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Optimization of Extraction Conditions for Phenolic Compounds from Potato Tubers: LC-MS Phenolic Profile as a Powerful Tool to Assess the Genotypes, Vegetation Period, and Production Systems of Potato

Aleksandra Dramićanin [1,*], Nikola Horvacki [2], Uroš Gašić [3,*] and Dušanka Milojković-Opsenica [1]

[1] Department of Analytical Chemistry, Center of Excellence for Molecular Food Sciences, Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, 11158 Belgrade, Serbia; dusankam@chem.bg.ac.rs
[2] Innovation Centre of the Faculty of Chemistry Ltd., Studentski trg 12-16, 11158 Belgrade, Serbia; nhorvacki@chem.bg.ac.rs
[3] Department of Plant Physiology, Institute for Biological Research "Siniša Stanković"—National Institute of the Republic of Serbia, University of Belgrade, Bulevar Despota Stefana 142, 11108 Belgrade, Serbia
* Correspondence: akosovic@chem.bg.ac.rs (A.D.); uros.gasic@ibiss.bg.ac.rs (U.G.)

Abstract: Five different extraction methods were assessed to select an optimal procedure for extracting the phenolic antioxidants from potato tubers. Total phenolic content and antioxidant capacity were determined for each type of extraction. In total, 144 samples of four potato varieties from three production systems, over a period of three years, were analyzed. The results show that TPC and RSA tests can be used as parameters for differentiating potato parts and variety and to distinguish the samples depending on ripening time and the production system. Higher values of TPC and RSA were observed in samples from the organic cultivation system compared to integral and conventional cultivation in the same cultivar. Finally, by the employment of UHPLC-LTQ Orbitrap XL, fifty-nine phenolic compounds were identified. It was concluded that the phenolic profile is a powerful tool for confirming botanical origin, distinguishing between genotypes, and distinguishing various production systems of potato.

Keywords: potato; organic/integral/conventional type of production; advanced chemometrics; total phenolic content; antioxidant capacity; UHPLC-DAD MS/MS; UHPLC-LTQ Orbitrap XL

Academic Editors: Adela Ramona Moise and Daniel Severus Dezmirean

Received: 18 November 2024
Revised: 24 January 2025
Accepted: 31 January 2025
Published: 2 February 2025

Citation: Dramićanin, A.; Horvacki, N.; Gašić, U.; Milojković-Opsenica, D. Optimization of Extraction Conditions for Phenolic Compounds from Potato Tubers: LC-MS Phenolic Profile as a Powerful Tool to Assess the Genotypes, Vegetation Period, and Production Systems of Potato. *Processes* **2025**, *13*, 396. https://doi.org/10.3390/pr13020396

1. Introduction

Potato accumulates a large number of secondary metabolites, including phenolic compounds and many other phytochemicals, as protection against the harmful effects of mechanical bruising, light, and damage from predators such as bacteria, fungi, viruses, and insects [1,2]. In addition to contributing to the pigmentation and sensory characteristics of this plant crop [3], phenolic compounds from potato can reduce the risk of cancer, cardiovascular diseases, and type 2 diabetes. They participate in preventing damage to proteins, lipids, carbohydrates, and DNA caused by free radicals [4,5]. Therefore, potato is one of the most important sources of antioxidants in human nutrition [6]. Based on metabolic relationships and structural composition, there are three main groups of antioxidants present in potato [7]. The first group consists of aromatic phenolic compounds, including flavonoids such as anthocyanins and flavonols, and the amino acids tyrosine, phenylalanine, and tryptophan produced via the shikimate metabolic pathway. The second group includes isoprenoid antioxidants such as carotenoids and tocopherols, while the

third group encompasses antioxidants related to the functions of ascorbate and glutathione in the redox system, including ascorbic acid [8].

Phenolic compounds such as chlorogenic acid, catechin, *p*-coumaric acid, ferulic acid, caffeic acid, and protocatechuic acid and flavonols (kaempferol, quercetin, myricetin) were observed in relevant concentrations in potato tubers in multiple studies [9–11]. Phenol concentrations, including anthocyanins, in potatoes are related to the color, mass, and skin, with the bulk or peel of the potato potentially being fully or partially pigmented [12–14]. Potato peel has also drawn attention as a natural antioxidant in nutrition due to its high phenol content, believed to be ten times higher than the concentration in the core, constituting about 50% of all phenols in potato tubers [15].

In order to find potential indicators of differences between the potato varieties of different origins and lengths of vegetation period from three production systems, this study aimed to evaluate a simple procedure for phenol fingerprinting of potato tubers from three types of production—conventional, integral, and organic.

Five different extraction solvents were employed, and all five extraction types were assisted with ultrasound in the same thermal regime. Total phenolic content (TPC) and antioxidant capacity (RSA) for each extraction type and for a total of 144 samples were determined (48 per year, in a period of three years of production, namely 24 bulk and 24 peel samples from four potato varieties: Red Fantasy, Laura, Marabel, and Jelly). The results were analyzed to select the best method for extracting phenolic compounds. Considering the obtained results and their statistical processing, the optimization process was reduced from five to two procedures. For further optimization and the selection of the potentially best extraction method, the quantification of phenolics in the peel and bulk of the potato samples in combination with processing the obtained data with advanced chemometric tools was performed.

Quantification of phenolic compounds in the samples was performed using UHPLC-DAD MS/MS. Eleven phenolic compounds were quantified in 48 potato extract samples, with 24 samples for each extraction method. In this work, UHPLC-LTQ Orbitrap XL was used to define criteria for describing and classifying various potato cultivars. This approach is used for the first time, to the best of our knowledge, although this methodology was already used for the determination of phenols and the characterization of potato samples [16–18]. Also, in recent years there have been studies focusing on a smaller number of phenolic compounds such as the reports of Vinod Kumar et al. (2024) [19], Cebulak et al. (2023) [20], and Makori et al. (2022) [9]. In a less recent study, Shepherd et al. (2010) performed a metabolomic analysis of potato tubers in regard to their life cycle segmented into six stages of development including developing and mature tubers, sprouting mature tubers, and mature tubers, by the utilization of three MS-coupled methods [21]. Similarly to our study, Oertel et al. (2017) have profiled 57 potato samples by the implementation of ultra-high-resolution time-of-flight mass spectrometry and detected 21 anthocyanins and 31 other phenolic compounds [22]. In our study, an untargeted approach was also implemented, which resulted in identification of fifty-nine phenolic compounds in potato tuber samples. Furthermore, in combination with advanced chemometric analysis, it was determined that biomarkers derived from the detailed phenolic profiles (with an emphasis on phenolic acids and flavonoids) of potato tubers could be a powerful tool for confirming their botanical origin, as well as to distinguishing potato genotypes, distinguishing samples with different lengths of vegetation period, and characterizing the response of potato tubers to various agronomic practices, i.e., production systems.

2. Materials and Methods

2.1. Reagents and Standards

2.1.1. Determining Total Phenolic Contents and Antioxidant Capacity

Reagents and standards for determining TPC (total phenolic content), TEAC (Trolox Equivalent Antioxidant Capacity), and radical scavenging activity (RSA): Methanol (HPLC-grade) and FC reagent were procured from Merck (KGaA, Darmstadt, Germany). 2,2-Diphenyl-1-picrylhydrazyl (DPPH) was purchased from Fluka Chemie AG (Buchs, Switzerland). Trolox, gallic acid standard, and anhydrous sodium carbonate were obtained from Sigma-Aldrich (Steinheim, Germany). For the preparation of all standard solutions and dilutions, ultrapure water was used (MicroPure water purification system, 0.055 mS/cm, TKA, Thermo Fisher Scientific, Niederelbert, Germany). Ethanol 96% (v/v) and HCl 37% (v/v) were obtained from Zorka Pharma (Šabac, Serbia), and acetone from Merck (Germany). All reagents were of analytical grade. Syringe filters (13 mm, 0.45 µm PTFE membrane) were purchased from Supelco (Bellefonte, PA, USA).

