% phase B from 75 to 77 min, 100% phase B from 77 to 79 min, and then maintained for 3 min, 10% phase B from 82 to 85 min. Mass spectrometry condition was set at 45 psi gas pressure; 300 °C of nitrogen gas, 5 L/min of flow rate; 250 °C of sheath gas, 11 L/min of flow rate. The capillary voltage was 3.5 kV, and the voltage of the nozzle was 500 V. For MS/MS, electrospray ionization (ESI) was utilized in operating both negative and positive ion modes. The mass spectra were obtained over the *m/z* range of 50–1300 amu

with collision energies 10, 15, and 30 eV for fragmentation. Data analysis was performed using Agilent LC-MS-QTOF MassHunter data acquisition software version B.03.01.

2.6. HPLC-PDA Analysis

Agilent 1200 series HPLC (Agilent Technologies, Santa Clara, CA, USA) equipped with a photodiode array (PDA) detector was used to quantify targeted polyphenol [33]. With the exception of sample injection volume of 20 μL, the rest of the conditions were consistent with the LC-ESI-QTOF-MS/MS section. Samples were measured at wavelengths of 280, 320, and 370 nm. Agilent MassHunter software version B.03.01 was used for data analysis.

2.7. Statistical Analysis

One-way analysis of variance (ANOVA) and Tukey's test were applied to compare different groups' mean values ($p < 0.05$). Data were analyzed by Minitab 18.0 (Minitab, LLC, State College, PA, USA). The results are expressed as mean $\pm$ standard deviation (SD).

3. Results and Discussion

3.1. Polyphenol Estimation (TPC, TFC and TTC)

Kiwifruit have been considered an excellent source of polyphenols [15]. The results showed that the highest phenolic percentage recovery or yield was calculated in SunGold (21.7%), followed by Hayward (17.2%) and round organic Hayward (12.8%). The phenolic content in ethanol extracts of three cultivars of rejected kiwifruit samples were determined by TPC, TFC, and TTC. As illustrated in Table 1, SunGold possessed the highest phenolic content (0.72 $\pm$ 0.01 mg GAE/g fw), while round organic Hayward displayed the lowest phenolic content. Previously, Wang, et al. [9] reported TPC values of four different Chinese-grown cultivars, including Red Sun, Cuiyu, Hayward, and Qinmei, which ranged from 0.78 $\pm$ 0.01 to 0.87 $\pm$ 0.04 mg GAE/g fw. According to Bursal and Gülçin [19], the TPC in 1 mg lyophilized water extract from Hayward kiwifruit grown in Turkey measured 0.42 $\pm$ 0.07 mg GAE/g fw. In this study, the TPC value of our rejected Hayward was higher than that of previously reported TPC from fresh Hayward kiwifruit. Previously, a study on sliced pitaya fruit by Xiaoan, et al. [34] observed that accumulation of phenolic content in the fruit was increased after injuring and cutting of the fruit. This may be a reason why higher TPC was observed in rejected kiwifruit compared with fresh and undamaged kiwifruit.

Table 1. Polyphenol content and antioxidant activity of three kiwifruit cultivars.

Antioxidant Assays	Hayward	SunGold	Round Organic Hayward
TPC (mg GAE/g)	0.58 $\pm$ 0.07 [b]	0.72 $\pm$ 0.01 [a]	0.22 $\pm$ 0.05 [c]
TFC (mg QE/g)	0.05 $\pm$ 0.09 [a]	0.03 $\pm$ 0.07 [b]	0.01 $\pm$ 0.01 [c]
TTC (mg CE/g)	-	0.01 $\pm$ 0.01	-
DPPH (mg AAE/g)	0.12 $\pm$ 0.01 [b]	0.31 $\pm$ 0.05 [a]	0.09 $\pm$ 0.02 [c]
FRAP (mg AAE/g)	0.15 $\pm$ 0.01 [b]	0.48 $\pm$ 0.04 [a]	0.11 $\pm$ 0.03 [c]
ABTS (mg AAE/g)	0.43 $\pm$ 0.03 [b]	0.69 $\pm$ 0.07 [a]	0.27 $\pm$ 0.01 [c]
RPA (mg AAE/g)	0.09 $\pm$ 0.02 [a]	0.03 $\pm$ 0.05 [c]	0.07 $\pm$ 0.04 [b]
•OH-RSA (mg AAE/g)	0.04 $\pm$ 0.01 [b]	0.07 $\pm$ 0.03 [a]	0.01$\pm$ 0.02 [c]
FICA (mg EDTA/g)	0.11 $\pm$ 0.04 [b]	0.19 $\pm$ 0.07 [a]	-
TAC (mg AAE/g)	0.57 $\pm$ 0.04 [a]	0.11 $\pm$ 0.01 [c]	0.19 $\pm$ 0.02 [b]

Values expressed as mean $\pm$ standard deviation per gram fresh weight (fw). Values within the same rows with different superscript letters ([a,b,c]) indicate that they are significantly different from each other ($p < 0.05$). TPC, total phenolic content; TFC, total flavonoid content; TTC, total tannin content; DPPH, 2,2′-diphenyl-1-picrylhydrazyl assay; FRAP, ferric reducing antioxidant power assay; ABTS, 2,2′-azino-bis-3-ethylbenzothiazoline-6-sulfonic acid assay; RPA, reducing powder assay; •OH-RSA, hydroxyl radical scavenging activity; FICA, ferrous ion chelating activity; TAC, total antioxidant capacity; GAE, gallic acid equivalents; QE, quercetin equivalents; CE, catechin equivalents; AAE, ascorbic acid equivalents and EDTA, ethylenediaminetetraacetic acid.

Flavonoids are commonly found phenolic compounds in plants, which are well-regarded for their antioxidative effects [35]. In this study, TFC of Hayward was sig-

nificantly higher than SunGold and round organic Hayward. Kheirkhah, et al. [36] reported a higher TFC value of New Zealand-grown Hayward, ranging from 1.40 ± 0.01 to 16.18 ± 0.05 mg QE/g dw. The difference was observed perhaps due to the difference in sample extraction technique and growing regions. Dea, et al. [37] reported the highest flavonoids level in green tomato and found a slight decrease during ripening. The decline in TFC of rejected kiwifruit may be attributed to long storage time and over-ripening.

In terms of TTC value, we found trace amounts of tannins in SunGold ethanol extract (0.01 ± 0.01 mg CE/g fw), and no tannin content was detected in Hayward and in round organic Hayward extracts. Previously a study reported higher TTC value in methanol extract of freeze-dried South Korea-grown Hayward [11]. Another study also reported a higher TTC value of 3.12 ± 0.2 mg CE/g in organically Korea-grown Hayward using methanol as a solvent [15]. Compared with our result, it is possible that methanol may be more suitable for extracting higher yields of tannins. Additionally, sample preparation methods, genotypes, and growing regions may all affect TTC value. Importantly, bioactive secondary metabolites in plants contribute to antioxidant capacity; thus, changes in their level may influence the measured antioxidant activity of kiwifruit.

3.2. Antioxidant Activities (DPPH, FRAP, ABTS, RPA, •OH-RSA, FICA, and TAC)

Polyphenols, flavonoid, and vitamin C in plants contribute significantly to antioxidant capacity [38]. Results shown in Table 1 demonstrate that kiwifruit are an excellent source of bioactive compounds. It has been suggested that different growing areas, cultivars, solvents, and extraction approaches influence polyphenol content and antioxidant activity [9]. In this study, the antioxidant activities were evaluated through DPPH, FRAP, ABTS, RPA, OH-RSA, and TAC assays and are expressed as mg AAE/g fw, while FICA is expressed as mg EDTA/g fw.

As presented in Table 1, the antioxidant activities of the three kiwifruit cultivars were significantly different. In short, FRAP, ABTS, and •OH-RSA assays saw highest value from SunGold, then Hayward, and lastly round organic Hayward. RPA and TAC assay saw highest values from Hayward, then from round organic Hayward, and lastly from SunGold. Our results are consistent with previous research, where golden kiwifruit showed significantly higher antioxidant capacity in DPPH, FRAP, and ABTS assays, compared with Hayward [9]. In this study, SunGold possessed the highest TPC value, corresponding to the strongest scavenging activity, while round organic Hayward recorded the worst values of TPC and worst values in most antioxidant assays. This result is consistent with Li-Li, et al. [39], where they reported a positive correlation between TPC value and antioxidant capacity. According to Inil, et al. [40], antioxidant capacity is affected more prominently by TPC than TFC. This may suggest why Hayward exhibited lower antioxidant capacity than SunGold in DPPH, FRAP, and ABTS assays, although Hayward possessed higher TFC value.

In the DPPH assay, three cultivars' results ranged from 0.09 ± 0.02 to 0.31 ± 0.05 mg AAE/g fw, while SunGold had the highest values. Higher DPPH results of golden kiwifruit (0.9–1.21 mg AAE/g fw) were reported previously [40]. In the ABTS assay, free radical scavenging activity of SunGold was the greatest. Previously, Hwang, et al. [41] reported higher ABTS values of five cultivars of Korea-grown kiwifruit, which varied from 5.8 ± 0.1 to 39.0 ± 0.3 mg AAE/g dw. The variability in the results may be due to different growing areas and sample preparation methods. Latocha, et al. [42], who extracted using methanol and phosphate-buffered saline solution, also reported higher ABTS values of Hardy kiwifruit with values ranging from 1.52–1.63 mg AAE/g fw and 2.51–3.05 mg AAE/g fw, respectively. The choice of extraction solution may explain the difference observed, as well as the difference in cultivar and growing regions.

In FRAP assay, the antioxidant capacity was determined by the ability to reduce Fe^{3+} to Fe^{2+}. Similar to the above two assays, SunGold exhibited significantly higher FRAP values than Hayward and round organic Hayward. A previous study reported higher antioxidant capacity of different China-grown kiwifruit cultivars, including Red Sun, Cuiyu, Hayward, and Qinmei, in which their antioxidant potentials were determined by FRAP assay [9].

Jeong, et al. [43] also reported higher FRAP values in Korea-grown Hardy kiwifruit, in which they observed 1.35 to 2.35 mg AAE/g fw in their sample. Different growing areas and cultivars may have led to the observed difference [44].

In RPA assay, Hayward showed the highest antioxidant potential followed by organic Hayward and SunGold. Meanwhile, SunGold exhibited the highest value from the OH-RSA assay. Previously, few studies were conducted to elucidate the antioxidant potential of kiwifruit using RPA and •OH-RSA methods. To the best of our knowledge, this is the first time that RPA and •OH-RSA were conducted on rejected kiwifruit samples and limited data are available for comparison. However, several studies have conducted RPA and •OH-RSA methods and suggested that antioxidant activity is positively correlated with phenolic content. Metal chelating assay is also another widely performed antioxidant assay, which determines sample antioxidant potential by measuring a sample's ability to compete with ferrozine for ferrous ion. Transition metals such as iron and copper may undergo Fenton reaction and or other redox reactions that generate hydroxyl radicals, in which accumulation of these metals could cause damaging effects to cells [45]. Thus, chelating metals is considered to be a way of reducing reactive oxidative species. Polyphenols contain numerous hydroxyl groups and are considered to be excellent candidates for chelating metals [46]. In our study, SunGold recorded the highest FICA value of 0.19 ± 0.07 mg EDTA/g, nearly 2 times higher than Hayward's 0.11 ± 0.04 mg EDTA/g, while organically grown Hayward did not record any metal chelating capacity in our assay. In a previous study, Hayward and various other cultivars of kiwifruit recorded potent metal chelating capacity [46].

