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Assessment of Antioxidant Capacity, Heavy Metal, Mineral and Protein Contents of Some Medicinal Plants Selected in Van, Turkey

Van İlinden Seçilmiş Bazı Tıbbi Bitkilerin Antioksidan Kapasite, Ağır Metal, Mineral ve Protein İçeriklerinin Değerlendirilmesi

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ÖZET

Amaç: *Rosa canina* L., *Malus domestica* L., *Prunus persica* L Siebold & Zucc., *Cydonia oblonga* Mill., *Armenica vulgaris* Lam., ve *Pyracantha coccinea* M.Roem., *Rosaceae* familyasına ait, gıda, parfüm, kozmetik, boya, içecek gibi çok çeşitli sanayi kollarında kullanılan, ekonomik ve tıbbi kullanım açısından önemli meyvelerdir. Tıbbi bitkiler hastalıklara karşı doğal bileşenleri ile etki gösterseler de toksik ve istenmeyen yan etkilere neden olabilirler. Bitkilerin tedavi, gıda veya kozmetik amaçlı kullanılmadan önce ağır metal, mineral, protein ve antioksidan kapasiteleri açısından incelenmesi insan sağlığı ve gıda güvenliği açısından önemlidir. Van-Türkiye'de kültürü yapılan bazı tıbbi bitkilerin ağır metal (Al, Cr, Cu, Co, Zn), mineral (Fe, Mg, Na, Ca, K), protein ve antioksidan kapasiteleri belirlenerek, gıda ve tıbbi kullanım açısından güvenliklerini değerlendirildi.
Materyal ve Metot: Liyofilize edilen bitkiler yaş yakma (mikrodalga) cihazıyla çözünürleştirildikten sonra ICPOES cihazında Al, Cr, Cu, Co, Zn, AAS cihazında Fe, Mg, Na, Ca, K elementleri analiz edildi. Protein analizleri Gerthardt Dumatherm yöntemiyle yapıldı. Antioksidan kapasite analizi için Cuprac yöntemi kullanıldı.
Bulgular: Tespit edilen değerler (mg kg^{-1}) şu şekildedir: Al 10.753-20.407, Co 0.007-9.664, Cr 0.119-0.411, Cu 2.409-6.554, Zn 23.426-33.891, Ca 743.0-2501.7, Fe 31.7-117.6, K 3555.2-4202.9, Mg 498.7-1982.9, Na 839.8-1616.0 ve Protein (%) 1.45-5.53 aralığında gözlendi. Bitkilerin Cuprac değerleri 1.13-3.62 arasında değişirken, standart olarak kullanılan sentetik antioksidanlar α-tokoferol ve BHT için Cuprac değeri sırasıyla 2.14 ve 3.21 µmol TE g^{-1}DW olarak tespit edildi. Özellikle *Rosa canina* ekstraktının, α-tokoferol ve BHT ile karşılaştırılabilir düzeyde yüksek aktivite (3.65) gösterdiği tespit edildi.
Sonuç: Yüzyıllar boyunca insanoğlu hastalıkların tedavisinde bitkilerden yararlanmıştır. Sentetik ilaçların ciddi yan etkileri nedeniyle günümüzde de birçok hastalığın tedavisi tıbbi bitkilerle yapılmaktadır. Ancak tıbbi bitkilerin özellikle ağır metal miktarları açısından incelenerek bilinçli tüketilmesi uzun vadede ciddi sağlık sorunlarının önüne geçecektir. Çalışmada, Van halkı tarafından kültürü yapılan, tedavi amaçlı kullanılan ve meyve olarak tüketilen Rosaceae familyasına ait bazı bitkilerin ağır metal miktarlarının insan tüketimi ve tıbbi kullanım için güvenli olduğu, mikro besin, protein ve sağlıklı beslenme ve tedavi edici kullanımlar için antioksidan kapasitelerinin istenilen düzeyde olduğu tespit edildi.

Anahtar Kelimeler: Tıbbi bitkiler, Rosaceae, Ağır metal, Mineral, Protein, Antioksidan kapasite.

