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Effects of Roasting on the Antioxidant Status and Phenolic Profiles of Commercial Turkish Hazelnut Varieties (*Corylus avellana* L.)

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ABSTRACT: The effect of roasting on the antioxidant status and phenolic profiles of seven commercial Turkish hazelnut varieties (namely, Çakıldak, Foşa, Karafındık, Mincane, Palaz, Sivri, and Tombul) was assessed. Samples were examined for their total phenolics, oxygen radical absorbance capacity (ORAC) values, condensed tannins, and phenolic acids (free and bound forms). Significant losses ($p < 0.05$) in total phenolics (~66.3%), ORAC values (~41.6%), condensed tannins (~75.2), and phenolic acids (~42.7) were noted when the hazelnuts were roasted. Some variations both between and within natural and roasted hazelnuts were observed ($p < 0.05$). Phenolic acids were mainly found in the bound form. Gallic, protocatechuic, *p*-coumaric, and ferulic + sinapic acids were present in all hazelnut varieties, albeit to different extents, and the first two were dominant. Mincane, in roasted form, had the highest total phenolics, ORAC values, condensed tannins, and phenolic acids. This was due to the presence of some skin in roasted Mincane. No skin was left in all other varieties upon roasting. The present work suggests that roasting results in a significant loss in the antioxidant status and phenolic profiles because of the removal of the skin, which is a rich source of phenolics. It is highly recommended to consume natural hazelnut instead of the roasted counterpart to take advantage of all of the functional benefits of this nut.

KEYWORDS: *Natural hazelnuts, roasted hazelnuts, total phenolics, ORAC value, condensed tannins, phenolic acids*

INTRODUCTION

Hazelnut (*Corylus avellana* L.) belongs to the Betulaceae family and is a popular tree nut worldwide; it is mainly distributed along the coasts of the Black Sea region of Turkey, southern Europe (Italy, Spain, Portugal, and France), and in some areas of the United States (Oregon and Washington). Hazelnut is also grown in New Zealand, China, Azerbaijan, Chile, Iran, and Georgia. Turkey is the world's largest producer of hazelnuts (510 000 megatons in 2011, in shell basis), contributing around 63.6% to the total global production, followed by Italy (15.6%), Azerbaijan (5.6%), Georgia (4.4%), the United States (4.3%), and Spain (3.1%). Other countries contribute only 3.4% to the total global production.[1]

A total of 18 varieties (Acı, Cavcava, Çakıldak, Foşa, Ham, İncekara, Kalınkara, Kan, Karafındık, Kargalak, Kuş, Mincane, Palaz, Sivri, Tombul, Uzunmusa, Yassı Badem, and Yuvarlak Badem) of hazelnuts are cultivated in Turkey.[2,3] Only seven varieties of hazelnuts (Tombul, Çakıldak, Foşa, Karafındık, Mincane, Palaz, and Sivri) are considered as major commercial varieties.[3] The production of the remaining varieties is less than 10% to the total production in Turkey.

Hazelnut may be consumed as natural (raw) or preferably roasted. The main purpose of roasting is to improve the desirable flavor, color, crispy, and crunchy texture of products.[4−7] As a parallel to this study, we assessed the effects of roasting on taste-active components,[2] oil and fatty acid composition,[3] and flavor characteristics[7] of 18 Turkish hazelnut varieties. It is, therefore, of great interest to assess how the roasting effects the antioxidant status and phenolic profiles of commercial Turkish hazelnut varieties. Little is known about the antioxidant status and phenolic profiles of roasted hazelnuts,[8] despite the fact that the antioxidant activity and phenolic profiles of some natural hazelnut varieties have been reported.[9−13] The objective of this study was to evaluate the effect of roasting on the antioxidant status and phenolic profiles of seven commercial Turkish hazelnut varieties.