In TAC assay, previously, Suleria, et al. [47] reported higher TAC values in kiwifruit peels and concluded that fruit peels have more antioxidant activities as compared with pulps. Therefore, bioactive compounds that display antioxidant activities are likely distributed in different plant parts. In our assay, Hayward and organic Hayward exhibited stronger antioxidant capacity than golden kiwifruit, which was not consistent with the TPC result or TFC result. However, according to Guorong, et al. [48], vitamin C is another major antioxidant in kiwifruit contributing to antioxidant capacity. Thus, it is possible that vitamin C and or other phytochemicals instead of phenolic compounds may also be contributing to the assay's observed antioxidant capacity in the Hayward samples.

3.3. LC-ESI-QTOF-MS/MS Based Characterization of Phenolic Compounds

In this study, untargeted LC-ESI-QTOF-MS/MS qualitative analysis in both positive and negative ionization modes was conducted to analyze phenolic compounds in the three kiwifruit varieties. Based on the *m/z* value and MS spectra (Supplementary Figure S1), phenolic compounds from kiwifruit samples were tentatively characterized according to Agilent LC-MS Qualitative Software and Personal Compound Database and Library (PCDL). To further characterize the phenolics, mass error < ± 5 ppm and PCDL library score > 80 were selected.

In this study, LC-MS/MS enabled the tentative characterization of 97 phenolic compounds in three kiwifruit samples, including phenolic acids (28), flavonoids (54), lignans (5), stilbene (1), and other polyphenols (9), as listed in Table 2.

Table 2. LC-ESI-QTOF-MS/MS characterization of phenolic compounds in different kiwifruit samples.

No.	Molecular Formula	Proposed Compounds	RT (min)	Ionization (ESI$^+$/ESI$^-$)	Molecular Weight	Theoretical (m/z)	Observed (m/z)	Error (ppm)	MS^2 Product Ion	Kiwifruit
				Phenolic Acid						
				Hydroxybenzoic Acids						
1	$C_{13}H_{16}O_{10}$	Gallic acid 4-*O*-glucoside	10.541	[M–H]$^-$	332.0743	331.0670	331.0668	−0.6	169, 125	SG
2	$C_{13}H_{16}O_9$	Protocatechuic acid 4-*O*-glucoside	11.005	[M–H]$^-$	316.0794	315.0721	315.0717	−1.3	153	* SG, HW
3	$C_{13}H_{16}O_8$	4-Hydroxybenzoic acid 4-*O*-glucoside	11.054	[M–H]$^-$	300.0845	299.0772	299.0770	−0.7	255, 137	SG
4	$C_7H_6O_3$	2-Hydroxybenzoic acid	11.783	** [M–H]$^-$	138.0317	137.0244	137.0247	2.2	93	* SG, HW
5	$C_7H_6O_5$	Gallic acid	12.893	** [M–H]$^-$	170.0215	169.0142	169.0140	−1.2	125	* SG, HW
6	$C_8H_8O_5$	3-*O*-Methylgallic acid	13.079	[M+H]$^+$	184.0372	185.0445	185.0452	3.8	170, 142	HW
7	$C_7H_6O_4$	2,3-Dihydroxybenzoic acid	15.580	[M–H]$^-$	154.0266	153.0193	153.0196	2.0	109	* HW, SG
8	$C_9H_{10}O_5$	3,4-*O*-Dimethylgallic acid	19.314	** [M+H]$^+$	198.0528	199.0601	199.0597	−2.0	153, 139, 125, 111	HW, * SG
9	$C_{23}H_{28}O_{11}$	Paeoniflorin	34.596	[M–H]$^-$	480.1632	479.1559	479.1583	5.0	449, 357, 327	SG
				Hydroxycinnamic Acid						
10	$C_9H_8O_2$	Cinnamic acid	12.479	** [M–H]$^-$	148.0524	147.0451	147.0453	1.4	103	* SG, OHW
11	$C_9H_8O_3$	m-Coumaric acid	19.437	[M–H]$^-$	164.0473	163.0400	163.0397	−1.8	119	* SG, HW
12	$C_{15}H_{18}O_9$	Caffeoyl glucose	19.603	[M–H]$^-$	342.0951	341.0878	341.0875	−0.9	179, 161	* SG, HW
13	$C_9H_8O_4$	Caffeic acid	19.619	[M–H]$^-$	180.0423	179.0350	179.0350	0.0	143, 133	SG
14	$C_{15}H_{16}O_{10}$	Caffeic acid 3-*O*-glucuronide	22.273	** [M–H]$^-$	356.0743	355.0670	355.0671	0.3	179	* HW, SG
15	$C_{18}H_{16}O_8$	Rosmarinic acid	22.273	[M–H]$^-$	360.0845	359.0772	359.0755	−4.7	179	HW
16	$C_{16}H_{20}O_9$	Ferulic acid 4-*O*-glucoside	23.330	[M–H]$^-$	356.1107	355.1034	355.1031	−0.8	193, 178, 149, 134	* SG, HW
17	$C_{10}H_{10}O_4$	Ferulic acid	23.366	[M–H]$^-$	194.0579	193.0506	193.0505	−0.5	178, 149, 134	* HW, SG
18	$C_{15}H_{18}O_8$	*p-Coumaric acid 4-O-glucoside*	23.764	[M–H]$^-$	326.1002	325.0929	325.0924	−1.5	163	* HW, SG
19	$C_{16}H_{18}O_{10}$	Ferulic acid 4-*O*-glucuronide	24.592	[M–H]$^-$	370.0900	369.0827	369.0829	0.5	193	HW
20	$C_{11}H_{12}O_5$	Sinapic acid	26.166	[M–H]$^-$	224.0685	223.0612	223.0604	−3.6	205,163	* HW, SG
21	$C_{43}H_{48}O_{21}$	1-Sinapoyl-2,2′-diferuloylgentiobiose	26.763	** [M–H]$^-$	900.2688	899.2615	899.2579	−4.0	613,201	* HW, SG
22	$C_{16}H_{18}O_9$	3-Caffeoylquinic acid	30.606	[M–H]$^-$	354.0951	353.0878	353.0883	1.4	254, 190, 144	HW
23	$C_{29}H_{36}O_{15}$	Verbascoside	31.531	[M–H]$^-$	624.2054	623.1981	623.1984	0.5	477, 461, 315, 135	SG
24	$C_{16}H_{18}O_8$	3-p-Coumaroylquinic acid	32.031	[M–H]$^-$	338.1002	337.0929	337.0923	−1.8	265, 173, 162	* HW, SG
25	$C_{33}H_{40}O_{18}$	1-Sinapoyl-2-feruloylgentiobiose	60.158	** [M–H]$^-$	724.2215	723.2142	723.2121	−2.9	529, 499	SG

Table 2. *Cont.*

No.	Molecular Formula	Proposed Compounds	RT (min)	Ionization (ESI+/ESI−)	Molecular Weight	Theoretical (*m/z*)	Observed (*m/z*)	Error (ppm)	MS² Product Ion	Kiwifruit
				Hydroxyphenylacetic Acid						
26	3,4-Dihydroxyphenylacetic acid	$C_8H_8O_4$	24.924	** [M–H]−	168.0423	167.0350	167.0349	−0.6	149, 123	* HW, OHW, SG
27	2-Hydroxy-2-phenylacetic acid	$C_8H_8O_3$	31.517	** [M–H]−	152.0473	151.0400	151.0402	1.3	136,92	* HW, SG
				Hydroxyphenylpropanoic Acid						
28	Dihydroferulic acid 4-*O*-glucuronide	$C_{16}H_{20}O_{10}$	33.025	[M–H]−	372.1056	371.0983	371.0990	1.9	195	HW
				Flavonoids **Flavonols**						
29	Patuletin 3-*O*-glucosyl-(1->6)-[apiosyl(1->2)]-glucoside	$C_{33}H_{40}O_{22}$	21.872	[M–H]−	788.2011	787.1938	787.1907	−3.9	625, 463, 301, 271	SG
30	Myricetin 3-*O*-rutinoside	$C_{27}H_{30}O_{17}$	25.766	[M–H]−	626.1483	625.1410	625.1395	−2.4	301	SG
31	Quercetin 3-*O*-glucosyl-xyloside	$C_{26}H_{28}O_{16}$	27.754	[M–H]−	596.1377	595.1304	595.1306	0.3	265, 238, 116	* SG, HW
32	Kaempferol 3,7-*O*-diglucoside	$C_{27}H_{30}O_{16}$	30.785	** [M–H]−	610.1534	609.1461	609.1462	0.2	447, 285	SG
33	Kaempferol 3-*O*-glucosyl-rhamnosyl-galactoside	$C_{33}H_{40}O_{20}$	31.382	[M–H]−	756.2113	755.2040	755.2035	−0.7	285	SG
34	Kaempferol 3-*O*-(2″-rhamnosyl-galactoside) 7-*O*-rhamnoside	$C_{33}H_{40}O_{19}$	40.112	[M–H]−	740.2164	739.2091	739.2060	−4.2	593, 447, 285	SG
35	Quercetin 3-*O*-xylosyl-glucuronide	$C_{26}H_{26}O_{17}$	43.207	[M+H]+	610.1170	611.1243	611.1255	2.0	479, 303, 285, 239	HW
36	Quercetin 3′-*O*-glucuronide	$C_{21}H_{18}O_{13}$	45.016	** [M–H]−	478.0747	477.0674	477.0653	−4.4	301	* SG, HW
37	Myricetin 3-*O*-rhamnoside	$C_{21}H_{20}O_{12}$	45.314	[M–H]−	464.0955	463.0882	463.0871	−2.4	317	SG
38	Quercetin 3-*O*-arabinoside	$C_{20}H_{18}O_{11}$	47.948	[M–H]−	434.0849	433.0776	433.0751	−5.0	301	SG
39	Isorhamnetin 3-*O*-glucuronide	$C_{22}H_{20}O_{13}$	53.962	** [M–H]−	492.0904	491.0831	491.0809	−4.5	315, 300, 272, 255	* SG, HW
40	Isorhamnetin	$C_{16}H_{12}O_7$	85.555	** [M–H]−	316.0583	315.0510	315.0510	0.0	300,271	SG
				Flavanols						
41	(+)-Gallocatechin	$C_{15}H_{14}O_7$	21.925	** [M–H]−	306.0740	305.0667	305.0667	0.0	261, 219	HW
42	(+)-Catechin 3-*O*-gallate	$C_{22}H_{18}O_{10}$	22.306	** [M–H]−	442.0900	441.0827	441.0805	−5.0	289, 169, 125	HW
43	(+)-Catechin	$C_{15}H_{14}O_6$	24.159	** [M–H]−	290.0790	289.0717	289.0714	−1.0	245, 205, 179	* SG, HW
44	Procyanidin dimer B1	$C_{30}H_{26}O_{12}$	26.498	** [M–H]−	578.1424	577.1351	577.1338	−2.3	451	* HW, SG
45	4′-*O*-Methyl-(-)-epigallocatechin 7-*O*-glucuronide	$C_{22}H_{24}O_{13}$	27.607	[M–H]−	496.1217	495.1144	495.1160	3.2	451, 313	* HW, SG