ABSTRACT

Objective: *Rosa canina* L., *Malus domestica* L., *Prunus persica* L Siebold & Zucc., *Cydonia oblonga* Mill., *Armenica vulgaris* Lam., and *Pyracantha coccinea* M.Roem. are important fruits of the Rosaceae family, used in a wide variety of industries such as food, perfume, cosmetics, paint, beverage, and for economic and medical purposes. Although medicinal plants act with their natural components against diseases, they can cause toxic and undesirable side effects. It is important in terms of human health and food safety to examine plants for their heavy metal, mineral, protein and antioxidant capacities before they are used for treatment, food or cosmetic purposes. The heavy metals (Al, Cr, Cu, Co, Zn), minerals (Fe, Mg, Na, Ca, K), protein and antioxidant capacities of some medicinal plants grown in Van-Turkey were determined and their safety in terms of food and in medical uses were evaluated.
Material and Method: After the lyophilized plants were solubilized with a wet burning (microwave) device, Al, Cr, Cu, Co, Zn, Fe, Mg, Na, Ca, K elements were analyzed in the ICPOES device. Protein analyzes were performed by the Gerthardt Dumatherm method. Cuprac method was used for antioxidant capacity analysis.
Results: The measured values were ranged between (in mg kg^{-1}) Al 10.753-20.407, Co 0.007-9.664, Cr 0.119-0.411, Cu 2.409-6.554, Zn 23.426-33.891, Ca 743.0-2501.7, Fe 31.7-117.6, K 3555.2-4202.9, Mg 498.7-1982.9, Na 839.8-1616.0 and Protein (%) 1.45-5.53. Detected heavy metal amounts are in general within acceptable limits determined by WHO (World Health Organization). While the Cuprac values of the plants ranged between 1.13 and 3.62, the Cuprac values for the standard synthetic antioxidants α-tocopherol and BHT were determined as 2.14 and 3.21 µmol TE g^{-1}DW, respectively. In particular, it was determined that *Rosa canina* extracts showed high activity (3.62 µmol TE g^{-1}DW) comparable to α-tocopherol and BHT.

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Conclusion: For centuries, human beings have benefited from plants in the treatment of diseases. Due to the severe side effects of synthetic drugs, people in the modern world also turn to medicinal plants for the treatment of many diseases. However, conscious consumption of medicinal plants by examining them especially in terms of heavy metal amounts will prevent serious health problems in the long run. The study showed that the heavy metal amounts of some plants belonging to the Rosaceae family, which are cultured, used for therapeutic purposes and consumed as fruit by the people of Van, are safe for human consumption and medical uses, and their micronutrient, protein and antioxidant capacities are at the desired level for healthy nutrition and therapeutic uses.

Keywords: Medicinal plants, Rosaceae, Heavy metal, Mineral, Protein, Antioxidant capacity.

INTRODUCTION

Medicinal plants are plant and plant-derived products used for their therapeutic properties all over the world for hundreds of years. The main reason why the demand for herbal resources has continued to increase in recent years is that synthetically produced drugs cause negative effects that will harm different organs of the body while curing the disease in question. The World Health Organization (WHO, 1998) reports that 80% of the world's population primarily benefit from medicinal plants for the prevention and healing of diseases. Thanks to the phytochemicals they contain, medicinal plants show therapeutic properties such as antioxidant (Ryu et al., 2006), antibacterial (Dzoyemet al., 2018), anti-inflammatory (Su, X et al., 2017), anti-cancer (Ahmed et al., 2016), cardioprotective (Razavi-Azarkhiavi et al., 2016), immune system strengthening (Vasantha Rupasinghe et al., 2015), calming and protecting the skin from UV radiation (Korać and Khambholja, 2011).

A biological antioxidant is defined as any substance that retards or inhibits the oxidation of that substrate, even in small amounts, when compared to concentrations of oxidizable substrates (Halliwell, 2001). Antioxidants are responsible for the defense mechanism of the organism against pathologies due to the attack of free radicals, therefore, the intake of plant-derived antioxidants plays a role in the prevention of degenerative diseases caused by oxidative stress, such as cancer, Parkinson's, Alzheimer's or atherosclerosis diseases (Pisoschi and Negulescu, 2012). Antioxidants are small molecular weight, endogenous or exogenous compounds that can reduce or eliminate the effects of free radicals. For this reason, it is recommended to consume various fruits and vegetables with antioxidant effect in order to prevent diseases that may arise. Since antioxidants obtained from plant sources are more advantageous and preferable than synthetic ones, they have become important compounds sought both as food supplements and for use in the food, pharmaceutical or cosmetic industry.