MATERIALS AND METHODS

Samples. Seven sun-dried (3 days at ~20−25 °C) native Turkish hazelnut varieties (namely, Çakıldak, Foşa, Karafındık, Mincane, Palaz, Sivri, and Tombul) were procured from the Hazelnut Research Institute in Giresun, Turkey, at the beginning of the harvest season of 2010. All hazelnut varieties (1 kg from each variety) were from the same location/field to make a true comparison. The natural hazelnut samples were kept in shell in a control cabinet (at 5 °C with relative humidity of 65−70%) at the Food Institute (TÜBİTAK Marmara Research Centre, Gebze, Turkey) until they were analyzed. The hazelnuts were shelled before analysis.

Reagents and Standards. All chemical reagents were obtained from Sigma-Aldrich-Fluka Co., Ltd. (Prolab, Istanbul, Turkey), unless otherwise stated.

Roasting of Hazelnuts. The hazelnuts were cracked and then kept at room temperature for 3 h. They were roasted at 140 °C for 30 min with an air velocity of 1 m/s (model CS02-KF Hazelnut Roasting Oven, Ceselsan Machinery, Ltd., Giresun, Turkey). The same temperature and time were applied for all hazelnut varieties, regardless of the kernel size.

Extraction of Phenolic Compounds. The procedure of sample preparation for total phenolics, total antioxidant activity, condensed tannins, and phenolic acids was based on the study by Rosa et al.[14] Hazelnut kernels were finely ground and then defatted by mixing with

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hexane (1:10, w/v, for 3 min, 3 times) in a homogenizer (model DI 25 basic IKA, Staufen, Germany) at ambient temperature. Defatted kernels (5 g) were mixed with 50 mL of 80% acetone, and phenolic compounds were extracted by mixing at 50 °C for 30 min. Afterward, the extract was centrifuged (5000*g* for 2 min at room temperature). The residue was re-extracted twice under the same conditions, and supernatants were combined. Then, the solvent was removed from the combined supernants under vacuum at 40 °C (model Büchi Anniversary Eddition, Zurich, Switzerland), and the remaining water in the concentrated extract was removed by lyophilization for 72 h at −45 °C [Christ Epsilon 2-4 Lyo-Screen-Control (LSC), Osterode am Harz, Germany]. Dried extracts were stored in tightly sealed glass vials at −20 °C.

Determination of the Total Phenolic Content. The total phenolics were determined using Folin− Ciocalteu's phenol reagent. Extracts were dissolved in methanol (3 mg/mL), and the analysis was performed on the diluted samples as mentioned by Rosa et al.[14] The content of total phenolics was calculated on the basis of the standard curve using gallic acid as the standard. The results were expressed as milligrams of gallic acid equivalents per 100 g of sample (mg of GAE/100 g).

Determination of the Oxygen Radical Absorbance Capacity (ORAC). The ORAC values were determined using a microplate reader (FLUOStar Omega, BMG Labtech, Ortenberg, Germany) according to ORAC assay. Extracts were dissolved in methanol (3 mg/mL), and the analysis was performed on the diluted samples as mentioned by Wu et al.[9] ORAC values were calculated using the Trolox and the sample concentration and net area under the fluorescein decay curve (AUC). Data were expressed as micromoles of Trolox equivalents per 100 g of fresh sample (μmol of TE/100 g).

Determination of the Condensed Tannins. The condensed tannins (proanthocyanidins) were assayed calorimetrically (FLUOStar Omega, BMG Labtech, Ortenberg, Germany) according to a vanillin assay. Extracts were dissolved in methanol (3 mg/mL), and the analysis was performed on the diluted samples as mentioned by Rosa et al.[14] The content of condensed tannins was calculated on the basis of the standard curve using catechin as the standard. The results were expressed as milligrams of catechin equivalents per 100 g of fresh sample (mg of CE/100 g).

Extraction, Hydrolysis, Identification, and Quantification of Phenolic Acids. Phenolic acids were assessed according to the high-performance liquid chromatography (HPLC) method by Matilla et al.,[15] with slight modifications. A total of 0.3 g of freeze-dried sample was homogenized in 7 mL of a mixture of methanol, containing 2 g/L butylated hydroxyanisole (BHA) and 10% acetic acid (85:15, v/v). The mixture was sonicated for 30 min and made up to a volume of 10 mL with HPLC-grade water. After mixing, 1 mL was filtered through a Gelman Acrodisc LC13 PVDV 0.45 μm pore size syringe filter (Pall Life Sciences, Ann Arbor, MI) for HPLC analysis of free phenolic acids.

