



Article

Bioactive Compounds in the Residue Obtained from Fruits of Some Cultivars of *Lonicera caerulea*

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Abstract: This paper aimed to investigate the bioactive compounds in the dry powder residue of honeysuckle cultivars after extracting the juice. Based on the analyses performed on the total content of phenolic compounds, flavonoids, anthocyanins, tannins, carotenoids and vitamin C, the results indicated that dried *Lonicera caerulea* residue represented a rich source of phenolic compounds (8041.36 mg GAE 100 g⁻¹), of which about 80% were tannins (6432.10 mg GAE 100 g⁻¹). The flavonoid content varied around 2436.95 mg CE 100 g⁻¹. Vitamin C (185 mg 100 g⁻¹), lycopene and β -carotene (over 2.5 and 2.8 mg 100 g⁻¹, respectively) were also quantified. Among the phenolic acids, chlorogenic acid predominated (316 mg 100 g⁻¹), followed by cryptochlorogenic acid (135 mg 100 g⁻¹) and neochlorogenic acid (32 mg 100 g⁻¹). Flavonoids were mainly represented by catechin (2594 mg 100 g⁻¹) and anthocyanins (1442 mg 100 g⁻¹). Similar amounts of epicatechin and rutin were measured (156 mg 100 g⁻¹ and 148 mg 100 g⁻¹), while the isoquercetin concentration was below 15 mg 100 g⁻¹. In conclusion, the high level of phytochemicals and the diverse composition of dry *Lonicera caerulea* residue support its high nutraceutical value and high health-promoting potential.



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1. Introduction

Lonicera caerulea, commonly known as blue honeysuckle or honeyberry (*Caprifoliaceae*) is closely related to other edible berries such as blueberries and cranberries. The fruit, usually bluish-purple in color and having a sweet and sour flavor, is a rich source of antioxidants and other bioactive compounds that may have health-promoting properties [1]. Also known as “haskap” or “blue honeysuckle”, the fruits have significant nutritional and therapeutic importance [2,3] and have been included in the group of so-called “super-fruits” [4]. Rich in antioxidants, especially anthocyanins and vitamin C, with an important role in protecting cells against damage caused by free radicals, honeysuckle fruits reduce the risk of cardiovascular disease, diabetes and other medical conditions [5]. Vitamin C in honeysuckle fruits supports the immune system and improves the body’s ability to fight infections and diseases [1,6,7]. The phenolic group is very diverse in *Lonicera* species and is the main contributor to their antioxidant activity. About 186 chemicals have been reported to be identified in *Lonicera*, including phenolic acids, flavonoids, triterpenoids, carotenoids and fatty acids [1]. From the category of plant secondary metabolic products, not only hydroxycinnamic acids, hydroxybenzoic acids, flavanols, flavones, isoflavones, flavonols, flavanones and anthocyanins but also iridoids are present in honeysuckle berries in exceptional amounts [5,8,9]. A high content of polyphenolic compounds in *Lonicera*

fruits was also reported by other authors [10,11]. Some of the health-promoting activities of *Lonicera* fruit consumption have also been attributed to its anthocyanin content [12,13]. In addition to having antioxidant and anti-inflammatory activities, anthocyanins have a broad spectrum of colors, making this class of compounds a potential replacement for synthetic dyes used in most industries (food, textile and cosmetics). *Lonicera* fruits are used both fresh and in various food products such as jams, syrups and drinks due to their pleasant taste and nutritional properties. Fruits, similarly to vegetables, represent a considerable part of the food chain, and the industry of processing them generates many by-products. The residues resulting from the processing of *Lonicera* fruits have unique nutritional value [14–16] that can be influenced by the cultivar, environmental factors, orchard technology and processing technology. Although there are numerous studies on the chemical composition of *Lonicera* fruits [17], there are few reports on the biologically active compounds from the residue obtained after juice production. Therefore, this study aimed to investigate the bioactive compounds in the dry powder residue of three *Lonicera* cultivars after juice extraction.

2. Materials and Methods

2.1. Materials and Preparation

The fruits were picked at their fully ripe stage, when they begin to detach easily from the branches. *Lonicera* fruits ('Cera', 'Loni' and 'Kami' cultivars) were harvested from plants in the experimental plots of ICDP Pitesti-Maracineni (E44°54'11" N 24°52'29" E, 287 m altitude). To obtain vegetable powder, the freshly harvested fruits (10 kg samples for each cultivar) were washed with drinking water, dried with a paper towel and pressed with an industrial hydraulic press (Voran series 100 P2), with a pressing power/force of 24 t, to obtain the juice. The pressed residue (pulp, peel, seeds) resulting after juice production was convectively dehydrated at 45 °C for 24 h with a Hestya DRY 15 industrial electric dehydrator until a water content of 10% was obtained. Next, samples of 200 g each of dehydrated residue were finely granulated with a grinder and stored in hermetically sealed glass containers at 4 °C in a dark place.

