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A New Bloody Pulp Selection of Myrobalan (*Prunus cerasifera* L.): Pomological Traits, Chemical Composition, and Nutraceutical Properties

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Abstract: A new accession of myrobalan (*Prunus cerasifera* L.) from Sicily (Italy) was studied for the first time for its chemical and nutraceutical properties. A description of the main morphological and pomological traits was created as a tool for characterization for consumers. For this purpose, three different extracts of fresh myrobalan fruits were subjected to different analyses, including the evaluation of total phenol (TPC), flavonoid (TFC), and anthocyanin (TAC) contents. The extracts exhibited a TPC in the range 34.52–97.63 mg gallic acid equivalent (GAE)/100 g fresh weight (FW), a TFC of 0.23–0.96 mg quercetin equivalent (QE)/100 g FW, and a TAC of 20.24–55.33 cyanidine-3-*O*-glucoside/100 g FW. LC-HRMS analysis evidenced that the compounds mainly belong to the flavonols, flavan-3-ols, proanthocyanidins, anthocyanins, hydroxycinnamic acid derivatives, and organic acids classes. A multitarget approach was used to assess the antioxidant properties by using FRAP, ABTS, DPPH, and β-carotene bleaching tests. Moreover, the myrobalan fruit extracts were tested as inhibitors of the key enzymes related to obesity and metabolic syndrome (α-glucosidase, α-amylase, and lipase). All extracts exhibited an ABTS radical scavenging activity that was higher than the positive control BHT (IC_{50} value in the range 1.19–2.97 µg/mL). Moreover, all extracts showed iron-reducing activity, with a potency similar to that of BHT (53.01–64.90 *vs* 3.26 µM Fe(II)/g). The PF extract exhibited a promising lipase inhibitory effect (IC_{50} value of 29.61 µg/mL).

Keywords: *Prunus cerasifera*; myrobalan; LC-MS analysis; antioxidant activity; lipase and carbohydrate hydrolyzing enzymes inhibitory effects

Citation: Sottile, F.; Napolitano, A.; Badalamenti, N.; Bruno, M.; Tundis, R.; Loizzo, M.R.; Piacente, S. A New Bloody Pulp Selection of Myrobalan (*Prunus cerasifera* L.): Pomological Traits, Chemical Composition, and Nutraceutical Properties. *Foods* **2023**, *12*, 1107. https://doi.org/10.3390/foods12051107

Academic Editors: Urszula Złotek and Małgorzata Sierocka

Received: 10 February 2023
Revised: 2 March 2023
Accepted: 3 March 2023
Published: 5 March 2023

1. Introduction

Among fresh fruit species, plums (genus *Prunus*) play a non-determinant role in terms of production and cultivated surfaces, yet it is traditionally found in many areas characterized by temperate climates. It is usually considered a minor stone fruit together with apricot mostly because it is compared to peach and nectarines, which accounts for wider diffusion and growing areas [1]. The species has a complex botanical classification because several species are traced back to the name plum, and its hybridizations, natural and/or induced, are widespread [2]. Domestic or European plums (*Prunus domestica* L.) are generally used for processing into dried plums, while Japanese plums (*Prunus salicina* Lindl.) are almost exclusively used for fresh consumption. The names of the two species highlight the links between the origin and geographical distribution, with the former being

more closely associated with the old continent and the latter with the Asian continent. However, these are genetically distant species characterized by different ploidy levels.

Myrobalan (*Prunus cerasifera* L.) is a diploid, widespread species in the Mediterranean. This species is credited with the origin of European plums via hybridization with the tetraploid *P. Spinosa*, and for this reason, myrobalan is considered genetically close to *P. domestica*, although with different ploidy [1]. It is widely used as rootstock for both plum and apricot trees, more rarely for peach [3,4] thanks mainly to its ability to produce adventitious roots that facilitate its propagation [5,6].

In many traditional fruit-growing areas, where intensive agriculture has not taken over, there are several edible fruiting myrobalan accessions, often small (hence referred to as cherry-plum), selected by farmers and passed down because of the consumption related to the gastronomic traditions of indigenous peoples [7]. For this reason, many studies have focused on characterizing the accessions that are locally grown and highly valued by consumers, often for the taste qualities of the fruits as well as their early ripening time [8]. This approach is very often based on the analysis of morphological data through the adoption of specific descriptor lists studied and approved on a global scale [9]. The morphological traits of flowers, leaves, fruits, and seeds are studied, as well as wood, crown, bud characteristics, tree habit, and phenotypic behavior by the age of maturity and flowering. More recently, it has been proposed to combine these observations with a molecular-scale evaluation model, which, however, becomes effective only when morphological analysis fails to separate different accessions and, in any case, only in the presence of an adequate bank of genetic information [10]. Over the past decade, on an international scale, many research centers have initiated several programs for biodiversity conservation and characterization in accordance with the provisions of the International Treaty on Plant Genetic Resources for Agriculture and Food [11]. This important agreement has given all participating countries a responsibility in the conservation of indigenous genetic resources through the development of national plans in which the main objective is to enable a description of biodiversity with comparable and recognized patterns. Many innovative approaches have been developed for preserving plum biodiversity from the risk of erosion and/or extinction [12]. It is well known that the myrobalan fruits are usually rich in fibers and antioxidants, evidencing an important role in terms of nutritional source [13]; however, cherry plums are not so widely diffused due to the low resistance of the fruit in the postharvest management. Given that germplasm conservation is a substantial contribution to preserving knowledge about all crops, the identification of new resources and their characterization is an indispensable tool for achieving sustainable development targets by reducing the risk of genetic erosion. Indigenous genetic diversity is now recognized as a tool for resilience, mitigating the climate crisis due to increased adaptation with less consumption of natural resources, especially soil and water. Genetic diversity can conserve those genes that are potentially useful in strengthening resistance to pathogens or adaptability to stresses [14]. On a global scale, this type of work is also of strategic importance with a view to achieving the Agenda 2030 goals [15]. The conservation of biodiversity of agricultural interest and its morphological and functional characterization is central to SDGs 1, 2, 3, 12, and 14, with the general convergence of all targets toward SDG 13 being related to urgent action on climate change mitigation and adaptation, which, in some ways, underlies all the goals [16].

The attention of consumers toward an increasingly healthy diet has led to an increase in the consumption of fruits, with reference to red fruits not only for their nutritional value but also for their characteristic taste and their well-known health properties [17]. In fact, these fruits, in addition to vitamins and minerals, are rich in compounds with several health properties, mainly phenolic acids such as *p*-coumaric acid, vanillic acid β-glucoside, protocatechuic acid, and caffeic acid, and flavonoids such as catechin, epicatechin, quercetin and cyanidin-3-*O*-glucoside [18–20].

Metabolic syndrome (MetS) is a complex disorder that is often associated with insulin resistance, high cholesterol and triglycerides levels, and abdominal obesity [21]. The role of oxidative stress in its pathogenesis was proved [22,23]. Găman et al. [24] evidenced that in

the pancreatic β cells of subjects affected by type 2 diabetes, oxidative stress can reduce insulin secretion and, consequently, glucose uptake.

Although research has elucidated many of the mechanisms underlying MetS, its treatment remains a challenge, given the complexity of this disease. For this reason, many research groups are looking for bioactive compounds from food products that can play a preventive role in the onset of this syndrome. Many of these compounds belong to the class of phenols and possess antihypertensive, antihyperglycemic, antihypercholesterolemic, antioxidant, and anti-inflammatory activity, and furthermore, they can produce body weight loss or prevent against body weight gain [25,26].

Among the potentially used preventing approaches to counteract MetS and obesity, the inhibition of α-glucosidase, α-amylase, and lipase was one of the most applied. In fact, the inhibition of carbohydrate hydrolyzing enzymes delays carbohydrate digestion with a consequent hypoglycaemic effect, whereas the inhibition of pancreatic lipase reduces the absorption of ingested fats with a consequent hypolipidemic effect [27,28].