After the samples were taken for analysis of free phenolic acids, 12 mL of HPLC-grade water containing 1% ascorbic acid, 0.415% ethylenediaminetetraacetic acid tetrasodium salt dihydrate (EDTA), and 5 mL of 10 M NaOH was added to a 50 mL test tube, sealed, and stirred overnight (about 16 h) at room temperature using a magnetic stirrer (0.8 cm in length). The solution was then adjusted to pH 2 with concentrated HCl, and the liberated phenolic acids were extracted 3 times with 15 mL of a mixture of cold diethyl ether (DE) and ethyl acetate (EA) 1:1 (v/v), by manually shaking and centrifuging. The organic layers were then combined. After the above alkaline hydrolysis was completed, an acid hydrolysis was performed by adding 2.5 mL of concentrated HCl into the test tube (containing the residue of alkaline hydrolysis) and incubating the tube in a water bath at 85 °C for 30 min. The sample was cooled, and further sample handling was performed in the same manner as after alkaline hydrolysis. The organic layers from the alkaline and acid hydrolyses were combined, evaporated to dryness, dissolved into 2 mL of methanol, filtered, and analyzed for total phenolic acids by HPLC.

Phenolic acids were analyzed using a Shimadzu HPLC system (LC-20AD pump, SPD-M20A DAD detector, SIL-20A HT autosampler, CTO-2OAC column oven, DGU-20A5 degasser, and CMB-20A communications bus module, Shimadzu Corporation, Kyoto, Japan). A total of 10 μL of the sample extracts was automatically injected into a Phenomenex 5u (ODS 2) column (250 mm, 3.20 mm inner diameter, 5 μm particles, Merck, Darmstadt, Germany) at 35 °C. The mobile phase (filtered through a 0.45 μm Millipore filter prior to use) consisting of 50 mM H_3PO_4 (pH 2.5) (solution A)/acetonitrile (solution B) at a total flow rate of 0.7 mL/min was programmed as isocratic elution: 95% A, for 0−5 min; linear gradient from 95 to 85% A, for 5−17 min; linear gradient from 85 to 80% A, for 17−40 min; linear gradient from 80 to 50% A, for 40−60 min; isocratic elution 50% A, for 60−65 min; linear gradient from 50 to 95% A, for 65−67 min; and post-time of 6 min before the next injection. The wavelengths of the diode array detector (DAD) were set at 259 nm for monitoring of protocatechuic acid, 270 nm for gallic acid, 309 nm for *p*-coumaric acid, and 323 nm for caffeic, ferulic, and sinapic acids. Tentatively identified phenolic acids were quantified on the basis of their peak areas and a comparison to a calibration curve obtained with the corresponding standards (caffeic, ferulic, gallic, gentisic, *m*-coumaric, *o*-coumaric, *p*-coumaric, protocatechuic, salicylic, sinapic, and vanillic acids). The results from free and bound hydrolyzates were calculated to represent total phenolic acids and expressed as milligrams of phenolic acids per 100 g of fresh sample.

Statistical Analysis. Results were expressed as the mean ± standard deviation (SD) (n = 3) for each analysis. Differences were estimated by analysis of variance (ANOVA) followed by Tukey's "honest significant difference" test. Differences were considered to be significant at $p \leq 0.05$. All statistical analyses were performed using the SPSS 18.0 version (SPSS, Inc., Chicago, IL).