2.1.2. Identification and Quantification of Phenols—Determination of Phenolic Profile

Standards of phenolic compounds used for quantification analysis (protocatechuic acid, 5-*O*-caffeoylquinic acid, *p*-hydroxybenzoic acid, caffeic acid, *p*-coumaric acid, quercetin-3-*O*-glucoside, naringin, quercetin-3-*O*-rhamnoside, kaempferol and ferulic acid) were obtained from Sigma-Aldrich (Steinheim, Germany).

2.2. Sample Preparation—Cultivation Experiments

Four potato varieties were used in this study: two middle early red peel varieties, Red Fantasy (F) and Laura (L); one early yellow peel variety, Marabel (M); and one late yellow variety, Jelly (J). Over three years (I, II, and III), the varieties were grown in field trials using four repetitions of randomized block design in three different production systems: organic (O), integral (I), and conventional (C). In our previous studies, field and test conditions were both reported [23,24].

2.3. Optimization of Phenol Extraction Method

In order to develop an optimal procedure for isolating the antioxidant fraction from potato tubers, five different extraction methods (E1–E5) were applied to samples from the last year of production. The extraction methods are modifications of described methods that utilize methanol [10,11,14,22], ethanol [25], and acetone [12]. All extractions were performed at room temperature in an ultrasonic bath. The solutions were collected and evaporated under vacuum to dryness at 40 °C (IKA RV5, IKA Werke, Staufen, Germany), dissolved, filtered (0.45 µm PTFE membrane filter), and stored at 4 °C until analysis. The performance of extraction methods was evaluated by their TPC and RSA values of obtained extracts. The following extraction conditions were assessed:

Extraction 1 (E1): Approximately 0.5 g of dried sample was extracted with 10 mL of 80% methanol for 20 min. The extract was centrifuged for 15 min at 3000 rpm. The supernatant was collected, and the extraction was repeated two more times. The residue after evaporation was dissolved in 5 mL of a methanol/water mixture (3:2).

Extraction 2 (E2): About 0.5 g of dried sample was extracted with 10 mL of an ethanol–water mixture (80:20, v/v) for 10 min. Subsequently, centrifugation was carried out at 4000 rpm for 15 min. The extraction was repeated three times. The residues after evaporation were dissolved in 5 mL of a methanol–water mixture (50:50, v/v).

Extraction 3 (E3): Approximately 0.5 g of dried sample was extracted with 10 mL of an acetone–water mixture (70:30, v/v) for 30 min. The extracts were centrifuged for 15 min at

4000 rpm. The supernatant was collected, and the extraction was repeated two more times. The residues after evaporation were dissolved in 5 mL of methanol.

Extraction 4 (E4): About 0.5 g of dried sample was extracted three times for 30 min each with 10 mL of methanol containing 1% HCl in the dark. The extracts were centrifuged at 4000 rpm for 15 min. The obtained dry residue was dissolved in 5 mL of a methanol/1% HCl mixture.

Extraction 5 (E5): Approximately 0.5 g of dried sample was extracted three times with 10 mL of a methanol–water mixture (70:30, v/v) containing 0.1% HCl for 30 min in the dark. The extracts were centrifuged for 15 min at 4000 rpm. The obtained dry residue was dissolved in 5 mL of water. Solid–liquid extraction was used for the purification of the extracts. C-18 column preconditioning was performed with 3 mL of methanol and 9 mL of ultrapure water. Samples were applied under vacuum without prior filtration. Sugar components were eluted from the column with 6 mL of water, and phenolic compounds were eluted with 1.5 mL of methanol.

2.4. Determining Total Phenol Content of Potato Tubers

The TPC in the samples was determined spectrophotometrically (Cintra 6 UV-Visible spectrophotometer, GBC, Keysborough, Australia), based on a modified Folin–Ciocalteu (FC) method described in the literature, with gallic acid as the standard [14]. To 0.5 mL of the diluted sample, 0.5 mL of ultrapure water and 2.5 mL of 10% FC reagent were added. The mixture was incubated for 5 min at room temperature. Then, 2 mL of 7.5% sodium carbonate was added. After incubating for 2 h at room temperature in the dark, the absorbance was measured at 765 nm. A series of standard solutions with concentrations of 20, 40, 50, 70, and 100 mg/kg were prepared, and a mixture of 1 mL of water and reagents was used as a blank. The results are expressed as milligrams of gallic acid equivalents (GAE) per kilogram of potatoes. All measurements were performed in duplicate.

2.5. Determining Antioxidant Capacity of Potato Tubers

A modified method from the literature was used for the measurement of antioxidant activity [14]. To 0.1 mL of the diluted sample or 0.1 mL of the standard solution, 4 mL of a 0.02 mg/mL DPPH solution was added. The resulting solutions were incubated for 60 min at room temperature in the dark and the absorbance was measured at 517 nm. A series of standard Trolox solutions with concentrations of 100, 200, 300, 400, 500, and 600 µM was prepared. A mixture of 0.1 mL of methanol and 4 mL of DPPH solution was used as a blank. The RSA was calculated as a percentage of the DPPH discoloration in reference to the blank. The results are expressed as mM TE (Trolox equivalent) per kilogram of dry potato sample.

2.6. Identification of Phenolic Compounds—Determination of the Phenolic Profile

For the separation and identification of metabolites from potato tuber samples, a UHPLC system was employed. The system consists of an Accela autosampler (Thermo Fisher Scientific, Bremen, Germany) and a quaternary Accela 600 pump connected to a high-resolution hybrid mass spectrometer (UHPLC-LTQ Orbitrap XL) with a heated electrospray ionization (HESI) ion source (Thermo Fisher Scientific, Bremen, Germany). The analytical column used for separation, Syncronis C18 (100 × 2.1 mm, 1.7 µm particle size), was obtained from Thermo Fisher Scientific. The mobile phase consisted of eluent A: water + 0.1% formic acid and eluent B: acetonitrile + 0.1% formic acid. Mass spectra were recorded in the negative mode, covering a full scan mass spectrum range of 100–1000 m/z. The other LC-MS parameters were previously described by Devrnja et al. (2022) [16]. The ChemDraw molecule editing software (version 12.0) was used as a reference library for calculating the mass of compounds of interest. The molecular formula of the unknown

compound was determined based on the recorded accurate mass of the molecular ion ($[M–H]^-$), while the MS^2 fragmentation allowed the elucidation of the structures of the unknown compounds.

2.7. Quantitative Analysis of Phenolic Compounds

Quantification of phenolic compounds in potato tuber samples was performed using a Dionex Ultimate 3000 UHPLC system equipped with a diode-array detector (DAD) and mass spectrometry detector (TSQ Quantum Access Max, Thermo Fisher Scientific, Basel, Switzerland) with a triple quadrupole mass detector (UHPLC-DAD MS/MS). The elution process was carried out on an analytical Syncronis C18 column thermostated at 40 °C. The mobile phase consisted of eluent A: water + 0.1% acetic acid and eluent B: acetonitrile with a concentration gradient: 5% B, 2.0 min; 5–95% B, 2.0–12.0 min; 95–5% B, 12.0–12.2 min; and 5% B until 15 min with a flow rate of 0.3 mL/min. For quantification of phenolics, both the molecular ion and the most intense fragment of the MS^2 spectrum were recorded for each standard. The Xcalibur software (version 2.2) was used for instrument control, data collection, and data analysis. The total content of each compound was determined by integrating peak areas, and the content was expressed as mg/kg.