Table 2. *Cont.*

No.	Molecular Formula	Proposed Compounds	RT (min)	Ionization (ESI⁺/ESI⁻)	Molecular Weight	Theoretical (*m/z*)	Observed (*m/z*)	Error (ppm)	MS² Product Ion	Kiwifruit
				Flavanols						
46	4″-*O*-Methylepigallocatechin 3-*O*-gallate	$C_{23}H_{20}O_{11}$	32.575	[M–H]⁻	472.1006	471.0933	471.0927	−1.3	169,319	SG
47	Prodelphinidin dimer B3	$C_{30}H_{26}O_{14}$	35.082	** [M+H]⁺	610.1323	611.1396	611.1363	−5.0	469, 311, 291	HW, * SG
48	Cinnamtannin A2	$C_{60}H_{50}O_{24}$	35.444	[M–H]⁻	1154.2692	1153.2619	1153.2629	0.9	739	HW
49	Procyanidin trimer C1	$C_{45}H_{38}O_{18}$	36.239	[M–H]⁻	866.2058	865.1985	865.2004	2.2	739, 713, 695	HW
				Flavanones						
50	Hesperetin 3′,7-*O*-diglucuronide	$C_{28}H_{30}O_{18}$	21.163	[M–H]⁻	654.1432	653.1359	653.1361	0.3	477, 301, 286, 242	HW
51	Neoeriocitrin	$C_{27}H_{32}O_{15}$	41.835	** [M–H]⁻	596.1741	595.1668	595.1644	−4.0	431, 287	SG
52	Hesperidin	$C_{28}H_{34}O_{15}$	52.573	[M+H]⁺	610.1898	611.1971	611.1962	−1.5	593, 465, 449, 303	SG
53	Hesperetin 3′-*O*-glucuronide	$C_{22}H_{22}O_{12}$	52.673	** [M–H]⁻	478.1111	477.1038	477.1039	0.2	301,175,113,85	* HW, SG
				Flavones						
54	Apigenin 7-*O*-glucuronide	$C_{21}H_{18}O_{11}$	15.812	** [M+H]⁺	446.0849	447.0922	447.0930	1.8	271, 253	OHW, * HW
55	Cirsilineol	$C_{18}H_{16}O_{7}$	26.744	[M+H]⁺	344.0896	345.0969	345.0962	−2.0	330, 312, 297, 284	HW
56	Apigenin 6,8-di-C-glucoside	$C_{27}H_{30}O_{15}$	38.423	[M–H]⁻	594.1585	593.1512	593.1512	0.0	503, 473	* SG, HW
57	Rhoifolin	$C_{27}H_{30}O_{14}$	39.665	[M–H]⁻	578.1636	577.1563	577.1559	−0.7	413, 269	SG
58	Apigenin 6-C-glucoside	$C_{21}H_{20}O_{10}$	41.736	** [M–H]⁻	432.1056	431.0983	431.0984	0.2	413, 341, 311	SG
59	Chrysoeriol 7-*O*-glucoside	$C_{22}H_{22}O_{11}$	56.598	** [M+H]⁺	462.1162	463.1235	463.1214	−4.5	445, 427, 409, 381	HW, * SG
60	6-Hydroxyluteolin 7-*O*-rhamnoside	$C_{21}H_{20}O_{11}$	57.938	** [M–H]⁻	448.1006	447.0933	447.0929	−0.9	301	* SG, HW
				Isoflavonoids						
61	6″-*O*-Acetylglycitin	$C_{24}H_{24}O_{11}$	14.046	[M+H]⁺	488.1319	489.1392	489.1410	3.7	285, 270	SG
62	2′-Hydroxyformononetin	$C_{16}H_{12}O_{5}$	17.906	** [M+H]⁺	284.0685	285.0758	285.0747	−3.9	270, 229	SG
63	Dihydrobiochanin A	$C_{16}H_{14}O_{5}$	22.255	[M+H]⁺	286.0841	287.0914	287.0925	3.8	269, 203, 201, 175	HW
64	6″-*O*-Malonylglycitin	$C_{25}H_{24}O_{13}$	37.252	[M+H]⁺	532.1217	533.1290	533.1274	−3.0	285, 270, 253	SG
65	Formononetin 7-*O*-glucuronide	$C_{22}H_{20}O_{10}$	39.234	[M–H]⁻	444.1056	443.0983	443.0989	1.4	267, 252	SG
66	6″-*O*-Acetyldaidzin	$C_{23}H_{22}O_{10}$	41.868	[M–H]⁻	458.1213	457.1140	457.1129	−2.4	221	SG
67	5,6,7,3′,4′-Pentahydroxyisoflavone	$C_{15}H_{10}O_{7}$	42.893	** [M+H]⁺	302.0427	303.0500	303.0487	−4.3	285, 257	* HW, SG
68	3′-Hydroxydaidzein	$C_{15}H_{10}O_{5}$	50.933	** [M+H]⁺	270.0528	271.0601	271.0613	4.4	253, 241, 225	SG
69	3′-Hydroxygenistein	$C_{15}H_{10}O_{6}$	56.581	** [M+H]⁺	286.0477	287.0550	287.0539	−3.8	269, 259	SG
70	3′,4′,7-Trihydroxyisoflavanone	$C_{15}H_{12}O_{5}$	83.053	** [M–H]⁻	272.0685	271.0612	271.0608	−1.5	177, 151, 119, 107	* SG, HW

Table 2. *Cont.*

No.	Molecular Formula	Proposed Compounds	RT (min)	Ionization (ESI⁺/ESI⁻)	Molecular Weight	Theoretical (m/z)	Observed (m/z)	Error (ppm)	MS² Product Ion	Kiwifruit
				Anthocyanins						
71	Cyanidin 3-O-(6''-p-coumaroyl-glucoside)	$C_{30}H_{27}O_{13}$	22.205	[M+H]⁺	595.1452	596.1525	596.1553	4.7	287	HW
72	Cyanidin 3-O-diglucoside-5-O-glucoside	$C_{33}H_{41}O_{21}$	27.297	** [M+H]⁺	773.2140	774.2213	774.2250	4.8	610, 464	SG
73	Cyanidin 3,5-O-diglucoside	$C_{27}H_{31}O_{16}$	28.804	** [M+H]⁺	611.1612	612.1685	612.1715	4.9	449, 287	HW, * SG
74	Delphinidin 3-O-xyloside	$C_{20}H_{19}O_{11}$	37.212	[M+H]⁺	435.0927	436.1000	436.0996	−0.9	303	HW
75	Delphinidin 3-O-galactoside	$C_{21}H_{21}O_{12}$	45.278	** [M+H]⁺	465.1033	466.1106	466.1113	1.5	303	HW
76	Pelargonidin 3-O-rutinoside	$C_{27}H_{31}O_{14}$	50.950	[M+H]⁺	579.1714	580.1787	580.1814	4.7	271, 433	SG
77	Delphinidin 3-O-glucosyl-glucoside	$C_{27}H_{31}O_{17}$	52.556	[M+H]⁺	627.1561	628.1634	628.1650	2.5	465, 3030	SG
				Dihydrochalcones						
78	3-Hydroxyphloretin 2'-O-xylosyl-glucoside	$C_{26}H_{32}O_{15}$	12.198	[M–H]⁻	584.1741	583.1668	583.1680	2.1	289	SG
79	3-Hydroxyphloretin 2'-O-glucoside	$C_{21}H_{24}O_{11}$	24.659	[M–H]⁻	452.1319	451.1246	451.1249	0.7	289, 273	HW
80	Phloridzin	$C_{21}H_{24}O_{10}$	56.168	[M–H]⁻	436.1369	435.1296	435.1295	−0.2	273	HW
				Dihydroflavonols						
81	Dihydromyricetin 3-O-rhamnoside	$C_{21}H_{22}O_{12}$	23.549	** [M–H]⁻	466.1111	465.1038	465.1031	−1.5	301	* HW, SG
82	Dihydroquercetin	$C_{15}H_{12}O_7$	38.674	[M–H]⁻	304.0583	303.0510	303.0518	2.6	285, 275, 151	HW
				Other Polyphenols						
				Hydroxybenzoketones						
83	2-Hydroxy-4-methoxyacetophenone 5-sulfate	$C_9H_{10}O_7S$	12.844	[M–H]⁻	262.0147	261.0074	261.0069	−1.9	181, 97	SG
				Furanocoumarins						
84	Isopimpinellin	$C_{13}H_{10}O_5$	11.626	** [M+H]⁺	246.0528	247.0601	247.0593	−3.2	232, 217, 205, 203	SG, *OHW
				Hydroxycoumarins						
85	Esculetin	$C_9H_6O_4$	27.972	[M–H]⁻	178.0266	177.0193	177.0183	-5.0	149, 133, 89	HW
86	Urolithin A	$C_{13}H_8O_4$	48.909	[M–H]⁻	228.0423	227.0350	227.0345	-2.2	198, 182	SG

Table 2. *Cont.*

No.	Molecular Formula	Proposed Compounds	RT (min)	Ionization (ESI$^+$/ESI$^-$)	Molecular Weight	Theoretical (*m/z*)	Observed (*m/z*)	Error (ppm)	MS^2 Product Ion	Kiwifruit
				Other Polyphenols						
87	Arbutin	$C_{12}H_{16}O_7$	7.393	** [M–H]$^-$	272.0896	271.0823	271.0824	0.4	109	* SG, OHW
88	Salvianolic acid B	$C_{36}H_{30}O_{16}$	27.074	[M–H]$^-$	718.1534	717.1461	717.1484	3.2	519, 339, 321, 295	SG
				Tyrosols						
89	Demethyloleuropein	$C_{24}H_{30}O_{13}$	12.181	[M–H]$^-$	526.1686	525.1613	525.1624	2.1	495	SG
90	Hydroxytyrosol 4-*O*-glucoside	$C_{14}H_{20}O_8$	14.338	[M–H]$^-$	316.1158	315.1085	315.1090	1.6	153, 123	HW
91	3,4-DHPEA-AC	$C_{10}H_{12}O_4$	25.537	[M–H]$^-$	196.0736	195.0663	195.0658	−2.6	135	HW
				Stilbenes						
92	4-Hydroxy-3,5,4′-trimethoxystilbene	$C_{17}H_{18}O_4$	29.782	[M+H]$^+$	286.1205	287.1278	287.1279	0.3	271, 241, 225	SG
				Lignans						
93	Enterolactone	$C_{18}H_{18}O_4$	4.234	** [M+H]$^+$	298.1205	299.1278	299.1279	0.3	281, 187, 165	SG, OHW, * HW
94	Schisandrol B	$C_{23}H_{28}O_7$	7.833	[M+H]$^+$	416.1835	417.1908	417.1896	−2.9	224, 193, 165	OHW
95	Schisandrin C	$C_{22}H_{24}O_6$	11.013	[M+H]$^+$	384.1573	385.1646	385.1632	−3.6	386	OHW
96	7-Oxomatairesinol	$C_{20}H_{20}O_7$	19.212	[M+H]$^+$	372.1209	373.1282	373.1293	2.9	358, 343, 328, 325	OHW
97	Todolactol A	$C_{20}H_{24}O_7$	22.552	[M–H]$^-$	376.1522	375.1449	375.1454	1.3	313, 137	SG

Ionization mode with ** represents that the compound was detected in both positive and negative modes, but only one mode's data are presented. For compounds found in more than one samples, only results for samples with * are shown in the table. Kiwifruit samples mentioned in abbreviations are Hayward "HW", round organic Hayward "OHW", SunGold "SG". RT is short for retention time.

