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Effect of Preservation Methods on Fat-Soluble Vitamins and Stress Biomarkers in *Rhus coriaria* L. (Sumac) of Different Regions

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ABSTRACT
The number of fat-soluble vitamins and stress biomarkers in *Rhus coriaria* L. samples taken from different regions was determined by HPLC before and after being subjected to different preservation methods. For this purpose, one group of the samples was analyzed immediately, while the other two groups one of which oiled, and the other group is kept as is for six months. It was determined that the amounts of vitamin A, E, ß-carotene and lycopene in fresh sumac samples varied between 1.12 - 2.77, 84.40 - 230.65, 2.48 - 5.31 and 8.10 - 26.90 µg (g dw)$^{-1}$, respectively. The highest loss of vitamins was observed in an unoiled group of samples. The amounts of GSH, GSSG, MDA, 4-HNE, and GSH/GSSG in the same samples varied between 1004.12 - 2550.42, 422.54 - 1375.38, 13.95 - 31.30, 7.12 - 15.40 µg (g dw)$^{-1}$, and 1.16 - 3.49, respectively. While the amount of GSH and GSH/GSSG ratio in the stored sumac samples for six months decreased, on the other hand amount of MDA, GSSG, and 4-HNE increased. Differences in all examined parameters in fresh, unoiled, and oiled sumac samples are statistically significant (P<0.05). It was observed that the changes of the studied parameter in all sumac samples were lower in stored oiled samples.

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Muhafaza Yöntemlerinin Farklı Bölge Sumaklarındaki (*Rhus coriaria* L.) Yağda Çözünen Vitaminler ve Stres Biyomarkırları Üzerine Etkisi

ÖZET
Farklı bölgelerde yetişen ve farklı muhafaza yöntemleri uygulanan sumak örneklerindeki yağda çözünen vitaminler ile stress biomakırlarının miktarı HPLC ile belirlendi. Bu amaçla öğütülen örneklerden bir grup hemen analizlenirken, diğerleri ise iki kısma ayrılıp, bir kısmı yağlanırken diğer kısım olduğu gibi altı ay bekletildikten sonra analiz edildi. Taze sumak örneklerindeki A ve E vitamini, □-karoten ve likopen miktarlarının sırasıyla 1.12 – 2.77, 84.40 - 230.65, 2.48 – 5.31 ve 8.10 – 26.90 µg (g dw)$^{-1}$, arasında değiştiği gözlendi. Sonuçlardan, vitamin A, E, β-karoten ve likopen kaybının yağlanmadan bekletilen grupta fazla olduğu gözlenmiştir (P<0.05). Örneklerdeki GSH, GSSG, MDA, 4-HNE ve GSH/GSSG miktarları sırasıyla 1004.12 - 2550.42, 422.54 - 1375.38, 13.95 - 31.30, 7.12 - 15.40 µg (g dw)$^{-1}$ ve 1.16- 3.49 arasında değiştiği görülmüştür. Bekletilen sumak örneklerindeki GSH ve GSH/GSSG miktarı azalırken, MDA, GSSG ve 4-HNE miktarlarının arttığı tespit edilmiştir. Taze, yağlanmış ve yağlanmamış sumak örneklerindeki incelenen parametrelerdeki değişimlerin istatiksel olarak anlamlı (P<0.05) olduğu görülmüştür. Yağlanmış örneklerdeki değişimlerin yağlanmamış örneklere göre daha az olduğu görülmektedir.

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INTRODUCTION

Rhus coriaria (Sumac), which can grow all over the world, especially in subtropical and temperate climates, is a medicinal plant that is also used as a spice (Shabbir, 2012). It is reported that in the traditional medicine of the Middle East and Iran, sumac has been used for centuries in the treatment of diseases such as dysentery, diarrhea, hemorrhoids, and gout, as well as for healing wounds and lowering blood sugar, cholesterol, and uric acid levels. It is also stated that sumac contains antibacterial, antifungal, antiviral, antioxidant, anti-inflammatory, hepatoprotective, xanthine oxidase inhibition, hypoglycemia, and cardiovascular protective activities (Morshedloo et al., 2018). The fruits and leaves of the sumac plant, which has great economic value, are used in the kitchen, medicine, leather, and dye industries (Abu-Reidah et al., 2015; Güvenç et al., 2017). Studies have reported that it contains many physiologically active components such as tannins, anthocyanins, organic acids including malic and citric acid, fatty acids, vitamins, flavonoids, and terpenoid derivatives (Shabbir, 2012; Khalil et al., 2021; Özcan et al.,2021).

Vitamins are organic molecules that have regulatory functions in the living system, act as catalysts in metabolic events, and help the efficient use of nutrients in energy production. Vitamins are divided into two groups: water-soluble and fat-soluble (Kennedy, 2016). Fat-soluble vitamins are essential for living systems due to their different physiological functions in metabolism. Carotenoids have antioxidant functions in plants and animals (Yuan et al., 2020). It is stated that carotenoid compounds are of great importance for human health in protecting against many diseases, and in the treatment of some diseases, and are also necessary for the continuation of normal life functions (Eggersdorfer and Wyss, 2018). Vitamin A, which has important roles in vision, gene expression, reproduction, embryonic development, growth, and immune function, is provided by foods of animal and plant origin (Karaağaç and Pınarlı, 2023). Vitamin E regulates heart, vascular, nerve, and brain functions, helps heal wounds, and increases the durability of DNA molecules. It also has the ability to protect cells from damage caused by free radicals occurring in the body (Stevens, 2021). It is reported that lycopene not only helps repair damaged cells in the body but also has a protective effect against types of cancer and chronic diseases because antioxidant properties (Zengin and Kurt, 2018).