Therefore, herein, we report, for the first time, the pomological characteristics, chemical profile, and nutraceutical properties of different extracts obtained from *Prunus cerasifera* cv 'Alimena', a new bloody pulp cultivar from Sicily. The anthocyanin (TAC), flavonoid (TFC), and total phenol (TPC) contents were spectrophotometrically measured. The complete phytochemical profile was assessed using LC-ESI/LTQOrbitrap/MS analysis. A multitarget approach was applied to assess antioxidant activity (ABTS, DPPH, *β*-carotene bleaching, and FRAP assays). The inhibitory activity against key enzymes involved in MetS was also assessed.

2. Materials and Methods

2.1. Chemicals and Reagents

All chemicals utilized in this study were purchased from VWR International (Milan, Italy) and Sigma-Aldrich Chemical Co., Ltd. (Milan, Italy).

2.2. Plant Material

The research was carried out on a new accession of *Prunus cerasifera* L. named 'Alimena' and identified in an agricultural area in the territory of Alimena, Sicily (Italy) at an altitude of 675 m s/l, (37°41′25″ N; 14°05′53″ E). From the selected natural tree, budsticks have been collected for developing a small experimental orchard with 50 trees grafted onto *P. cerasifera* myrobalan 29C.

The orchard was established in 2015, and standard growing techniques have been applied since then. The planting density was 5 m × 5 m, fully irrigated during summer and managed by adopting spontaneous cover crops during the winter-spring season. Winter and summer pruning was performed yearly; fruit thinning was not necessarily due to a regular crop density recorded at fruit set.

2.3. Morphological Description

Morphological description was carried out by applying the Guidelines for the Characterization of Plant, Livestock and Microbial Genetic Resources approved based on the National Agricultural Biodiversity Plan of the Italian Ministry of Agriculture [29]. The Guidelines were drafted based on the international descriptors approved by UPOV [30] and contain references to plant traits considered essential for the characterization of plum tree accessions with the aim of distinguishing and defining their uniqueness.

Application of the guidelines involves the observation of multiple characters related to the tree and morphological characteristics of vegetative and reproductive organs. Leaves and wood samples were taken from mature trees during the vegetative-reproductive season, and at the same time, all observations of tree habits were recorded. At maturity, a sample of 100 fruits was subjected to morphological analysis (height, width, and thickness of the drupe and stone), as well as to qualitative analysis (skin and pulp color, titratable acidity, and soluble sugar content). For this purpose, fruits were randomly taken from the mass

harvested at maturity from 5 plants of the same age. The samples were transported to the laboratory with refrigerated facilities so as not to suffer any damage or spoilage.

2.4. Extraction Procedure

A total of 500 g of ripe fruits of *P. cerasifera* were cleaned, stone removed, and homogenized into puree (PA, 380 g) using a food processor. To determine the water quantity, 50 g of puree, once freeze-dried, to give 7.90 g of extract (content of water: 84.2%). Three hundred grams of PA were extracted for seven days at r.t. with 600 mL of acetone. The solvent was evaporated to give, after freeze-drying, 35.5 g of dry extract (PB). Then, 2.5 g of PB, after dilution with deionized water (≈15 mL) and then extracted with butanol (8 × 10 mL). The butanolic extracts were evaporated to give, after freeze-drying, 0.63 g of dry material (PC). The aqueous layer was freeze-dried to give 1.8 g of extract (PD). As an alternative extraction method, 20 g of PA was mixed with organic solution [≈120 mL, acetone/methanol/water/formic acid (40:40:20:0.1, *v*/*v*/*v*/*v*)] [31,32] and the mixture was allowed to stand at 4 °C for 24 h. The crude was filtered and washed with 120 mL of the same solution. The supernatants were combined, evaporated under vacuum at 37 °C, and freeze-dried to obtain 2.51 g of new extract (PF).

2.5. Total Phenol (TPC), Flavonoid (TFC), and Anthocyanin Contents (TAC)

Total phenol content (TPC) and total flavonoid content (TFC) were evaluated as previously described by Leporini et al. [33,34]. The differential pH method was used for total anthocyanin content (TAC) quantification [35].

2.6. LC-HRMS Analysis

The LC-ESI/HRMS analysis was carried out on a system of liquid chromatography consisting of a Thermo Ultimate RS 3000 UHPLC coupled online to a Q-Exactive hybrid quadrupole Orbitrap high-resolution mass spectrometer (UHPLC-Q-Orbitrap) (Thermo Fisher Scientific, Bremen, Germany), fitted with a HESI II (heated electrospray ionization) probe, working in both negative and positive ionization mode.

In order to allow the chromatographic separation, a Luna C-18 column (RP-18, 2.0 × 150 mm, 5 nm; Waters; Milford, MA, USA), set at a temperature of 30 °C, and a linear gradient, obtained by using mobile phase 0.1% formic acid in water, *v*/*v* (A), and 0.1% formic acid in acetonitrile, *v*/*v* (B), from 5 to 55% of B, in 20 min, at a flow rate of 0.2 mL/min, were used. 5 µL of each extract, dissolved in water/acetonitrile 1:1 *v*/*v* (0.25 mg/mL), were injected by the autosampler.

To allow negative and positive ions analysis, the HESI source parameters were set as follows: spray voltage at −2.50 kV and 3.30 kV, respectively; sheath gas at 50 arbitrary units (a.u.); auxiliary gas at 10 and 15 a.u., respectively; auxiliary gas heater temperature at 300 °C; capillary temperature at 300 °C; S-lens RF value at 50 a.u.

HRMS and HRMS/MS analyses were carried out by experiments of full (mass range: *m*/*z* 150–1400) and data-dependent scan (dd-MS^2 topN = 5) at resolutions of 70,000 and 17,500, respectively. A normalized collision energy (NCE) of 30 was used. For each sample, three replicates were performed. Data collection and analysis were carried out by using the manufacturer's software (Xcalibur 2.2).

2.7. In Vitro Evaluation of Antioxidant Potential and Relative Antioxidant Capacity Index

The antioxidant activity was assessed by using two radical scavenging test: 2,2-azino-*bis*(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) and 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging activity, *β*-carotene bleaching test and Ferric Reducing Ability Power (FRAP). All the procedures were previously detailed [36]. The Relative Antioxidant Capacity Index (RACI) was applied to evaluate the sample characterized by the highest activity [33].

2.8. Pancreatic Lipase Inhibitory Activity

The evaluation of pancreatic lipase inhibitory activity was assessed as previously described by Loizzo et al. [37].

2.9. Evaluation of α-Amylase and α-Glucosidase Inhibitory Activity

For α-amylase and α-glucosidase inhibitory activity tests, the procedure previously reported was adopted [36].

2.10. Statistical Analysis

Linear regression, assessment of repeatability, calculation of average, relative standard deviation (SD), and Pearson's correlation coefficient (r) were calculated by using Microsoft Excel 2010 software (Redmond, WA, USA). The results were expressed as the means of three different experiments ± SD. The inhibitory concentration 50% (IC_{50}) was calculated by using Prism GraphPad Prism version 4.0 for Windows (GraphPad Software, San Diego, CA, USA).

Parametric data were statistically analyzed by using one-way analysis of variance (ANOVA) followed by Tukey's posthoc test by using Prism GraphPad Prism version 4.0 for Windows. Differences at * $p < 0.05$ were statistically significant, while at ** $p < 0.01$, they were highly significant.

3. Results and Discussion

3.1. Morphological Data

All data related to the description of morphological traits provided by the applied descriptors are given in Table 1. All data related to the measurements of the fruits, seeds, and leaves, as well as of the fruit quality characteristics, are given in Table 2. The data reported revealed that the 'Alimena' accession had morphological characteristics of uniqueness, mainly related to the average fruit size (41.3 g), which is generally larger than that of the other *P. cerasifera* cultivars known in the Mediterranean basin. The color of the skin and pulp, therefore, give these fruits distinguishable traits that are unmatched in the varietal panorama of myrobalans, confirming, moreover, the character of low resistance to handling and transport.

Table 1. Application of criteria for describing the morphological traits of plum tree accessions on 'Alimena' myrobalan based on a list of descriptors prepared under the National Agricultural Biodiversity Plan.

