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Research Paper / Araştırma Makalesi

Physicochemical and Phytochemical Properties of Different Extracts of Sumac Plant (*Rhus coriaria* L.) Grown in Tunceli, Türkiye

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ABSTRACT

In this study, sumac plant (*Rhus coriaria* L.) naturally grown in Tunceli (Türkiye) was collected from 5 different provinces and investigated for their phytochemical properties. In sumac samples, pH, color, ash amount, total phenolic content (TPC), 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging capacity, metal chelating capacity, copper (II) ion reducing antioxidant capacity (CUPRAC), reducing power, mineral matter content, organic acids as tartaric acid, malic acid and citric acid, phenolic compounds as gallic acid, vanillic acid, caffeic acid, routine, resveratrol, (-)- epicatechin, and (+)- catechin hydrate contents were determined. The highest TPC was found in the acidified methanol extract (AME) and the DPPH free radical scavenging capacity was found in the acidified acetonitrile extract (AAE). It was determined that all extracts of sumac sample 5 (S5) collected from Pertek district, metal chelating capacity was higher than the other samples but lower than the metal chelating capacity of ethylene diamine tetra acetic acid (EDTA). CUPRAC was detected at the highest concentration of 118.0±3.0 mg caffeic acid equivalent kg^{-1} (mg CAE kg^{-1}) in the AME, at the lowest 10.2±0.6 mg CAE kg^{-1} in the AAE for S5 sample. It was found that the reducing powers of all samples were found to be lower than the reducing power of synthetic antioxidants (butylhydroxytoluene (BHT), α tocopherol, and vitamin C), and the samples were rich in mineral substances, the predominant organic acid was malic acid, and phenolic compound was gallic acid.

Keywords: Antioxidant capacity, Phenolic substance, Mineral, Organic acid, Sumac

Tunceli'de Yetişen Sumak Bitkisinin (*Rhus coriaria* L.) Farklı Ekstraktlarının Fizikokimyasal ve Fitokimyasal Özellikleri

ÖZ

Bu çalışmada, Tunceli'de doğal olarak yetişen sumak bitkisinin (*Rhus coriaria* L.) 5 farklı bölgeden toplanarak fitokimyasal bileşenleri araştırılmıştır. Sumak örneklerinde pH, renk, kül miktarı, toplam fenolik madde (TFM), 2,2-difenil-1-pikrilhidrazil (DPPH) serbest radikal temizleme kapasitesi, metal şelatlama kapasitesi, bakır (II) iyonu indirgeme antioksidan kapasitesi (CUPRAC), indirgeme kuvveti, mineral madde içeriği, tartarik asit, malik asit ve sitrik asit gibi organik asitler, gallik asit, vanilik asit, kafeik asit, rutin, resveratrol, (-)- epikateşin ve (+)- kateşin hidrat gibi fenolik bileşikler belirlenmiştir. En yüksek TFM miktarı asitlendirilmiş metanol ekstraktında (AME) ve DPPH serbest radikal süpürme kapasitesi asitlendirilmiş asetonitril ekstraktında (AAE) bulundu. Pertek bölgesinden toplanan sumak örneğinden (S5) elde edilen tüm ekstraktların metal şelatlama kapasitesi diğer numunelere göre daha yüksek, ancak etilen diamin tetra asetik asit (EDTA) metal şelatlama kapasitesinden ise daha düşük olduğu bulunmuştur. CUPRAC değerinin S5 örneğinin AME'nda en yüksek, 118,0±3,0 mg kafeik asit eşdeğeri kg^{-1} (mg KAE kg^{-1}), AAE'ında ise en

düşük, 10,2±0,6 mg KAE kg^{-1} olduğu tespit edilmiştir. Tüm örneklerin indirgeme kuvvetinin sentetik antioksidanların (bütil hidroksitoluen (BHT), α tokoferol, ve vitamin C), indirgeme kuvvetinden daha düşük olduğu ve örneklerin mineral maddelerce zengin olduğu, baskın organik asidin malik asit ve fenolik bileşiğin gallik asit olduğu belirlenmiştir.

Anahtar Kelimeler: Antioksidan kapasite, Fenolik madde, Mineral, Organik asit, Sumak

INTRODUCTION

Sumac (*Rhus coriaria* L.), which belongs to *Anacardiaceae* family, is a small tree that reaches a height of 4 m and with imparipinnate leaves [1, 2]. It is shrub with reddish-brown colored fruit and with one seed fruit which is 4–6 mm slightly fleshy, lenticular drupes, surrounded by short glandular hairs. It is usually wild grown in the Mediterranean region extending from the Canary Island to Iran and Afghanistan besides southeast of Anatolia-Türkiye [1–4]. Sumac is traditionally used as a spice and flavoring agent in several Mediterranean and Middle Eastern countries including Iran, Lebanon, Jordan, and Syria as well as Türkiye, and has a widespread preference in medicine and nutritional applications [3]. For enhancing taste of vegetable dishes, it has been preferable as a condiment both in Türkiye and Iran [4]. Because of antibacterial, hypolipidemic, antiinflammatory, antifungal, hypoglycemic and antioxidant activities. It has used in many area including cosmetic, dying agent, nutrition especially in pharmacy and other industries [1, 3, 5]. Sumac is a rare plant that is frequently preferred in traditional medicine as medicinal herb, due to these superior and versatile properties [6].

As reported in various studies about sumac composition, over 200 components such as phenolic compounds, flavonoids, organic acids, terpenoids, anthocyanins and their derivates compounds have been isolated from the sumac plant [3]. On the other hand, as can be understood from the studies conducted to evaluate its potential antibacterial, antifungal and antioxidant effects, it has also been proven that the sumac in question has analgesic, antilipidemic and hypoglycemic effects [5]. Because of the various phytochemical components which contains such as bioactive compounds and phenolic compounds, sumac has been frequently used as a treatment agent for various diseases including diabetes, stomach pain, smallpox, hypertension, dysentery, diarrhea, paralysis, hematemesis, ophthalmia, diuresis, atherosclerosis, measles, and liver disease, tooth and gum diseases. Moreover, it has been preferred for cancer treatment in traditional medicine [1, 3, 7].

Sumac, a natural antibacterial agent, is also used as a natural preservative in food products, as well as an ingredient in beverages and sauces, and as a natural acidifier in recipes. Based on previous investigations, it has been clearly reported that sumac addition to foods or water can have a beneficial effect on both human and animal health [1]. Recently, the hypoglycemic effect and chemopreventive effect of sumac, which is frequently consumed as herbal medicine due to its anti-fibrogenic, antimicrobial and anti-inflammatory activities, has also attracted the attention of many researchers [2]. In addition, it has been reported that the alcohol extract of sumac is genoprotective and hydroalcoholic extracts inhibit skin proinflammatory mediators significantly, and it is emphasized that this activity is due to the tannins it contains [2].