2.2. Chemicals and Reagents

The following chemicals and reagents were used: methanol; hydrochloric acid; distilled water; hexane; ethanol; acetone; Folin–Ciocalteu reagent (Merck-Sigma-Aldrich, Darmstadt, Germany); sodium carbonate; sodium nitrite; aluminum chloride; sodium hydroxide; potassium chloride; sodium acetate; 2,6-dichlorophenolindophenol sodium salt dihydrate; sodium bicarbonate; phosphoric acid; acetonitrile; and standards of gallic acid monohydrate, catechin hydrate, cyanidin chloride, ascorbic acid, epicatechin, rutin hydrate, quercetin dihydrate, isoquercetin, chlorogenic acid, cryptochlorogenic acid and neochlorogenic acid (Merck-Sigma-Aldrich, Germany).

2.3. Laboratory Equipment

A Vortex Mixer VX-200 Corning-Labnet system, an ultrasonic bath with a heater (ULTR-2L0-001) and a Labnet Spectrafuge 6c centrifuge were used to obtain extracts from the plant material. Colorimetric determinations were performed with a UV–Vis spectrophotometer (Perkin Elmer Lambda 25). HPLC analyses were performed using the SHIMADZU LC-20AT HPLC system equipped with a quaternary pump, a solvent degasser, an autosampler and a UV–Vis detector with a photodiode (DAD).

2.4. Analysis Methods

2.4.1. Determination of Total Content of Phenolic Compounds

The total polyphenolic content was estimated by the spectrophotometric method, following the methodology proposed by Cosmulescu et al. [18]. A methanolic extract of homogenized plant material was used for the analysis. To obtain the methanolic extract, 1 g dry powdery honeysuckle residue was treated with 10 mL methanol 8:2 v/v, vortexed for 2 min at 3000 rpm and subjected to ultrasonic treatment (40 kHz), followed by cen-

trifugation for 15 min at 3000 rpm, and the resulting supernatant was finally filtered. The extract (0.5 mL) was added to a 10 mL flask containing 7 mL of distilled water and 0.5 mL of Folin–Ciocalteu reagent. After 5 min, 2 mL of 10% sodium carbonate solution was added, and the mixture was allowed to stand for 2 h in the dark at room temperature. The absorbance of samples was measured, and the concentration of polyphenols was estimated. A blank sample was prepared from 0.5 mL of Folin–Ciocalteu reagent, 2 mL of 10% sodium carbonate solution and 7.5 mL of distilled water. The concentration of polyphenols was calculated using the calibration curve for gallic acid, performed under the same conditions as for the samples, and the absorbances of the resulting solutions were measured at 765 nm. Polyphenol content was expressed as mg gallic acid equivalent per 100 g dry residue (mg GAE 100 g^{−1}).

2.4.2. Determination of the Total Content of Tannins

The tannin content was determined with the methodology proposed by Cosmulescu et al. [19], with some modifications. For analysis, a volume of 1 mL of aqueous extract was added to a 10 mL flask containing 2 mL of distilled water and 2 mL of Folin–Ciocalteu reagent. After 5 min, 5 mL of 10% sodium carbonate solution was added. After 60 min of rest, the absorbance of samples was measured at 760 nm, and the concentration of tannins was expressed in mg GAE 100 g^{−1} dry weight of plant material. To obtain an aqueous extract, 1 g of dry powdery honeysuckle residue was treated with 10 mL of distilled water and vortexed for 2 min at 3000 rpm, followed by 30 min of ultrasonication at 80 °C. The mixture was subsequently centrifuged for 15 min at 3000 rpm, and the supernatant was used for analyses.

2.4.3. Determination of Total Content of Flavonoids

The flavonoid content was determined using the methodology proposed by Trandafir et al. [20], with minor modifications. A volume of 1 mL of methanolic extract was added to a 10 mL volumetric flask containing 4 mL of distilled water and 0.3 mL of 5% sodium nitrite. The mixture was allowed to stand 5 min, and then 0.3 mL of 10% aluminum chloride was added to the volumetric flask. After another 5 min of rest, 2 mL of a solution of 1 M sodium hydroxide was added, and the volume of the sample was adjusted with distilled water to 10 mL. The absorbance of the solution was measured at 510 nm. Total flavonoid content was expressed as mg catechin equivalent per 100 g dry honeysuckle residue (mg CE 100 g^{−1}).

2.4.4. Determination of Total Anthocyanin Content

The pH differential method applicable to the determination of monomeric anthocyanin, expressed in fruit as cyanidin-3-glucoside, was used as the reference approach. This method is suitable for determining the total content of monomeric anthocyanins based on structural changes in the anthocyanin chromophore as a function of pH (between pH 1.0 and 4.5). A volume of extract was mixed with 0.025 M potassium chloride buffer (pH 1.0), and another portion was mixed with 0.4 M sodium acetate buffer (pH 4.5). Following 30 min at room temperature (~25 °C), the absorbances were recorded at wavelengths of 520 and 700 nm for solutions at pH 1.0 and pH 4.5, respectively. Cyanidin-3-glucoside chloride was used as a standard, and the results are expressed in mg cyanidin-3-glucoside equivalent per 100 g^{−1} dry weight matter.