Conversion of Oxidized Glutathione (GSSG) to Reduced glutathione (GSH) is important in terms of preventing free radical damage (Gill et al., 2013). While GSSG is an indicator of oxidative stress, it also inhibits protein synthesis, GSH has many physiological functions like preventing the harmful effects of drugs (Mendoza-Cózatl et al., 2005). GSH and GSSG are important indicators of cellular redox status and organismal health and are in balance in the cell, and disruption of the balance against GSH causes negative effects. Therefore, reduced glutathione to oxidized glutathione ratio is also known as a stress indicator (Cnubben et al., 2001). Radical compounds cause lipid peroxidation of fatty acids in cell membranes. Lipid peroxides transform into compounds such as Malondialdehyde (MDA) and 4-Hydroxyneoneal (4-HNE), which are indicative of lipid peroxidation (Gaweł et al., 2004).

Foods are sensitive to various environmental factors such as moisture, light, oxygen, and microorganisms, and these factors can cause spoilage (Redfearn et al., 2023). He et al. (2023) report that ginger oil is turned into a film and used to preserve foods such as bread, meat, fish, and fruit. Some biochemical parameters in foods change depending on shelf life. Sumac in many cultures generally consumed in ground form together with food.

Aimed of this study is to determine the fat-soluble vitamins and stress biomarkers in sumac samples grown in different regions according to time and storage characteristics (vegetable oil/fat-free). In addition to comparing the effect of storage conditions, ground sumac samples were divided into three portions, fresh; analyzed immediately, and oiled and unoiled samples analyzed after 6 months.

MATERIAL AND METHODS

Materials:

All sumac samples from Türkiye and Iraq were obtained fresh from public markets. 500 grams of fresh sumac samples from each region were homogenized and 3 different portions were taken and mixed thoroughly. Then, samples were dried in an oven at 60 °C for 10 hours. From each group of samples, 25 grams were taken from 3 different portions of the sample, ground in a mixer, sieved, and separated from their seeds, then samples were sieved in a 100-mesh sieve (Retsch AS 200). These samples were then divided into three groups one of the groups was oiled by spraying sunflower oil, the second group of samples kept as is and the third group of samples (fresh) was analyzed immediately. On the other hand, the other two groups, oiled and unoiled, were packaged and stored in the refrigerator for six months. At the end of six months, sumac samples were analyzed.

Methods:

Determination of vitamin A, E, ß-Carotene, Lycopene, and 4-HNE 1.0-gram sumac sample was taken, 6.0 mL of ethanol was added and vortexed, then sonicated in an ice water bath (Wise Clean, WUC-AO3H, 170 W) 10 times for 30 seconds for each sample. Sonicated samples were centrifuged at 8000 rpm for 10 min, then 1.0 mL n-hexane was added to each tube and centrifuged again at 4000 rpm for 6 min. The n-hexane phase was transferred to a glass tube and this process was repeated twice. Hexane was removed under vacuum at 30 °C, and then 1.0 mL of methanol was added to the residue in the tube and transferred to HPLC vials. In HPLC, analyses were carried out on an Inertsil ODS-3 column (25.0 cm x 4.6 mm x 5.0 µm) using a mixture of methanol and water (95:5) as the mobile phase (İbrahim et al. 2017).

Determination of GSH, GSSG, and MDA The amounts of GSH, GSSG, and MDA in sumac samples were determined by HPLC on the SGE Walkosil II 5Cl8 RS (15cm x 4.6 mm x 5 µm) column, using 50 mM $NaClO_4$ solution containing 0.1% H_3PO_4 as the mobile phase (İbrahim et al. 2017).

Statistical Analysis:

All analyses were repeated three times. Findings were subjected to One-Way ANOVA using SPSS 26.0 for MS Windows, and the results are given mean ±error. Power analysis was conducted using G*Power version 3.1.9.7 (Faul et al., 2007) to determine the minimum sample size required to test the study hypothesis. Results indicated the required sample size to achieve 0.80 power (1-□) for detecting a medium effect, at a significance criterion of α = 0.05, with the effect size of 0.45 was n = 99 for One-way ANOVA. Differences between group means were analyzed for significance using the Tukey HSD test and statistical significance was expressed as $p<0.05$. Significant differences in table rows are indicated by superscript capital letters (A-C) while the same letter indicates there is no statistical difference between groups. Similarly, the same small letters in the table column indicate that there is no significant difference ($p>0.05$) within the regions.

RESULTS and DISCUSSIONS

Vitamins are micronutrients necessary for the growth and development of living things, and fat-soluble vitamins are stored in the body and play a role in maintaining homeostasis (Yuan et al., 2020). Some biochemical parameters in foods change depending on shelf life. Sumacs are generally offered for consumption in ground form with foods.

The amounts of vitamins A and E, ß-carotene, lycopene, GSH, GSSG, GSH/GSSG, MDA, and 4-HNE found as a result of different treatments applied to sumac grown in different regions are given in Tables 1-9.