3.3.1. Phenolic Acids

As shown in Table 2, a total of 28 phenolic acids were tentatively characterized in Hayward, SunGold, and round organic Hayward kiwifruit, which includes hydroxybenzoic acids (9), hydroxycinnamic acids (16), hydroxyphenylacetic acids (2), and hydroxyphenylpropanoic acid (1). Hydroxycinnamic acid was the predominant sub-class, followed by hydroxybenzoic acid.

Hydroxybenzoic Acids

In this study, a total of nine hydroxybenzoic acid derivatives were identified. Five of them were detected in both SunGold and Hayward. Compound **4** ([M–H]$^-$ *m/z* at 137.0247), compound **5** ([M–H]$^-$ *m/z* at 169.0140), and compound **7** ([M–H]$^-$ *m/z* at 153.0196) were tentatively characterized as 2-hydroxybenzoic acid, gallic acid, and 2,3-dihydroxybenzoic acid based on the product ions at *m/z* 93, at *m/z* 125, and at *m/z* 109, respectively. All three fragment ions were generated from the loss of CO_2 (44 Da) from their respective precursor ions [49,50]. Previously, Dawes and Keene [51] also identified protocatechuic acid and dihydroxybenzoic acid derivative in Hayward kiwifruit juice. 3-*O*-methylgallic acid (compound **6**) was found only in Hayward, which was previously found by Gabriela, et al. [52] in wild berries.

There were three compounds detected only in SunGold in negative ionization mode, including gallic acid 4-*O*-glucoside (compound **1**), 4-hydroxybenzoic acid 4-*O*-glucoside (compound **3**), and paeoniflorin (compound **9**). 4-hydroxybenzoic acid 4-*O*-glucoside was previously characterized in strawberry by Fotiric Aksic, et al. [53] and in *Cedrus brevifolia* by Douros, et al. [54]. According to Sroka and Cisowski [55], gallic acid, protocatechuic acid, and 2,3-dihydroxybenzoic acid demonstrated good DPPH radical scavenging ability, reaching elimination of 75%, 41%, and 47%, respectively. In our study, gallic acid, protocatechuic acid, and 2,3-dihydroxybenzoic acid was present only in SunGold and Hayward samples, and the presence of these phenolic compounds may have contributed to their relatively higher antioxidant activities.

Hydroxycinnamic Acids

In this study, hydroxycinnamic acid derivatives were the most predominant phenolic acids in the three kiwifruit samples. In this work, a total of 16 hydroxycinnamic acids were tentatively identified. Compound **13** was detected in the SunGold sample with *m/z* 179.0350 and was suggested to be caffeic acid based on the fragmentation in MS^2 spectrum, which displayed product ions at *m/z* 143 (M–H–36, loss of 2 H_2O) and *m/z* 133 (M–H–46, loss of HCOOH) [56]. Caffeic acid was previously found in many fruits, such as blueberry, carambola, citrus, mango, papaya, peach, and plum [57]. Our study also characterized three caffeic acid derivatives, including caffeoyl glucose (compound **12**), caffeic acid 3-*O*-glucuronide (compound **14**), and 3-caffeoylquinic acid (compound **22**). Caffeic acid and 3-caffeoylquinic acid have been reported to possess a marked ability to inhibit lipid peroxidization and to scavenge hydrogen peroxide and free radicals [55].

Compound **10** detected in round organic Hayward and SunGold samples was tentatively characterized as cinnamic acid. Previously, cinnamic acid was characterized in wild edible mushrooms (*R. patagonica*) by Toledo, et al. [58]. Compound **20** was tentatively identified as ferulic acid, which was previously found in pineapple, papaya and orange [57]. Two ferulic acid derivatives were identified in kiwifruit samples, including ferulic acid 4-*O*-glucoside and ferulic acid 4-*O*-glucuronide. Ferulic acid 4-*O*-glucuronide was previously reported to be found in glechomae herba by Luo, et al. [59].

Furthermore, 1-sinapoyl-2-feruloylgentiobiose (compounds **25**) was characterized in *Brassica* plant by Sousa, et al. [60]. Sinapic acid (compound **23**) detected in both SunGold and Hayward samples was previously found in citrus fruits [61]. To the best of our knowledge, this is the first time that 1-sinapoyl-2-feruloylgentiobiose and sinapic acid were identified in rejected kiwifruit.

Hydroxyphenylacetic Acids and Hydroxyphenylpropanoic Acids

Compound **26** was observed in all three kiwifruit extracts in different modes and was tentatively characterized as 3,4-dihydroxyphenylacetic acid. Previously, no study recorded the observation of 3,4-dihydroxyphenylacetic acid in kiwifruit, but it was detected in Danhong injection and olive oil [62].

Compound **28** (dihydroferulic acid 4-*O*-glucuronide) was detected only in the negative ionization mode with the [M–H]$^-$ precursor ions at *m/z* 371.0990. The characteristic loss of the glucuronide (176 Da) moiety was observed, which produced the product ions at *m/z* 195 and at *m/z* 181 from compound **28** [63].

3.3.2. Flavonoids

Flavonoids are phytochemicals with excellent antioxidant potential and were the most abundant class of phenolic compounds present in the rejected kiwifruit samples. A total of 54 flavonoids were identified and further divided into eight subclasses, including flavonols (12), flavanols (9), flavones (7), flavanones (4), dihydrochalcones (3), dihydroflavonols (2), anthocyanins (7), and isoflavonoids (10).

Flavonols

There were three kaempferol derivatives, including compound **32** (kaempferol 3,7-*O*-diglucoside, [M–H]$^-$ at *m/z* 609.1462); compound **33** (kaempferol 3-*O*-glucosyl-rhamnosyl-galactoside, [M–H]$^-$ at *m/z* 755.2034); and compound **34** (kaempferol 3-*O*-(2''-rhamnosyl-galactoside) 7-*O*-rhamnoside, [M–H]$^-$ at *m/z* 739.2060); which were detected in both negative and positive modes. In the MS^2 fragmentation of compound **32**, the characteristic product ions at *m/z* 447 and *m/z* 285 were observed, representing the loss of glucoside and the consecutive loss of glucoside from the parent ion [64]. In terms of compounds **33** and **34**, product ions at *m/z* 285 (loss of the sugar unit) enabled the identification of kaempferol 3-*O*-glucosyl-rhamnosyl-galactoside [65], while peaks at *m/z* 593 [M–H-$C_6H_{10}O_4$], *m/z* 447 [M–H-$2C_6H_{10}O_4$], and *m/z* 285 [M–H-$2C_6H_{10}O_4$-$C_6H_{10}O_5$] allowed for the identification of kaempferol 3-O-(2''-rhamnosyl-galactoside) 7-O-rhamnoside [66]. Previously, compounds **32** and **34** were identified in different fruits, such as peach, pear, and papaya [67].

There were four compounds characterized as quercetin derivatives in the present work. Quercetin 3-*O*-glucosyl-xyloside (compound **31**) was detected in both SunGold and Hayward samples, and the compound was previously characterized in phalsa (*Grewia asiatica*) fruit by Koley, et al. [68]. Compounds **35** and **38** were identified as quercetin 3-*O*-xylosyl-glucuronide and quercetin 3-*O*-arabinoside, respectively. Compound **36** detected in SunGold and Hayward samples was tentatively characterized as quercetin 3'-*O*-glucuronide. Our results are in line with Zhu, et al. [69], who also found quercetin 3'-*O*-glucuronide in kiwifruit.

Flavanols

In our study, catechin derivatives were the main flavanols found in Hayward and SunGold extracts. Hayward showed a higher diversity of flavanols, while there was no flavanol detected in round organic Hayward extract. A total of four catechin derivatives were identified in both SunGold and Hayward extracts. Compound **42** was present in Hayward, and with [M–H]$^-$ *m/z* at 441.0805 and fragments at *m/z* 289 [M–H-$C_7H_5O_4$], *m/z* 169 [M–H-$C_7H_5O_4$-C_8H_8O], and *m/z* 125 [M–H-$C_7H_5O_4$-C_8H_8O-CO_2], it was identified as (+)-catechin 3-*O*-gallate [70]. Compound **43** was tentatively identified as (+)-catechin ([M–H]$^-$ *m/z* at 289.0714), based on the fragmentation that showed the product ions at *m/z* 245, *m/z* 205, and *m/z* 179, corresponding to the loss of CO_2 (44 Da), flavonoid A ring (84 Da), and flavonoid B ring (110 Da) from the precursor ion, respectively [49]. Previously, (+)-catechin had been reported in kiwifruit by Pérez-Burillo, et al. [11].

Compounds **45** and **46** were identified as 4'-*O*-methyl-(-)-epigallocatechin 7-*O*-glucuronide and 4''-*O*-methylepigallocatechin 3-*O*-gallate, respectively. Previously, the presence of catechin, epicatechin, and epigallocatechin gallate in Hayward kiwifruit was also reported [20].

Flavanones and Flavones

A total of four flavanones were identified in extracts of Hayward, SunGold, and round organic Hayward, of which two of the flavanones were hesperetin derivatives. Compounds 50 and 53 were tentatively identified as hesperetin 3′,7-*O*-diglucuronide and hesperetin 3′-*O*-glucuronide based on *m/z* at 653.1361 and *m/z* 477.1039. The presence of hesperetin 3′,7-*O*-diglucuronide was confirmed by the product ions at *m/z* 477 [M–H–glucuronide, loss of 176 Da], *m/z* 301 [M–H-2 glucuronides, loss of 352 Da], *m/z* 286 [M–H–2 glucuronides–CH₃, loss of 367 Da], and *m/z* 242 [M–H–2 glucuronides–OCH₂-CHO] [71]. The tentative identity of hesperetin 3′-*O*-glucuronide was determined by the product ions at *m/z* 301 [M–H–glucuronyl moiety, loss of 176 Da], *m/z* 175 [M–H–hesperetin, loss of 302 Da], *m/z* 113 [M–H–hesperetin–CO_2–H_2O, loss of 364 Da], and *m/z* 85 [M–H–hesperetin–CO_2–H_2O–CO, loss of 392 Da] [72].

