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Screening of Bioactive Compounds from *Rosa canina* L. Peel and Seed Herbal Dust Using Eco-Friendly Extraction Techniques

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Abstract

The rising demand for sustainable and circular approaches in the agro-industrial sector has generated interest in repurposing herbal tea residues as sources of high-value bioactive compounds. This work focusses on recovering phytochemicals from *Rosa canina* L. peel and seed dust (by-products of processing of herbal tea in filter tea bags) using green extraction techniques. Two environmentally friendly technologies were used: ultrasound-assisted extraction (UAE) with a sonotrode and subcritical fluid extraction (SBFE). The extracts were qualitatively profiled using (HR) LC-ESI-QToF-MS/MS and quantified using HPLC-PDA. Both by-products contained phenolic substances, including gallic acid derivatives, ellagic acid, and flavonoids such as quercetin and quercetin-3-*O*-glucoside (only in the peel). Additionally, Folin–Ciocalteu's assay was used to determine Total Phenolic content (TP). The extraction efficiency was considered in terms of phenolic compound recovery and total phenolic content obtained under the respective experimental conditions. The maximum TP for SBFE was reported in samples extracted with ethanol–water (48:52) at 180 °C, producing 3876.67 GAE mg/L for peel and 1648.57 GAE mg/L for seeds. In the UAE, extraction with ethanol–water (48:52) for 10 min yielded the maximum TP of 2773.81 GAE mg/L for peel and 957.86 GAE mg/L for seeds. These findings highlight the potential of *R. canina* infusion by-products as long-term sources of bioactive compounds for use in nutraceutical, cosmetic, and pharmaceutical industries.

Keywords: by-products; herbal dust; LC-MS/MS; green extractions; phenolic compounds

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1. Introduction

Rosa canina L., often known as dog rose or briar rose, is a perennial shrub from the *Rosaceae* family that is primarily found in Europe, the Middle East, and parts of Asia. This plant has remarkable botanical characteristics, including a climbing or sprawling habit, thorny stems, and flowers ranging in colour from white to pale pink. The leaves are serrated and complex, made up of five to seven leaflets. The plant produces small, fleshy fruits with seeds known as hips, which range in colour from red to orange. These rose hips are particularly notable for their high concentration of minerals and bioactive elements such as vitamins, flavonoids, and fatty acids [1,2]. The biochemical composition of *R. canina* is rich

in phytochemicals, which add to its health advantages. Notably, the fruits are known for their high vitamin C content, which is sometimes quoted as being higher than that of many citrus fruits, making them an important source of this crucial nutrient [2]. Furthermore, they include antioxidants, such as flavonoids and polyphenols, which have been related to a variety of health benefits, including anti-inflammatory and antioxidant capabilities [3,4]. *R. canina* has been demonstrated to have considerable antioxidant capacity, potentially benefiting disorders including osteoarthritis and other inflammatory diseases [5]. *R. canina* has recently gained popularity as an herbal tea ingredient, thanks to its rich flavour profile and therapeutic benefits. This herbal tea, derived primarily from the plant's dried portions, is helpful not only for its refreshing effects but also for its numerous health advantages. Its significant antioxidant activity is thought to improve general health and may aid in the prevention of chronic diseases [6]. *R. canina* in herbal teas promotes hydration while also supplying critical minerals and phytochemicals that improve immune function and reduce inflammation [7].

Herbal teas, defined as water-based infusions produced from diverse plant materials, are widely drunk for their supposed health advantages, which include antioxidant, anti-inflammatory, and antibacterial activities [8,9]. Herbal tea is commonly prepared by infusing plant pieces in hot water to extract beneficial chemicals [6]. Notably, global demand for herbal teas is increasing, driven by a growing awareness of health and wellness, creating a sizable market for these goods [6]. Considering that agricultural waste and by-products from the food industry contain certain amounts of valuable bioactive compounds, there is a tendency to further exploit them as starting materials for extraction. Therefore, by-products generated in filter-tea factories, i.e., fine herbal powder, have great potential to be valorised to obtain a large number of bioactive compounds, depending on the type of plant raw material itself. Typically, the share of this by-product is 10% to 15% of the total processed material. When it comes to fruits that are processed into tea bags, this proportion is even higher, ranging from 10% to 35% [10,11]. One example is *R. canina*, where up to 35% of the plant mass is obtained as a by-product during processing and is therefore separated in the processing process [12].

The popularity of *R. canina* as an herbal tea mirrors larger market trends towards natural, plant-based therapies. As the market grows, many herbal tea products contain a range of ingredients, frequently blending *R. canina* with other herbs to improve flavour and nutritional value [13]. This implies an increasing interest in both the beverages and the health claims associated with them. Furthermore, customer feedback frequently emphasises the importance of ingredient quality and origin, resulting in a rising demand for ethically and sustainably harvested herbal products [6].

R. canina cultivation produces a variety of useful by-products in addition to tea preparations. The leaves, petals, and roots can all be used to make herbal treatments, cosmetics, and functional meals, allowing for a more holistic approach, using the entire plant [6]. This integration fosters sustainability in the herbal product market by ensuring that each of the various portions of the plant is valued, thus minimising waste and boosting the economic feasibility of growing methods.