2.4.5. Determination of Carotenoid Content (Lycopene and β-Carotene)

The concentration of carotenoids, expressed in mg 100 g^{−1} plant material, was determined in the resulting supernatant according to the previously mentioned procedure, and the concentrations of lycopene and β-carotene were calculated using molar extinction coefficients of 184,900/M cm at 470 nm and 172,000/M cm at 503 nm for lycopene and 108,427/M cm at 470 nm and 24,686/M cm at 503 nm, respectively, for β-carotene in hexane.

2.4.6. Determination of Vitamin C Content

Vitamin C was determined using the indophenol titration method. According to the protocol, the vegetal material was mixed with 70 mL of cold extraction solution. This cold extraction solution consisted of 30 mg of metaphosphoric acid, 80 mL of acetic acid and distilled water added to 1000 mL, stored at 4 °C. The mixture was homogenized in a blender for 1 min and then filtered, centrifuged at $9000 \times g$ (4 °C) for 20 min and brought to a final volume of 100 mL. To quantify the ascorbic acid content, 10 mL of the extract was titrated with 2,6-dichloroindophenol solution until a distinct rose-pink color that persisted for more than 5 s. The 2,6-dichloroindophenol solution was standardized daily with ascorbic acid solution. The results were expressed in $\text{mg } 100 \text{ g}^{-1}$ [19].

2.4.7. Determination of Phenolic Compounds through HPLC–DAD

A SHIMADZU LC-20AT HPLC system equipped with quaternary pump, solvent degasser, autosampler, photodiode array detector and thermostatic column oven was used to quantify polyphenolic compounds in the extract. The separation of compounds was performed on a Kinetex C18 column, $4.6 \times 150 \text{ mm}$, $5 \mu\text{m}$ particles (Agilent Technologies, Santa Clara, CA, USA), using a two-component (A and B) mobile phase, a 45 min analysis time, a column temperature of 35 °C and a flow rate of 0.8 mL min^{-1} (solvent A: water + phosphoric acid, $\text{pH} = 2.3$; solvent B: acetonitrile). The injection volume of standards/samples was $10 \mu\text{L}$. Standard solutions were prepared in methanol at a concentration level of 1 mg mL^{-1} . Linear gradient elution was performed as follows: 0–28 min, 5–50% B; 28–38 min, 50–65% B; 38–40 min, 65–30% B; 40–41 min, 30–5% B; 41–45 min, 5% B. Spectral values were recorded in the 200–600 nm range for all peaks. The wavelengths used for the quantification were 280 nm, 320 nm and 360 nm. For quantification of polyphenolic compounds in the samples, calibration curves were first made in the working concentration range: $2.5\text{--}35 \mu\text{g mL}^{-1}$ (catechin, epicatechin, rutin, ellagic acid, daidzein, quercetin); $3.35\text{--}46.9 \mu\text{g mL}^{-1}$ (caffeic acid); $2.69\text{--}37.63 \mu\text{g mL}^{-1}$ (coumaric acid); $3.63\text{--}50.75 \mu\text{g mL}^{-1}$ (chlorogenic acid and its isomers, neochlorogenic and cryptochlorogenic acids) and $4\text{--}56 \mu\text{g mL}^{-1}$ (isoquercetin). The identification of compounds of interest was performed based on retention times, considering the 5% coefficient of variance accepted by the supplier when qualifying the equipment, the confirmation of purity of specific peaks being carried out at the wavelength characteristic of each class of compounds. The results obtained were expressed in $\text{mg } 100 \text{ g}^{-1}$ and $\text{mg } 100 \text{ g}^{-1}$ chlorogenic acid equivalent, respectively (for chlorogenic acid and its isomers, neochlorogenic and cryptochlorogenic acids).

2.4.8. Statistical Analysis

All analyses were performed in triplicate, and data were reported as the mean $\pm$ standard deviation (SD). Results were processed in Excel (Microsoft Office 2010) and SPSS Trial Version 28.0 (SPSS Inc., Chicago, IL, USA). Data were subjected to analysis of variance (one-way ANOVA; $p \leq 0.05$), and Duncan's multiple range test (DMRT) post hoc tests were used to measure specific differences between sample means. Different letters used on the bar charts (a, b) represent statistical significance between the bars or groups according to DMRT. The Pearson correlation coefficient was used to measure the strength of the linear correlation between the determined parameters.

