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Quantitative Analysis of Phenolic Compounds and Mineral Contents of *Rosa canina* L. Waste Seeds

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ABSTRACT

Natural products play an important role in medicine. They have been used extensively in folk medicine to treat various illnesses. In this work, quantitative analysis of phenolic compounds in methanol, acetonitrile and dichloromethane extracts of *Rosa canina* L. waste seeds were investigated by liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) LC-MS/MS. Mineral analysis of *R. canina* seeds was determined by inductively coupled plasma–atomic emission spectrometry (ICP-OES). Fe, Mn, K and Zn were found as chief elements. Quantitative analysis revealed that catechin was the major flavonoid in all extracts. This work offers a viewpoint for recycling the *R. canina* waste seeds into the economy due to their bioactive content.

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Introduction

Plants have gained great importance in the drug discovery and development process due to their secondary metabolite contents (Erenler et al., 2016; Sevindik et al., 2017; Bose et al., 2019; Fascella et al., 2019; Mamat et al., 2020). After the development of spectroscopy in 19th century, the secondary metabolites were identified in the plants and usage of these compounds in pharmacy has accelerated. The bioactive compounds are found in root, steam, leaf, fruit and seeds (Mohammed et al., 2019; Ungurean et al., 2020). The identification and quantification of bioactive compounds into the plants play a significant role for usage in the food and pharmacy (Dąbrowska et al., 2019; Mohammed et al., 2020). Moreover, most of these compounds are beneficial for human diet (Parikh and Patel 2017; Mohammed et al., 2021). Although a lot of waste products including bioactive compounds form from the factories, the effective usage of these waste products is limited (Szentmihályi et al., 2002; Ahmed et al., 2016).

These waste materials have increased steadily with the population growth worldwide. Most of these waste materials are generally converted into fertilizers or animal feed low economic value by simple technology (Rostamizadeh et al., 2020). In addition, these waste materials cause serious environmental problems during disposal, transportation and storage due to their volatile and moisture content. Indeed, these wastes contain bioactive compounds which are used in food and medicinal industry (Engels et al., 2012; Flavio Ortega-Arellano et al., 2019; Choudhary et al., 2020) However, these bioactive compounds have been garbage without being evaluated. Converting these waste materials into valuable products is important in terms of the country's economic and environmental problems. *Rosa canina* L. is a shrub distributed throughout Europe, West Asia, northwest Africa, and Europe (Selahvarzian et al., 2018). This plant has been used effectively in traditional medicine to tread various diseases such as infection, common cold, gastrointestinal disorders, urine disease and inflammation

(Pehlivan et al., 2018; Turan et al., 2018). It is also effective for reducing osteoarthritis symptoms (Winther et al., 1999; Selahvarzian et al., 2018; Gruenwald et al., 2019). *R. canina* included ascorbic acid, carotenoids, and phenolic compounds, fatty acids (Demir et al., 2014). *R. canina* is processed in products including tea, jam, and nectar. *R. canina* seeds consist of nearly 50% polyunsaturated fatty acids, which are used in cosmetic industry due to their healing effect on skin (Ilyasoğlu, 2014).

Herein, quantitative analysis of phenolic compounds, mineral analysis and antioxidant activity of *R. canina* seeds were investigated. *R. canina* seeds are the waste products from the factory. This study provides a perspective on recycling waste products to the economy.

Material and Methods

Material and Reagents

Solvents and reagents were analytical grade and purchased from Sigma-Aldrich Co. (St. Louis. MO. USA) Merck KGaA (Darmstadt. Germany). Deionized water was obtained from a Milli–Q water purification system (Millipore. USA).

Plant Material and Extraction

R. canina fruits were collected from Tokat-Turkey in August/2019. Seeds were manually separated, washed, dried then grinded to powder prior to use. Samples were extracted using methanol (MeOH), dichloromethane (DCM), acetonitrile (ACN). 0.5 g seed powder was extracted in a tube with 10 mL solvent. The sample was vortexed for 2 min and centrifuged for 10 min. The obtained supernatant was filtered and stored at +4 °C for further analysis.