Rosa canina L., *Malus domestica* L.**,** *Prunus persica* L Siebold & Zucc., *Cydonia oblonga* Mill., *Armenica vulgaris* Lam., and *Pyracantha coccinea* M. Roem., belonging to Rosaceae family, occur especially in a wide region from Asia to the Caucasus and are generally known for their delicious and healthy fruits. Rosaceae fruits are reported to be used as a cough suppressant and expectorant in abdominal pain, colds, bronchitis and diabetes, against tonsillitis, hepatitis, asthma, heart and vascular occlusion diseases (Fındıcak, 2019). These fruits contain secondary compounds, phytoestrogens, phenolic compounds, flavonoids, antioxidants and protective molecules, which play an important role in the body's defense against diseases and cancer (Yau et al., 2002; Shulaev et al., 2008). In addition to their therapeutic properties, medicinal plants can cause various side effects and heavy metal toxicity. The World Health Organization (WHO) recommends the examination of medicinal plants in terms of mineral and heavy metal levels (WHO, 1998).

The aim of this study is to determine the heavy metal (Al, Cr, Cu, Co, Zn), mineral (Fe, Mg, Na, Ca, K), % protein and antioxidant capacities of some medicinal plants grown in Van-Turkey and to evaluate their safety in terms of food and in medical uses. Although medicinal plants act with their natural components against diseases, they can cause toxic and undesirable side effects. It is important in terms of human health and food safety to examine plants for heavy metal, mineral, protein and antioxidant capacities before they are used for treatment, food or cosmetic purposes.

MATERIAL and METHOD

Plant material and sample preparation

Plants were identified by specialist Dr. Fevzi Özgökçe. Fruits of *Rosa canina* L., *Malus domestica* L., *Prunus persica* L Siebold & Zucc., *Cydonia oblonga* Mill., *Armenica vulgaris* Lam., and *Pyracantha coccinea* M.Roem. were collected from Van city in Turkey (latitude: 38.57791850 N38°34′′ and longitude: 43.26287760 E43°15′′). According to the fruit period, the fruits collected in July-August and September were cut into thin slices and dried in the shade. Dried fruits were ground with a grinding mill (IKA, A11 basic Analytical mill) in the laboratory. After the pulverising process they were lyophilized (LyoQuerst-Telstar) at -80°C at 0.05 psi pressure for 48 hours and stored at -20°C until analyses.

Extraction procedure for antioxidant capacity analyses

The lyophilized samples were extracted with 80% acidic methanol (80 ml methanol+ 19.9% purified water + 0.1% acetic acid) in a ratio 1/10 (w:v). It was covered with aluminium foil and left at room temperature (22 ±2°C) for 24 hours. Then it was centrifuged (Hitachi-High speed refrigerated centrifuge-CR22N) at 15,320 g (10,000 rpm) for 20 min at 4°C. The supernatant (upper liquid) was filtered with a 0.45µm syringe tip filter and taken into an amber Eppendorf tube. The supernatant portion was evaporated (Heildolph) within 24 hours. Methanol was removed by evaporation at 45°C, 110rpm for 40 minutes. The residue was completely removed from the flask and lyophilized (LyoQuerst-Telstar) at -80°C at 0.05 psi pressure for 48 hours. The extracts were dissolved in methanol at 1 mg/ml and filtered through 0.45 µm filters and kept in an ultrasonic bath at 25°C for 30 minutes and used in antioxidant studies.

Microwave procedure for mineral and heavy metal analyses

2 ml of H_2O_2 and 6 ml of HNO_3 were added to 200 mg of dried plant sample and dissolved in Teflon tubes at 200˚C, 35 bar pressure, for 45 minutes in Milestone Ethos Easy Microwave digestion system. After the microwave, the samples were taken into 50 ml tubes and filled with Ultrapure Milli-Q water, so that the final volume was 50 ml. After the plant samples were solubilized by Milestone Ethos Easy Microwave digestion system (microwave wet digestion) device, analysed with atomic absorption spectrometry (AAS-ICE 3000 series Thermo Scientific) and inductively coupled plasma optical emission spectrometry (ICP-OES Icap 6000 series, Thermo scientific) instruments.

ICPOES and AAS analyses procedure

Thermo scientific Inorganic Ventures IV-Stock-8 solution (100µg ml-1 5.0 HNO3 % (v/v), 125ml d=1.042g ml-1 lot: F2-MEB 418147) was used as standard solution for ICPOES and AAS devices. The calibration curve was linear and from five point. Co, Cr, Cu, Mn, Al and Zn amounts were detected with ICPOES. Ca, Fe, K, Mg, Na amounts were detected with AAS devices. Analyses were performed in triplicate. All elemental amounts are calculated in mg kg^{-1} dry weight.