Owing to the advantages of using the sumac plant in different areas, there are various studies in the literature on different parts such as stick, leaf and fruit. Abu-Reidah et al.[8] extracted the fruit epicarps' using methanol and investigated phytochemical composition by using high performance liquid chromatography-mass spectrometry method (HPLC-MS). Al-Boushi et al. [9] determined phenolic compounds by using HPLC in leaves and sticks. Gallic acid, 4- hydroxyl benzoic acid, synergic acid, and vanillic acid concentrations were found higher in leaves than in sticks, only caffeic acid concentration was higher in sticks than in leaves. Ereifej et al. [10] extracted sumac fruit by various solvents at various temperatures and they reported that total phenolic content was significantly affected by solvent type and temperature.

The main goal of the present study was carried out a detailed investigation about sumac grown naturally in Tunceli, Türkiye. Sumac samples were collected from five different provinces in Tunceli. pH, color, ash amount, total phenolic content (TPC), DPPH free radical scavenging capacity, metal chelating capacity, CUPRAC, reducing power, mineral matter content, organic acids as tartaric acid, malic acid and citric acid, phenolic compounds as gallic acid, vanillic acid, caffeic acid, routine, resveratrol, (-)- epicatechin and (+)- catechin hydrate contents were determined and evaluated. In this context, various sumac extracts including water, acidified methanol were prepared and investigated. This study is the most comprehensive study on Tunceli (Türkiye) sumac.

MATERIALS and METHODS

Materials

Sumac plant samples were collected from different districts of Tunceli (Türkiye) province. Collected places are given in Figure 1. The collected sumac samples were cleaned and dried at room temperature, then separated from the seeds. The cleaned and dried samples were ground with a grinder. All analyses were performed by using ground samples and triplicate.

(a) (b)

Figure 1. (a) Image of sumac, (b) Sampling points of sumac samples (S1: Mazgirt, S2: Tunceli-Center, S3: Çemişgezek, S4: Pülümür, S5: Pertek)

Methods

pH

Five grams of ground sumac was taken and 10 mL of ultra-pure water was added. After vortexing 5 min, pH was measured with digital pH meter (Thermo Scientific, Orion3Star, MA, USA) [11].

Color Analysis

Hunter (L, a, b) color values were measured by colorimeter (Chroma Meter, CR-400, Konica Minolta Sensing, Inc., Osaka, Japan) at room temperature in the appropriate light [11].

Ash Content Amount

For the determination of ash, 3 g of ground sumac sample was weighed and placed in a beaker. The temperature of the ash oven (Nuve Furnace, MF110, Ankara, Turkey) was gradually increased and kept at 450°C until white ash was obtained. Samples were cooled in desiccator and then weighed [12].

Preparation of Samples for Antioxidant Capacity Tests

For antioxidant tests sumac samples were extracted using 3 different solvents, as acidified methanol, acidified acetonitrile and acidified water. 3 g of sumac sample was taken and 20 mL of acidified solvent was added. After shaking for 2 h using the orbital shaker (Orbital Shaker, JSOS-500, JS Research Inc. Gonju, Korea), then centrifuged 5 min at 3000 rpm. The obtained supernatant was passed through a 0.45 µm injection filter and stored in a refrigerator until to be used for antioxidant tests [13].

Total Phenolic Content

The total phenolic content (TPC) in the extracted samples was determined by some modifications to the method developed by Singleton and Rossi [14] using the Folin-Ciocalteu reagent. 0.1 mL of the gallic acid standards at different concentrations was added and then 5 mL of pure water and 0.5 mL of Folin-Ciocalteu solution were added and vortexed. The solution was incubated in the dark at room temperature for 3 min. After addition of 1.5 mL of 2% Na_2CO_3 vortexed and again incubated for 2 h at room temperature in the dark. The absorbances were determined by using ultraviolet visible (UV-Vis) spectrophotometer (Shimadzu, UV-1601, Kyoto, Japan) at 760 nm. The blank sample was done at same way by using ultra pure water instead of sumac extract. Gallic acid was used as standard. Using gallic acid standard graph, the TPC of the samples was calculated. The TPC was then expressed in terms of mg gallic acid equivalent kg^{-1} dry weight (mg GAE kg^{-1} dw).

2,2-Diphenyl-1-picrylhydrazyl (DPPH) Free Radical Scavenging Capacity

Blois [15] method was applied by making some modifications for determination DPPH free radical scavenging capacity. 0.1 mL was taken from the sumac samples extract and the final volume was completed to 3 mL with methanol. After addition of 1 mL of DPPH solution mixture was vortexed and incubated at room temperature in the dark for 30 min. Then, absorbance of mixture was measured by UV-Vis spectrophotometer at 517 nm. The same procedure was carried out using methanol instead of sumac extract for the control solution. The inhibition values were calculated according to the following formula (Eq. 1).

DPPH Free Radical Scavenging Capacity (%) = [(Absorbance of control - Absorbance of sample) / Absorbance of control] × 100 (1)

Metal Chelating Capacity

For the determination of chelating capacity of iron (II) ions, Dinis et al. [16] method was carried out by applying some changes. 1 mL of sumac extracts at different concentrations was taken. 3.7 mL of ultra pure water and 100 µL of 2 mM $FeCl_2$ were added and vortexed. Mixture was incubated at room temperature in the dark for 30 min. Then added 200 µL 5 mM of ferrozine and vortexed for 10 min at the same conditions. Absorbance measurements were done at 562 nm by UV-Vis spectrophotometer. Ethylene diamine tetra acetic acid (EDTA) was used as standard. The same procedure was

carried out using ultra pure water instead of sumac extract for the control solution.

Copper (II) Ion Reducing Antioxidant Capacity (CUPRAC)

For the determination of CUPRAC Apak et al. [17] method was used. 1 mL of 1.0×10^{-2} M $CuCl_2$, 7.5×10^{-3} M neocuproine and 1 M NH_4Ac (pH 7) was taken. 0.5 mL sumac extract and 0.5 mL of ultra pure water were added to this solution. The solution was vortexed and then incubated 30 min in the dark. Absorbance was determined at 450 nm. Caffeic acid at different concentrations was used as standard and all procedures were repeated for standards. The same procedure was carried out using pure water instead of the sample as the control solution. The CUPRAC values of the samples were expressed in mg caffeic acid equivalent kg^{-1} dry weight (mg CAE kg^{-1} dw).