GIBA Code	UPOV Code	Descriptor	Reference Cultivar	Level of Expression
1	1	High	Tree vigor Valor	7
2	-	Upright	Tree habit Jefferson	2
6	61	Early	Blooming time Ruth Gerstetter	3
10	38	Rounded	Flower: shape of the petals Czar	3
12	17	Medium	Leaf blade: Length/Width ratio D'Ente	5
13	18	Elliptic	Leaf blade: shape D'Ente	2

Table 1. *Cont.*

GlBA Code	UPOV Code	Descriptor	Reference Cultivar	Level of Expression
20	62	Early	Ripening time Bonne de Bry	3
21	43	Small	Fruit dimension Hauszwetsche	3
22	44	Rounded	Fruit shape Fortune	3
23	50	Red	Skin color Victoria	6
24	51	Red	Pulp color Bountiful	6
25	52	Medium	Fruit consistency Zucchella	5
26	53	High	Pulp sweetness Imperial Prune	7
27	54	Adherent	Seed-pulp adherence Jori's Plum	3
29	56	Elliptic large	Seed shape Regina Claudia	3

All data related to measurements of fruits, seeds, and leaves, as well as for fruit quality characteristics, are given in Table 2.

Table 2. Data on morphological descriptive traits related to fruit, seed, and leaf.

	Fruit		Seed		Leaf	
	Length	**Width**	**Length**	**Width**	**Length**	**Width**
cm	3.32 ± 0.06	3.41 ± 0.09	2.14 ± 0.02	1.48 ± 0.06	6.11 ± 0.11	3.31 ± 0.04

Data are reported to mean ± Standard Deviation (SD) (n = 3).

3.2. Total Phytochemical Content (TPC, TFC, and TAC)

The pulp obtained from the *P. cerasifera* 'Alimena' fruits was subjected to different extractions with several solvents (acetone, butanol, water, methanol, etc.) to evaluate the impact of the solvent on the phytochemical content. The presence of several compounds with different structures and polarities can drastically affect their solubility [38]. Polar solvents (MeOH, EtOH, and water) were used for the isolation of polyphenols and glycosides from plants. The most common ones are mixtures of water with ethanol and methanol. Ethanol is a good solvent for polyphenol extraction and is safe for human consumption, whereas acetone and ethyl acetate have been used for the extraction of medium molecular weight metabolites, such as terpenoids and flavonoid aglycones [39].

The PF sample resulted in the richest TPC and TFC, with values of 97.63 mg gallic acid equivalent (GAE)/100 g FW and 0.96 mg quercetin equivalent (QE)/100 g FW, respectively, followed by the PC samples, whereas PD was richest in TAC (55.33 mg cyanidine-3-*O*-glucoside/100 g FW) (Table 3).

Table 3. Phytochemicals content in the selection of myrobalan bloody pulp fruits extract.

Sample	TPC (mg GAE/100 g FW)	TFC (mg QE/100 g FW)	TAC (Cyanidine-3-*O*-glucoside/100 g FW)
PF	97.63 ± 6.45 [a]	0.96 ± 0.08 [a]	39.38 ± 2.09 [b]
PC	89.61± 2.98 [b]	0.80 ± 0.06 [b]	20.24 ± 1.45 [c]
PD	34.52 ± 2.85 [c]	0.23 ± 0.04 [c]	55.33 ± 3.83 [a]
Sign.	**	**	**

Data are reported as mean ± standard deviation (SD) (n = 3). Differences within and between groups were evaluated by one-way ANOVA, followed by Tukey's multiple-range test. The results followed by different letters in the same column are significantly different. ** Significance at $p < 0.05$.

Previously, the TPC content of *P. cerasifera* 'Mirabolano', *P. domestica* cv 'President', and *P. salicina* cv 'Shiro' at different stages of development was analyzed [40]. All plumes exhibited the highest TPC at the date of commercial harvesting—at about 100 days for 'Mirabolano', 130 days for 'President', and more than 110 days for "Shiro". TPC values in a range from 1.34 to 6.11 g/kg FW were found for the red and purple myrobalan plum fruits, respectively [31]. Values from 1.74 to 3.75 g/Kg FW were recorded for the Stanley and French Damson fresh plums, respectively [41].

A lower TPC content was found by Gündüz et al. [8], who investigated *P. cerasifera* selections from Turkey and found values between 136.8 to 583.1 mg GAE/kg FW for 'Ozark Premier', and 'Selection No. 3', respectively. On the contrary, our data are lower than those found for *P. divaricata* "Demal" and *P. domestica* 'Sugar plum', with TPC values of 169.6 and 172.4 mg GAE/100 g, respectively [40]. TFC values from 12.1 to 29.1 mg rutin equivalent/100 g were found for 'Demal' and *P. domestica* 'Red plum', respectively [42]. TPC values ranging from 177–365 mg GAE/100 g were found for *P. divaricate* yellow and black, respectively [43].

Gil et al. [44] analyzed several Californian flesh plums and found that 'Black Beaut' was richer in TPC and TCC in comparison to 'Angeleno', 'Red Beaut', 'Wickson', and 'Santa Rosa' cultivars. Moreover, several research papers demonstrated that qualitative and quantitative variability in TPC, is often related to different genetic factors and developmental stages [45].

Our data on TAC are in line with those reported for *P. cerasus* varieties 'Kántorjánosi', 'Újfehértói fürtös', and 'Debreceni bötermö' (TAC values of 21, 56, and 63 mg cyanidine-3-*O*-glucoside/100 g FW, respectively) but lower than those found for the varieties 'Csengödi csokros' and 'Cigánymeggy (TAC values of 295 and 206 mg cyanidine-3-*O*-glucoside/100 g FW, respectively) [46]. A higher TAC was found for *P. domestica* 'Santa Rosa' and 'African Rose', with values of 164.13 and 326.83 mg cyanidine-3-*O*-glucoside/100 g FW, respectively, and for *P. cerasifera* from Georgia (109.77 mg cyanidine-3-*O*-glucoside/100 g FW) [47,48].

3.3. LC-HRMS Analysis

The LC-HRMS profiles of the PC, PD, and PF extracts highlighted the occurrence of several metabolites in *P. cerasifera*, the structures of which could be assigned by a comparison between the molecular formulae, fragmentation patterns, and retention times and the literature data and metabolite databases, allowing us to putatively identify hydroxycinnamic acid derivatives, flavonols, flavan-3-ols and proanthocyanidins, anthocyanins, organic acids, sugar alcohols (and their derivatives), glycosylated hydroxybenzaldehyde and benzylic alcohol derivatives, glycosyl terpenates, and glycosylated aliphatic alcohol derivatives (Table 4) [37,49–54]. Except for compounds **28** and **67**, which were previously described in the Rosaceae family [55,56] but not in the genus *Prunus*, and for compounds **35**, **36**, **43**, and **54** described in families other than Rosaceae [57–59], to the best of our knowledge, most of these compounds have already been detected in plants belonging to the genus *Prunus* [60–73] but not in the species *cerasifera*. Only compounds **1**, **2**, **5**, **7**, **10**, **12**, **15**, **18**, **20**, **29**, **34**, **42**, **58**, and **75** have already been described in this species [31,45,74–78].