For quantitative analysis, a calibration curve was obtained by injection of known concentrations (0.25-10 ppm) of mix phenolic standards ($R^2 = 0.99$). Concentration of the standard compound in the methanol extract was determined using the peak area in the standard chromatogram. The analysis was carried out in triplicate for each concentration.

LC-MS/MS Analysis

The UHPLC (Thermo Fisher Scientific Inc. Boston. USA) system consisting of Ultimate 3000 RSLC system with binary pumps and S surveyor autosampler (Thermo Scientific Inc. San Jose. CA. USA) was used for the chromatographic separation of phenolic compounds (Wu et al., 2007; Yaman, 2020). Chromatographic separation was performed on a ODS HYPERSİL column (4.6×250 mm 5 µm, Thermo Fisher Scientific Inc. Boston. USA). The mobile phase was made up from solvent A (water with 0.1% formic acid) and solvent B (methanol). The gradient profile was set as follows: the method started at 100% mobile phase A and was held for the first 1.0 min. 25 min 5% A, 30 min 100% mobile phase B. The pump flow rate was 0.7 mL/min, the column temperature was held at 30°C. The sample injection volume was 20 µL. The analysis was carried out in triplicate for each concentration.

Mass spectrometric detection was performed with a TSQ Quantum Access Max API mass spectrometer (Thermo Fisher Scientific Inc. Boston. USA) equipped with electrospray ionisation (ESI). The operating conditions in negative/positive ionization mode were as follows: capillary temperature at 300ºC, vaporizer temperature at 350ºC, sheat gas pressure (Arb) at 30, aux gas pressure (Arb) at 13, sprey voltage (V) (positive polarity) at 4000, sprey voltage (V) (negative polarity) at 2500, discharge current (µA) at 4.0. The internal standards were used for calibration.

Determination of the Mineral Elements

Mineral analysis of *R. canina* waste seeds were determined by inductively coupled plasma–atomic emission spectrometry on a Thermo Scientific iCAP 6500 (ICP-OES) (Zhang et al., 2017). The calibration curve was represented using different concentrations (from 1ppb to 2000 ppb) of each element (Ca, Cd, Co, Ni, Mo, Pb, Mg, P, K, Na, Cu, Fe, Mn, Zn, Cr, Se) before analysing the plant samples. Microwave digestion technique was used for ICP analysis. Samples (0.5 g) were weighted and digested in concentrated HNO_3/H_2O_2 (Ngigi and Muraguri, 2019). The digest solutions were analysed as triplicates. The amounts of macro/micro elements in the samples are expressed as mg g^{-1} and mg kg^{-1}(Ercisli, 2007).

Results and Discussion

Several studies reported to chemical composition in different rose seeds. *R. canina* seeds are very common because they are a rich source of bioactive metabolites. However, to our knowledge currently few reports is available on the chemical composition, and nutritional value of *R. canina* waste seeds.

Multi Element Analysis

Methods of acid digestion and quantification by ICP-OES were proposed to calculate the content of Ca, Cd, Co, Ni, Mo, Pb, Mg, P, K, Na, Cu, Fe, Mn, Zn, Cr, Se in *R. canina* seed samples (Table 1.)

The quantification of macro and micro elements is exceedingly important, because there has been an increase in their consumption as a functional food. Some of these elements were given beloved as the limit of detection (LOD). Macro elements (Ca, Mg, P, K, Na) are in the concentration range of 0.236 to 11.71 mg g^{-1}. Micro elements (Cu, Fe, Mn, Zn, Se) were determined in the concentration range of 2.47 to 17.52 mg kg^{-1}. While macro elements are acting directly muscle and nervous system, micro elements are important for biochemical reactions such as immune and hormone system (Maatallah et al., 2020).