Reducing Power

Reducing power was determined according to Oyaizu [18] method by making some changes. This method is based on the reduction of Fe^{3+} to Fe^{2+} by the antioxidant substances. 1 mL of sumac extracts at different concentrations was taken. 2.5 mL of phosphate buffer and 2.5 mL of 1% $K_3Fe(CN)_6$ were added, vortexed and incubated at 50°C for 20 min. After addition of 2.5 mL of 10% trichloroacetic acid, it was centrifuged. 2.5 mL of supernatant was taken. 2.5 mL of ultra pure water and 0.5 mL of 0.1% $FeCl_3$ solution were added and vortexed. The absorbance was determined at 700 nm. Ultra pure water was used instead of the sumac extract for the control solution and the same procedure was carried out. The increase in absorbance was evaluated as the reducing power capacity of the sumac extract.

Mineral Matter Content

For the analysis of mineral content, 0.3 g of sumac sample was taken and 5 mL of concentrated nitric acid was added on it. Then it was solubilized by applying the steps given in Table 1 in the microwave oven (Berghof Speedwave 2, Berghof, Eningen, Germany) [19].

Table 1. Microwave oven digestion steps

Step	1	2	3
Temperature (°C)	145	190	100
Power (%)	75	90	40
Time (min)	5	10	10

Samples solubilized in microwave oven were centrifuged and clear solutions were obtained. The obtained clear solutions were analyzed by flame atomic absorption spectrometer (FAAS) (PerkinElmer AAnalyst 800, Shelton, CT, USA) according to operation conditions in Table 2.

Table 2. Operation conditions of FAAS

Element	Acetylene flow rate (L min^{-1})	Air flow rate (L min^{-1})	Wave length (nm)	Slit range (nm)
Ca	2.0	17.0	422.7	0.7
Cu	2.0	17.0	324.8	0.7
Fe	2.0	17.0	248.3	0.2
K	2.0	17.0	766.5	0.7
Mg	2.0	17.0	285.2	0.7
Mn	2.0	17.0	279.5	0.2
Na	2.0	17.0	589.0	0.2
Zn	2.0	17.0	213.9	0.7

Organic Acid Composition

The amount of organic acid was determined by making some changes on the method developed by Bevilacqua and Califano [20]. For determination of organic acids (citric acid, malic acid, and tartaric acid), 3 g of sumac sample was taken and 20 mL 0.004 M H_2SO_4 was added. After shaking for 2 h in an orbital shaker, centrifuged 15 minutes at 3000 rpm. Obtained supernatant was passed through 0.45 µm injection filter and then SEP-PAK C18 cartridge. 1 mL of solution was taken and analyzed by high performance liquid chromatography (HPLC) (Schimadzu, Prominence LC-20A) method. HPLC apparatus was equipped with diode array detector (DAD) (SPD-M20A), column oven (CTO-10ASVP), pump (LC-20AT), and degasser (DGU-20A5). H_2SO_4 (0.004 M) was used as mobile phase and flow rate was 1 mL min^{-1}. A 5 µM 4.6×250 mm (Inertsil ODS-3) column was used and temperature was set to 30°C. Sample volume was 20 µL.

Phenolic Compounds Composition

For the determination of phenolic compounds (gallic acid, vanillic acid, caffeic acid, routine, resveratrol, (-)- epicatechin and (+)- catechin hydrate), 3 g of sumac sample was taken and 20 mL of acidified water was added. The mixture was shaked for 2 h in an orbital shaker and then centrifuged 15 minutes at 3000 rpm. The supernatant was passed through a 0.45 µm injection filter. UniverSil HS C18 (5µm, 250×4.6 mm) column was used for HPLC analysis. Methanol and 2% acetic acid were used as mobile phase in gradient elution [13].

RESULTS and DISCUSSION

pH

The measured pH values of the sumac samples are given in Table 3. The highest pH was determined in S2 (3.28±0.23) sample and the lowest pH was determined in S3 (2.78±0.15) sample. Fereidoonfara et al. [21], analyzed Iranian sumac samples and samples pH values were varied in the range from 2.66 to 3.90, and Caliskan and Dirim [22] found sumac extracts pH in the range from 3.13 to 3.23.

Table 3. pH, ash amount and color (L, a, and b) values of sumac samples

Sample	pH	Ash amount (%)	L	a	b
S1	2.99±0.14	4.0±0.4	35.6±1.2	7.6±0.4	20.7±0.2
S2	3.28±0.23	5.0±0.3	37.6±1.2	7.6±0.2	19.1±0.4
S3	2.78±0.15	5.3±0.5	23.1±0.8	13.5±0.2	12.8±0.2
S4	2.83±0.25	4.3±0.4	43.0±0.7	9.5±0.8	19.0±0.8
S5	2.94±0.26	4.6±0.4	34.6±2.4	9.7±0.8	17.3±0.4

Ash

The ash contents (%) of the sumac samples are given in Table 3. Among the sumac samples, the highest ash content was found in sample S3 and the lowest in sample S1. It was observed that the amount of ash varied between 4.0±0.4% and 5.3±0.5%. Ash amount of Syrian sumac was determined as 2.66±0.33% and Chinese sumac as 5.37±0.14% [23]. The ash content of the sumac extracts obtained by spray drying at different temperatures was investigated in the range of 1.15 and 3.37% on a wet basis [22].

Color

Color values of sumac samples are given in Table 3. The L value is between 0 and 100, and the darker value increases as it approaches 0, while the lighter value increases as it approaches 100. The sample S4 has the highest L value, that is, the brightest. The sample with the lowest L value is the sample S3 and has a darker color than the others. a value takes + and - value and "+" denotes redness, "-" denotes greenery. Since a was positive in the results, the highest degree of redness was found in the sample S3, and at least in the samples S1 and S2. b value takes the value of "+" and "-" and denotes "+" yellowness, while "-" denotes blueness. Again, since the b value results were positive, the highest degree of yellowness was found in the sample S1 and the least in the sample S3. Caliskan and Dirim [24] detected the L* value of sumac berries and sumac extract 36.77±0.89 and 32.17± .13, respectively. a* value of sumac berries and sumac extract 8.00±1.29 and 2.25±0.08, respectively. b* value of sumac berries and sumac extract 5.56±0.55 and 0.93±0.03, respectively.