The study of *R. canina* and other herbal preparations is consistent with a growing body of literature emphasising the link between nutrition, particularly the intake of herbal teas, and health outcomes. Several studies have shown that regular use of herbal teas can lower the risk of chronic illnesses and provide other health advantages [9,14]. As research into the effects of various herbal elements progresses, knowing their interactions and potential synergies may help shape future therapeutic uses.

R. canina is an excellent example of a traditional plant that has gained popularity in modern health practices due to its rich biochemical composition and numerous ap-

plications, particularly as an herbal tea. The utilisation of herbal dust, a by-product of industrial processing that has received limited attention, constitutes an innovative and sustainable approach. This is due to the fact that it valorises by-products that have been scarcely investigated in previous studies, thereby contributing novel insights into their phytochemical potential. In order to further understand their potential valorisation as sources of bioactive chemicals, it is crucial to examine *R. canina* L. seed and peel herbal dust by-products independently and assess how they react to green extraction methods such as Subcritical Fluid Extraction (SBFE) and Ultrasound-Assisted Extraction (UAE) with a sonotrode. Due to their direct delivery of energy, increased cavitation and milder thermal exposure, UAE with a sonotrode and SBFE typically outperform traditional methods like maceration and Soxhlet in terms of extraction efficiency and time. In optimal UAE conditions, numerous matrices demonstrate enhanced yields or bioactivity. In comparison to maceration or Soxhlet, SBFE, which includes subcritical water, offers adjustable polarity, solvent recyclability, and decreased solvent residues. It frequently achieves equivalent or greater polyphenol yields and preserves thermolabile chemicals [15,16]. Quantitative analysis was conducted using HPLC-PDA, while qualitative analysis was performed using (HR) LC-ESI-QToF MS/MS. Furthermore, the Folin–Ciocalteu assay was used to establish the total phenolic content. Continued study into herbal products will strengthen their position in a health-conscious dietary landscape.

2. Materials and Methods

2.1. Chemicals and Reagents

All the chemicals were of analytical grade. The solvents used for the extraction were purchased from J.T. Baker (Radnor, PA, USA). Methanol and 85% *w*/*w* phosphoric acid were purchased from Sigma-Aldrich (Steinheim, Germany). LC-MS grade acetonitrile, formic acid, and H_2O were purchased from Merck (Darmstadt, Germany). The standards of gallic acid, catechin, chlorogenic acid, epicatechin, naringin, isoquercitrin (quercetin 3-*O*-glucoside), ellagic acid and quercetin that were used for HPLC assay were obtained from Sigma-Aldrich (Steiheim, Germany) and were of HPLC grade. Folin–Ciocalteu's phenol reagent was purchased from Sigma-Aldrich Chemie (Steiheim, Germany). Milli-Q pure water was used during experiments, and analytical measurements were obtained by the Milli-Q Millipore (Sigma-Aldrich) system (conductivity $\leq$ 0.054 µS/cm).

2.2. Sample and Sample Preparation

R. canina L. seed and peel herbal dust, with a particle diameter of less than 0.315 mm, was supplied by a local herbal filter tea producer, Fructus (Bačka Palanka, Serbia). The raw material was directly used for subsequent extraction techniques without further processing.

2.3. Extraction Techniques

2.3.1. Ultrasound-Assisted Extraction (UAE) with Sonotrode

The UAE employed an ultrasonic probe (UP400St, Hielscher Ultrasonics GmbH, Teltow, Germany). In brief, 1 g of herbal dust was deposited in 20 mL of three distinct solvents (100% water, 48:52 *v*/*v* EtOH:H_2O, and 96:4 *v*/*v* EtOH:H_2O, with two different extraction periods of 3 min and 10 min throughout the experiment. Amplitude and impulse level were kept constant at 100%, and the temperature was maintained below 60 °C. The extracts were filtered using a PTFE 0.45 µm filter before further analysis [17]. The extraction parameters used in this study (ultrasound amplitude, extraction time, and solvent composition) were selected based on previous studies and the authors' prior experience with similar plant matrices [17]. Ethanol–water mixtures were chosen as green solvents that are commonly used for the extraction of phenolic compounds. Solvent ratios

of 48:52 and 96:4 (EtOH:H_2O, v/v) were selected to evaluate the influence of solvent polarity on the extraction efficiency of phenolic compounds.