RESULTS AND DISCUSSION

Total Phenolics. A large variation in total phenolics was observed among natural (ranging from 178 mg of GAE/100 g in Foşa to 727 mg of GAE/100 g in Palaz) and roasted (ranging from 50 mg of GAE/100 g in Tombul to 195 mg of GAE/100 g in Mincane) hazelnut varieties (Table 1). The average loss for total phenolics of the seven roasted hazelnuts was around 66.3%, being lowest in Mincane (42.1%) and highest in Tombul (88.4%). The large variations in the loss of total phenolics among roasted hazelnut varieties were the presence of some skin. For example, not all skin was removed in Mincane even upon roasting. The loss of total phenolics in roasted hazelnuts could be due to the removal of the skin, which contains the majority of phenolics[10,16−18] or thermal

Table 1. Total Phenolic Content (mg of GAE/100 g) of Natural and Roasted Turkish Hazelnut Varieties[a]

hazelnut variety	total phenolics in natural hazelnuts	total phenolics in roasted hazelnuts	loss in roasted hazelnuts (%)
Çakıldak	246 ± 11 a	84 ± 4 a	65.8
Foşa	178 ± 8 b	78 ± 4 a	56.2
Karafındık	411 ± 17 c	157 ± 7 b	61.8
Mincane	337 ± 11 d	195 ± 4 c	42.1
Palaz	727 ± 33 e	148 ± 6 d	79.6
Sivri	486 ± 18 f	143 ± 3 d	70.5
Tombul	432 ± 21 c	50 ± 1 e	88.4

[a]Data are expressed as the mean ± SD (n = 3) on a fresh weight basis. Means ± SD followed by the same letter, within a column of natural and roasted hazelnuts, are not significantly different ($p > 0.05$). Average loss = 66.3%. Moisture content for natural hazelnut varieties: Çakıldak (5.77%), Foşa (5.03%), Karafındık (4.37%), Mincane (4.28%), Palaz (4.03), Sivri (4.38%), and Tombul (4.62%). Moisture content for roasted hazelnut varieties: Çakıldak (1.71%), Foşa (1.92%), Karafındık (0.88%), Mincane (0.83%), Palaz (1.02), Sivri (1.14%), and Tombul (0.90%).

degradation of certain phenolic compounds. To compare the results on fresh weight basis versus dry weight basis, the moisture content of natural and roasted hazelnuts are provided in the *footnote* of Table 1.

Wu et al.[9] measured the total phenolic content of 10 different tree nuts. Pecan had the highest total phenolics (2016 mg of GAE/100 g), whereas pine nut had the lowest total phenolics (68 mg of GAE/100 g). Hazelnut contained the fourth largest content of total phenolics, after pecan, walnut, and pistachio, overall at 835 mg of GAE/100 g (range between 430 and 1169 mg of GAE/100 g). The present values for natural hazelnuts are within the range of United States Department of Agriculture (USDA) values.[19] This may be due to the hazelnut varieties analyzed and environmental differences, such as harvesting year and climate. Recently, Schmitter et al.[8] investigated the potential effect of skin removal and roasting on individual and total phenolic content and antioxidantive potential of six hazelnut cultivars. They found that the content of total phenolics and antioxidant potential decreased when skin was removed. Roasting had a significant negative effect on individual phenolics but not the total phenolic content and antioxidant potential of kernels. From both current and Schmitter et al. studies, there is clear evidence that the majority of phenolics and antioxidants are located in the skin rather than the kernel.

ORAC. The ORAC values of natural hazelnuts showed significantly higher ($p < 0.05$) values compared to their roasted counterparts (Table 2). Significant differences ($p < 0.05$) existed within most varieties in both natural and roasted hazelnuts. The ORAC values in natural hazelnut varieties ranged from 4020 μmol of TE/100 g in Foşa to 11422 μmol of TE/100 g in Palaz, whereas the values for roasted hazelnuts ranged from 2217 μmol of TE/100 g in Tombul to 6762 μmol of TE/100 g in Mincane. Wu et al.[9] evaluated ORAC values of 10 different types of nuts. Considering all of the studied nuts, hazelnut had the third highest ORAC value (9645 μmol of TE/100 g), with pecan and walnut having the highest. The ORAC values of natural hazelnuts are within the range of their results.