Total Phenolic Content

The TPC in the acidified methanol extract (AME), acidified acetonitrile extract (AAE), and acidified water extract (AWE) of the sumac plant was determined by Folin Ciocalteu reagent. Linear regression equation and correlation coefficient were calculated as $y = 0.0007x+0.0598$ and $R^2 = 0.09973$, respectively. The TPC of samples of various extracts are given in Table 4.

Table 4. TPC and CUPRAC values of sumac samples

	TPC (mg GAE kg^{-1})			CUPRAC (mg CAE kg^{-1})		
Sample	AME	AAE	AWE	AME	AAE	AWE
S1	1100±44	494±40	672±50	90.3±2.5	69.1±2.5	100.0±5.7
S2	1388±33	350±5	754±47	96.0±0.3	26.0±0.3	52.3±1.1
S3	811±48	269±14	331±33	54.5±2.3	17.0±0.8	20.0±0.2
S4	797±5	231±10	631±64	53.3±1.0	34.0±0.9	41.2±0.3
S5	1929±63	526±67	904±39	118.0±3.0	10.2±0.6	70.0±1.3

As seen in Table 4, when the extracts of the same sumac in different solvents were compared, the highest TPC was determined in AME. This is followed by AWE and AAE, respectively. TPC of AME of different sumac samples were S5>S2>S1>S3>S4, respectively. TPC of different sumac samples from the highest to the lowest S5>S1>S2>S3>S4 for AAE and S5>S2>S1>S4>S3 for AWE. When the TPC of all samples in different solvents were compared, it was detected that the sample S5 was highest in terms of TPC.

Romeo et al. [25], extracted sumac fruit and leaf with water and different proportions of ethanol-water mixtures. The sumac leaf TPC was found higher than fruit. TPC of sumac fruit in different solvents were found to be in the range of 2.80±0.01-9.47±0.01 g GAE kg^{-1}, and in range of 15.22±0.13-29.38±0.24 g GAE kg^{-1} in the leaf. In a study, the TPC was determined by extracting Syrian and Chinese sumac samples under different experimental conditions such as ethanol concentration, extraction time, particle size and ratio of solvent amount to sumac amount. Optimum experimental conditions were found to be the same for Syrian and Chinese sumac samples except extraction time. Under optimum conditions, the TPC was determined as 159.32 mg GAE g^{-1} for Syrian sumac and 150.68 mg GAE g^{-1} for Chinese sumac [16]. Bashash et al. [27], extracted sumac samples with different solvents and compared TPC. TPC was found highest in extract of methanol in brown sumac fruit, in extract of ethanol-methanol mixture in brown sumac powder and in ethanol extract in red sumac powder samples. In all samples water extract TPC were the lowest. Bursal and Köksal [28], calculated water and ethanol extracts of sumac samples' TPC as GAE (per 1 mg extract). The TPC of ethanol and water extract were found as 15 µg GAE and 63 µg GAE, respectively. Zannou et al. [29] used acidic deep eutechtic solvents and conventional solvents to extract sumac samples by using homogenate and ultrasound assisted extraction methods. TPC was found highest, 124.96 ± 3.43 mg GAE g^{-1}, by ultrasound assisted extraction method.

DPPH Free Radical Scavenging Capacity

The inhibition (%) graphs of the DPPH free radical scavenging capacity of the sumac samples and different extracts are given in Figure 2. It was found that the DPPH free radical scavenging capacity of the samples extracted with acidified acetonitrile was the highest in all samples. The DPPH free radical scavenging capacity of samples extracted with acidified water was the lowest in samples S1 and S5, while the DPPH free radical scavenging capacity of samples extracted with acidified methanol was found to be the lowest in samples S2, S3, and S4.

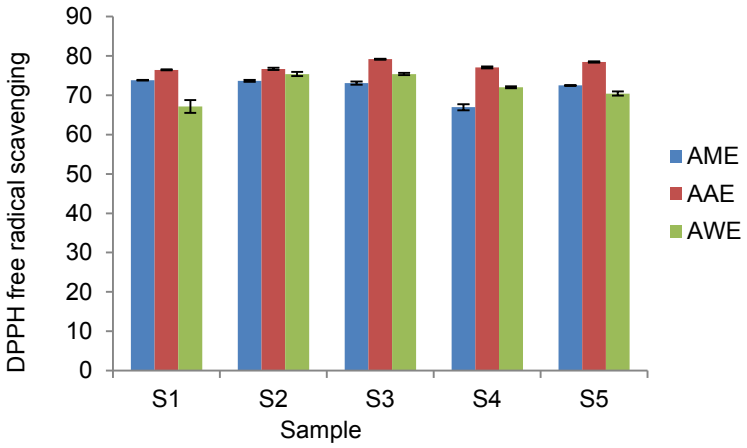


Figure 2. DPPH radical scavenging capacity of AME, AAE, AWE of sumac samples

DPPH free radical scavenging capacities of AME were 74.0±0.1% for S1, 73.7±0.3% for S2, 73.1±0.4% for S3, 67.0±0.8% for S4, and 72.5±0.2% for S5, in AAE, DPPH free radical scavenging capacities were 76.5±0.1% for S1, 76.7±0.3% for S2, 79.2±0.1% for S3, 77.1±0.2% for S4, and 78.5±0.1% for S5 and in AWE, DPPH free radical scavenging capacities were 67.2±1.6% for S1, 75.4±0.5% for S2, 75.4±0.3% for S3, 72.0±0.2% for S4, and 70.4±0.5% for S5, respectively.

Kossah et al. [30], reported 0.01 mg L^{-1}-1 mg L^{-1} of Syrian sumac extracts' DPPH radical scavenging capacity in the range of 34.53%±0.25 -95.42%±0.01. In a study, the leaves and fruits of the sumac plant were extracted with ethanol, and then pure extracts were obtained by removing the ethanol with a rotary evaporator. The obtained pure extracts were used for analysis. The DPPH radical scavenging capacity of sumac leaf was found in the range of 59%-100% and the fruit DPPH radical scavenging capacity was in the range of 39%-92% [31].

Metal Chelating Capacity

Metal ions can cause lipid peroxidation to form free radicals and lipid peroxides. Therefore, metal chelating capacity shows antiradical and antioxidant properties [28]. The metal chelating capacity of the sumac plant in AME, AAE and AWE was determined. EDTA was used for the standard graphic (Figure 3) and the metal chelating capacity of the extracts was compared with the metal chelating capacity of EDTA (Figure 4).

Metal chelating capacity of EDTA was found higher than AME (Figure 4(a)), AAE (Figure 4(b)) and AWE (Figure 4(c)). When different extracts of sumac samples compared among themselves S5 has the highest metal chelating capacity. Sample S5's in AME metal chelating capacity value was close to EDTA's metal chelating capacity. At the same time, the metal chelating capacities of other extracts were found to be much lower than that of EDTA, and the metal chelating capacities of the samples in these extracts were found to be close to each other.