2.3.2. Subcritical Fluids Extraction (SBFE)

Jokić et al. [18] provided a detailed description of their handmade subcritical water extraction apparatus. The extractor for subcritical extraction consists of a cylindrical thick-walled vessel with a stopper that is secured with a screw cap, and all elements are made of AISI 304 stainless steel in order to reduce the influence of the material on the composition of the obtained extracts, given that the extraction is carried out at high pressure and temperature values (Figure S1). On the extractor stopper, as a connection, a Hermeto® (Bijuk HPC, Zagreb, Croatia) coupling is used, to which a seamless tube made of AISI 316Ti is connected, through which the pressure is maintained with nitrogen through a nitrogen cylinder tank with a reduce valve (Nitrogen purity 5.0 Messer, reduce valve 200/50 bar). In addition to the aforementioned coupling, there is also a blind tube on the stopper that leads to the centre of the cylinder and is intended for positioning the temperature sensor in the centre of the extractor. A magnetic stirrer is used to mix the sample in the extractor itself, while an insulated air chamber with a fan, heater and temperature controller is used to maintain the temperature. The herbal dust (1 g/20 mL) was placed in a 500 mL stainless steel extraction vessel (AISI 304, Bijuk HPC, Zagreb, Croatia). The extractions were performed at four different temperatures (120 °C, 140 °C, 160 °C, and 180 °C) for the three solvents: 50:50% and 96:4 EtOH:H_2O% v/v and distilled H_2O. A gasket and extractor stopper were placed on top of the extractor, and tightness was achieved by tightening the screw cap. The pressure maintenance tube in the system was installed and tightened using a hand tool to prevent nitrogen leakage. The extractor was placed in a thermostatic air-ventilated heating chamber with very precise temperature regulation and fast heating possibility for good heat transfer. The control valve was carefully opened, and the extractor was filled with nitrogen, with the pressure previously set to 50 bar. After pressurising the extractor with nitrogen, a temperature sensor was placed in the designated place to monitor the temperature in the centre of the extractor. The thermostatic chamber was closed, and the desired extraction temperature was set on the thermostatic chamber, enabling direct heat transfer to the extractor. Turning on the magnetic stirrer enabled mixing of the material and solvent throughout the extraction time. When the temperature in the centre of the extractor reached 1 °C lower than the set temperature, the extraction time countdown began. After 30 min, the thermo chamber was turned off and opened, and the extractor was immersed in cold water using gloves to accelerate the cooling of the system. After cooling the contents of the extractor to a temperature below 60 °C, the nitrogen control valve was closed, and by slightly opening the high-pressure valve, the extractor pressure was equalised to atmospheric pressure. After equalising the pressures, the entire system was disassembled (which included removing the high-pressure valve, screw cap, and extractor plug), and the sample solution was filtered. The experiment then proceeded to further manipulation and analysis of the sample.

2.4. High-Resolution LC-ESI-QToF-MS/MS

The extracts were then subjected to qualitative analysis using an ion mobility QToF LC-MS system consisting of a 1290 Infinity II UPLC coupled to a 6560 IM-QToF mass spectrometer (Agilent Technologies, Palo Alto, CA, USA), following the method described by De Luca et al. [19]. The performance of the instruments was verified using an Agilent tuning mix, while continuous mass correction was ensured by reference masses at m/z 112.9855 and 966.0007. Analyses were conducted utilising an electrospray ionisation (ESI) source operating in negative ion mode, with optimised parameters. MS/MS data were

acquired using collision energies calculated by linear interpolation. Mass spectra were recorded in the 40–1300 m/z range. The chromatographic separation was achieved on a Kinetex EVO C18 column (150 × 2.1 mm, 1.7 µm, 100 Å), which was maintained at a temperature of 55 ± 1 °C. The mobile phase was composed of 0.1% formic acid in water (A) and acetonitrile with 0.1% formic acid (B), and elution was performed using gradient elution at a flow rate of 0.3 mL/min. The injection volume was 4 µL. The acquisition and processing of data was conducted using MassHunter Workstation software v. B.09.00. (Agilent Technologies), with the extraction of molecular features being undertaken through the utilisation of the MassHunter Qualitative Analysis v. 10.0 (Agilent Technologies) tool. The metabolites were tentatively identified through a comparison of the LC-MS/MS data with the METLIN PCDL database, Sirius®, MZmine®, and publicly available natural product databases (KNApSAcK®, PubChem®, Coconut®), in addition to literature-reported fragmentation patterns.

2.5. HPLC-PDA Analyses

The quantification of bioactive compounds in UAE and SBFE extracts of *R. canina* peel and seed herbal dust was performed by HPLC with UV detection following the method described by Krivošija et al. [20]. The chromatographic separation was achieved using a Cosmosil 5C18-MS-II column (250 × 4.6 mm, 5 µm; Nacalai Tesque, Kyoto, Japan), using an Agilent 1260 Infinity II HPLC system (Agilent Technologies, Waldbronn, Germany). This system was equipped with a quaternary pump, PDA detector, column oven, autosampler, and fraction collector. The mobile phases consisted of 0.1% formic acid in ultrapure water (A) and 0.1% formic acid in methanol (B), applied under gradient elution at a flow rate of 1.0 mL/min with a total run time of 65 min and a 15 min re-equilibration step between runs. The column temperature was maintained at 50 °C, and the injection volume was 10 µL. The detection process was conducted across a range of wavelengths (240–360 nm) utilising the PDA detector, while the verification of peak purity was conducted through the utilisation of ChemStation Edition software C.01.08 (OpenLab CDS). Quantification was carried out using the external standard method, with calibration curves for individual polyphenols prepared in the range of 1–50 mg/L ($R^2 > 0.99$).

2.6. Determination of Total Phenolic Content via Spectrophotometric Assay

The total phenolic content (TP) in UAE and SBFE extracts of *R. canina* peel and seed herbal dust was determined using the Folin–Ciocalteu method [21]. Absorbance was measured at a wavelength of 750 nm, employing a UV-Vis spectrophotometer with a single-beam system (LLG-uniSPEC 2, LLG Labware, Meckenheim, Germany). Quantification was carried out using an external calibration curve of gallic acid (0–1000 mg/L; $R^2 = 0.9991$). All measurements were performed in triplicate, and the results were expressed as milligrams of gallic acid equivalents per gram of dried extract (mg GAE/g DE).