Seven flavones were tentatively identified in the current work. Compound **55** was detected only in positive mode and was characterized as cirsilineol based on the [M + H]⁺ at *m/z* 345.0962. In the MS² spectrum, major fragments at *m/z* 330 [M + H–CH₃], *m/z* 312 [M + H–CH₃–H_2O], *m/z* 297 [M + H–2CH₃–H_2O], and 284 [M + H–CH₃–H_2O-CO] were recorded, which led to the identification of cirsilineol [73]. Three apigenin glucoside derivatives were also identified in three kiwifruit extracts, including apigenin 7-*O*-glucuronide (compound **54**), apigenin 6,8-di-*C*-glucoside (compound **56**), and apigenin 6-*C*-glucoside (compound **58**).

Isoflavonoids and Anthocyanins

A total of 10 isoflavonoids were identified in three kiwifruit cultivars. Among the three cultivars, SunGold was found to be the best source of isoflavonoids, with nine identified isoflavonoids. Four daidzein derivatives were found in SunGold, including 6″-*O*-acetyldaidzin (compound **66**) and 3′-hydroxydaidzein (compound **68**). Additionally, 6″-*O*-acetyldaidzin was identified by the intensive peaks at *m/z* 221, indicating the loss of $C_{15}H_8O_3$ (236 Da) from the precursor [74]. Previously, daidzein was found mainly in soy and soy products [75]. Two glyciteins were identified in SunGold sample in positive ionization mode, which included 6″-*O*-acetylglycitin (compound **61**) and 6″-*O*-malonylglycitin (compound **64**). To our best knowledge, characterization of daidzein and glycitein in kiwifruit is unprecedented.

A total of seven anthocyanins were found in three kiwifruit cultivars, among which cyanidin and delphinidin glycoside derivatives were highly represented. Anthocyanins—which are commonly found in berries such as gooseberry, black chokeberry, and blackcurrant—can act as antioxidant and have potential health effects in humans [76]. Compounds **71**, **72**, **73**, **74**, **75**, and **77** (Table 2) were tentatively identified as cyanidin 3-*O*-(6″-*p*-coumaroyl-glucoside), cyanidin 3-*O*-diglucoside-5-*O*-glucoside, cyanidin 3,5-*O*-diglucoside, delphinidin 3-*O*-xyloside, delphinidin 3-*O*-galactoside, and delphinidin 3-*O*-glucosyl-glucoside. Kähkönen, et al. [76] reported cyanidin-3-glucoside and cyanidin-3-rutinoside in blackcurrant. According to Hidalgo, et al. [77], both cyanidin-3-*O*-glucoside and delphinidin-3-*O*-glucoside possessed strong DPPH radical scavenging capacity, and these two anthocyanins may have contributed to the antioxidative effects in the antioxidant assays.

Dihydrochalcones and Dihydroflavonols

Three dihydrochalcones and two dihydroflavonols were observed in Hayward and SunGold samples, whereas none were detected in round organic Hayward sample. 3-hydroxyphloretin 2′-*O*-glucoside (compound **79**) was confirmed by fragment ions at *m/z* 289 [M–H–glucoside] and *m/z* 273 (phloretin) [78]. Compound **81** was tentatively identified as dihydromyricetin 3-*O*-rhamnoside. Previously, the presence of dihydromyricetin 3-*O*-rhamnoside was reported in red wine [79].

3.3.3. Other Polyphenols

From the rejected kiwifruit, a total of nine other polyphenols were identified, which were further divided into subclasses hydroxycoumarins (2), hydroxybenzoketones (1), furanocoumarins (1), tyrosols (3), and other polyphenols (2).

Hydroxycoumarins, Hydroxybenzoketones, and Furanocoumarins

Compound **85** with [M–H]$^-$ at *m/z* 177.0183 was found only in negative mode and was identified as esculetin. It was identified based on the product ions at *m/z* 149, *m/z* 133, and *m/z* 89, representing the loss of CO (28 Da), CO_2 (44 Da), and $2CO_2$ (88 Da), respectively, from the parent ion [80]. Isopimpinellin (compound **84**) was the only furanocoumarins found in round organic Hayward and SunGold kiwifruit.

Tyrosols and Other Polyphenols

Compound **88** was identified as salvianolic acid B, which was present in negative ionization mode and detected only in SunGold. Compound **90** and compound **91** were found in Hayward only in negative ionization mode. The two compounds were identified as hydroxytyrosol 4-*O*-glucoside and 3,4-DHPEA-AC based on the [M–H]$^-$ at *m/z* 315.1090 and *m/z* 195.0658, respectively. 3,4-DHPEA-AC was confirmed by the product ion at *m/z* 135 [M–H–$C_2H_4O_2$] [81], while hydroxytyrosol 4-*O*-glucoside was identified by the peaks at *m/z* 153 [M–H–glucoside] and *m/z* 123 [M–H–glucoside–CH_2O] [82]. Previously, tyrosols including *p*-HPEA-EDA, 3,4-DHPEA-AC and *p*-HPEA-AC were found in olive oil [83].

3.3.4. Lignans and Stilbenes

A total of five lignans were found in three kiwifruit cultivars, and round organic Hayward had the most abundant lignans. Compound **93** was present in both positive and negative modes and was identified as enterolactone, according to the [M + H]$^+$ at *m/z* 299.1279. Enterolactone produced product ions at *m/z* 281, *m/z* 187, and *m/z* 165, corresponding to the loss of H_2O (18 Da), $C_6H_8O_2$ (112 Da), and $C_9H_8O_2$ (134 Da) from the precursor ion, respectively [84]. Sapozhnikova, et al. [85] reported the presence of enterolactone in grape juice and green tea. Previously, there have been very few studies conducted to identify lignans in kiwifruit.

4-hydroxy-3,5,4′-trimethoxystilbene (compound **92**) was the only stilbene identified in SunGold. To our knowledge, this is the first time that 4-hydroxy-3,5,4′-trimethoxystilbene was reported in kiwifruit.

3.4. Distribution of Phenolic Compounds—Venn Diagram

The Venn diagrams of Hayward, SunGold, and organic Hayward were constructed to visually represent the distribution of phenolic compounds in different kiwifruit varieties. The phenolic compounds tentatively characterized in kiwifruit samples were divided into phenolic acid, flavonoids, and other phenolic compounds.

As shown in Figure 1A, a total of 320 phenolic compounds were identified in three kiwifruit varieties, of which 33 were phenolic compounds shared among all three cultivars, accounting for 10.3% of all phenolic compounds. Hayward and SunGold samples displayed similar phenolic profiles, with 55.3% of the total phenolic compounds identified in both cultivars, while only 12.2% of phenolic compounds were found in both Hayward and round organic Hayward. According to Figure 1B, 17.2% of phenolic acids were common in all samples. Hayward and SunGold samples had the most similar phenolic acids profile, while Hayward and round organic Hayward were dissimilar in their phenolic acids profile. Figure 1C indicates that the three studied kiwifruit cultivars shared fewer flavonoids, where only 3.2% of flavonoids were common among all samples. As shown in Figure 1D, 17.2% of other phenolic compounds were common among all samples. Notably, Hayward and SunGold had the highest proportion (49.5%) of shared other phenolic compounds.
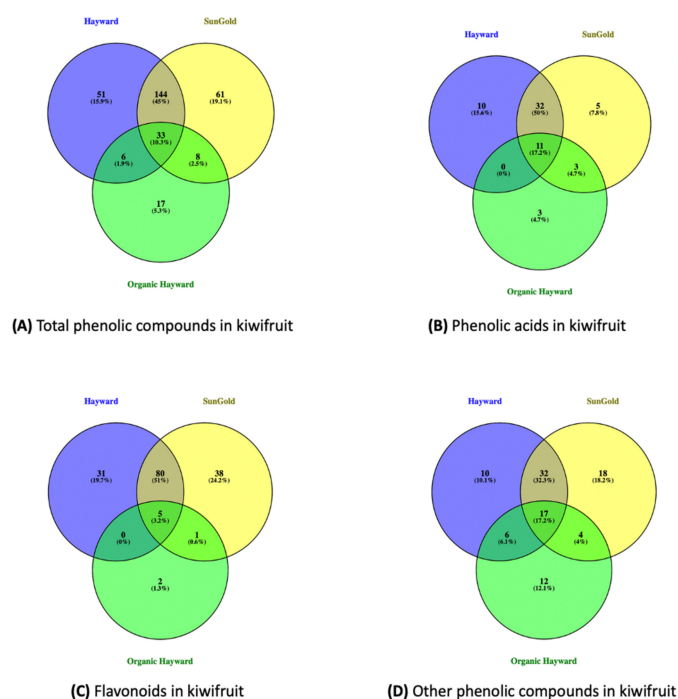
Figure 1. Venn diagram of phenolic compounds present in kiwifruit samples. The similarity of total phenolic compounds (**A**), phenolic acids (**B**), flavonoids (**C**), and other phenolic compounds (**D**) profiles between the three kiwifruit cultivars.

The three samples shared the least percentage of flavonoids, indicating that the difference in flavonoid levels may be one of the main reasons responsible for the observed difference in TPC, TFC, and antioxidant capacity. Previous research reported that green kiwifruit had richer phenolic acids and flavonoids contents and stronger antioxidant ability than golden kiwifruit [86]. For example, protocatechuic acid, (−)-epicatechin, (+)-catechin, neochlorogenic acid, and rutin found only in Hayward can act as free radicals and hydrogen peroxide scavengers, as well as lipid peroxidation inhibitors [55]. Moreover, Hayward and SunGold samples had the most comparable phenolic profile, while Hayward and round organic Hayward shared the fewest phenolic compounds. In addition to fruit varieties, growing conditions also can affect phenolic content and composition [11,87]. However, Park, et al. [12] stated that organically and conventionally grown kiwifruit exhibited similar bioactive compound content, but difference in polyphenol content was notable when comparing between cultivars. Further studies could be performed to elucidate the complex factors that influence the bioactive compound composition in kiwifruit.

3.5. HPLC-PDA Quantification

HPLC was deployed to quantify the phenolic compounds. As demonstrated in Table 3, a total of 10 phenolic compounds were targeted based on the LC-ESI-QTOF-MS/MS characterization, which included five phenolic acids (gallic acid, protocatechuic acid, *p*-hydroxybenzoic acid, chlorogenic acid, and caffeic acid) and five flavonoids (catechin, epicatechin, epicatechin gallate, quercetin, and kaempferol).

Table 3. Quantitative analysis of phenolic compounds in kiwifruit.