Table 4. Metabolites identified in PF, PC, and PD extracts.

n	R_t (min)	Compound	Molecular Formula	Error (ppm)	$[M-H]^-$ (*m*/*z*)	(−)HRMS/MS	$[M+H]^+$ (*m*/*z*)	(+)HRMS/MS	PF	PC	PD
1	1.72	Hexose sugar alcohol	$C_6H_{14}O_6$	0.34	181.0708	163.0601 ($C_6H_{11}O_5$), 101.0231 ($C_4H_5O_3$), 89.0231 ($C_3H_5O_3$), 71.0125 ($C_3H_3O_2$), 59.0126 ($C_2H_3O_2$)			√√	√√	√√
2	1.79	Quinic acid	$C_7H_{12}O_6$	0.71	191.0551	173.0445 ($C_7H_9O_5$), 127.0389 ($C_6H_7O_3$), 111.0440 ($C_6H_7O_2$), 93.0333 (C_6H_5O), 85.0282 ($C_4H_5O_2$)			√√	√√	√√
3	1.82	(Hexosyl sugar alcohol)-malic acid	$C_{10}H_{18}O_{10}$	0.32	297.0823	181.0708 ($C_6H_{13}O_6$), 133.0131 ($C_4H_5O_5$), 115.0024 ($C_4H_3O_4$), 101.0231 ($C_4H_5O_3$), 89.0231 ($C_3H_5O_3$), 71.0125 ($C_3H_3O_2$), 59.0125 ($C_2H_3O_2$)	321.0793 $[M+Na]^+$	205.0687 ($C_6H_{14}O_6Na$), 187.0582 ($C_6H_{12}O_5Na$), 157.0111 ($C_4H_6O_5Na$)	√√	√√	√√
4	1.85	Ketohexosyl-malic acid	$C_{10}H_{16}O_{10}$	−0.81	295.0669	179.0553 ($C_6H_{11}O_6$), 133.0130 ($C_4H_5O_5$), 101.0231 ($C_4H_5O_3$), 89.0231 ($C_3H_5O_3$), 71.0125 ($C_3H_3O_2$), 59.0125 ($C_2H_3O_2$)	319.0633 $[M+Na]^+$	301.0535 ($C_{10}H_{14}O_9Na$), 259.0432 ($C_8H_{12}O_8Na$), 229.0321 ($C_7H_{10}O_7Na$), 203.0530 ($C_6H_{12}O_6Na$), 185.0424 ($C_6H_{10}O_5Na$), 157.0110 ($C_4H_6O_5Na$)	√√	√√	√√
5	2.61	Citric acid	$C_6H_8O_7$	2.15	191.0190	111.0075 ($C_5H_3O_3$), 87.0074 ($C_3H_3O_3$)			√√	√√	√√
6	7.63	3-(*cis*)-*O*-caffeoylquinic acid	$C_{16}H_{18}O_9$	3.87	353.0881	191.0553 ($C_7H_{11}O_6$), 179.0340 ($C_9H_7O_4$), 135.0440 ($C_8H_7O_2$)			√√	√√	√
7	7.94	3-(*trans*)-*O*-Caffeoylquinic acid	$C_{16}H_{18}O_9$	3.86	353.0881	191.0552 ($C_7H_{11}O_6$), 179.0341 ($C_9H_7O_4$), 135.0440 ($C_8H_7O_2$)			√√	√√	√
8	8.43	Caffeoyl hexoside	$C_{15}H_{18}O_9$	3.94	341.0880	179.0339 ($C_9H_7O_4$), 161.0233 ($C_9H_5O_3$)			√√	√√	√

Table 4. *Cont.*

n	R_t (min)	Compound	Molecular Formula	Error (ppm)	$[M-H]^-$ (*m*/*z*)	(−)HRMS/MS	$[M+H]^+$ (*m*/*z*)	(+)HRMS/MS	PF	PC	PD
9	8.65	Coumaroyl dihexoside	$C_{21}H_{28}O_{13}$	3.82	487.1465	307.0817 ($C_{15}H_{15}O_7$), 163.0399 ($C_9H_7O_3$), 145.0283 ($C_9H_5O_2$)			√√	√√	√
10	8.74	Cyanidin 3-*O*-hexoside	$C_{21}H_{21}O_{11}$	1.52	447.0939 $[M-2H]^-$		449.1085 $[M]^+$	287.0556 ($C_{15}H_{11}O_6$)	√√	√√	√√
11	8.80	Dimeric B-type proanthocyanidins	$C_{30}H_{26}O_{12}$	3.49	577.1361	289.0721 ($C_{15}H_{13}O_6$)			√√	√	—
12	8.98	Cyanidin 3-*O*-hexoside	$C_{21}H_{21}O_{11}$	−0.24	447.0937 $[M-2H]^-$		449.1077 $[M]^+$	287.0553 ($C_{15}H_{11}O_6$)	√√	√√	√√
13	9.05	(Benzyl)hexose-hexoside	$C_{19}H_{28}O_{11}$	2.46	431.1559/477.1615 $[(M+FA)-H]^-$	269.1037 ($C_{13}H_{17}O_6$), 161.0445 ($C_6H_9O_5$), 113.0231 ($C_5H_5O_3$), 101.0231 ($C_4H_5O_3$)			√√	√√	√√
14	9.10	Coumaroyl dihexoside	$C_{21}H_{28}O_{13}$	2.57	487.1459	163.0390 ($C_9H_7O_3$), 145.0283 ($C_9H_5O_2$)			√√	√√	√
15	9.13	Cyanidin 3-*O*-rutinoside	$C_{27}H_{31}O_{15}$	−0.26	593.1517 $[M-2H]^-$	284.0324 ($C_{15}H_8O_6$)	595.1656 $[M]^+$	449.1083 ($C_{21}H_{21}O_{11}$), 287.0551 ($C_{15}H_{11}O_6$)	√√	√	√√
16	9.38	dimeric B-type proanthocyanidins	$C_{30}H_{26}O_{12}$	3.72	577.1362	289.0724 ($C_{15}H_{13}O_6$)			√√	√	—
17	9.45	3-*O*-coumaroylquinic acid	$C_{16}H_{18}O_8$	3.16	337.0929	191.0552 ($C_7H_{11}O_6$), 163.0390 ($C_9H_7O_3$), 119.0490 (C_8H_7O)			√√	√√	√
18	9.72	5-(*trans*)-*O*-caffeoylquinic acid	$C_{16}H_{18}O_9$	3.74	353.0880	191.0553 ($C_7H_{11}O_6$)			√√	√√	√
19	9.82	4-*O*-caffeoylquinic acid	$C_{16}H_{18}O_9$	3.86	353.0881	191.0553 ($C_7H_{11}O_6$), 179.0338 ($C_9H_7O_4$), 173.0445 ($C_7H_9O_5$), 135.0440 ($C_8H_7O_2$)			√√	√√	√
20	9.83	Catechin/Epicatechin	$C_{15}H_{14}O_6$	2.89	289.0715	245.0815 ($C_{14}H_{13}O_4$), 205.0500 ($C_{11}H_9O_4$), 179.0344 (C_9H_7O4)			√√	√√	√