2.8. Statistical Data Analysis

In order to optimize the extraction procedure of phenolic compounds and select a potentially best-suited method, non-parametric tests, namely the Friedman test and the Wilcoxon rank-sum test, were performed using the SPSS software package (IBM SPSS Statistics 20) based on the total phenolic content and antioxidant capacity. For further optimization, the phenolic profile was determined and phenols quantified, and the results obtained following LC-MS analyses were processed using the PLS Toolbox, v.6.2.1 in MATLAB 7.12.0 (R2011a) (MathWorks Inc., Natick, MA, USA). To gain a more comprehensive understanding of the data structure and to identify similarities, differences, and groupings, a principal component analysis (PCA) was conducted. Prior to multivariate analysis, all data were auto-scaled.

3. Results and Discussion

3.1. Optimization of Phenolic Compound Extraction Method

To develop an optimal procedure for isolating the antioxidant fraction from potato tubers, five different extraction methods were employed. The optimization process involved the selection of 24 potato samples, comprising 6 samples from each of the four varieties (2 samples for each variety from 3 cultivation systems). In these samples, the TPC and the RSA were determined for each extraction type. The obtained results are presented in Supplementary Materials Table S1. Non-parametric tests, the Friedman test and the Wilcoxon rank-sum test, were conducted to determine if there were statistically significant differences between the extraction types based on total phenolic content and antioxidant capacity. The objective was to identify the appropriate method for the extraction of phenolics. The results of these tests are shown in Table 1.

The highest content of total phenols and antioxidant capacity was determined in samples extracted with 80% methanol (extraction 1) and a mixture of acetone–water (70:30, v/v) (extraction 3) (Supplementary Materials Table S1, Figure 1). The results of the Friedman test and the Wilcoxon rank sum test indicate a statistically significant difference between these two extraction methods and the other three (Table 1); therefore, these two extraction methods were used for further analysis.

Table 1. Statistical tests for the total phenolic content extracted from potato samples using five extraction methods. Highlighted (bold) values indicate the presence of a statistically significant difference between extractions.

Wilcoxon Rank Test					**TPC**			
Differences	**E4**	**E3**	**E2**	**E1**				
	Z	***Z***	***Z***	***Z***	**Friedman's Test ***	**St. Dev.**	**Mean Value**	**Type of Extraction**
E1 (E2, E3, E4, E5)	**4.171**	**2.329**	**4.129**	/	N: 24 χ^2: 50,046 df: 4 Stat. significance: $p < 0.001$	1.26	3.74	E1
E2 (E1, E3, E4)	**2.418**	**2.971**	/	**4.129**		1.01	2.84	E2
E3 (E1, E2, E4, E5)	**3.929**	/	**2.971**	**2.329**		0.98	3.33	E3
E4 (E1, E2, E3)	/	**3.929**	**2.418**	**4.171**		0.71	2.61	E4
E5 (E1, E3)	0.257	**2.929**	1.344	**4.286**		1.25	2.70	E5
Wilcoxon Rank Test					**RSA**			
Differences	**E4**	**E3**	**E2**	**E1**				
	Z	***Z***	***Z***	***Z***	**Friedman's Test ***	**St. Dev.**	**Mean Value**	**Type of Extraction**
E1(E2, E4, E5)	**4.286**	1.286	**4.286**	/	N: 24 χ^2: 58,100 df: 4 Stat. significance: $p < 0.001$	7.05	19.67	E1
E2 (E1, E3, E5)	1.029	**3.800**	/	**4.286**		5.26	11.37	E2
E3 (E2, E4, E5)	**4.171**	/	**3.800**	1.286		6.72	17.92	E3
E4 (E1, E3, E5)	/	**4.171**	1.029	**4.286**		3.48	10.75	E4
E5 (E1, E2, E3, E4)	**2.714**	**2.743**	**3.243**	**3.829**		6.83	13.69	E5

* The values are considered statistically significantly different if the χ^2 value is >36.415.

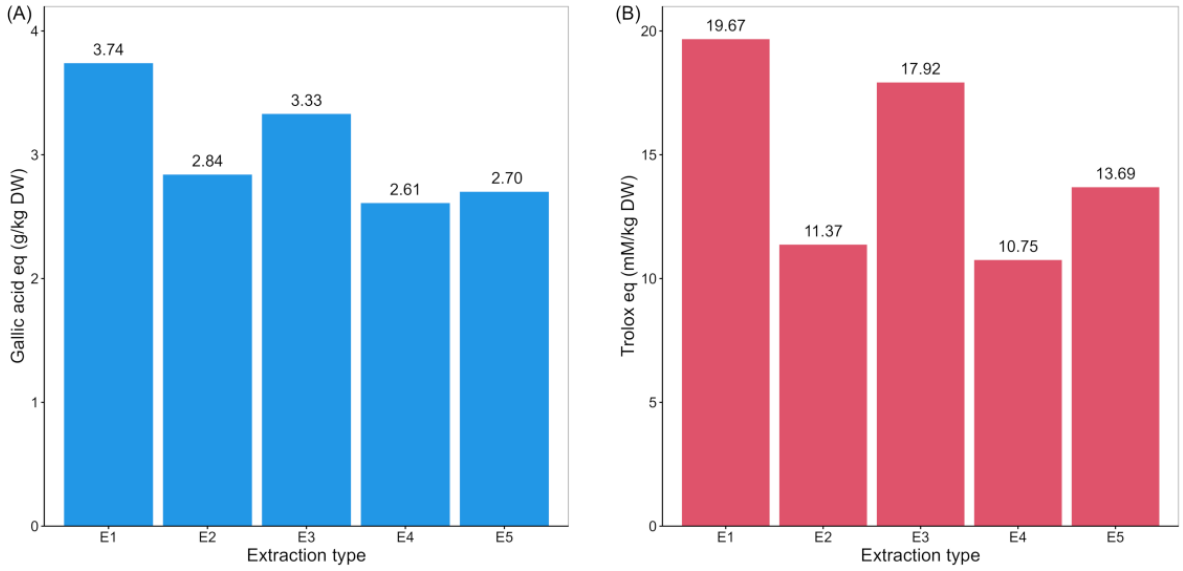

Figure 1. The total phenolic content (TPC; (**A**)) and radical scavenging activity (RSA; (**B**)) in extracts of potato samples from five different extraction methods.

To further optimize and select the potentially best extraction method, the quantification of phenolics was performed in samples extracted with 80% methanol and the mixture of acetone–water (70:30, *v*/*v*).

3.2. Quantitative Analysis of Phenolic Compounds in Potato Samples

In a total of 48 potato extract samples, 24 for each extraction type (extractions 1 and 3), eleven phenolic compounds were quantified by UHPLC-DAD MS/MS analysis. These compounds included six phenolic acids (protocatechuic acid, 5-*O*-caffeoylquinic acid, *p*-hydroxybenzoic acid, caffeic acid, *p*-coumaric acid, and ferulic acid), four glycosides (rutin, quercetin-3-*O*-glucoside, naringin, and quercetin-3-*O*-rhamnoside), and the flavonol kaempferol. The content of quantified phenolic compounds in the tested potato extracts from different potato varieties and production systems is presented in Supplementary Materials Table S2.

Multiple studies about the quantification of phenolic acids, such as chlorogenic, caffeic, *p*-coumaric, and ferulic acids, have been reported [1,26]. The results are diverse—heavily affected by the potato cultivar, the growth environment, and also the experimental procedure. A common observation is that chlorogenic acid is detected in high amounts in comparison to other quantified phenolic acids or flavonoids, along with caffeic acid which is usually ranked second. Similarly to our results, Ru et al. (2019) have detected chlorogenic acid in the range between 20.6 and 79.4 mg/kg DW and caffeic acid in the range between 9.5 and 66.6 mg/kg DW in yellow or white flesh potatoes [11].