Protein analyses

The leaves were dried in the dark at room temperature (22 ±2°C) and were ground with a grinding mill (IKA, A 11 basic Analytical mill). After the dried plant samples were ground, nitrogen and protein amounts were determined with the Dumatherm Nitrogen-Protein device (Gerthardt Analytical System, Germany). For analyses approximately 50 mg of pulverised plant sample was weighed and burned in aluminium tin cups at 900°C in the device to determine the amount of protein. Ethylenediamine tetraacetic acid (EDTA, Dumatherm, Germany) was used as a standard.

Cupric-Reducing Antioxidant Capacity (CUPRAC) Procedure

The CUPRAC assay of plant extracts was carried out using the method of Apak et al. (2008). Antioxidant activities of the prepared extracts were determined at four different concentrations according to the CUPRAC method based on copper (II) reduction. In the presence of antioxidant compounds in the samples, the Cu(II)-Neocuproin (Nc) complex is reduced to colored Cu(I)-Nc chelate and the absorbance of this chelate is measured at 450 nm. 10 mM CuCl2, 1 M CH3COONH4 buffer and 7.5 mM neocuproin were added to the plant extracts with final concentrations of 10, 25, 50, 100 µg/mL. After 1 hour, absorbance was measured at 450 nm (Apak et al., 2008). The absorbance values of the samples were evaluated against the standards. BHT (Butylated Hydroxy Toluene), α-tocopherol was used as standard and total antioxidant capacity, TEAC (Trolox equivalent antioxidant capacity) values were in the range of µg/ml for all extracts.

Statistical analysis

The experiment was designed according to the randomized blocks experimental design and was applied with 3 replications for each feature. Kolmogorov-Smirnov test with normal distribution control of the data obtained regarding the characteristics in the experiment and homogeneity control of subgroup variances were performed with Levene test. As a result of the control, the descriptive statistics of the data that met the conditions were calculated and evaluated with One-Way ANOVA analysis of variance. All statistical data were evaluated with the MINITAB 17 package program and Tukey multiple comparison test was used to determine different groups. Tukey test results were expressed as letters, and 5% significance level was used in the statistical analysis and interpretation of results.

RESULTS

The heavy metal levels of *Rosa canina* L., *Malus domestica* L.**,** *Prunus persica* L Siebold & Zucc., *Cydonia oblonga* Mill., *Armenica vulgaris* Lam., and *Pyracantha coccinea* M. Roem., detected by the ICPOES device (Al, Co, Cr, Cu, Zn) are given in Table 1 and mineral nutrients detected by AAS (Fe, Ca, Mg, Na, K) are given in Table 2. In this study, heavy metal and mineral amounts showed a wide variety. While there was no significant difference between *R. canina* and *P. coccinea* in terms of Al content, the difference has been observed between *A. vulgaris, P. persica, C. oblonga* and *M. domestica*. The lowest Al content has been detected in *M. domestica* (10.753 mg kg^{-1}) and the highest (20.407 mg kg^{-1}) in *P. persica.* A significant difference was observed in terms of Co content among all *Rosaceae* species. For Co the highest value (9.664 mg kg^{-1}) was detected in *P. coccinea* and the lowest (0.007 mg kg^{-1}) in *A. vulgaris*. While no statistically significant difference was observed between *P. persica* and *P. coccinea* in terms of Cr content, a statistically significant difference was found between *A. vulgaris, C. oblonga, M. domestica* and *R. canina*. The highest Cr amount (0.411 mg kg^{-1}) was detected in *P. coccinea* and the lowest (0.072 mg kg^{-1}) in *R. canina.* The amount of Cu was significantly different from each other in the six analysed Rosaceae species. While the highest Cu amount (6.554 mg kg−1) was detected in *P. coccinea*, the lowest (2.409 mg kg^{-1}) was in *A. vulgaris.* While there was no significant difference between the Zn amounts of *P. persica, C. oblonga, M. domestica* and *R. canina,* it was determined that the Zn amounts of *A. vulgaris* and *P. coccinea* were significantly different from each other and from other Rosaceae species. For Zn the highest amount (33.891 mg kg^{-1}) was detected in *P. coccinea* and the lowest (23.426 mg kg−1) in *A. vulgaris* (Table 1).