Vitamin A is necessary for epithelial tissue, health, and general growth and is effective in reproduction and bone growth (Stevens, 2021). The amount of vitamin A in fresh sumac samples from different regions varies between 1.30 ± 0.05 - 2.77 ± 0.06 µg (g dw)$^{-1}$. It was observed that the amount of vitamin A in sumac samples oiled and unoiled varied between 0.97 ± 0.03 - 2.34 ± 0.07, and 0.85 ± 0.04 - 2.00 ± 0.06 µg (g dw)$^{-1}$, respectively. The difference between fresh, unoiled, and oiled groups is statistically significant ($p<0.05$). The difference between the amounts of vitamin A in sumac samples grown in Maraş and Sheladize regions is statistically insignificant ($p>0.05$) (Table 1). Okonkwo and Ogu (2014) reported that the vitamin A contents in Myristica frangrans, Piper guineense, Monodora myristica, and Rosmarinus officinalis samples were 14.57, 7.08, 13.71, and 14.87 Ug (100 g)$^{-1}$, respectively. Pereira et al. (2011) found the vitamin A content in yellow guava, guabiroba, and uvaia to be 0.718, 6.838, and 37.834 µg equivalent to retinol (g dry matter)$^{-1}$, respectively.

Table 1 Amount of vitamin A in sumac samples (µg (g dw)$^{-1}$) (n= 33 each group)
Tablo 1. Sumak örneklerindeki A vitamini miktarı (µg (g kuru ağırlık)$^{-1}$) (her grupta n=33)

Region	Fresh group	Unoiled group	Oiled group
Maraş	^{d} 1.93 ± 0.05 ^{A}	^{c} 1.51 ± 0.04 ^{B}	^{e} 1.75 ± 0.04 ^{C}
Elazığ	^{d} 1.89 ± 0.06 ^{A}	^{c} 1.46 ± 0.05 ^{B}	^{e} 1.70 ± 0.04 ^{C}
Shelaza	^{c} 1.69 ± 0.07 ^{A}	^{b} 1.15 ± 0.04 ^{B}	^{d} 1.45 ± 0.04 ^{C}
Trawanish	^{b} 1.30 ± 0.05 ^{A}	^{a} 0.92 ± 0.04 ^{B}	^{b} 1.17 ± 0.04 ^{C}
Shahi	^{d} 1.88 ± 0.05 ^{A}	^{c} 1.45 ± 0.04 ^{B}	^{e} 1.70 ± 0.05 ^{C}
Charput	^{g} 2.77 ± 0.06 ^{A}	^{e} 2.00 ± 0.06 ^{B}	^{g} 2.34 ± 0.07 ^{C}
Süleymaniye	^{f} 2.56 ± 0.07 ^{A}	^{e} 1.90 ± 0.05 ^{B}	^{g} 2.20 ± 0.07 ^{C}
Kadana	^{c} 1.73 ± 0.05 ^{A}	^{b} 1.23 ± 0.04 ^{B}	^{d} 1.46 ± 0.04 ^{C}
Derişke	^{a} 1.12 ± 0.05 ^{A}	^{a} 0.85 ± 0.04 ^{B}	^{a} 0.97 ± 0.03 ^{C}
Ranya	^{e} 2.16 ± 0.09 ^{A}	^{d} 1.72 ± 0.05 ^{B}	^{f} 1.96 ± 0.06 ^{C}
Shalidize	^{c} 1.69 ± 0.06 ^{A}	^{b} 1.19 ± 0.04 ^{B}	^{c} 1.35 ± 0.04 ^{C}

Letters with different superscripts (a-g) within the same column and capital letters (A-C) within the row differ significantly $P<0.05$

Table 2. Amount of ß-carotene in sumac samples (µg (g dw)$^{-1}$) (n=33 each group)
Tablo 2. Sumak örneklerindeki β-karoten miktarı (µg (g kuru ağırlık)$^{-1}$) (her grupta n=33)

Region	Fresh	Unoiled group	Oiled group
Maraş	^{d} 4.46 ± 0.12 ^{A}	^{f} 3.70 ± 0.09 ^{B}	^{d} 3.98 ± 0.09 ^{C}
Elazığ	^{c} 4.21 ± 0.10 ^{A}	^{d} 3.52 ± 0.08 ^{B}	^{d} 3.85 ± 0.09 ^{C}
Shelaza	^{b} 3.61 ± 0.09 ^{A}	^{b} 2.82 ± 0.07 ^{B}	^{b} 3.06 ± 0.08 ^{C}
Trawanish	^{c} 4.12 ± 0.09 ^{A}	^{d} 3.47 ± 0.08 ^{B}	^{d} 3.90 ± 0.09 ^{C}
Shahi	^{c} 4.11 ± 0.11 ^{A}	^{d} 3.45 ± 0.10 ^{B}	^{d} 3.92 ± 0.10 ^{C}
Charput	^{c} 4.02 ± 0.08 ^{A}	^{c} 3.04 ± 0.07 ^{B}	^{c} 3.51 ± 0.07 ^{C}
Süleymaniye	^{e} 4.73 ± 0.10 ^{A}	^{e,f} 3.67 ± 0.07 ^{B}	^{f} 4.10 ± 0.09 ^{C}
Kadana	^{f} 5.31 ± 0.12 ^{A}	^{g} 4.30 ± 0.10 ^{B}	^{g} 4.90 ± 0.10 ^{C}
Derişke	^{b} 3.53 ± 0.09 ^{A}	^{b} 2.73 ± 0.07 ^{B}	^{b} 3.05 ± 0.08 ^{C}
Ranya	^{e} 4.86 ± 0.11 ^{A}	^{f} 3.77 ± 0.09 ^{B}	^{f} 4.15 ± 0.09 ^{C}
Shalidize	^{a} 2.48 ± 0.07 ^{A}	^{a} 1.85 ± 0.06 ^{B}	^{a} 2.15 ± 0.06 ^{C}