Table 4. *Cont.*

n	R_t (min)	Compound	Molecular Formula	Error (ppm)	$[M-H]^-$ (*m*/*z*)	(−)HRMS/MS	$[M+H]^+$ (*m*/*z*)	(+)HRMS/MS	PF	PC	PD
21	10.03	5-*O*-Feruloylquinic acid	$C_{17}H_{20}O_9$	3.40	367.1036	193.0499 ($C_{10}H_9O_4$), 191.1560 ($C_7H_{11}O_6$), 173.0448 ($C_7H_9O_5$), 161.0231 ($C_9H_5O_3$), 134.0363 ($C_8H_6O_2$)			√√	√√	—
22	10.19	Coumaroyl-(acetyl)hexose-hexoside isomer	$C_{23}H_{30}O_{14}$	3.70	529.1571	341.1092 ($C_{12}H_{21}O_{11}$), 307.0825 ($C_{15}H_{15}O_7$), 163.0389 ($C_9H_7O_3$), 145.0284 ($C_9H_5O_2$)			√√	√√	√
23	10.35	Dimeric B-type proanthocyanidins	$C_{30}H_{26}O_{12}$	1.12	577.1347	289.0720 ($C_{15}H_{13}O_6$)			√√	√	—
24	10.40	Benzylhexose pentoside	$C_{18}H_{26}O_{10}$	−1.36	401.1450/447.1504 $[(M+FA)-H]^-$	269.1031 ($C_{13}H_{17}O_6$), 161.0446 ($C_6H_9O_5$)	425.1412 $[M+Na]^+$	293.0997 ($C_{13}H_{18}O_6Na$)	√√	√√	√√
25	10.48	Feruloyl hexoside isomer	$C_{16}H_{20}O_9$	3.69	355.1037	193.0496 ($C_{10}H_9O_4$), 175.0391 ($C_{10}H_7O_3$)			√√	√√	—
26	10.49	(Benzyl)hexose-dihexoside	$C_{25}H_{38}O_{16}$	2.00	593.2089	415.1607 ($C_{19}H_{27}O_{10}$), 269.1032 ($C_{13}H_{17}O_6$)			√√	√√	√√
27	10.55	Coumaroyl-(acetyl)hexose-hexoside isomer	$C2_3H_{30}O_{14}$	0.31	529.1570	341.1088 ($C_{12}H_{21}O_{11}$), 307.0824 ($C_{15}H_{15}O_7$), 163.0391 ($C_9H_7O_3$), 145.0284 ($C_9H_5O_2$)	553.1530 $[M+Na]^+$	391.1009 ($C_{17}H_{20}O_9Na$), 349.0896 ($C_{15}H_{18}O_8Na$)	√√	√√	√
28	10.56	(Benzaldehyde)hexose-pentoside	$C_{18}H_{24}O_{11}$	3.59	415.1250/461.1310 $[(M+FA)-H]^-$	121.0282 ($C_7H_5O_2$)			√√	√√	√√
29	10.59	Methyl caffeoylquinate isomer	$C_{17}H_{20}O_9$	2.92	367.1034	179.0341 ($C_9H_7O_4$), 173.0449 ($C_7H_9O_5$), 161.0235 ($C_9H_5O_3$)			√√	√√	—
30	10.65	5-(*cis*)-*O*-caffeoylquinic acid	$C_{16}H_{18}O_9$	3.60	353.0880	191.0553 ($C_7H_{11}O_6$)			√√	√√	—
31	10.81	Feruloyl hexoside isomer	$C_{16}H_{20}O_9$	3.27	355.1035	193.0502 ($C_{10}H_9O_4$), 175.0391 ($C_{10}H_7O_3$)			√√	√√	—
32	10.85	Coumaroyl-(acetyl)hexose-hexoside isomer	$C_{23}H_{30}O_{14}$	3.75	529.1572	341.1088 ($C_{12}H_{21}O_{11}$), 307.0824 ($C_{15}H_{15}O_7$), 163.0391 ($C_9H_7O_3$), 145.0284 ($C_9H_5O_2$)			√√	√√	√

Table 4. *Cont.*

n	R_t (min)	Compound	Molecular Formula	Error (ppm)	$[M-H]^-$ (*m*/*z*)	(−)HRMS/MS	$[M+H]^+$ (*m*/*z*)	(+)HRMS/MS	PF	PC	PD
33	10.90	4-*O*-coumaroylquinic acid	$C_{16}H_{18}O_8$	3.18	337.0929	191.0557 ($C_7H_{11}O_6$), 173.0446 ($C_7H_9O_5$), 163.0387 ($C_9H_7O_3$)			√√	√√	√√
34	10.97	Catechin/Epicatechin	$C_{15}H_{14}O_6$	2.89	289.0715	245.0814 ($C_{14}H_{13}O_4$), 205.0503 ($C_{11}H_9O_4$), 179.0344 ($C_9H_7O_4$)			√√	√√	√
35	11.00	Feruloyl-(acetyl)hexose-hexoside isomer	$C_{24}H_{32}O_{15}$	2.47	559.1671	175.0391 ($C_{10}H_7O_3$)			√√	√√	—
36	11.26	Feruloyl-(acetyl)hexose-hexoside isomer	$C_{24}H_{32}O_{15}$	2.85	559.1673	175.0392 ($C_{10}H_7O_3$)			√√	√√	—
37	11.43	Coumaroyl-(acetyl)hexose-hexoside isomer	$C_{23}H_{30}O_{14}$	3.75	529.1572	341.1095 ($C_{12}H_{21}O_{11}$), 307.0820 ($C_{15}H_{15}O_7$), 163.0394 ($C_9H_7O_3$), 145.0284 ($C_9H_5O_2$)			√√	√√	√
38	11.51	Methyl coumaroylquinate isomer	$C_{17}H_{20}O_8$	3.83	351.1088	145.0283 ($C_9H_5O_2$)			√√	√√	√√
39	11.61	Dimethyl-hydroxy-decadienedioate hexoside	$C_{18}H_{28}O_{10}$	3.74	403.1614	241.1080 ($C_{12}H_{17}O_5$), 197.1178 ($C_{11}H_{17}O_3$), 181.0866 ($C_{10}H_{13}O_3$), 59.0126 ($C_2H_3O_2$)			√√	√√	√
40	11.81	Methyl coumaroylquinate isomer	$C_{17}H_{20}O_8$	3.83	351.1088	145.0284 ($C_9H_5O_2$), 119.0492 (C_8H_7O)			√√	√√	√√
41	11.93	Coumaroyl-(diacetyl)dihexoside isomer	$C_{25}H_{32}O_{15}$	3.00	571.1675	307.0824 ($C_{15}H_{15}O_7$), 163.0389 ($C_9H_7O_3$), 145.0284 ($C_9H_5O_2$)			√√	√√	√
42	12.22	Methyl caffeoylquinate isomer	$C_{17}H_{19}O_9$	2.97	367.1034	179.0341 ($C_9H_7O_4$), 161.0238 ($C_9H_5O_3$)			√√	√√	—

Table 4. *Cont.*

n	R_t (min)	Compound	Molecular Formula	Error (ppm)	$[M-H]^-$ (*m*/*z*)	(−)HRMS/MS	$[M+H]^+$ (*m*/*z*)	(+)HRMS/MS	PF	PC	PD
43	12.26	Hexyl-dihexoside isomer	$C_{18}H_{34}O_{11}$	3.27	471.2084 [(M + FA) − H]$^-$	263.1499 ($C_{12}H_{24}O_6$), 161.0444 ($C_6H_9O_5$), 101.0231 ($C_4H_5O_3$)			√√	√√	√
44	12.37	Coumaroyl-(diacetyl)dihexoside isomer	$C_{25}H_{32}O_{15}$	2.65	571.1673	341.1088 ($C_{12}H_{21}O_{11}$), 307.0834 ($C_{15}H_{15}O_7$), 163.0388 ($C_9H_7O_3$), 145.0283 ($C_9H_5O_2$)	595.1644 $[M+Na]^+$	391.1009 ($C_{17}H_{20}O_9Na$), 349.0900 ($C_{15}H_{18}O_8Na$), 331.0790 ($C_{15}H_{16}O_7Na$), 287.0756 ($C_{10}H_{16}O_8Na$), 167.0315 ($C_6H_8O_4Na$)	√√	√√	√
45	12.50	Delphinidin-3-*O*-rutinoside	$C_{27}H_{31}O_{16}$	0.18	609.1466 $[M-2H]^-$		611.1608 $[M]^+$	303.0501 ($C_{15}H_{11}O_7$)	√√	√	√√
46	12.59	Dimethyl-octadienedioate hexoside	$C_{16}H_{24}O_9$	2.93	359.1347	197.0810 ($C_{10}H_{13}O_4$), 153.0910 ($C_9H_{13}O_2$), 59.0125 ($C_2H_3O_2$)			√√	√√	√
47	12.64	Coumaroyl-(diacetyl)dihexoside isomer	$C_{25}H_{32}O_{15}$	1.30	571.1665	341.1084 ($C_{12}H_{21}O_{11}$), 307.0829 ($C_{15}H_{15}O_7$), 163.0390 ($C_9H_7O_3$), 145.0284 ($C_9H_5O_2$)	595.1636 $[M+Na]^+$	391.1004 ($C_{17}H_{20}O_9Na$), 349.0899 ($C_{15}H_{18}O_8Na$), 331.0804 ($C_{15}H_{16}O_7Na$), 287.0732 ($C_{10}H_{16}O_8Na$), 167.0317 ($C_6H_8O_4Na$)	√√	√√	√
48	12.66	Delphinidin-3-*O*-hexoside	$C_{21}H_{21}O_{12}$	0.34			465.1029 $[M]^+$	303.0502 ($C_{15}H_{11}O_7$)	√√	√√	√√
49	12.79	Dimeric A-type proanthocyanidins	$C_{30}H_{24}O_{12}$	1.45	575.1204	539.0960 ($C_{30}H_{19}O_{10}$), 423.0726 ($C_{22}H_{15}O_9$), 407.0771 ($C_{22}H_{15}O_8$), 327.0513 ($C_{17}H_{11}O_7$), 289.0723 ($C_{15}H_{13}O_6$), 287.0562 ($C_{15}H_{11}O_6$), 285.0409 ($C_{15}H_9O_6$)	577.1349	287.0552 ($C_{15}H_{11}O_6$)	√√	√√	√
50	12.92	Isorhamnetin 3-*O*-rutinoside	$C_{28}H_{32}O_{16}$	3.78	623.1630	315.0503 ($C_{16}H_{11}O_7$), 314.0431 ($C_{16}H_{10}O_7$)			√√	—	—
51	13.08	Quercetin-3-*O*-hexoside	$C_{21}H_{20}O_{12}$	0.12	463.0889	301.0346 ($C_{15}H_9O_7$)	465.1028	303.0502 ($C_{15}H_{11}O_7$)	√√	√√	√
52	13.12	Isorhamnetin-3-*O*-pentose-hexoside	$C_{27}H_{30}O_{16}$	1.18	609.1472	315.0509 ($C_{16}H_{11}O_7$)	611.1614	317.0657 ($C_{16}H_{13}O_7$)	√√	—	—