Table 1. Heavy metal levels of some medicinal plants belonging to *Rosaceae* family grown in Van

Plant	Al	Co	Cr	Cu	Zn
A. vulgaris	17.857 [b]	0.007 [f]	0.119 [d]	2.409 [e]	23.426 [c]
P. persica	20.407 [a]	5.079 [b]	0.388 [a]	5.168 [b]	26.967 [b]
C. oblonga	19.263 [ab]	1.314 [d]	0.149 [c]	3.773 [c]	27.252 [b]
M. domestica	10.753 [d]	1.776 [c]	0.207 [b]	3.208 [d]	25.759 [b]
R. canina	13.612 [c]	0.830 [e]	0.072 [e]	2.591 [e]	26.840 [b]
P. coccinea	13.612 [c]	9.664 [a]	0.411 [a]	6.554 [a]	33.891 [a]
P Value	0.000	0.000	0.000	0.000	0.000

The difference between means with the same letter in the same column is insignificant ($p<0.05$).

While there was no significant difference between the Ca amounts of *R. canina* and *P. coccinea*, there was a significant difference between the Ca amounts of *C. oblonga, M. domestica, C. oblonga, M. domestica, P. persica* and *A. vulgaris.* The highest Ca amount (2501.7 mg kg^{-1}) was detected in *P. coccinea*, while the lowest (743.0 mg kg^{-1}) in *M. domestica.* In terms of Fe and Na amounts, there was a significant difference only between *A. vulgaris* and *P. coccinea*, but no significant difference was found between other Rosaceae species. The detected highest and lowest mineral concentrations (in mg kg^{-1}) per plants were for Fe highest amount (117.6 mg kg^{-1}) in *P. coccinea* and the lowest (31.7 mg kg^{-1}) in *M. domestica,* for Na; the highest 1616.3 in *A. vulgaris* and the lowest 839.8 in *P. coccinea* (Table 2).

Table 2. Mineral levels of some medicinal plants belonging to *Rosaceae* family grown in Van

Plant	Ca	Fe	K	Mg	Na
C. oblonga	1834.0 [b]	44.4 [c]	3624.5 [d]	918.0 [b]	1107.0 [b]
M. domestica	743.0 [d]	31.7 [c]	3555.2 [d]	498.7 [c]	1051.1 [b]
R. canina	2497.7 [a]	45.8 [c]	3796.9 [c]	1965.0 [a]	941.1 [b]
P. persica	1101.3 [cd]	32.6 [c]	4023.4 [b]	567.1 [c]	928.9 [b]
A. vulgaris	1205.4 [c]	79.4 [b]	3881.7 [c]	877.5 [b]	1616.0 [a]
P. coccinea	2501.7 [a]	117.6 [a]	4202.9 [a]	1982.9 [a]	839.8 [b]
P Value	0.000	0.000	0.000	0.000	0.002

The difference between means with the same letter in the same column is insignificant ($p<0.05$).

Protein amounts were analysed with Gerthard Dumatherm protein device according to Dumas method. There was no wide range between the protein amounts of species. While in the terms of protein amounts there was no significant difference in *P. persica, M. domestica and C. oblonga* between each, a significant difference was observed between *R. canina* and *A. vulgaris*. The highest protein amount (5.53%) was in *R. canina* and lowest (1.45%) was detected in *M. domestica*. Protein concentrations (%) per plant were as follows: *R. canina* 5.53%; *M. domestica* 1.45%; *A. vulgaris* 5.48%; *C. oblonga* 1.58%; *P. persica* 2.19% and *P. coccinea* 4.39% (Table 3).

In the CUPRAC method evaluating total antioxidant capacity, TEAC (Trolox equivalent antioxidant capacity) values were in the range of mg/ml for all extracts, and 3.21 and 2.14 µg/ml for synthetic antioxidants BHT and α-tocopherol, respectively. In particular, it was observed that *Rosa canina* extracts showed high activity comparable to the standard antioxidants BHT and α-tocopherol and the sample extracts also showed increasing activities with increasing concentration. The Cuprac values (for 100 ppm) were as follows; for *Rosa canina* 3.62 µmol TE g^{-1} DW; for *M. domestica* 1.54 µmol TE g^{-1} DW, for *A. vulgaris* 1.13 µmol TE g^{-1} DW, for *C. oblonga* 2.00 µmol TE g^{-1} DW, for *P. persica* 1.92; for *P. coccinea* 3.24 µmol TE g^{-1} DW; for BHT 3.21 µmol TE g^{-1} DW and for α-Toc 2.14 µmol TE g^{-1} DW.