Letters with different superscripts (a-g) within the same column and capital letters (A-C) within the row differ significantly P<0.05

Table 3. Amount of lycopene in sumac samples (µg (g dw)$^{-1}$) (n=33)
Tablo 3. Sumak örneklerindeki likopen miktarı (µg (g kuru ağırlık)$^{-1}$) (n=33)

Region	Fresh	Unoiled group	Oiled group
Maraş	^{e} 11.13 ± 0.35 ^{A}	^{d} 8.41 ± 0.31 ^{B}	^{d} 9.76 ± 0.26 ^{C}
Elazığ	^{b} 8.10 ± 0.31 ^{A}	^{b} 5.38 ± 0.20 ^{B}	^{b} 7.00 ± 0.21 ^{C}
Shelaza	^{d} 10.38 ± 0.35 ^{A}	^{c} 7.55 ± 0.25 ^{B}	^{c} 8.80 ± 0.27 ^{C}
Trawanish	^{g} 22.16 ± 0.73 ^{A}	^{f} 16.17 ± 0.52 ^{B}	^{h} 18.26 ± 0.45 ^{C}
Shahi	^{c} 8.87 ± 0.32 ^{A}	^{b} 5.58 ± 0.15 ^{B}	^{b} 7.10 ± 0.22 ^{C}
Charput	^{h} 26.90 ± 0.80 ^{A}	^{g} 18.85 ± 0.53 ^{B}	^{g} 15.16 ± 0.47 ^{C}
Süleymaniye	^{f} 12.57 ± 0.43 ^{A}	^{e} 9.38 ± 0.33 ^{B}	^{e} 10.70 ± 0.36 ^{C}
Kadana	^{a} 7.08 ± 0.24 ^{A}	^{a} 4.30 ± 0.13 ^{B}	^{a} 5.98 ± 0.17 ^{C}
Derişke	^{h} 25.63 ± 0.77 ^{A}	^{g} 18.22 ± 0.50 ^{B}	^{i} 21.91 ± 0.70 ^{C}
Ranya	^{f} 13.30 ± 0.44 ^{A}	^{e} 9.65 ± 0.37 ^{B}	^{f} 11.30 ± 0.39 ^{C}
Shalidize	^{e} 11.63 ± 0.37 ^{A}	^{d} 8.55 ± 0.30 ^{B}	^{d} 9.84 ± 0.31 ^{C}

Letters with different superscripts (a-i) within the same column and capital letters (A-C) within the row differ significantly P<0.05

Table 4. Amount of Vitamin E in sumac samples (µg /(g dw)$^{-1}$) (n=33)
Tablo 4. Sumak örneklerindeki E vitamini miktarı (µg (g kuru ağırlık)$^{-1}$) (n=33)

Region	Fresh	Unoiled group	Oiled group
Maraş	^{e} 155.53 ± 3.84 ^{A}	^{e} 118.86 ± 3.92 ^{B}	^{e} 139.18 ± 4.06 ^{C}
Elazığ	^{b} 105.42 ± 3.69 ^{A}	^{b} 85.12 ± 3.08 ^{B}	^{b} 94.22 ± 3.19 ^{B}
Shelaza	^{a} 84.40 ± 3.22 ^{A}	^{a} 64.07 ± 2.58 ^{B}	^{a} 76.30 ± 2.91 ^{C}
Trawanish	^{c} 120.40 ± 4.22 ^{A}	^{c} 92.93 ± 3.36 ^{B}	^{c} 107.80 ± 3.50 ^{C}
Shahi	^{g} 212.51 ± 5.86 ^{A}	^{h} 180.67 ± 3.89 ^{B}	^{g} 197.29 ± 3.68 ^{C}
Charput	^{f}173.36 ± 4.94 ^{A}	^{g} 141.40 ± 3.84 ^{B}	^{f} 158.20 ± 3.89 ^{B}
Süleymaniye	^{d} 137.17 ± 3.99 ^{A}	^{d} 105.54 ± 3.34 ^{B}	^{d} 120.68 ± 3.40 ^{C}
Kadana	^{h}230.65 ± 6.55 ^{A}	^{i} 190.40 ± 5.16 ^{B}	^{h} 207.07 ± 5.29 ^{C}
Derişke	^{f} 164.74 ± 4.89 ^{A}	^{f} 127.87 ± 4.18 ^{B}	^{e} 145.22 ± 3.92 ^{C}
Ranya	^{g} 216.95 ± 6.34 ^{A}	^{h} 175.45 ± 4.99 ^{B}	^{g} 193.08 ± 5.17 ^{C}
Shalidize	^{a} 89.26 ± 3.04 ^{A}	^{a} 61.86 ± 2.59 ^{B}	^{a} 77.18 ± 2.81 ^{C}

Letters with different superscripts (a-i) within the same column and capital letters (A-C) within the row differ significantly P<0.05