3. Results

R. canina seed and peel dust, a by-product of the production of herbal tea in filter tea bags, was extracted using two different green extraction techniques (GETs). A total of twelve samples were processed by UAE and twenty-four by SBFE (see Table 1). The extraction parameters applied for each GET were selected based on the authors' previous experience and relevant literature [17,22].

Table 1. (**a**) *R. canina* peel and seed herbal dust samples obtained with UAE. A = 100%, I = 100%, temperature up to 60 °C (A: amplitude and I: impulse were constant parameters). (**b**) *R. canina* peel and seed herbal dust samples obtained with SBFE.

(**a**)			
	Sample	**Solvent**	**Time (Min)**
***Rosa canina* peel**	UV 1	H_2O	3
	UV 2	H_2O	10
	UV 3	EtOH:H_2O (48:52, *v*/*v*)	3
	UV 4	EtOH:H_2O (48:52, *v*/*v*)	10
	UV 5	96% EtOH	3
	UV 6	96% EtOH	10
	Sample	**Solvent**	**Time (Min)**
***Rosa canina* seeds**	UV 7	H_2O	3
	UV 8	H_2O	10
	UV 9	EtOH:H_2O (48:52, *v*/*v*)	3
	UV 10	EtOH:H_2O (48:52, *v*/*v*)	10
	UV 11	96% EtOH	3
	UV 12	96% EtOH	10
(**b**)			
	Sample	**Temperature**	**Solvent**
***Rosa canina* peel**	S 1	120 °C	H_2O
	S 2	120 °C	EtOH:H_2O (48:52, *v*/*v*)
	S 3	120 °C	96% EtOH
	S 4	140 °C	H_2O
	S 5	140 °C	EtOH:H_2O (48:52, *v*/*v*)
	S 6	140 °C	96% EtOH
	S 7	160 °C	H_2O
	S 8	160 °C	EtOH:H_2O (48:52, *v*/*v*)
	S 9	160 °C	96% EtOH
	S 10	180 °C	H_2O
	S 11	180 °C	EtOH:H_2O (48:52, *v*/*v*)
	S 12	180 °C	96% EtOH
	Sample	**Temperature**	**Solvent**
***Rosa canina* seeds**	S 13	120 °C	H_2O
	S 14	120 °C	EtOH:H_2O (48:52, *v*/*v*)
	S 15	120 °C	96% EtOH
	S 16	140 °C	H_2O
	S 17	140 °C	EtOH:H_2O (48:52, *v*/*v*)
	S 18	140 °C	96% EtOH
	S 19	160 °C	H_2O
	S 20	160 °C	EtOH:H_2O (48:52, *v*/*v*)
	S 21	160 °C	96% EtOH
	S 22	180 °C	H_2O
	S 23	180 °C	EtOH:H_2O (48:52, *v*/*v*)
	S 24	180 °C	96% EtOH

3.1. Qualitative Determination of Bioactive Compounds in R. canina Peel and Seed Herbal Dust

The forty-eight *R. canina* peel and seed herbal dust extracts were qualitatively analysed by (HR) LC-ESI-QToF MS/MS in the negative and positive ion modes (Table 2, Figures S2 and S3), and 8 different targeted compounds were quantified by HPLC-PDA analysis (Figures S4 and S5). Compounds were identified by comparing the measured *m*/*z* values with literature data and by comparing experimental MS/MS spectra with reported fragmentation patterns or spectra available in public mass spectral repositories [23], as well as with those of pure standards. The compounds detected in peel and seed by-product

extracts are listed in Table 2 according to their HPLC retention times, together with the experimentally derived molecular formulae, MS/MS data, mass error (Δ ppm), references used for identification, and the corresponding confidence levels [24].

Table 2. Compounds identified using (HR) LC-ESI-QToF MS/MS in *R. canina* peel and seed herbal dust.

No	Rt Min	Identity	[M-H]$^-$ *m/z*	Molecular Formula	Δ ppm	MS/MS * *m/z*	References	Level #
1	6.72	Gallic acid	169.0144	$C_7H_6O_5$	0.14	125.0252(100)	[25]	1
2	12.95	Catechin	289.0721	$C_{15}H_{14}O_{16}$	0.41	245.0828(100)/ 203.0699(61)/ 165.0184(59)	[25]	1
3	16.42	Chlorogenic acid	353.0881	$C_{16}H_{18}O_9$	2.56	191.0560(100)	[25,26]	1
4	17.77	Epicatechin	289.0732	$C_{15}H_{14}O_{16}$	0.15	245.0830(100)/ 203.0711(70)/ 165.0244(48)	[27]	1
5	30.57	Naringin	271.0618	$C_{15}H_{12}O_5$	2.15	-	[28]	1
6	30.88	Isoquercitrin (quercetin 3-*O*-glucoside)	463.0884	$C_{21}H_{20}O_{12}$	1.19	301.0336(39)/ 300.0280(100)	[28]	1
7	31.71	Ellagic acid	300.9990	$C_{14}H_6O_8$	2.55	-	[27]	1
8	38.76	Quercetin	301.0355	$C_{15}H_{10}O_7$	0.39	178.991(100)/ 107.0134(87)	[26]	1

* in parentheses, the relative intensity; # according to Blaženović et al. [24]. X: detected. -: not detected.