Table 4. *Cont.*

n	R_t (min)	Compound	Molecular Formula	Error (ppm)	$[M-H]^-$ (*m*/*z*)	(−)HRMS/MS	$[M+H]^+$ (*m*/*z*)	(+)HRMS/MS	PF	PC	PD
53	13.20	Abscisic acid hexoside	$C_{21}H_{30}O_9$	1.59			449.1789 $[M+Na]^+$	287.1258 ($C_{15}H_{20}O_4Na$)	√√	√√	—
54	13.26	Dicrotalic acid (Benzyl)hexoside	$C_{19}H_{26}O_{10}$	3.91	413.1458	269.1039 ($C_{13}H_{17}O_6$)			√√	√√	√
55	13.36	Quercetin-3-*O*-di-pentoside	$C_{25}H_{26}O_{15}$	1.65	565.1207	301.0325 (C_{15} H_9 O_7)	567.1354	303.0506 (C_{15} H_{11} O_{7+})	√√	√√	√
56	13.43	Dimeric A-type proanthocyanidins	$C_{30}H_{24}O_{12}$	1.35	575.1204	539.0959 ($C_{30}H_{19}O_{10}$), 407.0771 ($C_{22}H_{15}O_8$), 327.0507 ($C_{17}H_{11}O_7$), 289.0719 ($C_{15}H_{13}O_6$), 287.0560 ($C_{15}H_{11}O_6$), 285.0405 ($C_{15}H_9O_6$)	577.1348	287.0553 ($C_{15}H_{11}O_6$)	√√	√√	√
57	13.59	Quercetin-3-*O*-pentoside	$C_{20}H_{18}O_{11}$	1.98	433.0779	301.0345 ($C_{15}H_9O_7$)	435.0930	303.0503 ($C_{15}H_{11}O_7$)	√√	√√	√
58	13.68	Quercetin 3-*O*-rutinoside	$C_{27}H_{30}O_{16}$	1.18	609.1468	301.0349 ($C_{15}H_9O_7$)	611.1614	303.0516 ($C_{15}H_{11}O_7$)	√√	√√	√
59	13.84	Coumaroyl-(triacetyl)dihexoside isomer	$C_{27}H_{34}O_{16}$	3.81	613.1786	163.0387 ($C_9H_7O_3$), 145.0284 ($C_9H_5O_2$)			√√	√√	√
60	14.01	Quercetin-3-*O*-pentoside	$C_{20}H_{18}O_{11}$	1.06	433.0778	301.0349 ($C_{15}H_9O_7$)	435.0927/457.0744 $[M+Na]^+$	303.0501 ($C_{15}H_{11}O_7$)	√√	√√	√
61	14.16	Coumaroyl-(triacetyl)dihexoside isomer	$C_{27}H_{34}O_{16}$	1.21	613.1782	383.1196 ($C_{14}H_{23}O_{12}$), 307.0813 ($C_{15}H_{15}O_7$), 163.0393 ($C_9H_7O_3$), 145.0284 ($C_9H_5O_2$)	637.1747 $[M+Na]^+$	391.0995 ($C_{17}H_{20}O_9Na$), 373.0882 ($C_{17}H_{18}O_8Na$), 287.0734 ($C_{10}H_{16}O_8Na$), 167.0315 ($C_6H_8O_4Na$)	√√	√√	√
62	14.17	Quercetin-3-*O*-deoxyhexoside	$C_{21}H_{20}O_{11}$	3.36	447.0937	301.0349 ($C_{15}H_9O_7$)	449.1085		√√	√√	√
63	14.18	Isorhamnetin 3-*O*-hexoside	$C_{22}H_{22}O_{12}$	1.60	477.1044	314.0431 ($C_{16}H_{10}O_7$)	479.1192	317.0659 ($C_{16}H_{13}O_7$)	√√	—	—
64	14.32	Methyl (hexosyl)-*O*-coumarate isomer	$C_{16}H_{20}O_8$	0.86			363.1054 $[M+Na]^+$	201.0524 ($C_{10}H_{10}O_3Na$), 185.0427 ($C_6H_{10}O_5Na$)	√√	√√	—

Table 4. *Cont.*

n	R_t (min)	Compound	Molecular Formula	Error (ppm)	$[M-H]^-$ (*m*/*z*)	(−)HRMS/MS	$[M+H]^+$ (*m*/*z*)	(+)HRMS/MS	PF	PC	PD
65	14.33	Coumaroyl-(triacetyl)dihexoside isomer	$C_{27}H_{34}O_{16}$	1.03	613.1783	341.1087 ($C_{12}H_{21}O_{11}$), 163.0390 ($C_9H_7O_3$), 145.0284 ($C_9H_5O_2$)	637.1746 $[M+Na]^+$	391.0992 ($C_{17}H_{20}O_9Na$), 373.0886 ($C_{17}H_{18}O_8Na$), 287.0739 ($C_{10}H_{16}O_8Na$), 167.0317 ($C_6H_8O_4Na$)	√√	√√	√
66	14.36	Quercetin-3-*O*-(acetyl)hexoside	$C_{23}H_{22}O_{13}$	1.25	505.0996	300.0273 ($C_{15}H_8O_7$)	507.1140	303.0502 ($C_{15}H_{11}O_7$)	√√	√√	√
67	14.65	[(Dihydroxybenzoyloxy)-dihydroxyphenyl]acetate methyl ester	$C_{16}H_{14}O_8$	1.54	333.0620	197.0446 ($C_9H_9O_5$), 165.0183 ($C_8H_5O_4$)	335.0767	137.0235 ($C_7H_5O_3$)	√√	√√	√
68	14.68	Coumaroyl-(triacetyl)dihexoside isomer	$C_{27}H_{34}O_{16}$	1.31	613.1783	383.1187 ($C_{14}H_{23}O_{12}$), 341.1085 ($C_{12}H_{21}O_{11}$), 163.0390 ($C_9H_7O_3$), 145.0284 ($C_9H_5O_2$)	637.1747 $[M+Na]^+$	391.0998 ($C_{17}H_{20}O_9Na$), 373.0895 ($C_{17}H_{18}O_8Na$), 287.0758 ($C_{10}H_{16}O_8Na$)	√√	√√	√
69	14.91	Coumaroyl-(triacetyl)dihexoside isomer	$C_{27}H_{34}O_{16}$	1.31	613.1786	383.1197 ($C_{14}H_{23}O_{12}$), 341.1094 ($C_{12}H_{21}O_{11}$), 307.0833 ($C_{15}H_{15}O_7$), 163.0391 ($C_9H_7O_3$), 145.0283 ($C_9H_5O_2$)	367.1747 $[M+Na]^+$	391.1006 ($C_{17}H_{20}O_9Na$), 373.0890 ($C_{17}H_{18}O_8Na$), 287.0744 ($C_{10}H_{16}O_8Na$), 167.0317 ($C_6H_8O_4Na$)	√√	√√	√
70	15.14	Azelaic acid	$C_9H_{16}O_4$	2.86	187.0970	125.0960 ($C_8H_{13}O$)			√√	√√	√√
71	15.28	Quercetin-3-*O*-(Acetyl)rutinoside	$C_{29}H_{34}O_{17}$	1.28	651.1583	301.0351 ($C_{15}H_9O_7$)	653.1721		√√	√√	√
72	16.62	Coumaroyl-(tetraacetyl)dihexoside isomer	$C_{29}H_{36}O_{17}$	1.04	655.1893	163.0390 ($C_9H_7O_3$), 145.0284 ($C_9H_5O_2$)	679.1852 $[M+Na]^+$	373.0889 ($C_{17}H_{18}O_8Na$), 329.0846 ($C_{12}H_{18}O_9Na$)	√√	√√	√
73	16.86	Coumaroyl-(tetraacetyl)dihexoside isomer	$C_{29}H_{36}O_{17}$	1.31	655.1892	163.0395 (C_9H_7O3), 145.0285 ($C_9H_5O_2$)	679.1854 $[M+Na]^+$	433.1112 ($C_{19}H_{22}O_{10}Na$), 373.0940 ($C_{17}H_{18}O_8Na$), 209.0423 ($C_8H_{10}O_5Na$)	√√	√√	√
74	17.17	Coumaroyl-(tetraacetyl)dihexoside isomer	$C_{29}H_{36}O_{17}$	0.69	655.1893	383.1197 ($C_{14}H_{23}O_{12}$), 163.0393 ($C_9H_7O_3$), 145.0284 ($C_9H_5O_2$)	679.1849 $[M+Na]^+$	433.1115 ($C_{19}H_{22}O_{10}Na$), 391.1004 ($C_{17}H_{20}O_9Na$), 373.0901 ($C_{17}H_{18}O_8Na$), 329.0835 ($C_{12}H_{18}O_9Na$), 209.0422 ($C_8H_{10}O_5Na$)	√√	√√	√