Carotenoids, which protect living systems from free radicals, react with peroxide radicals and molecular oxygen. Carotenoids such as ß-carotene and lycopene exhibit antioxidant properties by blocking free radicals (Pereira et al., 2011). It was determined that the amount of ß-carotene in fresh sumac samples varied between 2.48 ± 0.07 - 5.31 ± 0.12, on the other hand, unoiled and oiled groups varied in between 1.85 ± 0.06 - 4.30 ± 0.10, 2.15 ± 0.06 - 4.90 ± 0.10 µg (g dw)$^{-1}$, respectively. ß-carotene loss in the unoiled group is higher than in the oiled group. While the lowest amount of ß-carotene was found in Shalidize sumac,

the highest amount was found in Kadana region sumac. It can be said that there is no significant difference between Derişke and Shelaza, Elazığ, Trawanish, Shahi, and Charput regions, as well as between Ranya and Süleymania regions. In terms of □-carotene, the difference between all groups is statistically significant ($p<0.05$) (Table 2). Aremu and Nweze (2017) found the amounts of vitamin A in Guava, Pawpaw, and Mango fruits as 504.10, 683.93, and 301.61 µg (100 g)$^{-1}$, and the amounts of ß-carotene as 3015.27, 4043.45 and 1797.21 µg (100 g)$^{-1}$, respectively. The amount of ß-carotene in A. sativum, Z. officinale, A. melegueta, and E. caryophyllata samples was reported to be 109.5, 226.8, 308.5 and 98.1 mg (100 g)$^{-1}$, respectively (Omotayo and Adepoju, 2013).

Table 5. Amount of GSH in sumac samples (µg (g dw)$^{-1}$) (n=33)
Tablo 5. Sumak örneklerindeki GSH miktarı (µg (g kuru ağırlık)$^{-1}$) (n=33)

Region	Fresh	Unoiled group	Oiled group
Maraş	^{f} 1912.23 ± 21.60 ^{A}	^{f} 1706.40 ± 19.63 ^{B}	^{f} 1810.07 ± 17.27 ^{C}
Elazığ	^{d} 1588.63 ± 18.77 ^{A}	^{d} 1375.14 ± 16.17 ^{B}	^{d} 1441.14 ± 14.48 ^{C}
Shelaza	^{k} 2550.42 ± 18.48 ^{A}	^{j} 2314.90 ± 17.65 ^{B}	^{j} 2426.56 ± 18.11 ^{C}
Trawanish	^{b} 1285.10 ± 13.89 ^{A}	^{b} 1125.44 ± 14.48 ^{B}	^{b} 1178.72 ± 13.68 ^{C}
Shahi	^{a} 1004.12 ± 12.57 ^{A}	^{a} 877.53 ± 12.25 ^{B}	^{a} 913.53 ± 11.68 ^{C}
Charput	^{e} 1759.33 ± 15.80 ^{A}	^{e} 1408.14 ± 15.11 ^{B}	^{e} 1559.14 ± 14.56 ^{C}
Süleymaniye	^{j} 2390.10 ± 16.56 ^{A}	^{i} 2098.39 ± 17.05 ^{B}	^{i} 2187.39 ± 17.57 ^{C}
Kadana	^{c} 1362.07 ± 12.76 ^{A}	^{c} 1169.70 ± 13.43 ^{B}	^{c} 1215.70 ± 13.43 ^{C}
Derişke	^{i} 2152.10 ± 16.02 ^{A}	^{h} 1943.06 ± 17.13 ^{B}	^{h} 2014.06 ± 16.63 ^{C}
Ranya	^{h} 2109.69 ± 15.86 ^{A}	^{h} 1915.95 ± 17.56 ^{B}	^{h} 2015.95 ± 17.04 ^{C}
Shalidize	^{g} 2050.29 ± 14.99 ^{A}	^{g} 1883.45 ± 16.72 ^{B}	^{g} 1969.12 ± 16.13 ^{C}

Letters with different superscripts (a-j) within the same column and capital letters (A-C) within the row differ significantly $P<0.05$

Table 6. Amount of GSSG in sumac samples (µg (g dw)$^{-1}$) (n=33)
Tablo 6. Sumak örneklerindeki GSSG miktarı (µg (g kuru ağırlık)$^{-1}$) (n=33)

Region	Fresh	Unoiled group	Oiled group
Maraş	^{f} 895.06 ± 13.92 ^{A}	^{f} 1147.68 ± 17.63 ^{B}	^{f} 1014.35 ± 15.45 ^{C}
Elazığ	^{k} 1375.38 ± 18.74 ^{A}	^{h} 1492.55 ± 19.43 ^{B}	^{i} 1272.55 ± 15.95 ^{C}
Shelaza	^{i} 992.85 ± 12.16 ^{A}	^{f} 1126.31 ± 14.32 ^{B}	^{f} 1027.31 ± 13.82 ^{C}
Trawanish	^{d} 806.53 ± 11.06 ^{A}	^{d} 1016.97 ± 12.79 ^{B}	^{d} 901.34 ± 11.46 ^{C}
Shahi	^{a} 422.54 ± 7.61 ^{A}	^{a} 519.87 ± 8.23 ^{B}	^{a} 488.21 ± 7.62 ^{C}
Charput	^{b} 503.85 ± 8.99 ^{A}	^{b} 606.96 ± 9.06 ^{B}	^{b} 560.62 ± 9.05 ^{C}
Süleymaniye	^{g} 921.06 ± 11.07 ^{A}	^{f} 1117.22 ± 13.04 ^{B}	^{g} 1052.22± 13.04 ^{C}
Kadana	^{c} 693.56 ± 9.51 ^{A}	^{c} 745.23 ± 9.98 ^{B}	^{c} 715.90 ± 9.35 ^{C}
Derişke	^{j} 1075.40± 13.86 ^{A}	^{g} 1227.24 ± 14.77 ^{B}	^{h} 1153.91 ± 13.89 ^{C}
Ranya	^{e} 859.07 ± 11.27 ^{A}	^{d} 1015.73 ± 12.84 ^{B}	^{e} 975.73 ± 12.26 ^{C}
Shalidize	^{h} 949.92 ± 11.84 ^{A}	^{e} 1084.80 ± 12.38 ^{B}	^{f} 1005.06 ± 12.81 ^{C}