Table .1 Mineral element content of *R. canina* waste seeds estimated from dried samples by ICP-OES

Mineral	Mean ± SD*
Macro-mineral (mg g-1. D.W)	
Calcium (Ca)	2.47 ± 13.25
Magnesium (Mg)	0.43 ± 1.47
Phosphorus (P)	2.56 ± 0.03
Potassium (K)	11.71 ± 0.73
Sodium (Na)	0.236 ± 0.24
Micro-mineral (mg kg-1.DW)	
Copper (Cu)	6.67 ± 0.01
Iron (Fe)	17.52 ± 0.02
Manganese (Mn)	13.43 ± 0.002
Zinc (Zn)	9.78 ± 0.002
Selenium (Se)	2.47 ± 0.007

*Values are means and standard deviation (SD) of 3 replicates.

Table 2. Representative phenolic compounds in different solvents of *Rosa canina* seed waste as determined by LC-MS/MS (mg/kg)

RT	Phenolics	ACN	DCM	MeOH	LOD	LOQ
10.21	Gallic acid	3.262	0.300	35.959	0.058	0.091
13.32	Catechin	59.705	20.040	297.831	0.097	0.121
13.82	Protocatechuic acid	0.700	0.840	2.489	0.422	1.405
13.90	Gentisic acid	nd	nd	2.365	0.026	0.039
14.36	Chlorogenic acid	nd	nd	nd	0.051	0.072
14.67	p-hydroxybenzoic acid	6.412	0.910	5.336	0.243	0.519
14.83	Epicatechin	nd	nd	nd	0.003	0.006
15.20	Caffeic acid	0.298	nd	1.180	0.042	0.058
15.27	4-OH benzaldehyde	1.138	nd	1.149	0.032	0.059
17.09	p-Coumaric acid	3.063	nd	4.561	0.069	0.109
18.25	Rutin	0.003	0.001	0.260	0.022	0.034
20.50	Naringenin	1.514	0.326	1.275	0.052	0.068
20.73	Quercetin	3.920	nd	6.251	0.141	0.181
22.06	Kaempferol	2.273	1.406	7.999	0.188	0.447

RT, Retention time. nd, Not detected.

Determination of Phenolic Compounds

The LC-MS/MS analysis of 18 phenolics resulted in quantification of 14 compounds. Sample was extracted in methanol (MeOH), acetonitrile (ACN), and dichloromethane (DCM). The most phenolic compounds were found in methanol extract.

Qualification of phenolic compounds was possible by comparison with retention time. Quantification of selected compounds was made based on calibration curves of available standards. 12 compounds were identified in the methanol extract of seeds. The catechin was found as a major compound in *R. canina* waste seeds (Takahashi et al., 2019). It was reported that catechin revealed significant biological activities including antioxidant, antidiabetic, antimicrobial, anticancer, anticoagulant, antihypertensive, antiulcer effects (Rodríguez-Delgado et al., 2001). The gallic acid was found as the second chief compound in the *R. canina* waste seeds (Nadpal et al., 2016; Elmastaş et al., 2017). The gallic acid was reported to possess antioxidant, anti- allergic, anti-inflammatory, anticancer, antimutagenic effects (Denardin et al., 2015).

Conclusions

Quantitative analysis of phenolic compounds and mineral contents of *R. canina* waste seeds were investigated. *R. canina* waste seeds were presented to contain important bioactive compounds that could be a row material in pharmacy and food industry. However, *R. canina* waste seeds are not being used effectively nowadays. This study provides a perspective in recycling the *R. canina* waste seeds into the economy.

Notes

The authors declare no competing financial interest.

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References

Ahmed A, Arshad MU, Saeed F, Ahmed RS, Chatha SAS. 2016. Nutritional probing and HPLC profiling of roasted date pit powder. Pakistan Journal of Nutrition, 15: 229–237.

Bose B, Tripathy D, Chatterjee A, Tandon P, Kumaria S. 2019. Secondary metabolite profiling, cytotoxicity, anti-inflammatory potential and in vitro inhibitory activities of Nardostachys jatamansi on key enzymes linked to hyperglycemia, hypertension and cognitive disorders. Phytomedicine, 55: 58–69.

Choudhary S, Kumar R, Dalal U, Tomar S, Reddy SN. 2020. Green synthesis of nanometal impregnated biomass – antiviral potential. Materials Science and Engineering C, 112.