Işnel [31] collected sumac samples Diyarbakır-Silvan. Metal chelating capacity was investigated in sumac fruit and leaves. As a result of the analysis metal chelating capacity was determined as %38-%100 in fruits and as %12-%60 in leaves.

Copper (II) Ion Reducing Antioxidant Capacity (CUPRAC)

The antioxidant capacity is calculated by using the ability of the Cu (II)-neocuproin complex formed by neocuproin to be reduced to Cu (I)-neocuproin chelate. Caffeic acid was used as standard for determination of copper (II) ion reducing antioxidant capacity. Caffeic acid calibration graph linear regression equation and correlation coefficient were obtained as $y = 0.0406x + 0.1352$ and $R^2 = 0.998$, respectively. Using this standard graph, CUPRAC amounts of the samples were calculated as caffeic acid equivalent (mg CAE kg^{-1}). CUPRAC values of AME, AAE and AWE of sumac plant are given in Table 4.

As seen in Table 4, when the extracts of the same sumac in different solvents were compared, the highest CUPRAC value in the sample S1 was seen in AWE, while the highest CUPRAC value in other samples was found in AME. AAE of all examples has the lowest CUPRAC value. AME of different sumac have the highest CUPRAC values, respectively, S5>S2>S1>S3>S4. AAE of different sumac has the highest CUPRAC values, respectively S1>S4>S2>S3>S5. AWE of sumac plants' CUPRAC values decreased respectively as S1>S5>S2>S4>S3.

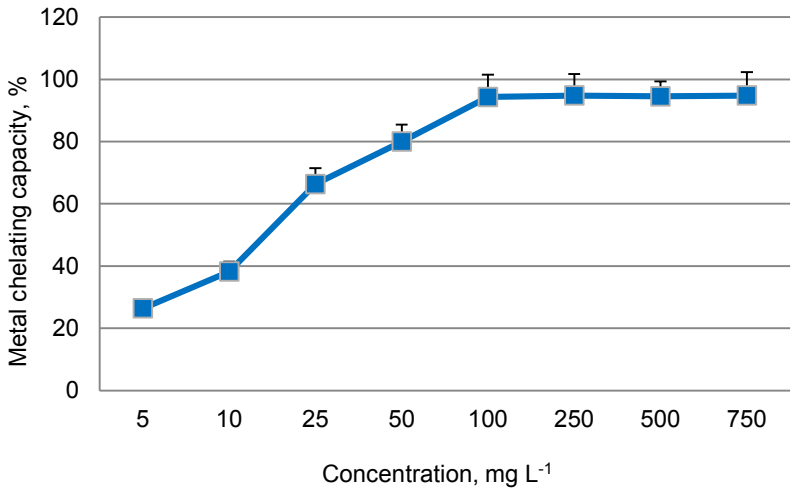
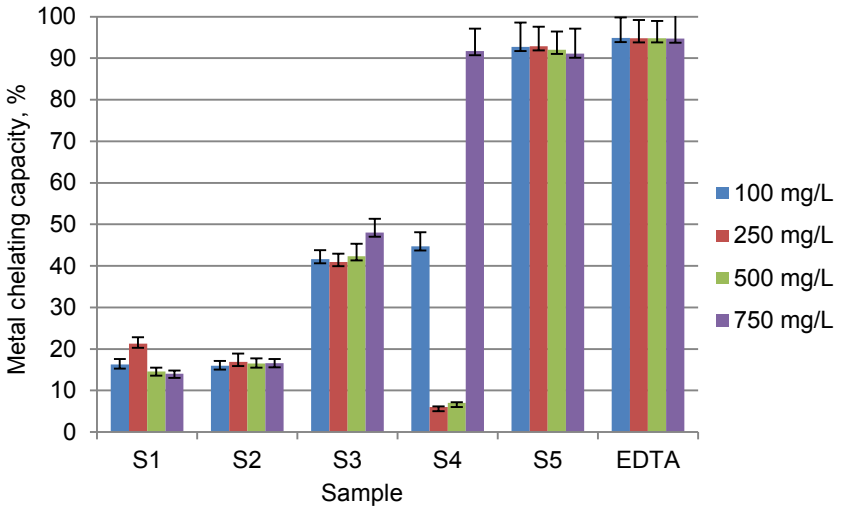
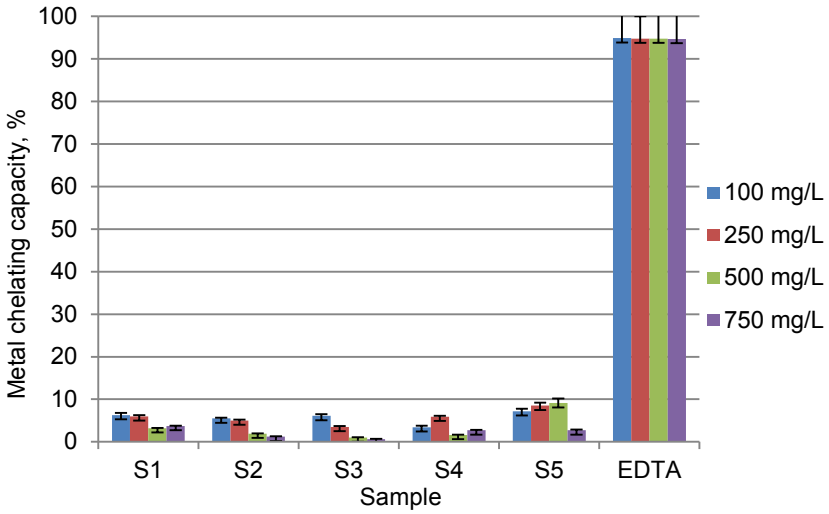


Figure 3. Calibration graph of EDTA



(a)