Letters with different superscripts (a-k) within the same column and capital letters (A-C) within the row differ significantly $P<0.05$

Table 7. GSH/GSSG ratios in sumac samples
Tablo 7. Sumak örneklerindeki GSH/GSSG oranı

Region	Fresh	Unoiled group	Oiled group
Maraş	2.14	1.49	1.78
Elazığ	1.16	0.92	1.13
Shelaza	2.57	2.06	2.36
Trawanish	1.59	1.11	1.31
Shahi	2.38	1.69	1.87
Charput	3.49	2.32	2.78
Süleymaniye	2.59	1.88	2.08
Kadana	1.96	1.57	1.70
Derişke	2.00	1.58	1.75
Ranya	2.46	1.89	2.07
Shalidize	2.16	1.74	1.96

Table 8. Amount of MDA in sumac samples (µg (g dw)$^{-1}$) (n=33)
Tablo 8. Sumak örneklerindeki MDA miktarı (µg (g kuru ağırlık)$^{-1}$) (n=33)

Region	Fresh	Unoiled group	Oiled group
Maraş	^{b} 18.66 ± 0.67 ^{A}	^{c} 22.79 ± 0.45 ^{B}	^{c} 20.53 ± 0.38 ^{C}
Elazığ	^{a} 13.95 ± 0.53 ^{A}	^{a} 16.46 ± 0.36 ^{B}	^{a} 15.12 ± 0.23 ^{C}
Shelaza	^{c} 22.80 ± 0.81 ^{A}	^{d} 26.57 ± 0.75 ^{B}	^{d} 24.90 ± 0.31 ^{C}
Trawanish	^{e} 28.37 ± 0.87 ^{A}	^{f} 32.09 ± 1.00 ^{B}	^{i} 30.52 ± 0.35 ^{C}
Shahi	$^{d, e}$ 27.25 ± 0.96 ^{A}	^{f} 32.34 ± 0.95 ^{B}	^{h} 29.47 ± 0.38 ^{C}
Charput	^{d} 26.19 ± 0.92 ^{A}	^{e} 30.39 ± 1.05 ^{B}	^{g} 28.46 ± 0.35 ^{C}
Süleymaniye	$^{c, d}$ 25.38 ± 0.87 ^{A}	^{e} 29.38 ± 1.05 ^{B}	^{f} 27.33 ± 0.37 ^{C}
Kadana	$^{c, d}$ 24.97 ± 1.00 ^{A}	^{e} 28.62 ± 1.00 ^{B}	^{e} 26.37 ± 0.29 ^{C}
Derişke	^{c} 24.14 ± 0.96 ^{A}	^{e} 29.73 ± 1.01 ^{B}	^{e} 26.06 ± 0.34 ^{C}
Ranya	^{b} 17.83 ± 0.61 ^{A}	^{b} 21.18 ± 0.63 ^{B}	^{b} 19.21 ± 0.26 ^{C}
Shalidize	^{f} 31.30 ± 1.02 ^{A}	^{g} 35.63 ± 1.02 ^{B}	^{j} 33.16 ± 0.45 ^{C}

Letters with different superscripts (a-j) within the same column and capital letters (A-C) within the row differ significantly P<0.05

Table 9. Amount of 4-HNE in sumac samples (µg (g dw)$^{-1}$) (n=33)
Tablo 9. Sumak örneklerindeki 4-HNE miktarı (µg (g kuru ağırlık)$^{-1}$) (n=33)

Region	Fresh	Unoiled group	Oiled group
Maraş	^{d} 11.69 ± 0.23 ^{A}	$^{b, c}$ 17.96 ± 0.62 ^{B}	^{d} 14.83 ± 0.61 ^{C}
Elazığ	^{a} 7.12± 0.19 ^{A}	^{a} 12.08 ± 0.46 ^{B}	^{a} 9.26 ± 0.35 ^{C}
Shelaza	^{e} 12.80 ± 0.35 ^{A}	^{b} 17.73 ± 0.64 ^{B}	^{d} 14.50 ± 0.48 ^{C}
Trawanish	^{e} 13.37 ± 0.40 ^{A}	^{c} 18.34 ± 0.74 ^{B}	$^{d, e}$ 15.20 ± 0.50 ^{C}
Shahi	^{c} 9.94 ± 0.32 ^{A}	^{b} 16.77 ± 0.58 ^{B}	^{c} 13.10 ± 0.42 ^{C}
Charput	^{e} 13.19 ± 0.40 ^{A}	^{c} 19.00 ± 0.73 ^{B}	^{e} 16.11 ± 0.49 ^{C}
Süleymaniye	^{f} 14.61 ± 0.47 ^{A}	$^{c, d}$ 20.07 ± 0.72 ^{B}	^{f} 17.51 ± 0.60 ^{C}
Kadana	^{a} 7.26 ± 0.21 ^{A}	^{a} 11.63 ± 0.46 ^{B}	^{a} 9.45 ± 0.37 ^{C}
Derişke	^{b} 8.14 ± 0.28 ^{A}	^{a} 12.14 ± 0.45 ^{B}	^{b} 10.48 ± 0.42 ^{C}
Ranya	^{f} 15.40 ± 0.47 ^{A}	^{d} 21.05 ± 0.77 ^{B}	^{f} 17.55 ± 0.50 ^{C}
Shalidize	^{e} 13.23± 0.39 ^{A}	^{c} 18.73 ± 0.66 ^{B}	^{e} 16.45 ± 0.54 ^{C}