Peak **1** was identified as gallic acid due to the [M-H]$^-$ at *m/z* 169.0144 with a fragment at 125.0252 and due to the comparison with pure standard and literature data [25]. Compound **2** was identified as catechin due to the [M-H]$^-$ at *m/z* 289.0721 with fragments at 245.0828, 203.0699, and 165.0184 and due to the comparison with pure standard and literature data [25]. Compound **3** was attributed to chlorogenic acid due to the [M-H]$^-$ at *m/z* 353.0881 with a fragment at 191.0560 (loss of a quinic acid unit) and due to the comparison with pure standard and literature data [25,26]. Compound **4** was identified as epicatechin due to the [M-H]$^-$ at *m/z* 289.0732 with fragments at 245.0830, 203.0711, and 165.0244 and due to the comparison with pure standard and literature data [27]. Compound **5** was identified as naringin due to the [M-H]$^-$ at *m/z* 271.0618 and due to the comparison with pure standard and literature data [28]. Compound **6** was identified as quercetin 3-*O*-glucoside (isoquercitrin) due to the [M-H]$^-$ at *m/z* 463.0884 and fragments at 301.0336 (loss of a quercetin unit) and 300.0280 and due to the comparison with pure standard and literature data [28]. Peak **7** was attributed to ellagic acid due to the [M-H]$^-$ at *m/z* 300.9990 and due to the comparison with pure standard and literature data [27]. Compound **8** was identified as quercetin aglycone due to the [M-H]$^-$ at *m/z* 301.0355 and due to the comparison with pure standard and literature data [26].

3.2. Quantitative Determination of Bioactive Compounds in R. canina Peel and Seed Herbal Dust and Influence of Extraction Technique on Selected Compounds Content

3.2.1. Ultrasound-Assisted Extraction (UAE) with Sonotrode

Regarding *R. canina* peel herbal dust extracted with UAE (Table 3), run UV4 (EtOH:H_2O 48:52, *v/v*, 10 min of extraction) was the one with the highest total phenolic content (116.66 mg/L). Run UV4 showed a significant content of catechin (16.44 mg/L) and ellagic acid (77.76 mg/L), followed by run UV3 (15.06 and 63.73 mg/L for catechin and ellagic acid, respectively). Interestingly, UV1 and UV2 (both extracted with H_2O), the ones with the lowest total phenolic content (14.97 and 17.99 mg/L, respectively), showed the highest content of gallic acid (10.90 and 12.91 mg/L, respectively), which was not found in

run UV5 and UV6. On the contrary, UV5 and UV6 (both extracted with 96% EtOH) were the only ones where epicatechin was found (2.61 and 3.11 mg/L, respectively). Overall, the longest time of extraction (10 min) showed the highest values.

Table 3. Quantification of phenolic compounds by LC-PDA method (mg/L of extract) in *R. canina* peel herbal dust extracted with UAE.

No [§]	Compound	UV 1	UV 2	UV 3	UV 4	UV 5	UV 6
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
1	Gallic acid	10.90	12.91	4.57	4.76	-	-
2	Catechin	-	-	15.06	16.44	3.66	3.89
3	Chlorogenic acid	0.85	1.20	1.70	1.89	0.43	0.55
4	Epicatechin	-	-	-	-	2.61	3.11
5	Naringin	-	-	1.63	1.66	0.70	0.28
6	Isoquercitrin (quercetin 3-*O*-glucoside)	-	-	7.01	7.38	2.08	3.79
7	Ellagic acid	3.22	3.88	63.73	77.76	9.71	14.66
8	Quercetin	-	-	1.59	1.77	0.83	1.05
	Total phenols	14.97	17.99	22.96	111.66	20.02	27.33

[§] peak number as reported in Table 2.

When examining *R. canina* seed herbal dust extracted with UAE (Table 4), only three compounds, gallic acid, catechin and ellagic acid, were found. UV10 was the one with the highest total phenolic content (30.18 mg/L), followed by UV9 (24.69 mg/L), both extracted with EtOH:H_2O 48:52, *v*/*v*. UV9 and UV10 showed the highest amount of catechin (11.78 and 14.45 mg/L, respectively), and ellagic acid (10.43 and 13.03 mg/L, respectively).

Table 4. Quantification of phenolic compounds by LC-PDA method (mg/L of extract) in *R. canina* seed herbal dust extracted with UAE.

No [§]	Compound	UV 7	UV8	UV 9	UV10	UV 11	UV 12
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
1	Gallic acid	3.66	4.80	2.48	2.70	-	-
2	Catechin	-	-	11.78	14.45	1.01	1.82
7	Ellagic acid	-	-	10.43	13.03	-	0.61
	Total phenols	3.66	4.80	24.69	30.18	1.01	2.43

[§] peak number as reported in Table 2.