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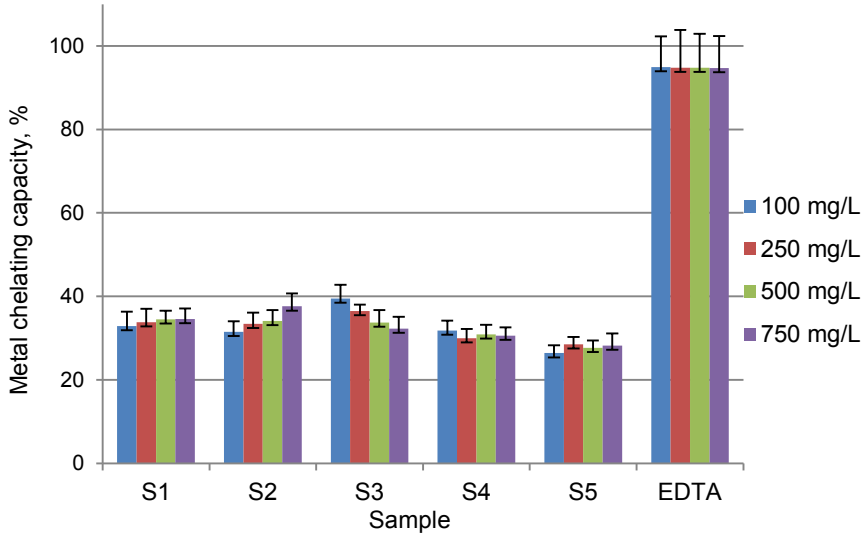

(c)

Figure 4. Metal chelating capacity of (a) EDTA and AME of sumac samples, (b) EDTA and AAE of sumac samples, (c) EDTA and AWE of sumac samples

Bursal and Köksal [28] stated in their study on sumac that the CUPRAC value of water extract is higher than ethanol extract. No other source has been found in the literature for the determination of CUPRAC in sumac. In the study in which the sumac plant grown in Şırnak was extracted with methanol for 24 h, the CUPRAC analysis value was reported as 3.33±0.17 mmol trolox equivalent antioxidant capacity (TEAC) g^{-1} [32].

Reducing Power

All of the sumac extracts used in the study were compared among themselves and synthetic antioxidants as butylhydroxytoluene (BHT), α tocopherol and vitamin C standards. When compared the reducing power of the sumac samples AME and synthetic antioxidants was changed as vitamin C>BHT>α tocopherol>S5>S1>S2>S4>S3, respectively. Sumac samples AAE and synthetic antioxidants was changed as vitamin C>BHT>α tocopherol>S5>S1>S2>S4>S3, and sumac samples AWE and synthetic antioxidants was changed as vitamin C>BHT>α tocopherol>S5>S2>S4>S1>S3, respectively. As a result, sample S5 had higher reducing power than others while sample S3 had the lowest reducing power in all of the solvents.

Al-Muwaly et al. [33] investigated Iraqi sumac seeds and extracted 24 h with distilled water, methanol and ethanol. The obtained extracts were dried in a lyophilizer, then they were dissolved with distilled water and used for analysis. The reducing power of the extracts prepared at different concentrations and ascorbic acid that used as a standard were determined. It was determined that the reducing force increased as the extract concentration increased. Statistically, the highest reducing force was determined as 2.103±0.397 in 117.64 ppm methanol extract. In another study reducing power of synthetic antioxidants, water extract and ethanol extract was compared and the reducing respectively decreased as BHA>trolox>BHT>α tocopherol>water extract>ethanol extract [28].

Mineral Concentration

Standard solutions of Ca, Fe, K, Mg, Mn, Na and Zn minerals were used in order to determine the mineral content of the sumac plant. Calibration values and mineral contents of sumac samples are given in Table 5. In terms of Fe content, S4 and S1 have the highest and lowest values, respectively. It was observed that the sample richest in Ca was S4 and the sample containing the least Ca was S1. In terms of K, S3 has the lowest value, while S5 has the highest value. In terms of Na content, S3 has the highest value and S5 is the lowest. S2 has the most Zn, while S3 is the sumac with the least Zn amount. The richest sample in Mn was S4 and the sample containing the least Mn was S3. The highest Mg amount was determined in S5 and the lowest in S3.

Özcan and Hacıseferoğulları [34] carried out mineral analysis of sumac samples collected from Mersin by using ICP-AES and element concentrations was found 144.53±3.76 mg kg^{-1} for Fe, 10.93±0.84 mg kg^{-1} for Zn, 855.95±17.63 mg kg^{-1} for Mg, 3661.57±25.71 mg kg^{-1} for Ca, 7963.35±47.85 mg kg^{-1} for K, 114.06±3.65 mg kg^{-1} for Na, and 10.49±1.32 mg kg^{-1} for Mn. Fe, Zn and Ca concentrations in sumac samples are lower than present study, and Mn concentrations are similar to present study. Ünver [11] reported that sumac samples collected from different provinces are rich in Al, Ca, K, Fe and Mg. Fe was in the range of 69-611 mg kg^{-1}, Zn was in the range of 3.70-6.92 mg kg^{-1}, Mg was in the range of 342.9-700.1 mg kg^{-1}, Ca was in the range of 1000.4-3577.5 mg kg^{-1}, K was in the range of 8094-17361 mg kg^{-1}, and Na was in the range of 730.9-1249.3 mg kg^{-1}. Kossah et al. [23], analyzed Syrian and Chinese sumacs and the mineral concentrations were found 174.15±0.18 mg kg^{-1}

and 180.00±0.67 mg kg^{-1} for Fe, 55.74±0.38 mg kg^{-1} and 17.20±0.38 mg kg-1 for Zn, 3155.53±0.41 mg kg^{-1} and 3098.00±0.52 mg kg^{-1} for Ca, 605.74±0.51 mg kg^{-1} and 871.00±0.42 mg kg^{-1} for Mg, 101.04±0.15 mg kg^{-1} and 183.00±0.26 for Na mg kg^{-1}, 7441.25±0.07 mg kg^{-1} and 5576.00±0.68 mg kg^{-1} for K, 10.57±0.39 mg kg^{-1} and 11.60±0.35 mg kg^{-1} for Mn, respectively.

Organic Acid

Citric acid, malic acid and tartaric acid were determined in sumac samples and organic acid standards were used for calibration curves. Calibration values for organic acids are given in Table 6. Figure 5 represents organic acids chromatogram including tartaric acid, malic acid and citric acid.

In the samples S1, S2, S3, S4 and S5, citric acid, malic acid and tartaric acid were determined (Table 7). The predominant organic acid in sumac samples is malic acid. Kossah et al. [23], determined that the sumac fruit grown in Syria contains more organic acid than the sumac fruit grown in China. The predominant organic acid in both sumac is malic acid. It has also been detected in small amounts of tartaric acid and citric acid in sumac in Syria and China. It has been revealed that the Syrian sumac fruit is more acidic than the Chinese sumac fruit. The concentration of malic acid among organic acids in sumac was 1568.04 mg kg^{-1}, citric acid 56.93 mg kg^{-1} and tartaric acid 2.15 mg kg^{-1}. In another study sumac samples that were different genotypes collected from Kahramanmaras province were analyzed and mean concentrations of citric acid and malic acid were calculated as 70.82 mg kg^{-1} and 1822.82 mg kg^{-1} [4].