Letters with different superscripts (a-f) within the same column and capital letters (A-C) within the row differ significantly P<0.05

The amount of lycopene in the fresh, unoiled and oiled group sumac samples varies between 7.08 ± 0.24 - 26.90 ± 0.80, 4.30 ± 0.13 - 18.85 ± 0.53, 7.00 ± 0.21 - 21.91 ± 0.70 µg (g dw)$^{-1}$, respectively. While the highest amount of lycopene was found in the sumac of Charput region, the least amount was found in the sumac of Kadana region. The difference between the lycopene content of fresh sumac samples regarding different regions together with fresh, unoiled, and oiled groups is statistically significant (p <0.05). It was observed that the loss of lycopene in the non-oiled group was greater than the loss in the oiled group (Table 4). It has been reported that the amount of lycopene in guava, papaya, rosehip, and red pepper varies between 52.3-55.0, 1.1-53.0, 6.8-7.1, and 10.8-26.2 µg g^{-1}, respectively (Zengin and Kurt, 2018).

Vitamin E has strong antioxidant properties and helps prevent cell membranes and lipoproteins from being damaged by oxidative stress. Vitamin E has a role in several physiological processes, including immunological function, inflammation control, gene expression regulation, and cognitive functioning (Dror and Allen, 2011). The amount of vitamin E in fresh sumac samples from different regions was found to vary in between 84.40 ± 3.22 - 230.65 ± 6.55 µg (g dw)$^{-1}$. The highest vitamin E was determined in Kadana region, while the lowest was determined in Shelaza region. While there is no statistical difference between the fresh sample of the Shelaza and Shalidize regions (p>0.05), all other regions are statistically different from each other (p<0.05). It was determined that vitamin E in the unoiled group sumac samples ranged between 61.86 ± 2.59 - 190.40 ± 5.16, while in the oiled group samples, it varied between 76.30 ± 2.91 - 207.07 ± 5.29 µg (g dw)$^{-1}$. Vitamin E in the oiled group of sumac samples was found to be higher than in the unoiled groups. In other words, vitamin E loss is less in the oiled group. The amounts of vitamin E in the fresh, unoiled, and oiled groups are statistically different (p <0.05) (Table 4). It was reported that the amount of ß-carotene in the ginger, garlic, turmeric, black pepper, and clove samples was 56.11, 68.17, 151.74, 92.14, and 83.43, and vitamin E was 10.23, 13.13, 11.24, 15.32 and 22.51 mg (100 g)$^{-1}$, respectively (Ayoade et al., 2023). Uhegbu et al. (2011) reported that the amount of vitamin E in P. Guineense and M. Myristica was 1.64 and 12.0 U (100 g)$^{-1}$, respectively.

It has been found that the amount of vitamin E in apricots grown under different conditions varies between 27.10 - 85.10 µg (100 g)$^{-1}$ (Kan et al., 2014). Çakmak et al. (2020) reported that the amounts of vitamin A, E, ß-carotene and lycopene in wild white Myrtus communis L. fruit were 1.85, 206.57, 5.89 and 9.79 µg (g dw)$^{-1}$, respectively. It was reported that the amounts of vitamins A, E, ß-carotene and lycopene in fresh fruits of Crataegus laevigata samples grown in the Elazığ region were 0.78, 0.83, 2.88 and 2.34 µg g^{-1}, respectively (İbrahim et al. 2017). It was observed that the loss in the amounts of vitamins A, E, □-carotene, and lycopene in sumac samples oiled less than in unoiled samples. It has been noted that parameters such as temperature and shelf life are important in the degradation of vitamins (Kala and Prakash, 2006). It has been reported that the loss of vitamins in chili pepper samples kept for a certain period in unoiled form is greater than in oiled samples (Karatas et al., 2017). Konfo et al. (2023) reported that essential oils, as natural antioxidants, are used in the preservation of foodstuffs. Falowo et al. (2019) reported that 2% and 4% basil essential oil applied to ground beef increased oxidative stability and preserved color during storage. Glutathione, an essential component for cellular immune system function, has a peptide structure and serves as the primary intracellular antioxidant. Additionally, it plays a role in amino acid transport in metabolism and the reduction of sulfhydryl groups in proteins (Mendoza-Cózatl et al., 2005).