No.	Compounds Name	Chemical Formula	RT (min)	SunGold (mg/g)	Hayward (mg/g)	Round Organic Hayward (mg/g)	Polyphenol Class
1	Gallic acid	$C_7H_6O_5$	6.836	4.58 ± 0.18 [a]	3.67 ± 0.19 [b]	-	Phenolic acids
2	Protocatechuic acid	$C_7H_6O_4$	12.569	1.39 ± 0.07 [c]	4.57 ± 0.27 [a]	2.64 ± 0.21 [b]	Phenolic acids
3	p-Hydroxybenzoic acid	$C_7H_6O_3$	20.240	2.34 ± 0.14 [b]	3.51 ± 0.21 [a]	1.34 ± 0.03 [c]	Phenolic acids
4	Chlorogenic acid	$C_{16}H_{18}O_9$	20.579	19.67 ± 0.78 [b]	23.98 ± 0.95 [a]	12.57 ± 0.62 [c]	Phenolic acids
5	Caffeic acid	$C_9H_8O_4$	25.001	-	4.57 ± 0.22	-	Phenolic acids
6	Catechin	$C_{15}H_{14}O_6$	19.704	14.21 ± 0.71 [b]	23.24 ± 1.16 [a]	17.54 ± 0.87 [b]	Flavonoids
7	Epicatechin	$C_{15}H_{14}O_6$	24.961	5.64 ± 0.23 [a]	5.67 ± 0.28 [a]	2.35 ± 0.11 [b]	Flavonoids
8	Epicatechin gallate	$C_{22}H_{18}O_{10}$	38.015	-	2.14 ± 0.13 [a]	1.21 ± 0.06 [b]	Flavonoids
9	Quercetin	$C_{15}H_{10}O_7$	70.098	24.59 ± 1.23 [a]	18.73 ± 0.75 [b]	12.45 ± 0.62 [c]	Flavonoids
10	Kaempferol	$C_{15}H_{10}O_6$	80.347	5.89 ± 0.29 [a]	2.98 ± 0.15 [b]	3.12 ± 0.16 [b]	Flavonoids

Values expressed as mean ± standard deviation per gram fresh weight (fw); *n* = 3 samples per variety. Values within the same rows with different superscript letters ([a,b,c]) indicate that they are significantly different from each other ($p < 0.05$).

In terms of phenolic acids, all three cultivars possessed relatively high chlorogenic acid levels. A previous study observed lower chlorogenic acid levels in different kiwifruit cultivars, including Hongshi, Jinshi, Jinlong, Hongyang, Jinhong, Honghua, Hort16A, Cuixiang, Xuxiang, and Hayward in the range of 20.94–235.75 µg/g dw. The observed differences may be attributed to the differences in sample genotype and extraction solvent [86]. Interestingly, Hayward exhibited the highest level of protocatechuic acid, *p*-hydroxybenzoic acid, and caffeic acid, with 4.57 ± 0.27, 3.51 ± 0.21, and 4.57 ± 0.22 mg/g, respectively. They also reported that gallic acid was the major individual hydroxybenzoic acid detected in kiwifruit, ranging from 9.12 µg/g DW to 53.76 µg/g dw [86]. The presence of protocatechuic acid has also been reported by Dawes and Keene [51]. In our study, Hayward exhibited abundant phenolic acids since five targeted phenolic acids were all detected in Hayward, whereas caffeic acid was not detectable in SunGold and round organic Hayward. Furthermore, gallic acid was not detected in the round organic Hayward sample.

Among the five targeted flavonoids, catechin and quercetin were the most abundant, ranging from 14.21–23.24 and 12.45–24.59 mg/g, respectively. Guo, et al. [88] found that flavanols were the most abundant phenolic compound detected in kiwifruit juice, accounting for 70% of the total phenolic content. The Hayward sample showed a higher level of catechin, epicatechin, and epicatechin gallate than the other two kiwifruit varieties, while epicatechin gallate was not detected in the SunGold sample. The SunGold sample had the highest quercetin and kaempferol levels, which were observed to be 24.59 ± 1.23 mg/g and 5.89 ± 0.29 mg/g, respectively. Previously, Nie, et al. [89] reported relatively lower epicatechin levels in Donghong kiwifruit, ranging from 81.09 to 100.09 µg/mg dw. Relatively lower quercetin levels in golden and green kiwifruit ranging from 4.50–41.94 µg/g dw were observed in a previous study, which may be due to the difference in extraction solvent utilized and the kiwifruit varieties being studied [86].

The Hayward sample recorded the highest levels of phenolic acid and flavonoids. Chlorogenic acid, catechin, and quercetin were the predominant phenolics found in our kiwifruit samples. Hydroxybenzoic acids, hydroxycinnamic acids, and their derivatives, such as protocatechuic acid, gallic acid, and caffeic acid, have been suggested to have excellent free radical scavenging ability [55]. Therefore, the presence of these phenolic compounds indicate that rejected kiwifruit could be exploited as a good source of natural antioxidants that would be beneficial as part of our diet, whether consumed despite their unfavorable appearance or after further processing into other commercial products.

4. Conclusions

The LC-ESI-QTOF-MS/MS analysis was performed to tentatively identify and characterize the phenolic compounds of kiwifruit. Based on the comparison of mass spectrometric data obtained under both negative and positive electron spray ionization modes, a

total of 97 phenolic compounds were tentatively identified, including 28 phenolic acids, 54 flavonoids, 5 lignans, 1 stilbene, and 9 other polyphenols. HPLC-PDA was utilized for the quantification of 10 individual phenolic compounds. Antioxidant assays were conducted for the evaluation of the antioxidant potential of kiwifruit samples. The three varieties of rejected kiwifruit exhibited a relatively high level of phenolic compounds and free radical scavenging activity. In particular, the SunGold variety displayed the greatest TPC result and showed the highest antioxidant potential in DPPH, FRAP, ABTS, OH-RSA, and FICA assays compared with Hayward and round organic Hayward. Overall, this study suggests that rejected kiwifruit are rich in phenolic compounds and could be an excellent source of antioxidants. The phenolic profile of rejected kiwifruit obtained in this study could deliver information and promote further utilization of rejected kiwifruit to reduce wastage.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/pr9050781/s1, Figure S1: LC-ESI-QTOF-MS/MS basic peak chromatograph (BPC) for characterization of phenolic compounds of rejected kiwifruit.

References

1. Stenmarck, Å.; Hanssen, O.J.; Silvennoinen, K.; Katajajuuri, J.-M.; Werge, M. *Initiatives on Prevention of Food Waste in the Retail and Wholesale Trades*; FAO: Rome, Italy, 2011; pp. 7–90.
2. Thyberg, K.L.; Tonjes, D.J., Jr. Drivers of food waste and their implications for sustainable policy development. *Conserv. Recycl.* **2016**, *106*, 110–123. [CrossRef]
3. Jiao, Y.; Quek, S.Y.; Gu, M.; Guo, Y.; Liu, Y. Polyphenols from thinned young kiwifruit as natural antioxidant: Protective effects on beef oxidation, physicochemical and sensory properties during storage. *Food Control* **2020**, *108*, 106870. [CrossRef]
4. Deng, J.; Liu, Q.; Zhang, C.; Cao, W.; Fan, D.; Yang, H. Extraction optimization of polyphenols from waste kiwi fruit seeds (actinidia chinensis planch.) and evaluation of its antioxidant and anti-inflammatory properties. *Molecules* **2016**, *21*, 832. [CrossRef] [PubMed]
5. Ma, T.; Lan, T.; Geng, T.; Ju, Y.; Cheng, G.; Que, Z.; Gao, G.; Fang, Y.; Sun, X. Nutritional properties and biological activities of kiwifruit (actinidia) and kiwifruit products under simulated gastrointestinal in vitro digestion. *Food Nutr. Res.* **2019**, *63*, 63. [CrossRef] [PubMed]
6. Richardson, D.P.; Ansell, J.; Drummond, L.N. The nutritional and health attributes of kiwifruit: A review. *Eur. J. Nutr.* **2018**, *57*, 2659–2676. [CrossRef]
7. Rasouli, H.; Farzaei, M.H.; Khodarahmi, R. Polyphenols and their benefits: A review. *Int. J. Food Prop.* **2017**, *20*, 1700–1741. [CrossRef]

8.   Yahfoufi, N.; Alsadi, N.; Jambi, M.; Matar, C. The immunomodulatory and anti-inflammatory role of polyphenols. *Nutrients* **2018**, *10*, 1618. [CrossRef]

9.   Wang, Y.; Zhao, C.-l.; Li, J.-y.; Liang, Y.-j.; Yang, R.-q.; Liu, J.-y.; Ma, Z.; Wu, L.J.B. Evaluation of biochemical components and antioxidant capacity of different kiwifruit (actinidia spp.) genotypes grown in china. *Biotechnol. Biotechnol. Equip.* **2018**, *32*, 558–565. [CrossRef]

10.   Peng, Y.; Lin-Wang, K.; Cooney, J.M.; Wang, T.; Espley, R.V.; Allan, A.C. Differential regulation of the anthocyanin profile in purple kiwifruit (actinidia species). *Hortic. Res.* **2019**, *6*, 1–16. [CrossRef]

11.   Pérez-Burillo, S.; Oliveras, M.J.; Quesada, J.; Rufián-Henares, J.A.; Pastoriza, S. Relationship between composition and bioactivity of persimmon and kiwifruit. *Food Res. Int.* **2018**, *105*, 461–472. [CrossRef]

12.   Park, Y.S.; Ham, K.-S.; Kang, S.-G.; Park, Y.-K.; Namiesnik, J.; Leontowicz, H.; Leontowicz, M.; Ezra, A.; Trakhtenberg, S.; Gorinstein, S. Organic and conventional kiwifruit, myths versus reality: Antioxidant, antiproliferative, and health effects. *J. Agric. Food Chem.* **2012**, *60*, 6984–6993. [CrossRef] [PubMed]

13.   Leontowicz, H.; Leontowicz, M.; Latocha, P.; Jesion, I.; Park, Y.-S.; Katrich, E.; Barasch, D.; Nemirovski, A.; Gorinstein, S. Bioactivity and nutritional properties of hardy kiwi fruit actinidia arguta in comparison with actinidia deliciosa 'hayward' and actinidia eriantha 'bidan'. *Food Chem.* **2016**, *196*, 281–291. [CrossRef]

14.   Testolin, R.; Huang, H.; Ferguson, A.R. *The Kiwifruit Genome*; Springer: Cham, Switzerland, 2016.

15.   Park, Y.S.; Leontowicz, H.; Leontowicz, M.; Namiesnik, J.; Suhaj, M.; Cvikrová, M.; Martincová, O.; Weisz, M.; Gorinstein, S. Comparison of the contents of bioactive compounds and the level of antioxidant activity in different kiwifruit cultivars. *J. Food Compos. Anal.* **2011**, *24*, 963–970. [CrossRef]

16.   Sobhani, M.; Farzaei, M.H.; Kiani, S.; Khodarahmi, R. Immunomodulatory; anti-inflammatory/antioxidant effects of polyphenols: A comparative review on the parental compounds and their metabolites. *Food Rev. Int.* **2020**, 1–53. [CrossRef]

17.   Rice-Evans, C.; Miller, N.; Paganga, G. Antioxidant properties of phenolic compounds. *Trends Plant Sci.* **1997**, *2*, 152–159. [CrossRef]

18.   Tingting, M.; Tian, L.; Tonghui, G.; Yanlun, J.; Guo, C.; Zhiluo, Q.; Guitian, G.; Yulin, F.; Xiangyu, S. Nutritional properties and biological activities of kiwifruit (actinidia) and kiwifruit products under simulated gastrointestinal in vitro digestion. *Food Nutr. Res.* **2019**, *63*, 1–17.