Dąbrowska M, Maciejczyk E, Kalemba D. 2019. Rose Hip Seed Oil: Methods of Extraction and Chemical Composition. European Journal of Lipid Science and Technology, 121: 1800440.

Demir N, Yildiz O, Alpaslan M, Hayaloglu AA. 2014. Evaluation of volatiles, phenolic compounds and antioxidant activities of rose hip (*Rosa* L.) fruits in Turkey. LWT - Food Science and Technology, 57: 126–133.

Denardin CC, Hirsch GE, Da Rocha RF, Vizzotto M, Henriques AT, Moreira JCF, Guma FTCR, Emanuelli T. 2015. Antioxidant capacity and bioactive compounds of four Brazilian native fruits. Journal of Food and Drug Analysis, 23: 387–398.

Elmastaş M, Demir A, Genç N, Dölek Ü, Güneş M. 2017. Changes in flavonoid and phenolic acid contents in some *Rosa* species during ripening. Food Chemistry, 235: 154–159.

Engels C, Gräter D, Esquivel P, Jiménez VM, Gänzle MG, Schieber A. 2012. Characterization of phenolic compounds in jocote (*Spondias purpurea* L.) peels by ultra-high-performance liquid chromatography/electrospray ionization mass spectrometry.: Food Research International, 46: 557–562.

Ercisli S. 2007: Chemical composition of fruits in some rose (Rosa spp.) species.: Food Chemistry 104: 1379–1384.

Erenler R, Sen O, Aksit H, Demirtas I, Yaglioglu AS, Elmastas M, Telci İ. 2016. Isolation and identification of chemical constituents from *Origanum majorana* and investigation of antiproliferative and antioxidant activities. Journal of the Science of Food and Agriculture, 96: 822–836.

Fascella G, D'Angiolillo F, Mammano MM, Amenta M, Romeo FV, Rapisarda P, Ballistreri G. 2019. Bioactive compounds and antioxidant activity of four rose hip species from spontaneous Sicilian flora. Food Chemistry, 289: 56–64.

Flavio Ortega-Arellano H, Jimenez-Del-Rio M, Velez-PardoC. 2019. Neuroprotective Effects of Methanolic Extract of Avocado Persea americana (var. Colinred) Peel on Paraquat-Induced Locomotor Impairment, Lipid Peroxidation and Shortage of Life Span in Transgenic knockdown Parkin Drosophila melanogaster. Neurochemical Research, 44: 1986–1998.

Gruenwald J, Uebelhack R, Moré MI. 2019. *Rosa canina* – Rose hip pharmacological ingredients and molecular mechanics counteracting osteoarthritis – A systematic review. Phytomedicine, 60: 152958.

Ilyasoğlu H. 2014. Characterization of Rosehip (*Rosa canina* L.) Seed and Seed Oil. International Journal of Food Properties, 17: 1591–1598.

Maatallah S, Dabbou S, Castagna A, Guizani M, Hajlaoui H, Ranieri AM, Flamini G. 2020. *Prunus persica* by-products: A source of minerals, phenols and volatile compounds. Scientia Horticulturae, 261: 109016.

Mamat SF, Azizan KA, Baharum SN, Noor NM, Aizat WM. 2020. GC-MS and LC-MS analyses reveal the distribution of primary and secondary metabolites in mangosteen (*Garcinia mangostana* Linn.) fruit during ripening. Scientia Horticulturae, 262: 109004.

Mohammed FS, Pehlivan M, Sevindik M. 2019. Antioxidant, antibacterial and antifungal activities of different extracts of *Silybum marianum* collected from Duhok (Iraq). International Journal of Secondary Metabolite, 6(4): 317-322.

Mohammed FS, Şabik AE, Sevindik E, Pehlivan M, Sevindik M. 2020. Determination of Antioxidant and Oxidant Potentials of *Thymbra spicata* Collected from Duhok-Iraq. Turkish Journal of Agriculture-Food Science and Technology, 8(5): 1171-1173.