Table 2. ORAC Values (μmol of TE/100 g) of Natural and Roasted Turkish Hazelnut Varieties[a]

hazelnut variety	ORAC values in natural hazelnuts	ORAC values in roasted hazelnuts	loss in roasted hazelnuts (%)
Çakıldak	7323 ± 269 a	5470 ± 199 a	25.3
Foşa	4020 ± 76 b	2846 ± 156 b	29.2
Karafındık	10457 ± 324 c	4486 ± 140 c	57.1
Mincane	7791 ± 298 ad	6762 ± 241 d	13.2
Palaz	11422 ± 597 c	3237 ± 125 e	71.7
Sivri	8184 ± 270 d	5784 ± 283 a	29.3
Tombul	6473 ± 263 e	2217 ± 76 f	65.7

[a]Data are expressed as the mean ± SD ($n = 3$) on a fresh weight basis. Means ± SD followed by the same letter, within a column of natural and roasted hazelnuts, are not significantly different ($p > 0.05$). Average loss = 41.6%.

The higher ORAC value in Mincane compared to other roasted hazelnuts could be due to the presence of polyphenolic compounds in the skin, such as condensed tannins, because they possess powerful antioxidant activity. A similar finding was also reported by Contini et al.,[20] who found that the extract from the skin of whole roasted hazelnut manifested the strongest activity, total phenols, and total tannins.

Hazelnut varieties retained an average of 58% of their ORAC values upon roasting. In other words, the average loss of ORAC values in roasted hazelnuts was 42%. This result is similar to the results by Arcan and Yemenicioğlu[21] and Schmitzer et al.[8] They reported a considerable reduction in antioxidant activity because of the removal of the skin in hazelnut. However, no statistical differences ($p > 0.05$) were observed among unroasted and roasted hazelnuts without skin, suggesting that thermal processing had a minor impact on the antioxidant activity of the hazelnut kernel. Hazelnut skin has been reported to possess strong antioxidant activity.[10,16,18] For example, in walnut, most of the polyphenolic compounds are remarkably located in the skin and less than 10% is retained when the walnut skin is removed.[22] This trend is the same for other tree nuts.[22,23] The ORAC values obtained in the present study showed the same trend as total phenolics and condensed tannins.

Chandrasekara and Shahidi[24] studied the effect of roasting on the content of phenolic compounds and antioxidant properties of cashew nut, kernel, and testa (skin). Cashew skin afforded a higher extract yield, total phenolics, proanthocyanidins, and various antioxidant activities [such as 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging capacity, hydroxyl radical scavenging capacity, ORAC, and Trolox equivalent antioxidant activity (TEAC)] in both soluble and bound fractions compared to that in whole cashew nut and kernel. The high-temperature-treated (130 °C for 33 min) cashew nut and skin showed a higher phenolic content and antioxidant activity than the low-temperature-treated (70 °C for 6 h) samples. The findings of their results suggest the notion that thermal processing enhances the antioxidant value of cashew kernels. Despite the fact that roasting (140 °C for 30 min) may also increase the total phenolic content and antioxidant activity of roasted hazelnuts, removal of skin in the roasted form had a significant impact on the loss of antioxidant phenolics,[24] because hazelnut skin possesses strong antioxidant activity and is a rich source of phenolic compounds.[10,16,18]

Condensed Tannins. In addition to their taste-active properties, tannins have been reported to possess antioxidant and antiradical properties.[25,26] The content of condensed tannins, expressed as milligrams of catechin equivalents per 100 g fresh sample, varied quite markedly among natural hazelnut varieties, from a low of 941 for Foşa to a high of 3163 for Palaz. A significant loss (~75.2%) was observed ($p < 0.05$) when hazelnuts were roasted (Table 3). This reveals that most of the condensed tannins are located in the skin of hazelnut. Several

Table 3. Condensed Tannin Content (mg of CE/100 g) of Natural and Roasted Turkish Hazelnut Varieties[a]

hazelnut variety	condensed tannins in natural hazelnuts	condensed tannins in roasted hazelnuts	loss in roasted hazelnuts (%)
Çakıldak	1017 ± 35 a	49 ± 2 a	95.1
Foşa	941 ± 35 a	52 ± 1 a	94.4
Karafındık	1487 ± 73 b	301 ± 11 b	79.7
Mincane	1186 ± 51 c	824 ± 29 c	30.5
Palaz	3163 ± 56 d	790 ± 38 c	75.0
Sivri	1826 ± 71 e	563 ± 30 d	69.2
Tombul	1476 ± 80 b	256 ± 13 b	82.7

[a]Data are expressed as the mean ± SD ($n = 3$) on a fresh weight basis. Means ± SD followed by the same letter, within a column of natural and roasted hazelnuts, are not significantly different ($p > 0.05$). Average loss = 75.2%.