To elucidate differences between extractions 1 and 3 to choose the best extraction method, the obtained results were used as input for PCA.

Principal component analysis (PCA) based on the content of phenolic compounds in 48 different potato samples resulted in a four-component model that explains 79.42% of the total variance in the data. The statistical parameters, including the number of principal components and the percentage of variance they explain, are presented in Supplementary Materials Table S3.

The results from the analysis of the first two principal components based on quantified phenolic compounds in potato samples extracted with extraction methods 1 and 3 (Supplementary Materials Table S2) are illustrated on score and loading plots (Figure 2) and explain 60.71% of the variability in the data.

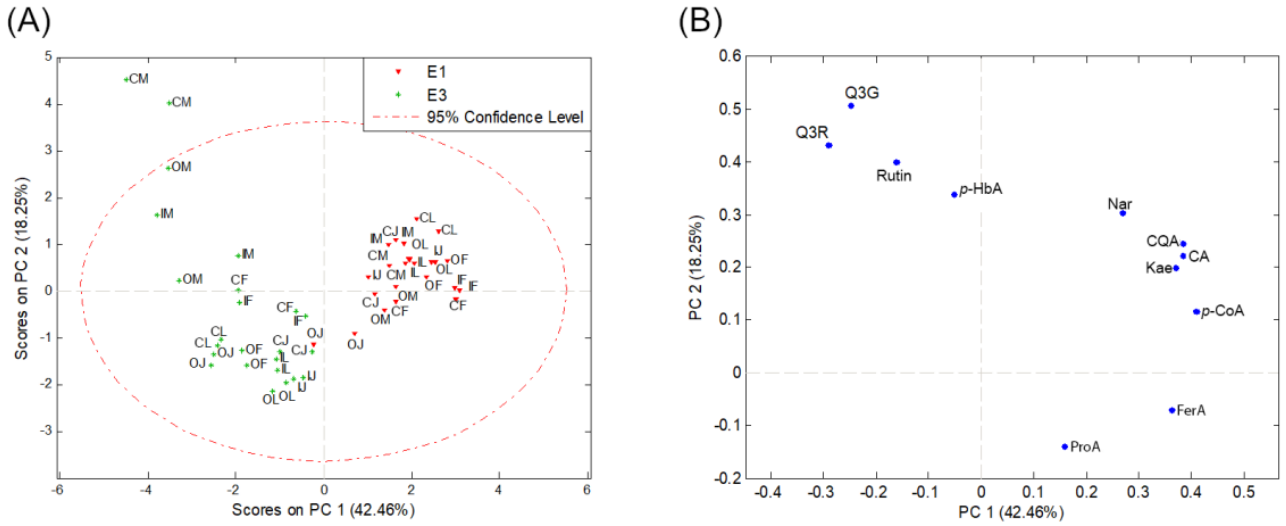

Figure 2. PCA score plot (A) and loading plot (B) based on the content of phenolic compounds extracted with 80% methanol (E1) and a mixture of acetone–water (70:30, *v*/*v*) (E3) in samples of four potato varieties (M—Marabel; F—Red Fantasy; L—Laura; J—Jelly) from three types of production systems (C—conventional; I—integral; O—organic production system). Protocatechuic acid—ProA; 5-*O*-caffeoylquinic acid—CQA; *p*-hydroxybenzoic acid—*p*-HbA; caffeic acid—CA; *p*-coumaric acid—*p*-CoA; quercetin-3-O-glucoside—Q3G; naringin—Nar; quercetin-3-*O*-rhamnoside—Q3R; kaempferol—Kae; ferulic acid—FerA.

On the score plot (Figure 2A), two distinct groups of objects can be observed along the PC1 axis. The first group consists of potato samples where phenolics were extracted with 80% methanol (extraction 1), and it separates from the second group composed of samples where extraction was performed with a mixture of acetone and water (70:30, *v*/*v*) (extraction 3). This separation is mainly influenced by phenolic acids (ProA, FerA, *p*-CoA, CA, CQA, *p*-HbA), Nar, and Kae (Figure 2B), which have higher concentrations in samples extracted with 80% methanol (extraction 1) compared to samples extracted with the extraction method 3 (Table 2, Figure 3). The concentrations of rutin, Q3G, and Q3R show the opposite trend (Figure 2B, Table 2). Specifically, their concentrations are higher in potato samples subjected to extraction method 3. Along the PC1 axis, *p*-CoA has the most positive impact, while Q3R has the most negative impact (Table 2, Figure 3).

Table 2. Descriptive statistics of phenolic compound content (mg/kg) in potato samples extracted with 80% methanol (E1) and a mixture of acetone–water (70:30, *v*/*v*) (E3). Protocatechuic acid—ProA; 5-*O*-caffeoylquinic acid—CQA; *p*-hydroxybenzoic acid—*p*-HbA; caffeic acid—CA; *p*-coumaric acid—*p*-CoA; quercetin-3-O-glucoside—Q3G; naringin—Nar; quercetin-3-*O*-rhamnoside—Q3R; kaempferol—Kae; ferulic acid—FerA.

Kae	Q3R	Nar	FerA	Q3G	*p*-CoA	Rutin	CA	*p*-HbA	CQA	ProA	Type of Extraction	
0.54	0.08	0.58	2.03	0.13	0.74	1.36	55.54	0.33	75.16	1.04	Mean	
0.55	0.08	0.61	1.94	0.13	0.75	0.74	54.20	0.32	76.59	1.05	Median	
0.10	0.04	0.21	0.50	0.04	0.18	1.25	9.77	0.12	17.48	0.19	Stdev	E1
0.39	0.03	0.23	1.26	0.08	0.26	0.18	41.60	0.14	31.17	0.67	Min	
0.72	0.20	1.07	3.14	0.23	1.21	4.49	74.08	0.65	108.75	1.42	Max	
0.39	0.16	0.34	0.80	0.21	0.20	2.64	28.02	0.30	26.07	0.97	Mean	
0.39	0.11	0.33	0.49	0.13	0.14	1.05	28.74	0.26	25.64	0.83	Median	
0.03	0.12	0.16	0.64	0.19	0.17	4.22	7.24	0.11	13.06	0.33	Stdev	E3
0.36	0.05	0.09	0.13	0.06	0.05	0.13	7.55	0.12	1.29	0.56	Min	
0.49	0.51	0.61	2.14	0.75	0.71	19.00	38.49	0.61	65.93	1.70	Max	