3. Results and Discussion

3.1. Determination of Total Content of Phenolic Compounds, Tannins, Flavonoids and Monomeric Anthocyanins

Dehydrated honeyberry residue represented an important source of compounds with biological activity (Table 1), among which the total phenolic content (TPC) reached, on average, $8041.36 \text{ mg } 100 \text{ g}^{-1}$, oscillating from 6664.40 ('Loni') to 9619.46 $\text{mg } 100 \text{ g}^{-1}$ ('Cera'). According to the results obtained, the predominance of tannins (TTC) was observed, with these compounds representing 80.5% of the total determined polyphenols. The mean concentration of tannins was $6432.10 \text{ mg } 100 \text{ g}^{-1}$, with the minimum content in 'Kami'

cultivar (4679.05 mg 100 g⁻¹) and the maximum in ‘Cera’ (8967.91 mg 100 g⁻¹). The average flavonoid content was 2436.95 mg 100 g⁻¹, and approximately 60.12% was represented by anthocyanins (TAC), with an average content of 1441.90 mg 100 g⁻¹ and variation limits between 1394.44 and 1511.36 mg 100 g⁻¹. In the study by Ochmian et al. [21], the total phenolic content was higher at the end of the harvest period, and the authors reported that anthocyanins were the dominant compounds. Anthocyanins accounted for up to 75% of total phenolic compounds, with variations depending on the cultivar and harvest time, in the study by Ochmian et al. [21]. In another study, Senica et al. [22] reported a total phenolic content in the range of 173.51–268.22 mg 100 g⁻¹ and between 85.97 and 112.53 mg 100 g⁻¹ total anthocyanins. Additionally, Kucharska et al. [6] reported higher values in honeyberry fruits, ranging from 151.74 to 655.21 mg 100 g⁻¹ for 30 *Lonicera* cultivars. The values obtained for dry residue are much higher than the data provided by the literature for fresh fruit. Previous reports have shown that *Lonicera* possesses a high polyphenol content, with pomace containing 4.3-fold more polyphenols than fresh berries [8,23].

Table 1. Statistical descriptors of total phenolic, tannin, flavonoid and anthocyanin content in honeyberries’ dry residue *.

Compounds **/Descriptive Statistics	TPC	TTC	TFC	TAC
Mean	8041.36	6432.10	2436.95	1441.90
Standard deviation (SD)	735.23	1451.36	235.31	42.89
Coefficient of variation (%)	9.14	22.56	12.24	2.97
Minimum	6664.40	4679.05	1858.88	1394.44
Maximum	9619.46	8967.91	2940.00	1511.36

* Values are expressed in mg 100 g⁻¹; ** TPC = total phenolic content, TTC = total tannin content, TFC = total flavonoid content, TAC = total anthocyanin content.

3.2. Determination of Carotenoid (Lycopene and β -Carotene) Content and Vitamin C Content

Carotenoids showed oscillations from 2.08 to 3.07 mg 100 g⁻¹ (mean value of 2.55 mg 100 g⁻¹) for lycopene and from 2.18 to 3.78 mg 100 g⁻¹ (mean value 2.86 mg 100 g⁻¹) for β -carotene. The values of vitamin C content were less dispersed around the mean of 184.73 mg 100 g⁻¹ (VC = 8.05%), varying between 167.38 and 212.01 mg 100 g⁻¹ (Table 2).

Table 2. Statistical descriptors of lycopene, β -carotene and vitamin C in honeyberries’ dry residue *.

Compounds/Descriptive Statistics	Lycopene *	β -Carotene	Vitamin C
Mean	2.55	2.86	184.73
Standard deviation (SD)	0.31	0.54	14.88
Coefficient of variation (%)	11.99	18.93	8.05
Minimum	2.08	2.18	167.38
Maximum	3.07	3.78	212.01

* Values are expressed in mg 100 g⁻¹.

3.3. Determination of Phenolic Compound Content

The phenolic acids identified in the *Lonicera* residue were chlorogenic acid (ChA), neochlorogenic acid (NChA) and cryptochlorogenic acid (CChA), and among the flavonoids, catechin (C), epicatechin (EC), rutin (R) and isoquercetin (IQ) were identified (Table 3). The variability of compounds was reduced, except for cryptochlorogenic acid (VC = 24.24%) and epicatechin (VC = 62.85%), and their average amount, expressed in mg 100 g⁻¹, was 316.29 (307–332.81) for chlorogenic acid, 32.35 (30.97–34.30) for neochlorogenic acid, 134.54 (96.37–173.41) for cryptochlorogenic acid, 2593.78 (2559.63–2627.43) for catechin, 155.86 (114.38–415.97) for epicatechin, 148.01 (131.40–168.39) for rutin and 14.56 (12.44–16.20) for isoquercetin.

Table 3. Statistical descriptors of chlorogenic acid, neochlorogenic acid, cryptochlorogenic acid, catechin, epicatechin, rutin and isoquercetin content in honeyberries' dry residue *.

Compounds **/Descriptive Statistics	ChA *	NChA	CChA	C	EC	R	IQ
Mean	316.28	32.35	134.54	2593.78	155.86	148.01	14.56
Standard deviation (SD)	10.34	1.13	32.61	27.56	97.95	15.71	1.38
Coefficient of variation (%)	3.27	3.48	24.24	1.06	62.85	10.61	9.45
Minimum	307.44	30.97	96.37	2559.63	114.38	131.40	12.44
Maximum	332.81	34.30	173.41	2627.43	415.97	168.39	16.20

* Values are expressed in mg 100 g⁻¹; ** ChA = chlorogenic acid, NChA = neochlorogenic acid, CChA = cryptochlorogenic acid, C = catechin, EpC = epicatechin, R = rutin, IQ = isoquercetin.