Again, UV7 and UV8 (both extracted with H_2O) showed the highest amount of gallic acid (3.66 and 4.80 mg/L, respectively), but in these samples, neither catechin nor ellagic acid was found. In runs UV11 and UV12 (both extracted with 96% EtOH), gallic acid was not detected. Again, the longest time of extraction (10 min) showed the highest values.

3.2.2. Subcritical Fluids Extraction (SBFE)

Considering *R. canina* peel herbal dust extracted with SBFE (Table 5), S11 and S12 (both extracted at 180 °C) were the samples with the highest total phenolic content (454.78 and 461.34 mg/L, respectively). Interestingly, the solvents used were EtOH:H_2O 48:52, *v*/*v* for S11 and 96% EtOH for S12. Despite that, in these two samples, gallic acid was not detected. The highest amount of gallic acid was found in S10 (55.78 mg/L), extracted at 180 °C, using H_2O as the solvent. Water was found to be the best solvent for the recovery of gallic acid, in line with UAE extracts. Curiously, catechin is absent in samples extracted with water (S1, S4 and S7) and in samples extracted at the highest temperature (S10–S12). The sample with the highest amount of catechin was S5 (89.34 mg/L), extracted with EtOH:H_2O 48:52,

v/*v* at 140 °C. Chlorogenic acid was found in all 12 extracts, as well as ellagic acid, which was found in large abundance in S11 (426.80 mg/L). Another noteworthy compound is epicatechin, which was identified mostly in samples extracted with 96% EtOH.

Table 5. Quantification of phenolic compounds by LC-PDA method (mg/L of extract) in *R. canina* peel herbal dust extracted with SBFE.

No §	Compound	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
1	Gallic acid	13.82	7.02	-	6.46	20.77	-	50.05	27.37	-	55.78	-	-
2	Catechin	-	28.44	25.09	-	89.34	52.12	-	38.97	35.94	-	-	-
3	Chlorogenic acid	1.64	2.25	1.55	1.12	1.86	1.58	2.50	2.44	1.66	2.77	2.60	2.59
4	Epicatechin	-	-	4.05	-	-	7.31	-	18.25	17.73	-	-	31.79
5	Naringin	1.12	2.01	2.05	2.75	4.28	2.40	5.83	7.24	3.25	-	13.17	9.02
6	Isoquercitrin (quercetin 3-*O*-glucoside)	-	5.52	4.92	-	3.86	4.72	-	2.08	4.15	-	-	3.86
7	Ellagic acid	1.12	105.63	99.05	4.28	206.22	150.89	137.67	318.91	246.30	114.42	426.80	404.52
8	Quercetin	-	2.34	2.26	-	4.13	3.37	-	7.01	6.65	-	9.21	9.56
	Total phenols	17.70	150.87	138.97	15.15	330.46	222.39	196.08	422.27	315.41	172.97	454.78	461.34

§ peak number as reported in Table 2.

Regarding *R. canina* seed herbal dust extracted with SBFE (Table 6), only four compounds were detected (gallic acid, catechin, ellagic acid and quercetin), aligning with UAE results, apart from quercetin, which was not detected in peel herbal dust. S20 was the sample with the highest total phenolic content (143.46 mg/L), followed by S17 (112.75 mg/L), both extracted with EtOH:H_2O 48:52, *v/v*, but set at different temperatures (160 and 140 °C, respectively). Interestingly, S20 showed the highest values for gallic acid and catechin (19.95 and 39.22 mg/L, respectively). Globally, the values were lower compared to peel extracts. Considerably, using H_2O as the solvent at 120 °C, all compounds were detected. S24 and S23 (extracted at 180 °C) showed the highest amount of ellagic acid (108.96 and 106.36 mg/L, respectively), confirming what was highlighted in S11 and S12. Quercetin was not detected in the H_2O extract (S13, S16 and S19), except for S22, where it was found in a low amount (0.45 mg/L). The highest values for quercetin were found in S24 and S23 (3.14 and 2.48 mg/L).

Table 6. Quantification of phenolic compounds by LC-PDA method (mg/L of extract) in *R. canina* seeds herbal dust extracted with SBFE.

No §	Compound	S13	S14	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
1	Gallic acid	-	6.06	-	4.26	11.39	-	16.30	19.95	-	18.39	-	-
2	Catechin	-	29.66	17.98	-	39.17	38.70	-	39.22	15.91	-	-	-
7	Ellagic acid	-	34.78	22.09	-	60.96	47.72	2.97	82.69	69.04	3.93	106.36	108.96
8	Quercetin	-	1.71	1.28	-	1.23	1.58	-	1.60	1.85	0.45	2.48	3.14
	Total phenols	-	72.21	41.35	4.26	112.75	88.00	19.00	143.46	86.80	22.77	108.84	112.10

§ peak number as reported in Table 2.

3.3. Total Phenolic Content in R. canina Peel and Seeds Herbal Dust Extracts

The spectrophotometric method was selected to determine the total phenolic compound quantification in the *R. canina* peel and seeds herbal dust extracts (Table 7). Namely, the Folin–Ciocalteu assay that is based on a redox reaction [29] was used.

Table 7. Total phenolic content (TP) values of *R. canina* peel and seed herbal dust extracts obtained with UAE and SBFE.