Table 4. *Cont.*

n	R_t (min)	Compound	Molecular Formula	Error (ppm)	$[M-H]^-$ (*m*/*z*)	(−)HRMS/MS	$[M+H]^+$ (*m*/*z*)	(+)HRMS/MS	PF	PC	PD
75	17.81	Quercetin	$C_{15}H_{10}O_7$	2.73	301.0351	178.9977 ($C_8H_3O_5$), 151.0025 ($C_7H_3O_4$), 121.0283 ($C_7H_5O_2$)			√√	√√	—
76	19.76	Coumaroyl-(pentaacetyl)dihexoside isomer	$C_{31}H_{38}O_{18}$	3.34	697.1998	145.0282 ($C_9H_5O_2$)			√√	√√	—
77	19.95	Coumaroyl-(pentaacetyl)dihexoside isomer	$C_{31}H_{38}O_{18}$	3.17	697.1996	145.0283 ($C_9H_5O_2$)			√√	√√	—

Legend: √√ = detectable; √ = detectable at low intensity level (1.1×10^3 < Normalized Level < 4.0×10^4); — = not detectable.

Among the most represented group of metabolites, the derivatives of hydroxycinnamic acid, some differences could be appreciated among the three *P. cerasifera* extracts (Table 4). PF and PC showed, in fact, a higher number of metabolites belonging to this class with respect to the PD extract. It is noteworthy that compounds **21**, **25**, **31**, **35**, and **36**, containing a feruloyl unit in their structure, and compounds **29**, **42**, and **64**, corresponding to methyl ester derivatives of quinic or coumaroyl acid, were not detectable in PD. Moreover, the caffeoyl- and coumaroyl-quinic acid isomers **6**–**7**, and **17**–**19**, along with the caffeoylhexose **8** and the coumaroyl dihexoside isomers **9** and **14** were detectable in PD at a minor intensity level with respect to the other two extracts, as well as the monoacylated forms of coumaroyldihexoside isomers (**22**, **27**, **32**, and **37**). Furthermore, in PD, the coumaroyldihexoside isomers with two to four acetyl groups were even less intense (**41**, **44**, **47**, **59**, **61**, **65**, **68**–**69**, and **72**–**74**), while the penta-acetylated forms (**76**–**77**) were not detectable at all (Table 4). It is noteworthy that compounds **41**, **44**, and **47** were more evident in PC than in PF.

Regarding the second most representative group of metabolites identified in *P. cerasifera*—flavonols—once again, the PF extract was the most complete of the three, highlighting, besides the quercetin derivatives, the occurrence of isorhamnetin derivatives (**50**, **52**, and **63**) that were not evident in the other two extracts. Furthermore, PC showed the occurrence of flavonols at higher intensity levels than PD (Table 4). Flavan-3-ols (**20** and **34**) and proanthocyanidins A-type (**49**, **56**) occurred in all tested extracts, even if at lower intensity in PD, which lacked the dimers of proanthocyanidins B-type (**11**, **16**, and **23**), which were, in turn, more evident in PF than in PC (Table 4). Glycosylated derivatives of cyanidin and delphinidin (**10**, **12**, **15**, **45**, and **48**) could be observed in PF, PC, and PD, with PC showing the occurrence of the rutinoside derivatives of both anthocyanins (**15** and **45**) at a minor intensity level.

Simple organic acids like **2** and **5** or the nonanedioic acid **70**, as well as derivatives of malic acid with sugar alcohol like sorbitol or galactitol (**3**), or with a ketohexose like fructose (**4**), were detectable in all tested extracts, unlike the glycosylated forms of the dicrotalic and abscisic acids (**54** and **53**), with the first being more evident in PF and PC and the second no detectable in PD (Table 4).

Analogously, the glycosylated derivatives of benzyl alcohol or hydroxybenzaldehyde (**13**, **24**, **26**, and **28**) (differing in sugars) could be highlighted in all the extracts, contrary to glycosylated terpenates (**39** and **46**), which were mainly present in PF and PC, as well as the glycosylated form of hexanol (**43**), likely due to their higher lipophilicity (Table 4).

3.4. 'Alimena' Myrobalan Antioxidant Potential

The antioxidant activities of myrobalan bloody pulp fruit extracts were assessed using different in vitro methods, namely FRAP, β-carotene bleaching test, ABTS, and DPPH assays (Table 5).

The PF sample showed the highest radical scavenging activity, with IC_{50} values of 19.61 and 1.19 µg/mL for the DPPH and ABTS assays, respectively.

In general, by comparing the data obtained from the two different radical scavenging tests, it was possible to note that the $DPPH^{\cdot}$ radical is less sensible than the $ABTS^{+}$ in our samples. In fact, IC_{50} values in the range 19.61–39.02 and 1.19–2.97 µg/mL for the DPPH and ABTS tests, respectively, were obtained. Data from the ABTS test are in the same order of potency as ascorbic acid. The 'Alimena' pulp extracts ferric-reducing potential was evaluated by FRAP testing, revealing reduced iron in the samples, with a potency comparable to the positive control BHT.

Pearson's correlation coefficient evidenced *r* values of 0.79, 0.80, and 0.91 for TPC, FRAP, ABTS, and DPPH, respectively. A similar trend was also observed for TFC, wherein *r* values of 0.73, 0.85, and 0.95 for FRAP, ABTS, and DPPH were recorded, respectively. No positive correlation was found for TAC and the antioxidant data.

Table 5. 'Alimena' Myrobalan Antioxidant Potential.

Sample	DPPH Test (IC_{50} μg/mL)	ABTS Test (IC_{50} μg/mL)	β-Carotene Bleaching Test (IC_{50} μg/mL)	FRAP Test (μM Fe(II)/g)
PF	19.61 ± 2.98 [a]	1.19 ± 0.06 [a]	39.38 ±2.09 [c]	58.72 ± 2.76 [b]
PC	29.63 ± 6.45 [b]	2.46 ± 0.08 [b]	11.32 ±1.76 [a]	64.90 ± 3.52 [c]
PD	39.02 ± 4.45 [c]	2.97 ± 0.09 [c]	20.24 ±1.45 [b]	53.01 ± 2.20 [a]
Sign.	**	**	**	**
Positive control				
Ascorbic acid	5.04 ± 0.81	1.72 ± 0.14		
Propyl gallate			0.09 ± 0.04	
BHT				63.26 ± 2.31

Differences within and between the groups were evaluated by one-way ANOVA followed by Tukey's multiple-range test. The results followed by different letters in the same column are significantly different. ** Significance at $p < 0.05$.