A study by Zadernowski et al. [24] showed that 61.1% of total phenolic acids from *Lonicera* fruits consisted of hydroxycinnamic acids (mainly chlorogenic and 3,5-di-caffeoylquinic acid) and their derivatives (p-coumaric acid and m-coumaric acid). Another study reported the presence of rosmarinic, vanillic and gentisic acids with values of 0.08% in total [25]. Regarding the levels of compounds identified in *Lonicera* fruits, according to the data of Senica et al. [26], the predominant compounds in the class of flavonols were quercetin and kaempferol derivatives, and flavanols were some of the least widespread substances, representing, on average, 11% of the total phenols. Among the flavonoids, catechin, epicatechin and procyanidins were mainly reported, but luteolin and diosmetin were reported as well, and the content of flavanols ranged from 8.15 to 24.20 mg 100 g⁻¹ in the study by Sharma and Lee [1].

The matrix of correlations between the components quantified in the *Lonicera* fruit residue (Table 4) indicated that the total level of polyphenols had a significant positive correlation with tannins ($r = 0.592^*$), anthocyanins ($r = 0.675^*$) and catechin ($r = 0.695^*$) and a significant negative correlation with cryptochlorogenic acid ($r = -0.668^*$). Tannins showed high concentrations in the samples where carotenoid levels were high ($r = 0.837^{**}$, $r = 0.794^*$) and chlorogenic acid levels were low ($r = -0.688^*$).

Anthocyanins were positively correlated with vitamin C ($r = 0.689^*$), chlorogenic acid ($r = 0.945^{***}$), neochlorogenic acid ($r = 0.912^{**}$), catechin ($r = 0.937^{***}$) and rutin ($r = 0.959^{***}$) but negatively with cryptochlorogenic acid ($r = -0.947^{\circ\circ\circ}$) and isoquercetin ($r = -0.919^{\circ\circ\circ}$). The correlation of lycopene with β -carotene was reduced (highly significant positive correlation, $r = 0.971^{***}$). As in the case of anthocyanins, a high level of vitamin C was determined in samples with a high content of chlorogenic acid ($r = 0.782^*$), catechin ($r = 0.760^*$), epicatechin ($r = 0.734^*$) and rutin ($r = 0.817^*$) but with reduced levels of cryptochlorogenic acid ($r = -0.748^*$) and isoquercetin ($r = -0.705^*$). Chlorogenic and neochlorogenic acids were positively correlated ($r = 0.897^{***}$) with catechin and rutin and showed a negative correlation with cryptochlorogenic acid and isoquercetin.

Cryptochlorogenic acid and isoquercetin presented the most negative correlations with the other compounds in the dried *Lonicera* residue, the only positive correlation being with each other. According to data in the literature, total phenolic content is correlated negatively with organic acids but shows a positive correlation with sugars [22,26]. Between cultivars, the oscillations of the compounds with antioxidant activity were, for the most part, significant (Table 5), and the effect size started at 4.07%, which was observed in the case of polyphenols, reaching 99.9%, which was observed for anthocyanins. The values of flavonoids, carotenoids and epicatechin varied without statistical significance. The influence of cultivar on the chemical composition of fruit residues has also been noted in other species [27].

Table 4. Correlation matrix of phenolic compounds, vitamin C, lycopene and β -carotene in dry honeyberry pomace.

		TTC	TFC	TAC	Vitamin C	Lycopene	β -Carotene	ChA	NChA	CChA	C	EC	R	IQ
TPC	Pearson Correlation	0.592 *	0.119	0.675 *	0.596	0.253	0.290	0.434	0.381	−0.668 °	0.695 *	0.608	0.643	−0.625
	Sig. (2-tailed)	0.043	0.713	0.046	0.090	0.512	0.449	0.243	0.312	0.049	0.038	0.082	0.062	0.072
TTC	Pearson Correlation	1	−0.210	−0.364	−0.439	0.837 **	0.794 *	−0.688 °	−0.503	0.353	−0.322	−0.272	−0.501	0.411
	Sig. (2-tailed)		0.513	0.336	0.237	0.005	0.011	0.040	0.168	0.351	0.398	0.479	0.169	0.272
TFC	Pearson Correlation		1	0.377	0.232	−0.292	−0.300	0.353	0.381	−0.358	0.366	0.199	0.398	−0.417
	Sig. (2-tailed)			0.318	0.547	0.445	0.432	0.352	0.312	0.344	0.332	0.607	0.288	0.264
TAC	Pearson Correlation			1	0.754 *	−0.152	−0.152	0.895 **	0.887 **	−0.999 °°°	0.997 ***	0.510	0.984 ***	−0.983 °°°
	Sig. (2-tailed)				0.019	0.696	0.696	0.001	0.001	0.000	0.000	0.160	0.000	0.000
Vitamin C	Pearson Correlation				1	−0.032	−0.042	0.782 *	0.583	−0.748 °	0.760 *	0.734 *	0.817 **	−0.705 °
	Sig. (2-tailed)					0.935	0.914	0.013	0.099	0.021	0.018	0.024	0.007	0.034
Lycopene	Pearson Correlation					1	0.971 ***	−0.494	−0.472	0.146	−0.110	0.142	−0.253	0.203
	Sig. (2-tailed)						0.000	0.176	0.199	0.708	0.779	0.716	0.511	0.600
β -Carotene	Pearson Correlation						1	−0.477	−0.470	0.143	−0.104	0.090	−0.249	0.221
	Sig. (2-tailed)							0.194	0.202	0.713	0.790	0.818	0.518	0.568
ChA	Pearson Correlation							1	0.897 **	−0.891 °°	0.873 **	0.474	0.951 ***	−0.892 °°
	Sig. (2-tailed)								0.001	0.001	0.002	0.197	0.000	0.001
NChA	Pearson Correlation								1	−0.888 °°	0.883 **	0.153	0.886 **	−0.890 °°
	Sig. (2-tailed)									0.001	0.002	0.695	0.001	0.001
CChA	Pearson Correlation									1	−0.997 °°°	−0.496	−0.982 °°°	0.982 ***
	Sig. (2-tailed)										0.000	0.174	0.000	0.000
C	Pearson Correlation										1	0.488	0.975 ***	−0.969 °°°
	Sig. (2-tailed)											0.182	0.000	0.000
EC	Pearson Correlation											1	0.564	−0.480
	Sig. (2-tailed)												0.114	0.191
R	Pearson Correlation												1	−0.971 °°°
	Sig. (2-tailed)													0.000