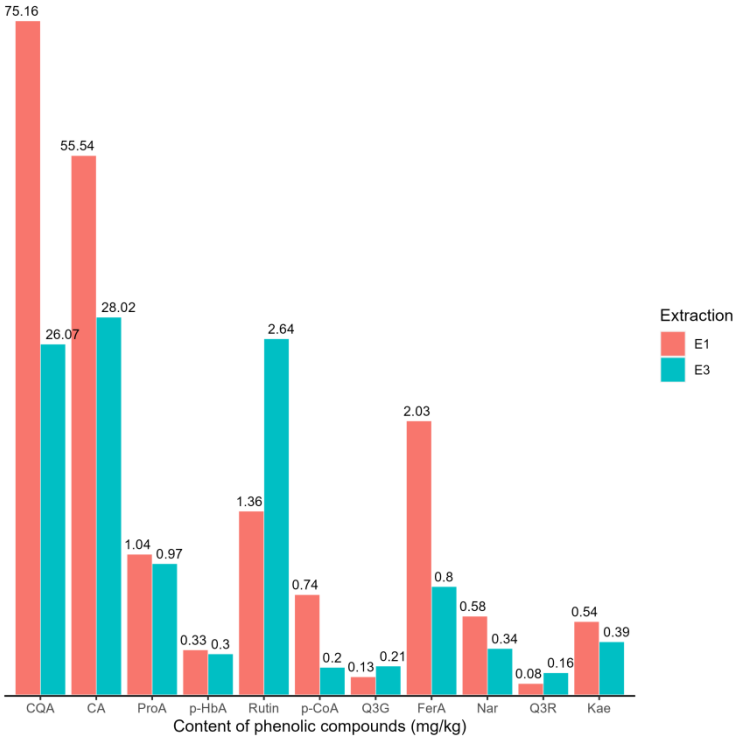

Figure 3. The content of phenolic compounds (mg/kg) in potato samples extracted with 80% methanol (E1) and a mixture of acetone–water (70:30, *v*/*v*) (E3). Protocatechuic acid—ProA; 5-*O*-caffeoylquinic acid—CQA; *p*-hydroxybenzoic acid—*p*-HbA; caffeic acid—CA; *p*-coumaric acid—*p*-CoA; quercetin-3-*O*-glucoside—Q3G; naringin—Nar; quercetin-3-*O*-rhamnoside—Q3R; kaempferol—Kae; ferulic acid—FerA.

Along the PC2 axis, Q3G has the most positive impact on sample separation, while ProA has the most negative impact (Figure 2B). Within object groups, based on quantified phenolics and PCA, no differences can be observed between potato varieties and production methods (Figure 2A).

Since the concentration ranges for each phenolic compound in the examined samples for both types of extractions are not greater than one order of magnitude (Supplementary Materials Table S2), a comparative *t*-test was performed to determine the presence of a statistically significant difference between these two extraction methods for each individual phenolic compound (Supplementary Materials Table S4).

Based on the results of the comparative *t*-test, it was demonstrated that there is a statistically significant difference between extractions 1 and 3 based on the content of CQA, CA, *p*-CoA, Q3G, FerA, Nar, Q3R, and Kae. As the concentration of these phenolic compounds is higher in samples extracted with 80% methanol (extraction 1) compared to samples extracted with the acetone–water mixture (70:30, *v*/*v*) (extraction 3), extraction 1 was selected as the potentially best method for extracting phenolic compounds from potato samples. In those samples from the third production year, the phenolic profile of both the peel and bulk of four potato varieties from three types of production systems was determined.

After the optimization process was completed, phenolic compounds were extracted using 80% methanol from potato samples from the first and the second production years. The obtained extracts were used to determine the total phenolic content and antioxidant capacity in the peel and bulk samples of four potato varieties from three types of production systems for all three production years. The results are presented in Supplementary Materials Table S5 and Figure S1.

Based on the results, it can be concluded that the total phenolic content and the antioxidant activity value for all three production years are higher in peel samples compared to bulk samples of potato tubers (TPC—3.79 g GAE/kg, 1.42 g GAE/kg; RSA—21.08 mmol TE/kg; 3.46 mmol TE/kg, respectively) (Supplementary Materials Table S5 and Figure S1). Overall, the obtained TPC values are comparable to the values described by Ru et al. [11], Leo et al. [10], Makori et al. [9], and Lachman et al. [25], which are between 0.8 and 3.0 g GAE/kg for whole potatoes and between 1.57 and 4.27 g GAE/kg for the peel. Higher values in bulk are described for red and purple potato cultivars, up to 23.5 g GAE/kg by Burgos et al. [14]. Regarding the antioxidant activity, Ru et al. obtained results between 0.21 and 3.09 mmol TE per kg of dried sample [11].

Regarding the potato varieties, observed for each production year individually and in the total average content for all three production years, higher total phenolic content and antioxidant activity values were found in samples of medium-early red varieties Red Fantasy (TPC—6.20 g GAE/kg; RSA—29.98 mmol TE/kg) and Laura (TPC—6.46 g GAE/kg; RSA—25.94 mmol TE/kg) compared to the medium-early white variety Marabel (TPC—4.78 g GAE/kg; RSA—22.05 mmol TE/kg) and the late white variety Jelly (TPC—3.42 g GAE/kg; RSA—18.18 mmol TE/kg) (Supplementary Materials Table S5 and Figure S1).

For all three production years, the TPC and RSA values are lowest in samples of the Jelly variety. This variety differs in the length of tuber vegetation, compared to the others, as it belongs to the late varieties. As for the types of production systems, observed by individual years, a universal trend of an increase or decrease in total phenolic content and antioxidant activity values based on whether the samples are from conventional, integral, or organic types of production cannot be discerned (Supplementary Materials Table S5 and Figure S1). However, when considering the average values of TPC and RSA over a three-year period, it can be noticed that the values for both parameters are highest in samples from the organic type of production (TPC—C: 5.29, I: 5.01, O: 5.34 g GAE/kg; RSA—C: 23.31, I: 23.45, O: 25.35 mmol TE/kg) (Supplementary Materials Table S5 and Figure S1).

3.3. Identification of Phenolic Compounds

In the qualitative analysis of the phenolic fraction of potato samples after extraction with 80% methanol, fifty-nine compounds were identified, including twenty-five phenolic acids and their derivatives, twenty-two phenolic glycosides (including flavonoid glycosides), and twelve flavonoid aglycones, including two isoflavones, three flavones, three flavonols, three flavanones, one flavanonol. A list of the identified compounds, retention times (t_R), molecular formulas, average monoisotopic mass values, and exact masses; MS/MS fragmentation data; and references that confirm the presence of the corresponding compound in *Solanum* species are provided in Table 3, while the peak areas obtained from full-scan MS spectra for all samples are provided in Supplementary Materials Table S6. The compounds were identified by comparing mass spectra and retention times (t_R) with available standards analyzed under the same conditions and by comparing the accurate mass, deprotonated molecules ($[M–H]^-$), and MS/MS fragmentation with corresponding spectral characteristics given in the literature [1,22,27–56]. Five of the detected phenolic acids derivatives are not yet described in *Solanum* species: two isomers of tetramethoxycinnamic acid hexuronide (peaks 23 and 24, Table 3), hydroxy-methoxy-benzoic acid pentosyl-hexoside (peak 29), dihydroxybenzoic acid pentosyl-hexoside (peak 31), and feruloylquinic acid hexoside (peak 41).

Table 3. Phenolic compounds identified in the bulk and peel of four potato varieties from three types of production using UHPLC-LTQ Orbitrap MS/MS.