Phenolic Compounds

Calibration values for phenolic compounds are given in Table 8. Since the amount of gallic acid has the highest value among the phenolic compounds in sumac. It was determined that gallic acid was the highest amount in the sample S1 (Figure 6) and the least in sample S3. + (-) catechin hydrate S2 is the most in the sample, while at least S1 is in the sample. - (-) epicatechin is in the sample numbered S4 at most and in the sample number S5 at least. Vanilic acid is mostly in the S1 sample of sumac and could not be determined in S4. While resveratrol could not be determined in S2 and S4, it showed the highest value in S5. Rutin and caffeic acid could not be determined in S4, but the highest values were found in the sample numbered S5.

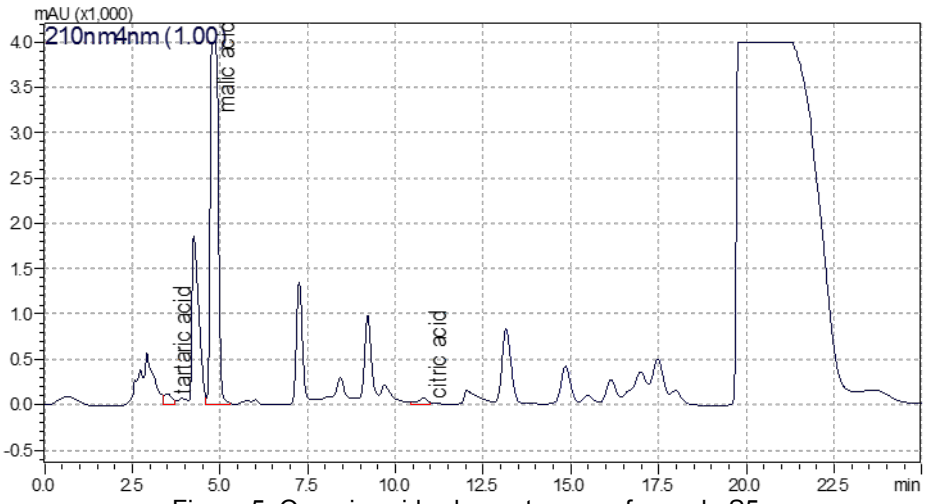

Figure 5. Organic acids chromatogram of sample S5

Table 5. Calibration values and mineral contents (mg kg^{-1}) of sumac samples

	S1	S2	S3	S4	S5	Linear regression equation and correlation coefficient
Ca	59153±1955	69011±4869	67747±2151	178174±10255	132360±12670	y = 0.0211x + 0.0004 R² = 0.9978
Fe	6117±724	10131±928	9236±199	16281±904	14776±635	y = 0.0202x - 0.002 R² = 0.9951
K	9490±594	7262±527	4259±183	4841±463	10297±329	y = 1.0324x - 0.0485 R² = 0.9999
Mg	1662±54	1676±79	532±30	1149±28	2022±191	y = 0.4537x + 0.009 R² = 0.9988
Mn	10.0±0.2	13.5±0.6	9.0±0.8	22.0±0.5	16.0±0.4	y = 1.0139x - 0.0205 R² = 1
Na	115±10	68±3	223±11	38±4	16±2	y = 0.9839x + 0.0245 R² = 0.9968
Zn	52±2	100±3	31±2	34±2	48±3	y = 0.2783x + 0.004 R² = 0.9997

Table 6. Calibration values of organic acids

Organic acid	Wavelength (nm)	Retention time (min)	LOD (mg L^{-1})	LOQ (mg L^{-1})	Linear regression equation and correlation coefficient
Citric	210	10.6	0.6061	2.0202	y = 1345.8x – 4335.5 R^2 = 0.9951
Malic	210	4.9	0.4320	1.4398	y = 1927.4x - 37877 R^2 = 0.9985
Tartaric	210	3.5	0.1735	0.5782	y = 2075.2x + 4713.6 R^2 = 0.9997

Table 7. Organic acid contents of sumac samples (mg kg^{-1})

Sample	Citric acid	Malic acid	Tartaric acid
S1	5559±490	156767±8200	1040±55
S2	2356±122	154885±6570	20360±358
S3	6916±433	207704±8875	2273±82
S4	1268±58	169515±5480	1993±124
S5	7463±215	219521±7758	6160±221

Table 8. Calibration values for phenolic compounds

Phenolic compound	Wavelength (nm)	Retention time (min)	LOD (mg L^{-1})	LOQ (mg L^{-1})	Linear regression equation and correlation coefficient
Gallic acid	280	10.14	0.0589	0.1963	y = 25982x – 6164.6 R^2 = 0.9989
+(-)Catechin hydrate	280	22.92	0.1149	0.3829	y = 7022.6x – 1253.3 R^2 = 0.9998
-(-) Epicatechin	280	34.83	0.1442	0.4806	y = 6741.4x - 4572,6 R^2 = 0.9982
Vanilic acid	280	29.94	0.0693	0.2310	y = 17509x – 3030.1 R^2 = 0.9998
Resveratrol	320	51.54	0.0128	0.0427	y = 75487x – 2297.2 R^2 = 0.9996
Rutin	360	50.82	0.0834	0.2781	y = 15755x + 3820.9 R^2 = 0.9988
Caffeic acid	320	31.77	0.0241	0.0805	y = 57030x – 6926.9 R^2 = 0.9997

The amounts of some phenolic compounds in the sumac samples are given in Table 9. In another study, gallic acid concentration (5.97±0.02 mg g^{-1}) of staghorn sumac fruit was found lower than present study [35]. Tohma et al.[7] used water and ethanol to determine phenolic compound in sumac samples. Gallic acid concentration was evaluated as 86.77 mg kg^{-1} and 19.31 mg kg^{-1}, in ethanolic and water extract, respectively. In ethanolic extract epicatechin and rutin did not detected but in water extract epicatechin was 21.2 mg kg^{-1} and rutin was 0.49 mg kg^{-1}. In another study gallic acid was detected as 67.56 mg g^{-1} in sumac samples collected in Çanakkale and detected 19.01 mg g^{-1} in sumacs collected in Siirt [11].