Our data on radical scavenging potential are better than those reported for Indian *P. cerasifera* with IC_{50} values of 10.09 and 45.40 μg/mL for ABTS and DPPH assays, respectively [79]. On the contrary, our data obtained by FRAP testing resulted lower than those found in the "Sugar plum" cultivar (563.8 μM Fe (II)/g) [44].

The variability of antioxidant activity during the harvesting of *P. domestica* cv 'President', *P. salicina* cv 'Shiro', and *P. cerasifera* myrobalan was investigated. By comparing the data on the 'Alimena' myrobalan with those obtained by Moscatello et al. [40], it emerges that at the commercial maturity stage, the radical scavenging DPPH activity of our samples is significantly higher, with IC_{50} values in the range 56.22–76.46 μg/mL vs. 19.61–39.02 μg/mL, while similar results can be observed with the plum 'President' (IC_{50} in the range 28.63–30.35 μg/mL). Similar results against DPPH were also found for the *P. domestica* 'African Rose' and 'Santa Rosa' extracts (IC_{50} values of 13.923 and 18.416 μg/mL, respectively) [47]. On the contrary, when comparing this with domesticated *P. domestica*, a higher DPPH activity was observed (IC_{50} in the range 5.2–6.6 μg/mL for black and red fruit, respectively) [43].

Recently, Popović et al. [75] explored different *Prunus* varieties from Serbia and found high variability in the ability of hydroalcoholic extract to counteract the $DPPH^{\cdot}$ radical (IC_{50} in the range 0.83–29.12 mg/mL for steppe cherry and red cherry plum, respectively). However, all data are lower than those found in our extracts.

FRAP values ranging from 11.20 to 44.83 mmol TE/g fresh weight (FW) were found for yellow and purple Chinese myrobalan plum extract, respectively [28], whereas the FRAP values ranged between 0.123 and 0.835 mmol TE/kg FW for 'Selection 33C 02' and 'Selection 31C 18', respectively [8].

The integration of antioxidant data into the PF sample saw the most active result in terms of antioxidant activity, with the lowest RACI value (0.71) (Figure S1).

3.5. Inhibition of Target Enzymes Useful for the Prevention and Treatment of Hyperglycaemia and Obesity

In our continuous search for foods that are able to prevent MeTs, we have investigated the ability of the bloody pulp of myrobalan, a new variety of Sicilian *Prunus*, to counteract the enzymes linked with hyperglycaemia and hyperlipidaemia. All investigated extracts exerted inhibitory enzyme activity in a concentration-dependent manner (Table 6). According to Nowicka et al. [80], the extract richest in flavonols (PF) exerted the highest α-amylase inhibitory activity (IC_{50} value of 34.48 μg/mL). Moreover, the PF sample was found to be more proficient in inhibiting pancreatic lipase, followed by the PD sample, with IC_{50} values of 29.61 and 38.16 μg/mL, respectively. Values from 49.76 to 78.87 μg/mL were found for the PC and PD samples, respectively, against α-glucosidase. The results of correlation analysis evidenced that a strong positive correlation was found between TPC

and α-glucosidase inhibitory activity (r = 0.96) and TAC and lipase inhibitory property (r = 0.80). A weak correlation was found between TFC and α-amylase (r = 0.56).

Table 6. Enzymes inhibitory activities by 'Alimena' myrobalan extracts.

Sample	Lipase (IC_{50} μg/mL)	α-Amylase (IC_{50} μg/mL)	α-Glucosidase (IC_{50} μg/mL)
PF	29.61 ± 1.45 [a]	34.48 ± 4.22 [a]	55.27 ± 2.97 [b]
PC	78.53 ± 2.96 [c]	54.49 ± 3.87 [c]	49.76 ± 2.76 [a]
PD	38.16 ± 1.89 [b]	51.50 ± 3.24 [b]	78.87 ± 3.56 [c]
Sign.	**	**	**
Positive control			
Orlistat	3.74 ± 1.01		
Acarbose		50.12 ± 1.13	35.55 ± 1.10

Data are reported as mean ± standard deviation (SD) (n = 3). Differences within and between the groups were evaluated by one-way ANOVA, followed by Tukey's multiple-range test. The results followed by different letters in the same column are significantly different. ** Significance at $p < 0.05$.

Our data on carbohydrate-hydrolyzing enzymes are in line with those reported by Kołodziejczyk-Czepas [81] for *P. spinosa*; they found IC_{50} values in a range from 15.43 to 90.95 μg/mL for hydroalcoholic extract and butanol fraction, respectively, against α-glucosidase, and from 33.47 to 110.12 μg/mL for ethyl acetate and butanol fraction, respectively, against α-amylase. A lower α-amylase inhibitory effect was found by testing the *P. ceraus* extracts, with IC_{50} values in a range from 330 to 892 μg/mL for the 'Cigánymeggy' and 'Kántorjánosi' varieties, respectively [46], and by Popović et al. [75], who investigated different *Prunus* species (IC_{50} values in the range 4.61–136.23 mg/mL for *P. fruticose* and *P. pissardi* 'Carriére', respectively). In the same work authors tested *Prunus* extracts against α-glucosidase and recognized a low inhibitory activity (IC_{50} values in the range 0.41–136.23 mg/mL).

Podsędek et al. [82] investigated the effect of water extract obtained from *P. persica* fruits from Poland and found lower α-glucosidase inhibitory activity in comparison to our data (IC_{50} value of 264.44 mg/mL) despite a higher TPC content.

Recently, Ullah et al. [83] demonstrated that *P. domestica* subsp. *syriaca* ('Mirabelle') was able to inhibit the key enzymes involved in MetS. In particular, the hydroethanolic extract inhibited α-amylase, α-glucosidase, and pancreatic lipase, with IC_{50} values of 7.01, 6.4, 6.0 mg/mL, respectively. All these values are higher than those found in this study.

A perusal analysis of the literature revealed that the inhibition of α-glucosidase should be related to the content of the hydroxycinnamic acid derivatives that are particularly abundant in PF and PC and that exert a more potent inhibitory activity against this enzyme [84].

4. Conclusions

The preservation of agro-biodiversity for the purpose of consumption is at the heart of the targets of SDG No. 12 (Responsible Production and Consumption), demonstrating that the spread of a model of sustainability goes through the choices of products that have very high environmental adaptation. For this reason, the identification of new accessions, their description, and in-depth knowledge of their quality characteristics represents a virtuous model of knowledge development for consumption. The growing awareness of consumers toward the possibility of preventing and/or treating pathologies through certain defined foods represents the driving force of the global market for these types of products. In this context, we have analyzed the chemical profile and bioactivity of three extracts of a new bloody pulp selection of myrobalan (*P. cerasifera*). The PF extract showed the most promising bioactivity, which is in agreement with its highest phytochemical content. Further in vivo studies are necessary to better understand the biological properties and potential applications for the development of functional foods or nutraceutical products that are useful to consumers with these types of health problems.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/foods12051107/s1, Figure S1. RACI values.

Author Contributions: Methodology: F.S., S.P., M.R.L. and R.T.; software validation: A.N.; formal analysis: A.N., N.B. and R.T.; data curation: A.N., N.B. and M.B.; writing—original draft preparation: M.R.L. and S.P.; writing—review and editing, S.P.; project administration. M.B. and F.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was carried out within the National Biodiversity Future Center S.c.a.r.l., Piazza Marina 61 (c/o Palazzo Steri) Palermo, Italy, and received funding from the European Union Next-Generation EU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR)—MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.4, C.I. CN00000033)—CUP UNIPA B73C22000790001; CUP UNISA D43C22001260001.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are available from the authors upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

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