Previously Reported in *Solanum*	MS/MS Fragments, (% of the Base Peak)	Δ ppm	Exact Mass, $[M–H]^-$	Calculated Mass, $[M–H]^-$	Molecular Formula, $[M–H]^-$	Identified Compounds	t_R, min	Peak No.
Phenolic acids and derivatives								
[27]	109(100), 123(8)	0.96	153.01838	153.01933	$C_7H_5O_4^-$	Protocatechuic acid	4.5	1
[28]	135(8), 173(3), 179(44), 191(100)	2.2	353.08561	353.08781	$C_{16}H_{17}O_9^-$	3-*O*-Caffeoylquinic acid	4.59	2
[28]	173(6), 179(7), 191(100)	2.51	353.08529	353.08781	$C_{16}H_{17}O_9^-$	5-*O*-Caffeoylquinic acid	5.1	3
[29]	93(100)	0.94	137.02348	137.02442	$C_7H_5O_3^-$	*p*-Hydroxybenzoic acid	5.21	4
[30]	134(6), 173(3), 193(100)	1.99	367.10146	367.10346	$C_{17}H_{19}O_9^-$	3-*O*-Ferruloylquinic acid	5.26	5
[31]	109(4), 119(7), 137(100), 163(4), 166(6)	1.2	181.04943	181.05063	$C_9H_9O_4^-$	Homovanillic acid	5.34	6
[22]	109(100), 125(4)	0.92	153.01842	153.01933	$C_7H_5O_4^-$	Gentisic acid	5.36	7
[28]	173(4), 179(6), 191(100)	2.04	353.08577	353.08781	$C_{16}H_{17}O_9^-$	5-*O*-Caffeoylquinic acid isomer	5.42	8
[32]	135(100)	1.03	179.03396	179.03498	$C_9H_7O_4^-$	Caffeic acid	5.58	9
[28]	179(100)	1.87	359.07537	359.07724	$C_{18}H_{15}O_8^-$	Rosmarinic acid	5.73	10
[30]	173(100), 193(6)	2.05	367.10141	367.10346	$C_{17}H_{19}O_9^-$	4-*O*-Feruloylquinic acid	5.8	11
[30]	173(100), 193(6)	1.84	367.10161	367.10346	$C_{17}H_{19}O_9^-$	4-*O*-Feruloylquinic acid isomer	6.01	12
[35]	91(2), 119(100)	1.08	163.03899	163.04007	$C_9H_7O_3^-$	*p*-Coumaric acid	6.23	13
[30]	173(10), 179(8), 191(4), 203(6), 299(4), 335(12), 353(100)	1.79	515.11771	515.1195	$C_{25}H_{23}O_{12}^-$	Dicaffeoylquinic acid	6.32	14
[22]	164(100), 179(22), 208(28)	1.52	223.05967	223.0612	$C_{11}H_{11}O_5^-$	Sinapic acid	6.43	15
[29]	89(6), 101(5), 107(4), 119(6), 123(4), 131(7), 136(100)	1.01	151.03906	151.04007	$C_8H_7O_3^-$	Vanillin	6.44	16
[32]	117(3), 134(89), 149(100), 178(54)	1.45	193.04918	193.05063	$C_{10}H_9O_4^-$	Ferulic acid	6.49	17
[30]	173(10), 179(8), 191(4), 203(6), 299(4), 335(12), 353(100)	2.22	515.11728	515.1195	$C_{25}H_{23}O_{12}^-$	Dicaffeoylquinic acid isomer	6.57	18
[34]	173(4), 335(5), 353(6), 397(100)	2.28	559.14344	559.14572	$C_{27}H_{27}O_{13}^-$	Caffeoyl-sinapoyl-quinic acid	7.1	19
[22]	99(3), 103(100), 115(3), 129(11)	1.09	147.04406	147.04515	$C_9H_7O_2^-$	Cinnamic acid	7.73	20
[35]	321(45), 443(71), 513(100), 543(51), 661(63), 687(46), 688(61)	0.33	705.16691	705.16724	$C_{32}H_{33}O_{18}^-$	Subulatin	5.12	21

Table 3. *Cont.*

Previously Reported in *Solanum*	MS/MS Fragments, (% of the Base Peak)	Δ ppm	Exact Mass, $[M–H]^-$	Calculated Mass, $[M–H]^-$	Molecular Formula, $[M–H]^-$	Identified Compounds	t_R, min	Peak No.
[36]	321(45), 443(71), 513(100), 543(51), 661(63), 687(46), 688(61)	0.02	705.16722	705.16724	$C_{32}H_{33}O_{18}^-$	Subulatin isomer	5.41	22
NA	193(7), 249(4), 267(100), 425(5)	2.1	443.1174	443.1195	$C_{19}H_{23}O_{12}^-$	Tetramethoxycinnamic acid hexuronide	5.45	23
NA	193(7), 249(12), 253(4), 267(100), 411(11), 425(14)	1.84	443.11766	443.1195	$C_{19}H_{23}O_{12}^-$	Tetramethoxycinnamic acid hexuronide isomer	5.75	24
[37]	134(7), 135(18), 161(23), 178(4), 179(100)	1.15	207.06513	207.06628	$C_{11}H_{11}O_4^-$	Ethyl caffeate	7.96	25
				Phenolic glycosides				
[38]	125(22), 167(12), 168(73), 169(24), 211(7), 223(7), 313(100)	1.01	331.06606	331.06707	$C_{13}H_{15}O_{10}^-$	Trihydroxybenzoic acid hexoside	3.45	26
[1]	108(11), 109(10), 152(43), 153(100), 163(9), 165(17), 225(9)	1.55	315.0706	315.07216	$C_{13}H_{15}O_9^-$	Dihydroxybenzoic acid hexoside	4.06	27
[39]	167(100)	1.38	329.08643	329.08781	$C_{14}H_{17}O_9^-$	Hydroxy-methoxy-benzoic acid hexoside	4.17	28
NA	152(12), 167(100), 293(11)	1.68	461.12838	461.13007	$C_{19}H_{25}O_{13}^-$	Hydroxy-methoxy-benzoic acid pentosyl-hexoside	4.3	29
[40]	182(3), 197(100)	1.48	359.09689	359.09837	$C_{15}H_{19}O_{10}^-$	Syringic acid hexoside	4.33	30
NA	152(77), 163(66), 177(67), 179(26), 207(37), 297(23), 315(100)	1.61	447.1128	447.11442	$C_{18}H_{23}O_{13}^-$	Dihydroxybenzoic acid pentosyl-hexoside	4.42	31
[39]	152(3), 167(100)	4.56	329.0985	329.10306	$C_{18}H_{17}O_6^-$	Hydroxy-methoxy-benzoic acid hexoside isomer	4.43	32
[40]	182(3), 197(100)	1.62	359.09675	359.09837	$C_{15}H_{19}O_{10}^-$	Syringic acid hexoside isomer	4.47	33
[34]	135(3), 179(100)	1.64	341.08617	341.08781	$C_{15}H_{17}O_9^-$	Caffeic acid hexoside	4.63	34
[41]	108(5), 109(6), 151(3), 152(25), 153(100), 163(3), 165(4)	1.75	285.05984	285.06159	$C_{12}H_{13}O_8^-$	Dihydroxybenzoic acid pentoside isomer	4.77	35
[34]	107(6), 135(100), 179(77)	1.89	341.08592	341.08781	$C_{15}H_{17}O_9^-$	Caffeic acid hexoside isomer 1	4.86	36
[42]	93(3), 137(100)	1.81	299.07543	299.07724	$C_{13}H_{15}O_8^-$	Hydroxybenzoic acid hexoside	4.9	37
[43]	137(3), 181(100)	0.91	343.10255	343.10346	$C_{15}H_{19}O_9^-$	Homovanillic acid hexoside	4.95	38