UAE	TP mg GAE/L DE											
Sample	**UV1**	**UV2**	**UV3**	**UV4**	**UV5**	**UV6**						
	2429.76	2344.05	2610.71	2773.81	227.38	256.67						
Sample	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**	**S11**	**S12**
	2020.71	2383.57	641.43	2036.43	2637.86	879.29	2786.90	3386.67	1177.86	1830.71	3876.67	1634.29
SBFE	**TP mg GAE/L DE**											
Sample	**UV7**	**UV8**	**UV9**	**UV10**	**UV11**	**UV12**						
	441.67	454.05	839.29	957.86	219.52	225.71						
Sample	**S13**	**S14**	**S15**	**S16**	**S17**	**S18**	**S19**	**S20**	**S21**	**S22**	**S23**	**S24**
	422.86	1023.57	347.14	691.43	1030.00	533.57	759.29	1089.29	634.29	925.00	1648.57	918.57

Overall, the highest total phenolic content (TP) values were detected in samples extracted with EtOH:H_2O 48:52, v/v and in SBFE extracts. TP was higher in *R. canina* peel herbal dust extracts, aligning with quantitative data (Section 3.2). Among SBFE peel extracts, the one with the highest TP was S11 (3876.67 mg GAE/L dm), extracted with EtOH:H_2O 48:52, v/v at 180 °C, followed by S8 (3386.67 mg GAE/L dm), extracted with EtOH:H_2O 48:52, v/v at 160 °C. Among SBFE seed extracts, the highest TP was found in S23 (1648.57 mg GAE/L dm), extracted with EtOH:H_2O 48:52, v/v at 180 °C, followed by S20 (1089.29 mg GAE/L dm), extracted with EtOH:H_2O 48:52, v/v at 160 °C. Among UAE peel extracts, the highest TP was found in U4 and U3 (2773.81 and 2610.71 mg GAE/L dm, respectively), both extracted with EtOH:H_2O 48:52, v/v. Among UAE seed extracts, the highest TP was found in U10 and U9 (957.86 and 839.29 mg GAE/L dm, respectively), both extracted with EtOH:H_2O 48:52, v/v. It is worth mentioning that the UAE samples extracted for 10 min showed the highest TP. Regarding the lowest TP values, among UAE extracts, the lowest were U5, U6, U11 and U12 (227.38, 256.67, 219.52 and 225.71 mg GAE/L dm, respectively), all extracted with 96% EtOH. Among SBFE extracts, the lowest TP values were S3 and S15 (641.43 and 691.43 mg GAE/L dm, respectively), both extracted with 96% EtOH at 120 °C.

4. Discussion

Considering what was discussed in Sections 3.2 and 3.3, the solvent plays a pivotal role in determining the extraction yield, with a 48:52 EtOH:H_2O mixture exhibiting optimal efficacy in terms of total polyphenol content. In comparison to pure water or highly concentrated ethanol, the 48:52 EtOH:H_2O mixture's intermediate polarity has been shown to enhance the solubility of a wide range of phenolic compounds and to increase solvent penetration into the plant matrix, thereby facilitating more effective extraction [30]. Conversely, water emerges as the least efficient solvent, yielding the lowest extraction yield. It is also important to consider additional parameters, including reaction time for UAE and temperature for SBFE, as these factors can significantly influence the outcome. The choice of solvent may also vary depending on the compound to be isolated, as demonstrated in Section 3.2, where it was shown that different solvents may be useful for the recovery of different compounds. The findings of the present study demonstrate that, in general, the yield of polyphenols, with a particular emphasis on ellagic acid, is higher in the context of SBFE as compared to the process of UAE. The intrinsic composition of the matrices exerts a significant influence on the resultant outcomes; the seeds contain a higher percentage of fatty acids, while the peels are characterised by a greater abundance of polyphenols, which may consequently impact the efficiency of extraction.

Nastić et al. [12] explored the *R. canina* herbal dust for its lipophilic content using Supercritical Carbon Dioxide Extraction. There are several studies that investigate the potential of *R. canina*, especially its seeds [31], but, to the best of our knowledge, there

are no studies on UAE with Sonotrode and SBFE employed on *R. canina* peel and seed herbal dust.

One of the most representative compounds found in the extracts was ellagic acid, known for its several biological activities such as antioxidant, anti-inflammatory, anticancer and antimicrobial activities [32,33]. Ellagic acid was found to be higher in peels rather than seeds, confirming what was previously estimated by Karczmarz et al. [34], who underlined the higher ellagic acid amount in the flesh rather than in the seeds of *R. canina* fruits. Other relevant compounds were catechin and quercetin aglycone, which were previously found as key compounds, with significant amounts in *R. canina* fruits (20.42 ± 0.47 and 13.82 ± 0.04 μg/g DW, respectively) [35]. Both catechin and quercetin have significant biological activity, but they are characterised by suboptimal bioavailability. Recent progress in the fields of nanobiotechnology and ligand design has focused on the enhancement of stability and effectiveness [36].