Table 9. Amounts of some phenolic compounds in sumac samples (mg kg^{-1})

Sample	Gallic acid	+(-)Catechin hydrate	-(-) Epicatechin	Vanilic acid	Resveratrol	Rutin	Caffeic acid
S1	15199±760	88±7	143±11	175±19	12±1	143±17	27±2
S2	14696±1175	228±23	131±8	33±2	ND*	86±8	34±3
S3	6093±305	129±8	163±8	15±1	59±3	50±3	5.0±0.5
S4	8629±690	119±7	599±54	ND	ND	ND	ND
S5	11045±773	142±14	93±6	88±10	237±19	183±13	52±5

*:ND: Not Detected

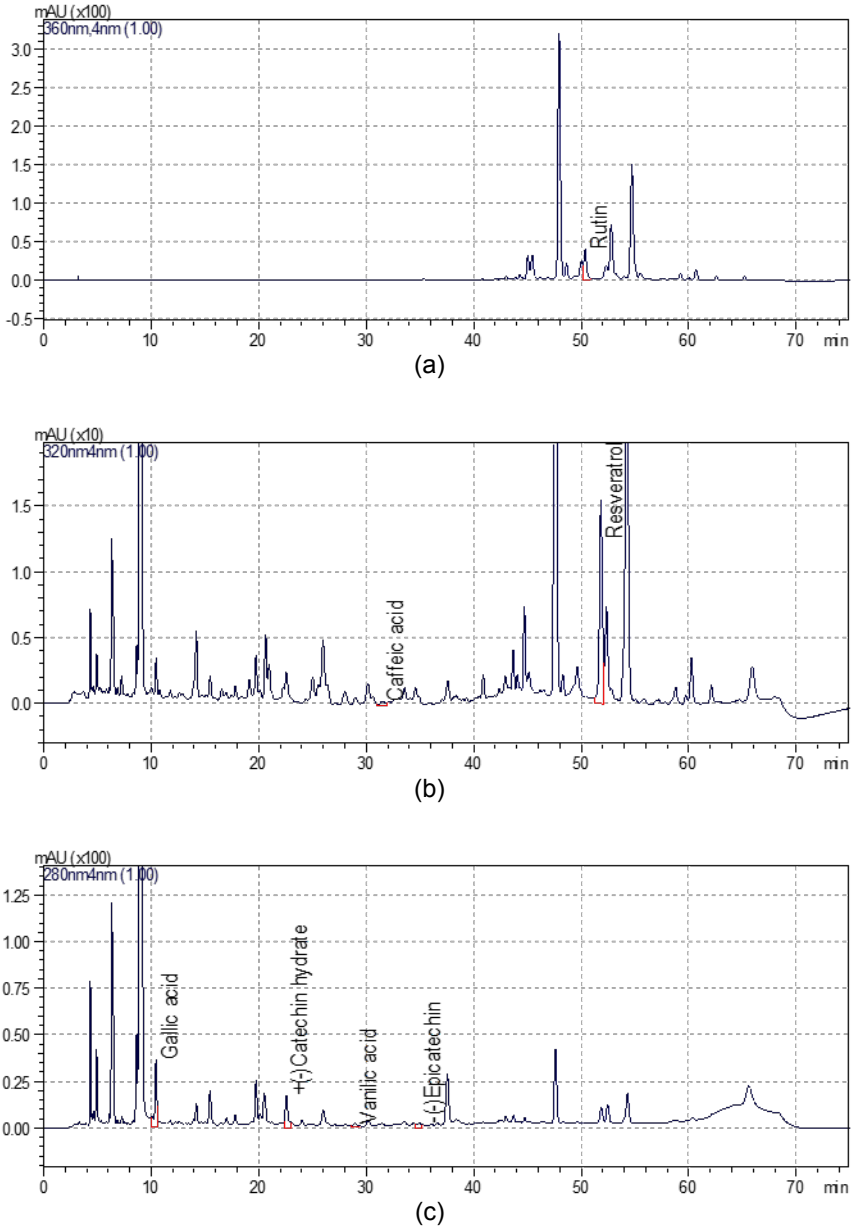

Figure 6. HPLC chromatogram of sample S1 at (a) 280 nm, (b) 320 nm, (c) 360 nm

CONCLUSION

In the present study, sumac samples were extracted using three different solvents and obtained results were presented:

- The pH values of sumac plants were found to be close to each other. It was determined that the pH value of S3 (2.78±0.15) was lower than the other samples, and S2 had the highest pH value (3.28±0.23).
- The lightest color has S4, the darkest color was seen in S3 sample and the others were found to be similar.
- The highest redness value was observed in S3 sample, the lowest value in S1 and S2 samples.
- The highest yellowness value is in S1 sample and the lowest in S3 sample. S2, S4, S5 showed similar results.
- Mineral content of sumac samples were found as for Ca (59153±1955 mg L^{-1}-178174±10255 mg L^{-1}), for (6117±724 mg L^{-1}- 16281±904 mg L^{-1}) Fe, for K (4259±183 mg L^{-1}-10297±329 mg L^{-1}), for Mg (532±30 mg L^{-1}-2022±191 mg L^{-1}), for Mn (9.0±0.8 mg L^{-1}-22.0±0.5 mg L^{-1}), for Na (16±2 mg L^{-1}-223±11 mg L^{-1}) and for Zn (31±2 mg L^{-1}-100±3 mg L^{-1}). Obtained results revealed that S5 was found to have the highest concentration in terms of K, but the lowest concentration in terms of Na. Ca, Fe and Mn concentrations were higher in S4 sample. It was determined that Na concentration was higher than the others in S3, while Zn, Mg, K and Mn were lower. Generally, the mineral content of sumac samples is high. As a result, the most abundant mineral in sumac in Tunceli province is Ca.
- Sumac samples DPPH radical scavenging capacities were found as AAE (76.5±0.1%-79.2±0.1%)>AWE

(67.2±1.6%-75.4±0.5%)>AME (67.0±0.8%-74.0±0.1%).

- Metal chelating capacities of extracted sumacs were decreased as EDTA>AWE>AME>AAE.
- While the highest CUPRAC value was obtained in the AME (118.0±3 mg CAE kg^{-1}), the lowest value was found in the AAE (10.2±3 mg CAE kg^{-1}).

The sumac plant analyzed in the study has its own color and taste and is therefore used as a spice. It was found that it is rich in minerals, organic acids and phenolic compounds that are of great importance for health, and its antioxidant capacity is high. It is also important that sumac grow naturally. Since the interest in natural nutrition has increased due to the increasing diseases in recent years, the consumption of naturally grown plants such as sumac should be encouraged. This plant, which is beneficial for human health in many ways, can be consumed by processing different products other than spices.

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DATA AVAILABILITY STATEMENT

The data that support this study are available in the article and accompanying online supplementary material.

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