*** Correlation is significant at level 0.001 (two-tailed); ** Correlation is significant at level 0.01 (two-tailed); * Correlation is significant at level 0.05 (two-tailed). Significant positive correlations were flagged by */**/***, while significant negative correlations were flagged by °/°°/°°°.

Table 5. Cultivar effect on levels of biologically active compounds in dehydrated honeyberry pomace.

Analyzed Constituent *	Sig.	Partial Eta Squared	Analyzed Constituent *	Sig.	Partial Eta Squared
TPC	0.043	0.407	ChA	0.000	0.977
TTC	0.001	0.773	NChA	0.008	0.803
TFC	0.939	0.014	CChA	0.000	0.999
TAC	0.000	0.999	C	0.000	0.997
Lycopene	0.114	0.516	EC	0.301	0.330
β -Carotene	0.102	0.533	R	0.000	0.998
Vitamin C	0.035	0.672	IQ	0.000	0.968

* TPC = total phenolic content, TTC = total tannin content, TFC = total flavonoid content, TAC = total anthocyanin content, ChA = chlorogenic acid, NChA = neochlorogenic acid, CChA = cryptochlorogenic acid, C = catechin, EC = epicatechin, R = rutin, IQ = isoquercetin.

The highest content of polyphenols (Figure 1) was determined in ‘Cera’ and ‘Loni’ cultivars (8708.88 and 7920.87 mg 100 g^{−1} respectively); ‘Cera’ was also distinguished by its concentration of tannins (8193.47 mg 100 g^{−1}). No significant differences were recorded in flavonoids content.

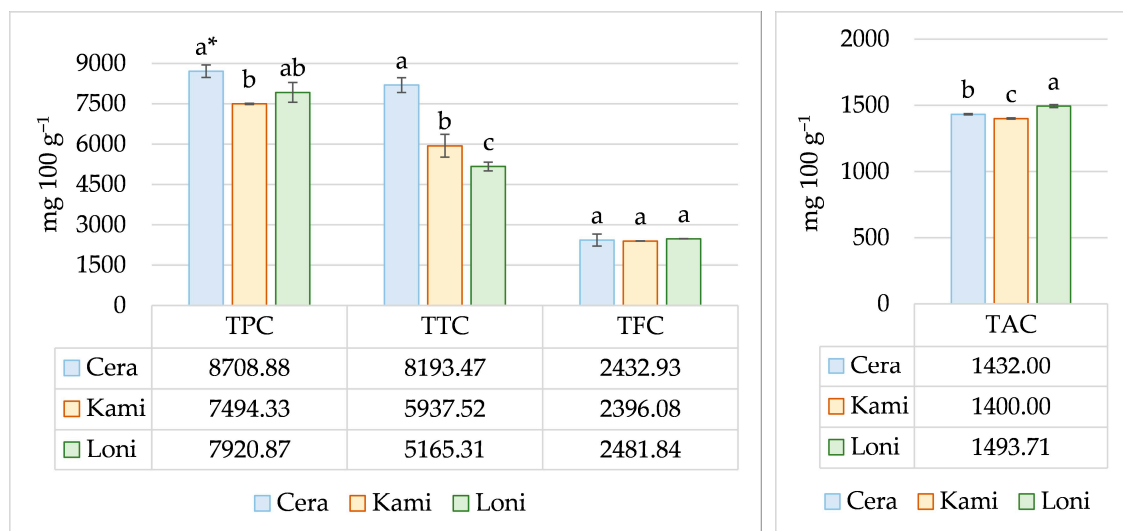


Figure 1. Total phenolic, tannin, flavonoid and anthocyanin content in dry honeyberry residue depending on cultivar. Different letters used on the bar charts (a, b, c) represent statistical significance between the bars or groups according to DMRT).