Mohammed FS, Pehlivan M, Sevindik E, Akgul H, Sevindik M, Bozgeyik I, Yumrutas O. 2021. Pharmacological properties of edible *Asparagus acutifolius* and *Asparagus officinalis* collected from North Iraq and Turkey (Hatay). Acta Alimentaria, 50(1): 136-143.

Nadpal JD, Lesjak MM, Šibul FS, Anačkov GT, Četojević-Simin DD, Mimica-Dukić NM, Beara IN. 2016. Comparative study of biological activities and phytochemical composition of two rose hips and their preserves: Rosa canina L. and Rosa arvensis Huds. Food Chemistry, 192: 907–914.

Ngigi AN, Muraguri BM. 2019. ICP-OES determination of essential and non-essential elements in *Moringa oleifera, Salvia hispanica and Linum usitatissimum*.: Scientific African 6: 165.

Parikh B, Patel VH. 2017. Quantification of phenolic compounds and antioxidant capacity of an underutilized Indian fruit: Rayan [Manilkara hexandra (Roxb.) Dubard]. Food Science and Human Wellness, 6(1): 10-19.

Pehlivan M, Mohammed FS, Sevindik M, Akgul H. 2018. Antioxidant and oxidant potential of *Rosa canina*. Eurasian Journal of Forest Science, 6(4): 22-25.

Rodríguez-Delgado MA, Malovaná S, Pérez JP, Borges T, García Montelongo FJ. 2001. Separation of phenolic compounds by high-performance liquid chromatography with absorbance and fluorimetric detection. Journal of Chromatography A, 912: 249–257.

Rostamizadeh E, Iranbakhsh A, Majd Ahmad, Arbabian S, MehreganI. 2020. Green synthesis of Fe_2O_3 nanoparticles using fruit extract of *Cornus mas* L. and its growth-promoting roles in Barley. Journal of Nanostructure in Chemistry, 10: 125–130.

Selahvarzian A, Alizadeh A, Baharvand PA, Eldahshan OA, Rasoulian B. 2018. Medicinal Properties of Rosa canina L. Herbal Medicines Journal, 3: 77–84.

Sevindik M, Akgul H, Pehlivan M, Selamoglu Z. 2017. Determination of therapeutic potential of *Mentha longifolia* ssp. *longifolia*. Fresen Environ Bull, 26(7): 4757-4763.

Szentmihályi K, Vinkler P, Lakatos B, Illés V, Then M. 2002. Rose hip (*Rosa canina* L.) oil obtained from waste hip seeds by different extraction methods. Bioresource Technology, 82: 195–201.

Takahashi M, Ozaki M, Miyashita M, Fukazawa M, Nakaoka T, Wakisaka T, Matsui Y, Hibi M, Osaki N, Shibata S. 2019. Effects of timing of acute catechin-rich green tea ingestion on postprandial glucose metabolism in healthy men. Journal of Nutritional Biochemistry, 73.

Turan S, Solak R, Kiralan M, Ramadan MF. 2018. Bioactive lipids, antiradical activity and stability of rosehip seed oil under thermal and photo-induced oxidation. Grasas y Aceites, 69: e248.

Ungurean C, Carpa R, Câmpean R, Maior MC, Olah NK. 2020. *Berberis* sp. extracts. Rom Biotechnol Lett, 25: 2132–2139.

Winther K, Rein E, Kharazmi A. 1999. The anti-inflammatory properties of rose-hip. Inflammopharmacology, 7: 63–68.

Wu J, lin Yee LP, Jiang ZH, Cai Z. 2007. One single LC-MS/MS analysis for both phenolic components and tanshinones in Radix Salviae Miltiorrihizae and its medicinal products. Talanta 73: 656–661.

Yaman C. 2020. Phytochemicals and antioxidant capacity of wild growing and in vitro *Hypericum heterophyllum*. Rom Biotechnol Lett 25: 2111–2117.

Zhang N, Li Z, Zheng J, Yang X, Shen K, Zhou T, Zhang Y. 2017. Multielemental analysis of botanical samples by ICP-OES and ICP-MS with focused infrared lightwave ashing for sample preparation. Microchemical Journal 134: 68–77.