19.   Bursal, E.; Gülçin, İ. Polyphenol contents and in vitro antioxidant activities of lyophilised aqueous extract of kiwifruit (actinidia deliciosa). *Food Res. Int.* **2011**, *44*, 1482–1489. [CrossRef]

20.   Jiao, Y.; Chen, D.; Fan, M.; Young Quek, S. Uplc-qqq-ms/ms-based phenolic quantification and antioxidant activity assessment for thinned young kiwifruits. *Food Chem.* **2019**, *281*, 97–105. [CrossRef]

21.   Tang, J.; Dunshea, F.R.; Suleria, H.A.R. Lc-esi-qtof/ms characterization of phenolic compounds from medicinal plants (hops and juniper berries) and their antioxidant activity. *Foods* **2020**, *9*, 7. [CrossRef] [PubMed]

22.   Subbiah, V.; Zhong, B.; Nawaz, M.A.; Barrow, C.J.; Dunshea, F.R.; Suleria, H.A. Screening of phenolic compounds in australian grown berries by lc-esi-qtof-ms/ms and determination of their antioxidant potential. *Antioxidants* **2021**, *10*, 26. [CrossRef]

23.   Severo, J.; Tiecher, A.; Chaves, F.C.; Silva, J.A.; Rombaldi, C.V. Gene transcript accumulation associated with physiological and chemical changes during developmental stages of strawberry cv. Camarosa. *Food Chem.* **2011**, *126*, 995–1000. [CrossRef]

24.   Gouveia, S.; Castilho, P.C. Antioxidant potential of artemisia argentea l'hér alcoholic extract and its relation with the phenolic composition. *Food Res. Int.* **2011**, *44*, 1620–1631. [CrossRef]

25.   Zou, B.; Dong, X.-q.; Ge, Z.-Z.; Xu, Z.; Du, J.; Li, C.-M. Development of suitable standards for quantitative determination of persimmon phenol contents in folin-ciocalteu and vanillin assays. *Eur. Food Res. Technol.* **2014**, *239*, 385–391. [CrossRef]

26.   Alvarez-Jubete, L.; Wijngaard, H.; Arendt, E.K.; Gallagher, E. Polyphenol composition and in vitro antioxidant activity of amaranth, quinoa buckwheat and wheat as affected by sprouting and baking. *Food Chem.* **2010**, *119*, 770–778. [CrossRef]

27.   Chen, X.-X.; Feng, H.-L.; Ding, Y.-M.; Chai, W.-M.; Xiang, Z.-H.; Shi, Y.; Chen, Q.-X. Structure characterization of proanthocyanidins from caryota ochlandra hance and their bioactivities. *Food Chem.* **2014**, *155*, 1–8. [CrossRef]

28.   Ferreira, I.C.F.R.; Baptista, P.; Vilas-Boas, M.; Barros, L. Free-radical scavenging capacity and reducing power of wild edible mushrooms from northeast portugal: Individual cap and stipe activity. *Food Chem.* **2007**, *100*, 1511–1516. [CrossRef]

29.   Smirnoff, N.; Cumbes, Q.J. Hydroxyl radical scavenging activity of compatible solutes. *Phytochemistry* **1989**, *28*, 1057–1060. [CrossRef]

30.   Dinis, T.C.P.; Madeira, V.M.C.; Almeida, L.M. Action of phenolic derivatives (acetaminophen, salicylate, and 5-aminosalicylate) as inhibitors of membrane lipid peroxidation and as peroxyl radical scavengers. *Arch. Biochem. Biophys.* **1994**, *315*, 161–169. [CrossRef]

31.   Prieto, P.; Pineda, M.; Aguilar, M. Spectrophotometric quantitation of antioxidant capacity through the formation of a phosphomolybdenum complex: Specific application to the determination of vitamin e. *Anal. Biochem.* **1999**, *269*, 337–341. [CrossRef]

32.   Hong, Y.; Wang, Z.; Barrow, C.J.; Dunshea, F.R.; Suleria, H.A. High-throughput screening and characterization of phenolic compounds in stone fruits waste by lc-esi-qtof-ms/ms and their potential antioxidant activities. *Antioxidants* **2021**, *10*, 234. [CrossRef]

33.   Feng, Y.; Dunshea, F.R.; Suleria, H.A.R. Lc-esi-qtof/ms characterization of bioactive compounds from black spices and their potential antioxidant activities. *J. Food Sci. Technol.* **2020**, *57*, 4671–4687. [CrossRef] [PubMed]

34. Xiaoan, L.; Qinghong, L.; Fan, G.; Cong, H.; Peng, J.; Yonghua, Z. Effect of cutting styles on quality and antioxidant activity in fresh-cut pitaya fruit. *Postharvest Biol. Technol.* **2017**, *124*, 1–7.

35. Abbas, M.; Saeed, F.; Anjum, F.M.; Afzaal, M.; Tufail, T.; Bashir, M.S.; Ishtiaq, A.; Hussain, S.; Suleria, H.A.R. Natural polyphenols: An overview. *Int. J. Food Prop.* **2017**, *20*, 1689–1699. [CrossRef]

36. Kheirkhah, H.; Baroutian, S.; Quek, S.Y. Evaluation of bioactive compounds extracted from hayward kiwifruit pomace by subcritical water extraction. *Food Bioprod. Process.* **2019**, *115*, 143–153. [CrossRef]

37. Dea, A.; Ingrid, B.; Tanel, K.; Mati, R.; Marina, H.; Anne, L.; Tõnu, P. Changes in polyphenols contents and antioxidant capacities of organically and conventionally cultivated tomato (solanum lycopersicum l.) fruits during ripening. *Int. J. Anal. Chem.* **2017**, *2017*, 2367453.

38. He, X.; Fang, J.; Chen, X.; Zhao, Z.; Li, Y.; Meng, Y.; Huang, L. Actinidia chinensis planch.: A review of chemistry and pharmacology. *Front. Pharmacol.* **2019**, *10*, 236. [CrossRef] [PubMed]

39. Li-Li, Z.; Zhen-Yu, W.; Zi-Luan, F.; Shuang-Qi, T.; Jia-Ren, L. Evaluation of antioxidant and antiproliferative properties of three actinidia (actinidia kolomikta, actinidia arguta, actinidia chinensis) extracts in vitro. *Int. J. Mol. Sci.* **2012**, *13*, 5506–5518.

40. Inil, L.; Sungbin, I.; Cheng-Ri, J.; Ho Jin, H.; Youn-Sup, C.; Moo-Yeol, B.; Dae-Ok, K. Effect of maturity stage at harvest on antioxidant capacity and total phenolics in kiwifruits (actinidia spp.) grown in korea. *Hortic. Environ. Biotechnol.* **2015**, *56*, 841–848.

41. Hwang, J.-S.; Cho, C.H.; Baik, M.-Y.; Park, S.-K.; Heo, H.J.; Cho, Y.-S.; Kim, D.-O. Effects of freeze-drying on antioxidant and anticholinesterase activities in various cultivars of kiwifruit (actinidia spp.). *Food Sci. Biotechnol.* **2017**, *26*, 221–228. [CrossRef]

42. Latocha, P.; Wołosiak, R.; Worobiej, E.; Krupa, T. Clonal differences in antioxidant activity and bioactive constituents of hardy kiwifruit (actinidia arguta) and its year-to-year variability. *J. Sci. Food Agric.* **2013**, *93*, 1412–1419. [CrossRef]

43. Jeong, H.R.; Kim, K.J.; Lee, S.G.; Cho, H.S.; Cho, Y.S.; Kim, D.O. Phenolic profiles of hardy kiwifruits and their neuroprotective effects on pc-12 and sh-sy5y cells against oxidative stress. *J. Microbiol. Biotechnol.* **2020**, *30*, 912–919. [CrossRef]

44. Wang, Z.; Barrow, C.J.; Dunshea, F.R.; Suleria, H.A.R. A comparative investigation on phenolic composition, characterization and antioxidant potentials of five different australian grown pear varieties. *Antioxidants* **2021**, *10*, 151. [CrossRef]

45. Canabady-Rochelle, L.L.; Harscoat-Schiavo, C.; Kessler, V.; Aymes, A.; Fournier, F.; Girardet, J.-M. Determination of reducing power and metal chelating ability of antioxidant peptides: Revisited methods. *Food Chem.* **2015**, *183*, 129–135. [CrossRef] [PubMed]

46. Ozen, T.; Zenginbal, H.; Yazicioglu, E.; Gul, F.; Demirtas, I. A comparison investigation on antioxidant activities, physicochemical properties and phytochemical contents of kiwifruit genotypes and cultivars. *Int. J. Fruit Sci.* **2019**, *19*, 115–135. [CrossRef]

47. Suleria, H.A.R.; Barrow, C.J.; Dunshea, F.R. Screening and characterization of phenolic compounds and their antioxidant capacity in different fruit peels. *Foods* **2020**, *9*, 1206. [CrossRef]

48. Guorong, D.; Mingjun, L.; Fengwang, M.; Dong, L. Antioxidant capacity and the relationship with polyphenol and vitamin c in actinidia fruits. *Food Chem.* **2009**, *113*, 557–562.

49. Escobar-Avello, D.; Lozano-Castellón, J.; Mardones, C.; Pérez, A.J.; Sáez, V.; Riquelme, S.; von Baer, D.; Vallverdú-Queralt, A. Phenolic profile of grape canes: Novel compounds identified by lc-esi-ltq-orbitrap-ms. *Molecules* **2019**, *24*, 3763.

50. Wang, X.; Yan, K.; Ma, X.; Li, W.; Chu, Y.; Guo, J.; Li, S.; Zhou, S.; Zhu, Y.; Liu, C. Simultaneous determination and pharmacokinetic study of protocatechuic aldehyde and its major active metabolite protocatechuic acid in rat plasma by liquid chromatography-tandem mass spectrometry. *J. Chromatogr. Sci.* **2016**, *54*, 697–705. [CrossRef]

51. Dawes, H.M.; Keene, J.B. Phenolic composition of kiwifruit juice. *J. Agric. Food Chem.* **1999**, *47*, 2398–2403. [CrossRef]

52. Gabriela, S.; Simona, L.; Tomescu, A.; Sirbu, R. Evaluation of antioxidant capacities and phenols composition of wild and cultivated berries. *Rev. Chim.* **2019**, *70*, 373–377.