Anthocyanins (CTA) were present in a higher quantity in the variety ‘Loni’ (1432.00 mg 100 g^{−1}; Figure 1), and vitamin C (Figure 2) predominated in the same cultivar (200.85 mg 100 g^{−1}), exceeding by at least 12.5% the amounts determined in the other two varieties. The total amounts of anthocyanins identified varied significantly within the cultivars in the study conducted by Raudonė et al. [28]. The variation of carotenoids (Figure 2) was nonsignificant. Carotenoids are natural pigments that are present in fruits and vegetables and make an important contribution to human health.

Among the phenolic acids present in the residue (Figure 3), chlorogenic and neochlorogenic acids predominated in the ‘Loni’ cultivar (329.86 and 33.61 mg 100 g^{−1}, respectively), and cryptochlorogenic acid dominated in ‘Kami’ (172.33 mg 100 g^{−1}). In all cases, ‘Cera’ var. occupied an average position. Contrary to our results, Oszmiański et al. [24] found higher amounts of chlorogenic acid (1109.8–1303.52 mg 100 g^{−1}) and a lower content of cryptochlorogenic acid (15.58–19.82 mg 100 g^{−1}) in dehydrated fruit residues.

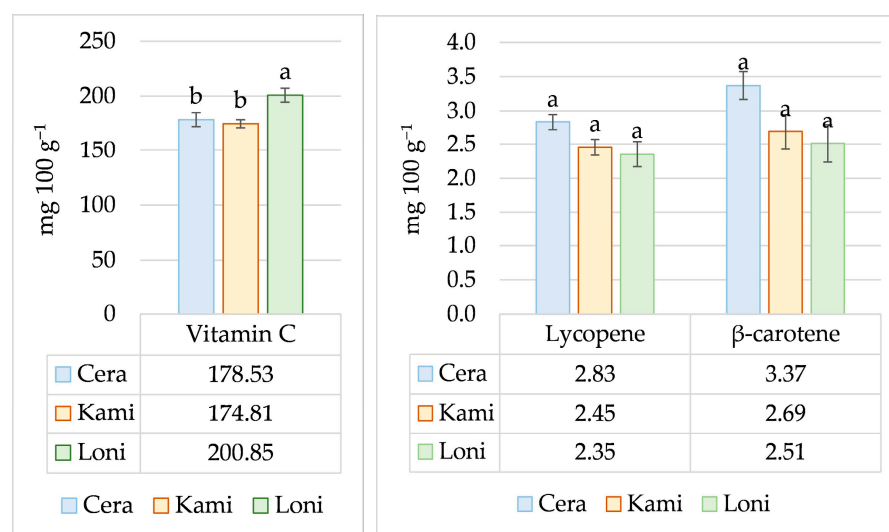


Figure 2. Vitamin C, lycopene and β -carotene content in dry honeyberry residue depending on cultivar. Different letters used on the bar charts (a, b) represent statistical significance between the bars or groups according to DMRT.

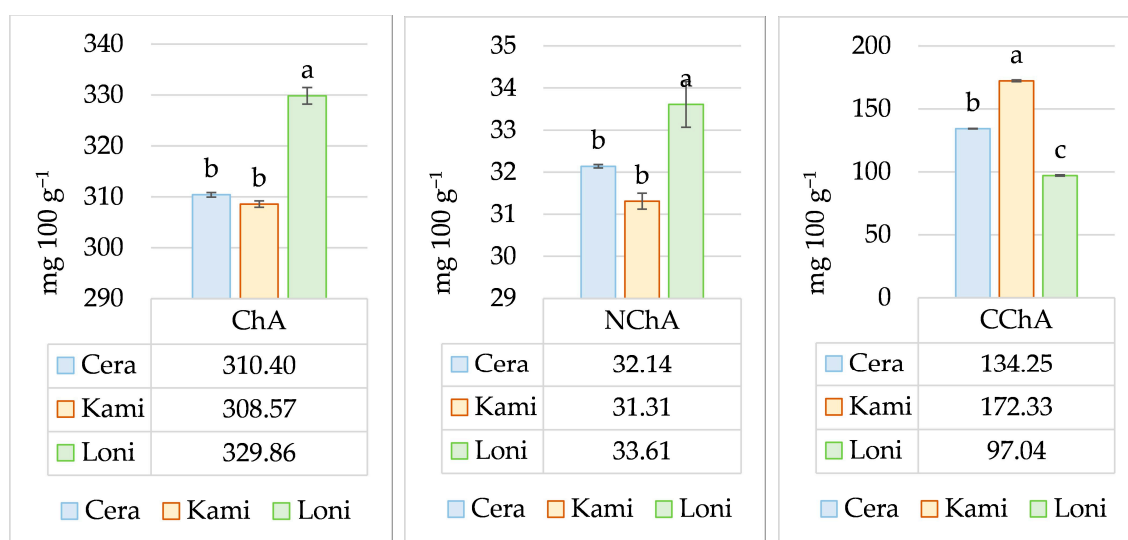


Figure 3. Content of chlorogenic (ChA), neochlorogenic (NChA) and cryptochlorogenic acids (CChA) in dry honeyberry residue depending on cultivar. Different letters used on the bar charts (a, b, c) represent statistical significance between the bars or groups according to DMRT.