Table 3. *Cont.*

Previously Reported in *Solanum*	MS/MS Fragments, (% of the Base Peak)	Δ ppm	Exact Mass, $[M–H]^-$	Calculated Mass, $[M–H]^-$	Molecular Formula, $[M–H]^-$	Identified Compounds	t_R, min	Peak No.
[41]	108(5), 109(9), 151(6), 152(32), 153(100), 163(5), 241(45)	1.85	285.05974	285.06159	$C_{12}H_{13}O_8^-$	Dihydroxybenzoic acid pentoside	4.97	39
[34]	107(6), 135(100), 179(77)	1.89	341.08592	341.08781	$C_{15}H_{17}O_9^-$	Caffeic acid hexoside isomer 2	5	40
NA	175(100), 353(10)	1.2	529.15508	529.15628	$C_{23}H_{29}O_{14}^-$	Feruloylquinic acid hexoside	5.12	41
[44]	271(25), 300(49), 301(51), 505(30), 591(100), 609(29), 753(13)	0.06	771.19887	771.19893	$C_{33}H_{39}O_{21}^-$	Kaempferol 3-*O*-[2‴-hexosyl-(2″-hexosyl)]-hexoside	5.34	42
[45]	259(40), 269(100), 287(69), 421(6), 431(21)	1.54	449.1074	449.10894	$C_{21}H_{21}O_{11}^-$	Dihydrokaempferol 3-*O*-hexoside	5.52	43
[34]	101(9), 113(8), 119(65), 159(7), 161(47), 163(100), 307(4)	1.72	325.09117	325.09289	$C_{15}H_{17}O_8^-$	Coumaric acid hexoside	5.9	44
[46]	179(3), 255(5), 271(5), 300(33), 301(100), 302(23), 343(7)	1.23	609.14488	609.14611	$C_{27}H_{29}O_{16}^-$	Quercetin 3-*O*-(6″-rhamnosyl)-hexoside	5.93	45
[47]	283(100)	0.02	445.11401	445.11402	$C_{22}H_{21}O_{10}^-$	Biochanin A 7-*O*-hexoside	6.17	46
[30]	257(3), 285(100), 286(10)	1.19	593.15	593.15119	$C_{27}H_{29}O_{15}^-$	Kaempferol 3-*O*-(6″-rhamnosyl)-hexoside	6.25	47
				Flavonoid aglycones				
				Isoflavones				
[48]	147(4), 176(7), 177(18), 283(34), 313(100), 327(31), 339(6)	2.57	357.09541	357.09798	$C_{19}H_{17}O_7^-$	Retusin	6.78	48
[49]	211(13), 239(64), 240(21), 265(3), 268(100), 269(7)	1.64	283.05956	283.0612	$C_{16}H_{11}O_5^-$	Biohanin A	9.19	49
				Flavones				
[50]	149(42), 151(25), 181(18), 201(35), 224(19), 225(100), 227(21)	1.22	269.04433	269.04555	$C_{15}H_9O_5^-$	Apigenin	8.44	50
[51]	145(10), 151(30), 169(11), 183(6), 187(15), 211(44), 213(100)	1.34	253.04929	253.05063	$C_{15}H_9O_4^-$	Chrysin	10.04	51
[52]	268(100)	1.8	283.0594	283.0612	$C_{16}H_{11}O_5^-$	Acacetin	10.54	52

Table 3. *Cont.*

Previously Reported in *Solanum*	MS/MS Fragments, (% of the Base Peak)	Δ ppm	Exact Mass, $[M–H]^-$	Calculated Mass, $[M–H]^-$	Molecular Formula, $[M–H]^-$	Identified Compounds	t_R, min	Peak No.
				Flavonols				
[53]	300(100) 151(60), 213(51), 229(51),	1.39	315.04963	315.05103	$C_{16}H_{11}O_7^-$	Isorhamnetin	8.09	53
[54]	239(48), 241(48), 257(49), 285(100)	1.85	285.03861	285.04046	$C_{15}H_9O_6^-$	Kaempferol	8.56	54
[48]	284(100)	1.62	299.05449	299.05611	$C_{16}H_{11}O_6^-$	Rhamnocitrin	8.81	55
				Flavanones				
[55]	145(8), 151(56), 169(11), 183(10), 187(16), 211(100), 213(33)	1.45	255.06483	255.06628	$C_{15}H_{11}O_4^-$	Pinocembrin	9.81	56
[56]	151(16), 164(84), 175(12), 226(12), 241(24), 243(100), 270(91)	1.51	285.07534	285.07685	$C_{16}H_{13}O_5^-$	Isosakuranetin	9.99	57
[56]	286(100)	1.98	301.06978	301.07176	$C_{16}H_{13}O_6^-$	Hesperetin	7.99	58
				Flavanonol				
[22]	201(4), 243(14), 259(100), 269(5)	2	287.05411	287.05611	$C_{15}H_{11}O_6^-$	Dihydrokaempferol	7.19	59

NA—not available.

To find potential indicators of differences between the four potato varieties of different origins and different lengths of vegetation period from three cultivation systems based on their phenolic profile in the bulk and peel of tubers, a PCA was conducted. The area under the peak of identified phenolic compounds was treated as a numerical variable. The results of PCA analysis of the phenolic profile are shown in Figure 4. The numbers in the score plots correspond to the numbers (Peak No.) in Table 3. The PCA analysis based on identified phenolic compounds in the peel of potato samples resulted in a ten-component model that explains 92.73% of the total variability, while PCA for the bulk samples resulted in an eight-component model explaining 94.13% of the variability. In both cases, the results indicate a separation of samples based on the potato variety to which they belong and the lengths of vegetation period. In the peel samples of potato tubers, based on the identified phenolic compounds, two groups of objects were separated along PC1, which explains 30.46% of the variability. The first group consists of samples of medium-early red potato varieties, Laura and Red Fantasy, while the second group of objects consists of white potato varieties, Marabel, and Jelly (Figure 4A). Along PC3, explaining 12.97% of the variability, it can be observed that there is a further separation within the white varieties Marabel and Jelly samples based on the lengths of vegetation period (Figure 4A). This is because Marabel is an early white variety, while Jelly is a late white variety. Therefore, it can be said that the phenolic profile can serve as an indicator of the difference between potato varieties (genotypes) and the lengths of vegetation period of potatoes.