53. Fotiric Aksic, M.; Tosti, T.; Sredojević, M.; Milivojević, J.; Meland, M.; Natić, M. Comparison of sugar profile between leaves and fruits of blueberry and strawberry cultivars grown in organic and integrated production system. *Plants* **2019**, *8*, 205. [CrossRef]

54. Douros, A.; Christopoulou, A.; Kikionis, S.; Nikolaou, K.; Skaltsa, H. Volatile components of heartwood, sapwood, and resin from a dated cedrus brevifolia. *Nat. Prod. Commun.* **2019**, *14*, 1934578X19859125. [CrossRef]

55. Sroka, Z.; Cisowski, W. Hydrogen peroxide scavenging, antioxidant and anti-radical activity of some phenolic acids. *Food Chem. Toxicol.* **2003**, *41*, 753–758. [CrossRef]

56. Lin, H.; Zhu, H.; Tan, J.; Wang, H.; Wang, Z.; Li, P.; Zhao, C.; Liu, J. Comparative analysis of chemical constituents of moringa oleifera leaves from china and india by ultra-performance liquid chromatography coupled with quadrupole-time-of-flight mass spectrometry. *Molecules* **2019**, *24*, 942. [CrossRef]

57. Ma, Y.Q.; Ye, X.Q.; Fang, Z.X.; Chen, J.C.; Xu, G.H.; Liu, D.H. Phenolic compounds and antioxidant activity of extracts from ultrasonic treatment of satsuma mandarin (citrus unshiu marc.) peels. *J. Agric. Food Chem.* **2008**, *56*, 5682–5690. [CrossRef]

58. Toledo, C.V.; Barroetaveña, C.; Fernandes, Â.; Barros, L.; Ferreira, I.C.F.R. Chemical and antioxidant properties of wild edible mushrooms from native nothofagus spp. Forest, Argentina. *Molecules* **2016**, *21*, 1201. [CrossRef] [PubMed]

59. Luo, Y.; Wen, Q.; Yang, S.; Feng, Y.; Tan, T. Chemical composition and anti-complement activity of glechomae herba collected in different months. *Biomed. Chromatogr.* **2020**, *34*, e4762. [CrossRef] [PubMed]

60. Sousa, C.; Valentão, P.; Rangel, J.; Lopes, G.; Pereira, J.A.; Ferreres, F.; Seabra, R.M.; Andrade, P.B. Influence of two fertilization regimens on the amounts of organic acids and phenolic compounds of tronchuda cabbage (brassica oleracea l. Var. Costata dc). *J. Agric. Food Chem.* **2005**, *53*, 9128–9132. [CrossRef]

61. Sun, Y.; Qiao, L.; Shen, Y.; Jiang, P.; Chen, J.; Ye, X. Phytochemical profile and antioxidant activity of physiological drop of citrus fruits. *J. Food Sci.* **2013**, *78*, C37–C42. [CrossRef]

62. Carrasco-Pancorbo, A.; Cerretani, L.; Bendini, A.; Segura-Carretero, A.; Del Carlo, M.; Gallina-Toschi, T.; Lercker, G.; Compagnone, D.; Fernández-Gutiérrez, A. Evaluation of the antioxidant capacity of individual phenolic compounds in virgin olive oil. *J. Agric. Food Chem.* **2005**, *53*, 8918–8925. [CrossRef] [PubMed]

63. Sasot, G.; Martínez-Huélamo, M.; Vallverdú-Queralt, A.; Mercader-Martí, M.; Estruch, R.; Lamuela-Raventós, R.M. Identification of phenolic metabolites in human urine after the intake of a functional food made from grape extract by a high resolution ltq-orbitrap-ms approach. *Food Res. Int.* **2017**, *100*, 435–444. [CrossRef] [PubMed]

64. Guijarro-Díez, M.; Nozal, L.; Marina, M.L.; Crego, A.L. Metabolomic fingerprinting of saffron by lc/ms: Novel authenticity markers. *Anal. Bioanal. Chem.* **2015**, *407*, 7197–7213. [CrossRef] [PubMed]

65. Kadam, D.; Palamthodi, S.; Lele, S.S. Lc–esi-q-tof–ms/ms profiling and antioxidant activity of phenolics from l. Sativum seedcake. *J. Food Sci. Technol.* **2018**, *55*, 1154–1163. [CrossRef] [PubMed]

66. Gong, L.; Haiyu, X.; Wang, L.; Xiaojie, Y.; Huijun, Y.; Songsong, W.; Cheng, L.; Ma, X.; Gao, S.; Liang, R.; et al. Identification and evaluation of the chemical similarity of yindan xinnaotong samples by ultra high performance liquid chromatography with quadrupole time-of-flight mass spectrometry fingerprinting. *J. Sep. Sci.* **2016**, *39*, 611–622. [CrossRef]

67. Santin, M.; Castagna, A.; Miras-Moreno, B.; Rocchetti, G.; Lucini, L.; Hauser, M.-T.; Ranieri, A. Beyond the visible and below the peel: How uv-b radiation influences the phenolic profile in the pulp of peach fruit. A biochemical and molecular study. *Front. Plant. Sci.* **2020**, *11*, 579063. [CrossRef]

68. Koley, T.K.; Khan, Z.; Oulkar, D.; Singh, B.; Bhatt, B.P.; Banerjee, K. Profiling of polyphenols in phalsa (grewia asiatica l) fruits based on liquid chromatography high resolution mass spectrometry. *J. Food Sci. Technol.* **2020**, *57*, 606–616. [CrossRef] [PubMed]

69. Zhu, M.; Huang, Y.; Wang, Y.; Shi, T.; Zhang, L.; Chen, Y.; Xie, M. Comparison of (poly)phenolic compounds and antioxidant properties of pomace extracts from kiwi and grape juice. *Food Chem.* **2019**, *271*, 425–432. [CrossRef]

70. Wang, J.; Jia, Z.; Zhang, Z.; Wang, Y.; Liu, X.; Wang, L.; Lin, R. Analysis of chemical constituents of melastoma dodecandrum lour. By uplc-esi-q-exactive focus-ms/ms. *Molecules* **2017**, *22*, 476. [CrossRef]

71. Zeng, X.; Su, W.; Bai, Y.; Chen, T.; Yan, Z.; Wang, J.; Su, M.; Zheng, Y.; Peng, W.; Yao, H. Urinary metabolite profiling of flavonoids in chinese volunteers after consumption of orange juice by uflc-q-tof-ms/ms. *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.* **2017**, *1061–1062*, 79–88. [CrossRef]

72. Zeng, X.; Su, W.; Zheng, Y.; Liu, H.; Li, P.; Zhang, W.; Liang, Y.; Bai, Y.; Peng, W.; Yao, H. Uflc-q-tof-ms/ms-based screening and identification of flavonoids and derived metabolites in human urine after oral administration of exocarpium citri grandis extract. *Molecules* **2018**, *23*, 895. [CrossRef]

73. Pandey, R.; Kumar, B. Hplc–qtof–ms/ms-based rapid screening of phenolics and triterpenic acids in leaf extracts of ocimum species and their interspecies variation. *J. Liq. Chromatogr. Relat. Technol.* **2016**, *39*, 225–238. [CrossRef]

74. Reed, K.A. Identification of Phenolic Compounds from Peanut Skin Using Hplc-msn. Ph.D. Thesis, Virginia Polytechnic Institute and State University, Blacksburg, VA, USA, 2009.

75. Soukup, S.T.; Al-Maharik, N.; Botting, N.; Kulling, S.E. Quantification of soy isoflavones and their conjugative metabolites in plasma and urine: An automated and validated uhplc-ms/ms method for use in large-scale studies. *Anal. Bioanal. Chem.* **2014**, *406*, 6007–6020. [CrossRef] [PubMed]

76. Kähkönen, M.; Heinämäki, J.; Ollilainen, V.; Heinonen, M. Berry anthocyanins: Isolation, identification and antioxidant activities. *J. Sci. Food Agric.* **2003**, *83*, 1403–1411. [CrossRef]

77. Hidalgo, M.; Sánchez-Moreno, C.; de Pascual-Teresa, S. Flavonoid–flavonoid interaction and its effect on their antioxidant activity. *Food Chem.* **2010**, *121*, 691–696. [CrossRef]

78. Petkovska, A.; Gjamovski, V.; Stanoeva, J.P.; Stefova, M. Characterization of the polyphenolic profiles of peel, flesh and leaves of malus domestica cultivars using uhplc-dad-hesi-msn. *Nat. Prod. Commun.* **2017**, *12*, 1934578X1701200111. [CrossRef]

79. Vitrac, X.; Monti, J.-P.; Vercauteren, J.; Deffieux, G.; Mérillon, J.-M. Direct liquid chromatographic analysis of resveratrol derivatives and flavanonols in wines with absorbance and fluorescence detection. *Anal. Chim. Acta* **2002**, *458*, 103–110. [CrossRef]

80. Ouyang, H.; Li, T.; He, M.; Li, Z.; Tan, T.; Zhang, W.; Li, Y.; Feng, Y.; Yang, S. Identification and quantification analysis on the chemical constituents from traditional mongolian medicine flos scabiosae using uhplc-dad-q-tof-ms combined with uhplc-qqq-ms. *J. Chromatogr. Sci.* **2016**, *54*, 1028–1036. [CrossRef]

81. Drira, M.; Kelebek, H.; Guclu, G.; Jabeur, H.; Selli, S.; Bouaziz, M. Targeted analysis for detection the adulteration in extra virgin olive oil's using lc-dad/esi–ms/ms and combined with chemometrics tools. *Eur. Food Res. Technol.* **2020**, *246*, 1661–1677. [CrossRef]

82. Wang, Y.; Vorsa, N.; Harrington, P.d.B.; Chen, P. Nontargeted metabolomic study on variation of phenolics in different cranberry cultivars using uplc-im—hrms. *J. Agric. Food Chem.* **2018**, *66*, 12206–12216. [CrossRef] [PubMed]

83. Gómez-Alonso, S.; Salvador, M.D.; Fregapane, G. Phenolic compounds profile of cornicabra virgin olive oil. *J. Agric. Food Chem.* **2002**, *50*, 6812–6817. [CrossRef] [PubMed]

84. Geng, C.-A.; Chen, H.; Chen, X.-L.; Zhang, X.-M.; Lei, L.-G.; Chen, J.-J. Rapid characterization of chemical constituents in saniculiphyllum guangxiense by ultra fast liquid chromatography with diode array detection and electrospray ionization tandem mass spectrometry. *Int. J. Mass Spectrom.* **2014**, *361*, 9–22. [CrossRef]

85. Sapozhnikova, Y.; Byrdwell, W.C.; Lobato, A.; Romig, B. Effects of uv-b radiation levels on concentrations of phytosterols, ergothioneine, and polyphenolic compounds in mushroom powders used as dietary supplements. *J. Agric. Food Chem.* **2014**, *62*, 3034–3042. [CrossRef] [PubMed]

86. Li, H.-Y.; Yuan, Q.; Yang, Y.-L.; Han, Q.-H.; He, J.-L.; Zhao, L.; Zhang, Q.; Liu, S.-X.; Lin, D.-R.; Wu, D.-T.; et al. Phenolic profiles, antioxidant capacities, and inhibitory effects on digestive enzymes of different kiwifruits. *Molecules* **2018**, *23*, 2957. [CrossRef] [PubMed]

87. Chen, Z.; Zhong, B.; Barrow, C.J.; Dunshea, F.R.; Suleria, H.A.R. Identification of phenolic compounds in australian grown dragon fruits by lc-esi-qtof-ms/ms and determination of their antioxidant potential. *Arab. J. Chem.* **2021**, *14*, 103151. [CrossRef]

88. Guo, J.; Yuan, Y.; Dou, P.; Yue, T. Multivariate statistical analysis of the polyphenolic constituents in kiwifruit juices to trace fruit varieties and geographical origins. *Food Chem.* **2017**, *232*, 552–559. [CrossRef]

89. Nie, X.-R.; Li, H.-Y.; Wei, S.-Y.; Han, Q.-H.; Zhao, L.; Zhang, Q.; Li, S.-Q.; Qin, W.; Wu, D.-T. Changes of phenolic compounds, antioxidant capacities, and inhibitory effects on digestive enzymes of kiwifruits (actinidia chinensis) during maturation. *J. Food Meas. Charact.* **2020**, *14*, 1765–1774. [CrossRef]