Catechin, epicatechin and rutin (Figure 4) accumulated in higher concentrations in the 'Loni' cultivar, at 2624.68 mg 100 g⁻¹, 230.79 mg 100 g⁻¹ and 167.68 mg 100 g⁻¹, and presented average values in 'Cera' cultivar. Moreover, isoquercetin also presented an average content in this cultivar but predominated in 'Kami' (16.07 mg 100 g⁻¹). Oszmiański et al. [24] reported that the dehydrated residue contained lower levels of the flavonoids catechin (1696.98–2013.13 mg 100 g⁻¹), epicatechin (52.22–80.55 mg 100 g⁻¹) and rutin (3.69–6.02 mg 100 g⁻¹) but higher levels of isoquercetin (53.21–61.86 mg 100 g⁻¹).

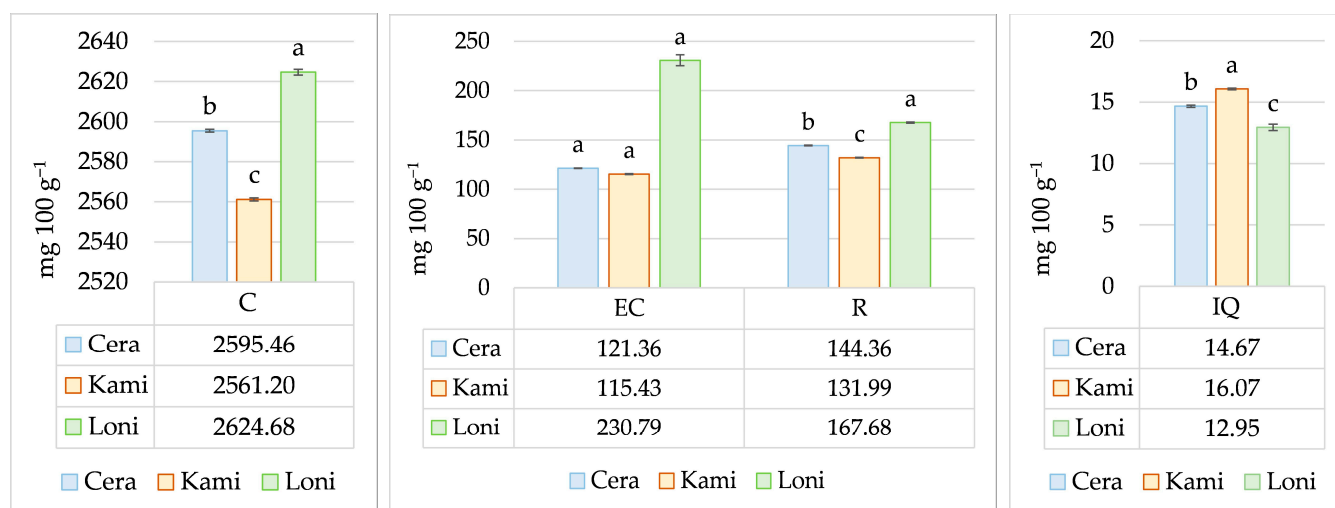


Figure 4. Catechin (C), epicatechin (EC), rutin (R) and isoquercetin (IQ) content in dry honeyberry residue depending on cultivar. Different letters used on the bar charts (a, b, c) represent statistical significance between the bars or groups according to DMRT.

4. Conclusions

The residues resulting from the processing of fruits and vegetables can represent a great loss of valuable nutrients. For this reason, the biotransformation of waste is receiving increasing attention because it can be used as a resource to obtain useful products with added value in the food, cosmetic and medical sectors. The dehydrated residue of *Lonicera* represents a rich source of phenolic compounds (with about 80% tannins), and it also contains vitamin C and carotenoids (lycopene, β -carotene). Based on the results obtained from three investigated *Lonicera* cultivars, the ‘Cera’ cultivar showed the richest polyphenolic profile, with a high content of polyphenols, especially tannins, anthocyanins, catechin, rutin, isoquercetin and cryptochlorogenic acid. The qualities of the residue obtained from the ‘Loni’ cultivar were also highlighted, with an average level of polyphenols but high levels of anthocyanins, catechin, epicatechin, rutin, vitamin C, chlorogenic acid and neochlorogenic acid. The highest levels of cryptochlorogenic acid and isoquercetin were found in the ‘Kami’ cultivar. In conclusion, this study helps raise the value of berry waste by demonstrating its diverse and rich content of bioactive compounds that, in the future, will be recovered and used according to market demands. *Lonicera* residue should not be treated as waste but should be recovered as useful materials from a circular economy perspective that can benefit industries, the environment and consumers.

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