The overall phenolic content ranges from 219.52 to 3876.67 mg GAE/L, suggesting *R. canina* peel and seed herbal dust as a valuable source of antioxidant compounds. This is in line with the findings of Roman et al. [37], who studied TP in different *R. canina* biotypes, using Folin-Ciocalteau's assay. One study reported TP values of 138.47 to 141.10 mg GAE/g extract for different extraction methods (ultrasonic, maceration, and Soxhlet) of *R. canina* fruits [28]. The high phenolic content measured by Folin–Ciocalteau's assay has been shown to correlate with strong antioxidant activities. As demonstrated by a substantial body of research, *R. canina* extracts have exhibited considerable antioxidant capacities in a variety of assays, including $DPPH^{\bullet}$ and $ABTS^{\bullet+}$, which is consistent with the elevated TP values obtained using Folin–Ciocalteu's method [28,38]. In contrast to the SBFE, which achieved higher extraction efficiency and selectivity but required more energy input and the use of pressurised, heated solvent, UAE showed lower energy requirements and minimal solvent consumption, enabling rapid extraction with moderate efficiency. This underscores the trade-offs between performance and sustainability for these green techniques [39].

This waste still contains significant levels of bioactive compounds. Recent research has concentrated on optimising extraction procedures to achieve maximum yield from both the fruit and waste elements. For instance, Lakka et al. [40] suggested that using novel extraction technologies such as Pulsed Electric Field (PEF) technology could allow for higher recovery of important substances from both the fruit and its by-products [40].

Future studies should determine the extraction yield to further evaluate the efficiency of the applied extraction techniques.

5. Conclusions

The analysis of the herbal dust derived from the peels and seeds of *R. canina* fruits provides significant insights into their biochemical composition and extraction efficiencies. The methodology employed, UAE using a sonotrode and SFBE, provided not only valuable information on the optimal conditions for maximising polyphenol recovery, but also enabled a high-resolution chemical mapping of the bioactive profile. The study identified distinct compositions of bioactive compounds in the peels and seeds, with ellagic acid and catechin being the main constituents. It also found that quercetin and quercetin 3-*O*-glucoside were the major flavonoids. Interestingly, the seeds exhibited lower compound diversity compared to the peels, probably due to their predominant fatty acid composition. The extraction methods employed exhibited variability depending on the solvent used and the specific parameters of the procedures. The optimal solvent identified was a 48:52 EtOH:H_2O mixture, which was significantly more effective than pure water, the solvent with the lowest extraction efficiency. Additionally, it was found that variations in extraction time for UAE and temperature for SBFE significantly influenced the overall

yield, highlighting the importance of carefully optimising these parameters. As they rely on different extraction mechanisms (acoustic cavitation in UAE and temperature-dependent solvent properties under subcritical conditions in SBFE), these were chosen as complementary green technologies. This facilitated the assessment of their comparative efficiency and selectivity in the recovery of phenolic compounds from *R. canina* matrices. While both techniques are regarded as environmentally friendly, SBFE at 40 bar requires pressurisation and heating, which increases energy consumption but improves extraction efficiency and selectivity. In contrast, UAE operates at ambient pressure with low energy input and short extraction durations. The findings of this study have direct industrial application, as standardised, high-antioxidant extracts are required in the nutraceutical and cosmetic industries. The identification of these compounds has provided evidence for their potential use in formulations intended for disorders associated with inflammation and oxidative stress, due to their strong antioxidant properties and well-established bioactivity. Moreover, the valuation of herbal dust, which has historically been regarded as a low-value processing by-product, demonstrates a sustainable strategy consistent with the principles of the circular economy. This work supports its conversion into a value-added raw material for functional components by demonstrating both its chemical richness and extractive feasibility, thereby reducing waste and improving resource efficiency. However, further studies evaluating the antioxidant activity of the obtained extracts are necessary to better correlate their chemical composition with their potential biological effects.

In summary, this study has clarified the relationship between extraction methods, solvent efficacy and chemical composition in *R. canina* fruits. The findings enhance the potential applications of this herbal resource and advocate for further studies into optimising extraction processes to improve the recovery of valuable bioactive compounds. Furthermore, the results emphasise the significance of herbal dust, which has historically been regarded as a processing by-product, as a prospective and sustainable source of phenolic compounds. This underscores the potential for its enhanced utilisation within circular economy and waste reduction strategies.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr14071086/s1, Figure S1: Subcritical Fluids Extraction (SBFE) Apparatus. 1. Nitrogen cylinder tank (200 bar), 2. Pressure reduce valve (200/50 bar), 3. Manometer 100 bar, 4. Extractor vessel (V = 0.5 dm^3, PN = 200 bar), 5. Thermostatic air ventilated heating vessel with thermo regulated control (TRC), 6. Thermo probe K-type (TRP), 7. High pressure valve (PN = 200 bar), 8. Magnetic stirrer; Figure S2: LC-MS/MS chromatogram of *Rosa canina* seeds in UAE and SBFE. Chromatographic conditions are described in the text. Peak identification is given in Table 2; Figure S3: LC-MS/MS chromatogram of *Rosa canina* peel in UAE and SBFE. Chromatographic conditions are described in the text. Peak identification is given in Table 2; Figure S4: HPLC chromatogram of S12 obtained with SBFE at λ = 260 (A), 270 (B), 250 (C), 280 (D), 240 (E), 330 (F), 360 (G) nm; Figure S5: HPLC chromatogram of UV4 obtained with UAE at λ = 260 (A), 270 (B), 250 (C), 280 (D), 240 (E), 330 (F), 360 (G) nm.

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