Table 3. % protein amounts and TEAC (Trolox equivalent antioxidant capacity) values of the extracts obtained from the CUPRAC method

Plant	Antioxidant Capacity (µmol TE g^{-1} DW)				% protein
	10 ppm	25 ppm	50 ppm	100 ppm	
R. canina	0.92 [b]	2.28 [a]	2.82 [b]	3.62 [a]	5.53 [a]
M. domestica	0.27 [e]	0.46 [h]	0.84 [g]	1.54 [f]	1.45 [c]
A. vulgaris	0.25 [e]	0.53 [g]	0.73 [h]	1.13 [g]	5.48 [a]
C. oblonga	0.35 [c]	0.71 [e]	1.31 [e]	2.00 [d]	1.58 [c]
P. persica	0.37 [c]	0.82 [d]	1.46 [d]	1.92 [e]	2.19 [c]
P. coccinea	0.97 [a]	2.21 [b]	2.91 [a]	3.24 [b]	4.39 [b]
BHT	0.91 [b]	1.44 [c]	2.32 [c]	3.21 [b]	-
a-Toc	0.31 [d]	0.63 [f]	1.13 [f]	2.14 [c]	-
P Value	0.000	0.000	0.000	0.000	0.000

The difference between means with the same letter in the same column is insignificant ($p<0.05$).

DISCUSSION

Trace elements and minerals show activity in biological systems by making complexes with metallo-enzyms and organic compounds (Kleczkowski et al. 2004). Cu and Zn with protein and components (e.g. methionine, cysteine, phytochelatins, metallothioneins, albumine) via the sulfur atom, Fe, Co, Cu and Mn with protein and components (e.g., histidine, tyrosine, glutamic acid, aspargine, metalloenzymes) via the oxygen atom, Cr with nucleic acids, Fe, Co, Ni with tetrapyrole ligands such as cobalamin, Al, Ni and Fe have also been reported to form complexes with small organic ligands such as citric acid (Kabata-Pendias, and Mukherjee, 2007). When heavy metals are above acceptable limits, they can cause immunological, neurological, endochronological disorders and psychological behavioural disorders in individuals (Dyer, 2007). Especially in high doses, heavy metals such as Cu are shown as the causes of digestive system cancers by showing carcinogenic and mutagenic effects (Khan et al., 2013) while high doses of Cr intake are associated with breast cancer (Pasha et al., 2010). Some metals such as Cd, Zn and Al are required for human metabolism within acceptable limits. However, they cause various degenerative diseases by showing toxic effects in high amounts. The excess of Al, Ni, Cr, Co, Fe and Zn has been reported as the causes of following disorders: Al: dementia, neurotoxicity, osteomalacia, Ni: gastric, liver and kidney damage, lung cancer, Co: neucrotic hepatitis, hyperglicemia, Cr: lung cancer, Fe: hemachromatosis, cardiac failure and Zn: anemia (Kabata-Pendias, and Mukherjee, 2007).