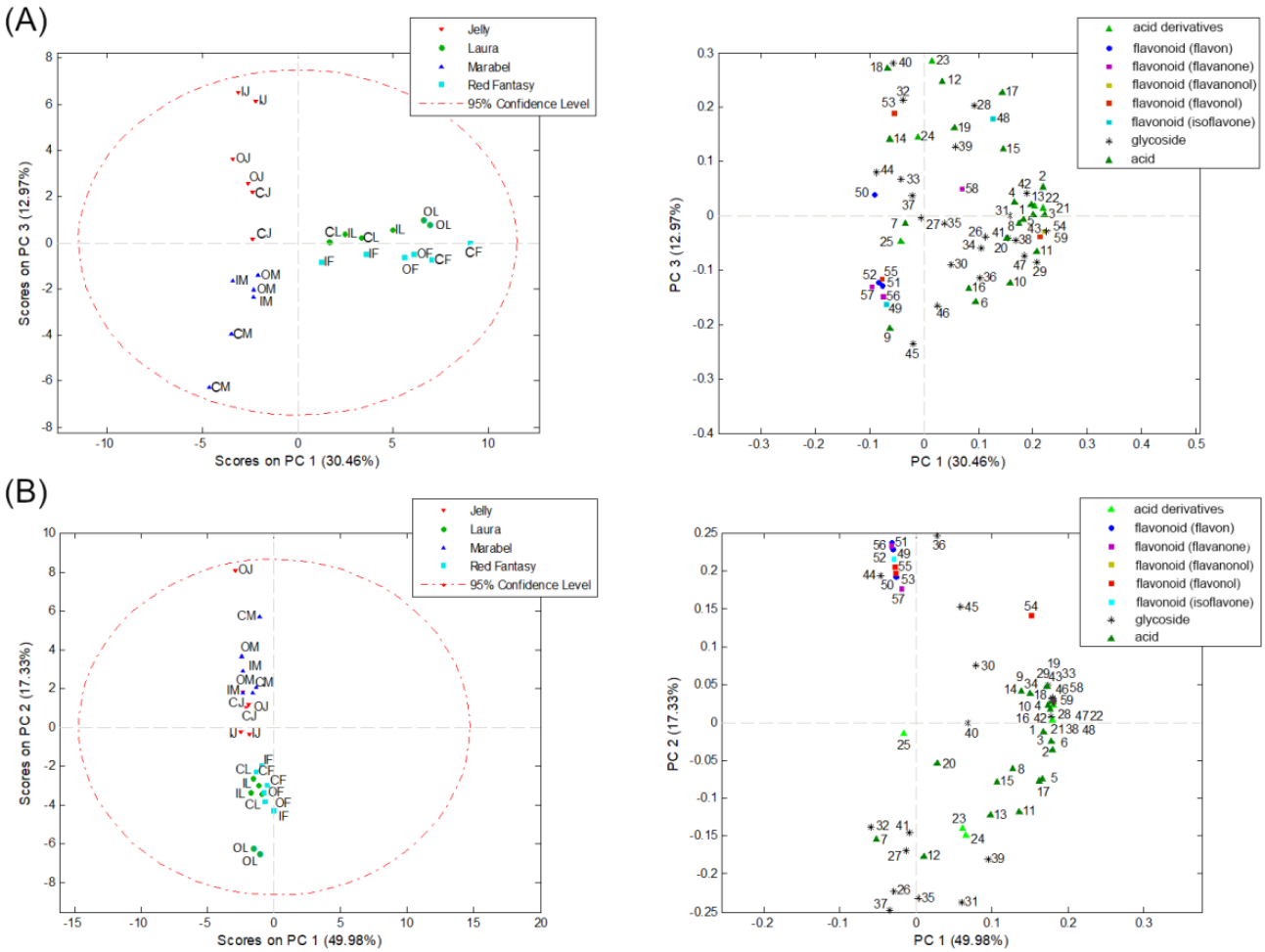

Figure 4. PCA based on the identified phenolic compounds in the peel (**A**) and bulk (**B**) samples of four potato varieties (M—Marabel; F—Red Fantasy; L—Laura; J—Jelly) from three types of production (C—conventional; I—integral; O—organic production system).

A similar trend can be observed in the bulk samples of potato tubers (Figure 4B), where there is also a separation between red and white peel color varieties along PC2. Phenolic acids, their derivatives, and glycosides identified in the red potato variety samples have the greatest influence on the separation, while white varieties have a higher proportion of identified classes of flavonoids. This is in line with the literature data confirming that secondary metabolites in potatoes contribute to their color and sensory characteristics [3]. The phenolic content in potatoes influences the tuber's color, and the bulk and/or peel of the potato can be completely or partially pigmented [14]. Additionally, there is a wide range of phenolic acids and anthocyanins quantified in varying concentrations depending on the potato variety, whereas red varieties mainly contain phenolic acids and glycosides [12,13], which is also confirmed in this paper.

4. Conclusions

This study aimed to optimize the extraction process to select an optimal procedure for isolating the antioxidant fraction from potato tubers and to evaluate potential biomarkers derived from the detailed phenolic profiles in order to differentiate the samples based on their botanical origin and system of production.

Five different extraction methods were evaluated. As the highest TPC and RSA values were found in samples extracted with 80% methanol and the acetone–water mixture (70:30, *v*/*v*), and the results indicated a statistically significant difference between these two extraction methods in comparison to the others, these two extraction methods were selected as the best for isolating phenolic compounds. The quantification and identification of phenolics in the peel and bulk of the potato samples were performed to select the better method among these two. The quantification of phenolic compounds in the samples was performed using UHPLC-DAD MS/MS. Eleven phenolic compounds were quantified in 48 potato extract samples, with 24 samples for each extraction method (extractions 1 and 3). The results indicated that 80% methanol (extraction 1) performed the best among the five examined methods.

This study concluded that the TPC and the RSA were higher in the peel samples compared to the bulk samples for all three production years. In terms of potato varieties, the content of total phenolics and antioxidant activity was higher in samples of medium-early red peel varieties, such as Red Fantasy and Laura, compared to medium-early white peel variety Marabel and late white peel variety Jelly. The average values of TPC and RSA over the three-year period were highest in samples from the organic production system.

Using UHPLC-LTQ Orbitrap XL, fifty-nine phenolic compounds were identified in potato tuber samples. In order to find potential indicators of differences between the four potato varieties of different origins and lengths of vegetation period from three production systems, a principal component analysis was conducted using the data on their phenolic profile in the bulk and peel of tubers. The results indicated a separation of samples based on the potato variety to which they belong and the lengths of vegetation period. The most significant influence on the separation was from phenolic acids, their derivatives, and glycosides identified in the red potato variety samples, while white varieties had a higher proportion of identified classes of flavonoids.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr13020396/s1, Supplementary Table S1. Total phenolic content (g GAE/kg) and radical scavenging activity (mmol TE/kg) in extracts of potato samples from five different extraction methods. C, I, O—type of production system (C—conventional; I—integral; O—organic); M, F, L, J—potato variety (M—Marabel; F—Red Fantasy; L—Laura; J—Jelly); III—third year of production; Table S2. Content of phenolic compounds (mg/kg) in potato samples extracted with 80% methanol (Extraction 1) and a mixture of acetone–water (70:30, *v*/*v*) (Extraction 3). C,

I, O—type of production (C—conventional; I—integral; O—organic), M, F, L, J—potato variety (M—Marabel; F—Red Fantasy; L—Laura; J—Jelly); protocatechuic acid—ProA; 5-*O*-caffeoylquinic acid—CQA; *p*-hydroxybenzoic acid—*p*-HbA; caffeic acid—CA; *p*-coumaric acid—*p*-CoA; quercetin-3-O-glucoside—Q3G; naringin—Nar; quercetin-3-*O*-rhamnoside—Q3R; kaempferol—Kae; ferulic acid—FerA; Table S3. The number of principal components and the percentage of variance they explain; Table S4. Results of the comparative *t*-test; protocatechuic acid—ProA; 5-*O*-caffeoylquinic acid—CQA; *p*-hydroxybenzoic acid—*p*-HbA; caffeic acid—CA; *p*-coumaric acid—*p*-CoA; quercetin-3-O-glucoside—Q3G; naringin—Nar; quercetin-3-*O*-rhamnoside—Q3R; kaempferol—Kae; ferulic acid—FerA. Bold values indicate the presence of a statistically significant difference between extractions; Table S5. Total phenolic content (g GAE/kg) and antioxidant capacity (mmol TE/kg) in the peel and bulk of four potato varieties (M—Marabel; F—Red Fantasy; L—Laura; J—Jelly) from three types of production systems (C—conventional; I—integral; O—organic production) and three production years (I, II, and III); Table S6. Peak areas of phenolic compounds identified in the bulk and peel of four potato varieties from three types of production using UHPLC-LTQ Orbitrap MS/MS; Figure S1. Total phenolic content (g GAE/kg) and antioxidant capacity (mmol TE/kg) in samples of bulk and peel from four potato varieties (M—Marabel; F—Red Fantasy; L—Laura; J—Jelly) from three types of production (C—conventional; I—integral; O—organic production) presented for individual production years (I, II, and III) and as a three-year average content.

Author Contributions: Conceptualization, A.D. and D.M.-O.; methodology, A.D. and D.M.-O.; formal analysis, A.D., U.G. and N.H.; investigation, A.D. and U.G.; resources, D.M.-O.; data curation, A.D. and U.G.; writing—original draft preparation, A.D. and U.G.; writing—review and editing, D.M.-O.; visualization, A.D.; project administration, D.M.-O.; funding acquisition, D.M.-O. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Grant Numbers 451-03-66/2024-03/200007, 451-03-66/2024-03/200168, and 451-03-66/2024-03/200288).

Data Availability Statement: Data are contained within the article and Supplementary Materials.

Conflicts of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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