It was determined that the amount of GSH in fresh sumac samples varied between 1004.12 ± 12.57 - 2550.42 ± 18.48, while GSSG varied between 422.54 ± 7.61 - 1375.38 ± 18.74 µg (g dw)$^{-1}$. The highest amounts of GSH and GSSG were in Shelaza and Elazığ regions, respectively, on the other hand, the lowest amounts were observed in the Shahi region (Tables 5 and 6). The amounts of both GSH and GSSG in fresh sumac samples are statistically different according to every region ($p<0.05$). The amount of GSH in the unoiled and oiled group sumac samples was found to vary between 877.53 ± 12.25 - 2314.90 ± 17.65 and 913.53 ± 11.68 - 2426.56 ± 18.11 µg (g dw)$^{-1}$ respectively. It was determined that the amount of GSSG in the same samples varied between 519.87 ± 8.23 - 1492.55 ± 19.43 and 488.21 ± 7.62 - 1272.55 ± 15.95 µg (g dw)$^{-1}$. It was observed that while the amount of GSH in the stored sumac samples decreased, on the other hand, GSSG increased. This might be the result of oxidation during the waiting period of the samples. While the loss of GSH in unoiled samples was higher than in the oiled samples, the increase in the amount of GGSG was found to be greater in the unoiled samples. From these results, it can be said that oiling prevents oxidation of the samples forming a thin film in between air and the sumac surface. The differences between the sumac samples of all three groups in terms of both GSH and GSSG amounts are statistically significant ($p<0.05$) (Tables 5 and 6).

Cerit et al. (2020) reported that the amount of GSH in red pepper, turmeric, cardamom, and ginger was 42, 41, 112, and 1076 nM (g dw)$^{-1}$, respectively. Tesoriere et al. (2005) discovered that the levels of GSH in three distinct cultures of prickly pears ranged from 3.40 to 8.10 mg (100 g)$^{-1}$. The GSH/GSSG ratio is higher under normal conditions but decreases under stress (Kocsy et al., 2001). As seen in Table 7, the highest GSH/GSSG ratio was found in fresh sumac samples, while the lowest ratio was observed in unoiled sumac samples. These results confirm that oiling the samples partially reduces oxidation. It was reported that when hydrogen peroxide was applied to spinach, green banana, and red pepper for the disinfection process, the amount of GSSG increased compared to the control group, while the GSH and GSH/GSSG ratio decreased (Qiang et al., 2005). MDA and 4-HNE, which are formed as a result of the peroxidation of polyunsaturated fatty acids, are used as stress indicators (Barrera et al., 2018). As seen in table 8, the amount of MDA in fresh, unoiled and oiled sumac samples varied between (13.95 ± 0.53 - 31.30 ± 1.02, 16.46 ± 0.36 - 35.63 ± 1.02 and 15.12 ± 0.23 - 33.16 ± 0.45 µg (g dw)$^{-1}$), respectively. The lowest amount of MDA was observed in fresh sumac samples, while the highest amount was observed in an unoiled sample. The difference between MDA in the fresh, unoiled, and oiled groups is statistically significant ($p<0.05$). It has been reported that the MDA concentration in mature ber fruit (Ziziphus mauritiana Lam) is 4.498 nmol/g (Kumar et al., 2011). Çakmak et al. (2023) reported that the amount of MDA in fresh and sun-dried black Myrtus communis L. fruit were 5.32 and 6.80 µg (g dw)$^{-1}$. It was determined that the amount of 4-HNE in fresh, unoiled and oiled sumac samples from different regions varied between 7.12 ± 0.19 - 15.40 ± 0.47, 11.63 ± 0.46 - 21.05 ± 0.77, 9.26 ± 0.35 - 17.55 ± 0.50 µg (g dw)$^{-1}$, respectively. The lowest amount of 4-HNE in the fresh sumac sample was observed in the sumac of the Elazığ region, while the highest was observed in the Ranya region sumacs. In terms of the amount of 4-HNE, it can be said that there is no significant difference between the Elazığ and Kadana regions, Shelaza, Trawanish and Sheladize regions, and Ranya and Süleymania regions. The amount of 4-HNE in fresh, unoiled, and oiled groups of sumacs in the same regions is statistically different ($p<0.05$) (Table 9).

The highest amounts of GSSG, MDA, and 4-HNE were found in unoiled sumac samples. This might be explained that the oiling partially reduces oxidative stress. Muktar et al. (2023) found that the amounts of GSH, GSSG, MDA, and 4-HNE in bitter tomatoes as 364, 225, 1.50, and 24.57, respectively, and the same parameters in White Garden Egg were 1930, 962, 8.40 and 38.25 µg (g dw)$^{-1}$. Çakmak et al. (2020) found the

amounts of GSH, GSSG, MDA and GSH/GSSG ratios in wild white Myrtus communis L. fruits as 609.90, 184.24, 5.73 µg (g dw)$^{-1}$) and 3.31, respectively, while the same parameters in cultivated white Myrtus communis L. fruits were 571.80, 115.50, 4.50 µg (g dw)$^{-1}$ and 4.95, respectively.

CONCLUSION

Charput and Suleymaniye are richer in vitamin A, Kadana and Ranya are richer in □-carotene, Charput, Derişke and Trawanish are richer in lycopene. Kadana, Ranya, and Shahi sumacs are richer in vitamin E than other regions. Derişke and Trawanish are poorer in vitamin A, Sheladize is poorer in beta carotene, Kadana is poorer in lycopene, and Shelaza and Shalidize sumacs are poorer in vitamin E. While Shelaza is the richest in terms of GSH, Shahi region sumac has the lowest in terms of GSSG. Elazığ region sumac has the lowest amounts of MDA and 4-HNE. It was found that the changes in all the measured parameters of oiled sumac samples were lower than the unoiled samples. It can be concluded from these results that, to protect the sumac sample from degradation it should be oiled to preserve it for longer shelf life. The difference between regions in the amounts of fat-soluble vitamins, glutathione, and stress biomarkers might be due to geographical and ecological conditions.

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Author Contribution

Authors declare that they all contributed equally to the article.

Conflicting of Interest

All authors declare that there is no conflict of interest.

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