In this study, which was carried out with plants selected in Van, the amounts of Al and Zn were found to be quite high compared to other heavy metals. Heavy metals and minerals accumulate in plants according to the needs of the plant, the type of element and environmental factors (Lokeshwari and Chandrappa, 2006). The allowable limit for Zn by WHO (1998) is 27.4 mg kg^{-1} for edible plants. All other Rosaceae species have acceptable Zn amounts except *P. coccinea* (33.891 $mg.kg^{-1}$). The Co, Cu and Cr amounts of *P. coccinea* were also the highest among other plants subject to our study. Consistent with our study, Akgüç et al. (2002) found high levels of heavy metals in *P. coccinea* samples. Since this plant grows on the roadsides, it may collect heavy metals from the car exhausts in its fruits. The mineral and protein contents of plants can be affected by the characteristics of the environment in which they are grown, as well as change in different vegetation periods. In studies conducted with different medicinal plants, the amounts of Zn were found to be above the limits set by the WHO (1998). Pytlakowska et al. (2012) determined the amount of Zn between 56.6±0.2 mg kg^{1} and 75.5±0.3mg kg^{-1} in St. John's Wort, mint, lemon balm, sage and chamomile, while Karahan et al, (2020) reported the amount of Zn in medicinal plants in the range of 166.910-395.252 mg kg^{-1}. WHO's (1996) acceptable value for Cr is 1.30 $mg.kg^{-1}$and for Cu 10 $mgkg^{1}$. When Cr is taken in excess, it reacts with biological reducers to form reactive oxygen species, thus causing oxidative stress that damages DNA and protein synthesis (Görmez et al., 2019). The amount of Cr in our study is in the acceptable range (0.07-0.41 mg kg^{-1}). While Özcan (2004) determined the Cr concentrations in basil, rosemary, laurel and lavender at values ranging from 7.95 to 19.0 mg kg^{-1}, Divrikli et al. (2006) determined the Cr value in rosemary, basil and laurel between 0.1 and 9.7 mg g^{-1}, respectively. Cobalt is part of vitamin B-12. Its deficiency in humans seriously affects some biological processes. The amount of Co in some medicinal plants has been reported between 0.14 and 0.40 mg kg^{-1} (Başgel and Erdemoğlu, 2006). In our study the range is between 0.007 and 9.664 mg kg^{-1}. The specified limiting value information of the Co element was not found. For plant growth, Ca, Fe, K and Mg represent the most abundant metal component of many plants because of their important roles as components of chlorophyll, metalloenzymes and secondary metabolites. According to Karahan (2020), the acceptable values reported in the literature for metals are as follows: for Al 15-100 mg kg^{-1}, for Mg 100-1000 mg kg^{-1}, and for Fe 50-250 mg kg^{-1}. In our study Al amounts were between 10.75 and 20.40 mg kg^{-1} , Fe concentrations between 31.7 and 117.6 $mg.kg^{-1}$ while Mg between 567.1 and 1982.9 $mg.kg^{-1}$. The results were consistent with the results of Karahan et al., (2020) determined in different medicinal plants; Al in the range of 13.845 and 186.015 mg kg^{-1}, Mg 295-2225 $mg.kg^{-1}$ and Fe between 100-1228 $mg.kg^{-1}$.

Proteins break down and participate in the structure of nitrogenous bases that make up DNA, amino acids that form the basic building blocks of living things, secondary metabolites that act as defence against stress, and enzymes that take part in metabolic events. Protein ratios in our study (1.45%-5.48%), are below the amounts Kabir et al. (2016) reported in medicinal plants (8.15%-17.3%). However is consistent with the amounts (1.8 -9.3%) Rybicka et al. (2021) reported in various fruits. It is thought that the increase in the amount of protein increases the antioxidant capacity, especially since amino acids such as phenylalanine, which make up proteins, form the structure of antioxidant phenolics. Plants perceive heavy metals as oxidative stressors and activate their antioxidant mechanisms to protect themselves (Bajraktari et al., 2022). The Cuprac method is particularly suitable for the analysis of polyphenols with high antioxidant properties against reactive oxygen species. Fındıcak (2019), reported Cuprac values in the range of 7.5 to 21 in apple, pear, and rose hip and quince fruits belonging to the Rosaceae family. The BHA value of the same study was reported as 41.5 and the BHT value as 37. In our study, BHT 3.21 and α-Toc 2.14 were detected, while Cuprac values were between 1.13 and 3.62 (for 100ppm). Cuprac values of especially *R. canina* and *P. coccinea* were determined above the standards (BHT and α-Toc).

Conclusion

For centuries, human beings have benefited from plants in the treatment of diseases. Because of synthetic drugs' severe effects, people in the modern world also turn to medicinal plants for the treatment of many diseases. However, examining medicinal plants especially in terms of heavy metal amounts and conscious consumption will prevent serious health problems in the long term. The study showed that the heavy metal amounts of some plants belonging to the Rosaceae family, which are cultured, used

for therapeutic purposes and consumed as fruit by the people of Van, are safe for human consumption and medical uses, and their micronutrient, protein and antioxidant capacities are at the desired level for healthy nutrition and therapeutic uses. As a result detected heavy metal amounts *Rosa canina* L., *Malus domestica* L., *Prunus persica* L Siebold & Zucc., *Cydonia oblonga* Mill., *Armenica vulgaris* Lam., and *Pyracantha coccinea* M.Roem fruits selected from Van are within acceptable limits determined by WHO.
Research and publication ethics complied within this study.

Conflicts of Interest

The author reports no actual or potential conflicts of interest.

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