Table 4. Contents of Free Phenolic Acids (mg/100 g) in Natural and Roasted Turkish Hazelnut Varieties[a]

	gallic acid		protocatechuic acid	
hazelnut variety	natural	roasted	natural	roasted
Çakıldak	1.29 ± 0.02 a	0.00 ± 0.00 a	0.27 ± 0.02 a	nd
Foşa	0.85 ± 0.04 b	0.35 ± 0.03 b	0.73 ± 0.02 b	0.47 ± 0.04 a
Karafındık	1.16 ± 0.03 c	0.73 ± 0.04 c	0.49 ± 0.00 c	0.46 ± 0.03 a
Mincane	0.52 ± 0.02 d	0.42 ± 0.02 d	1.17 ± 0.06 d	0.76 ± 0.01 b
Palaz	0.18 ± 0.01 e	0.16 ± 0.00 e	0.38 ± 0.02 e	nd
Sivri	0.14 ± 0.00 e	0.08 ± 0.02 f	0.26 ± 0.01 a	nd
Tombul	0.13 ± 0.00 e	0.00 ± 0.00 a	0.15 ± 0.01 f	nd
average loss (%)		52.7		68.1

[a]Data are expressed as the mean ± SD (n = 3) on a fresh weight basis. Means ± SD followed by the same letter, within a column of natural and roasted hazelnuts, are not significantly different (p > 0.05). nd = not detected.

Table 5. Contents of Bound Phenolic Acids (mg/100 g) in Natural and Roasted Turkish Hazelnut Varieties[a]

	gallic acid		protocatechuic acid		p-coumaric acid		ferulic + sinapic acids	
hazelnut variety	natural	roasted	natural	roasted	natural	roasted	natural	roasted
Çakıldak	1.70 ± 0.03 a	0.23 ± 0.01 a	3.99 ± 0.05 a	2.84 ± 0.04 a	0.39 ± 0.03 a	0.18 ± 0.00 a	0.54 ± 0.03 a	0.41 ± 0.01 a
Foşa	1.85 ± 0.03 b	0.57 ± 0.03 b	4.06 ± 0.05 a	2.96 ± 0.01 a	0.24 ± 0.01 b	0.17 ± 0.00 a	0.75 ± 0.02 b	0.55 ± 0.01 b
Karafındık	3.32 ± 0.04 c	1.03 ± 0.01 c	3.27 ± 0.02 b	3.12 ± 0.07 b	0.23 ± 0.02 b	0.07 ± 0.01 b	0.54 ± 0.02 a	0.41 ± 0.02 a
Mincane	3.67 ± 0.05 d	1.63 ± 0.02 d	7.83 ± 0.02 c	7.43 ± 0.06 c	0.31 ± 0.00 c	0.14 ± 0.01 c	0.81 ± 0.02 bc	0.71 ± 0.01 c
Palaz	4.11 ± 0.02 e	0.60 ± 0.01 b	3.56 ± 0.03 d	2.60 ± 0.02 d	0.15 ± 0.00 d	0.12 ± 0.01 d	0.60 ± 0.04 a	0.33 ± 0.02 d
Sivri	3.93 ± 0.02 f	1.04 ± 0.05 c	3.17 ± 0.05 b	3.13 ± 0.03 b	0.47 ± 0.03 e	0.12 ± 0.00 cd	0.87 ± 0.03 c	0.62 ± 0.03 e
Tombul	2.31 ± 0.07 g	0.25 ± 0.00 a	2.54 ± 0.03 e	2.23 ± 0.02 e	0.33 ± 0.02 c	0.08 ± 0.00 b	0.75 ± 0.03 b	0.44 ± 0.01 a
average loss (%)		75.5		15.2		54.0		28.9

[a]Data are expressed as the mean ± SD (n = 3) on a fresh weight basis. Means ± SD followed by the same letter, within a column of natural and roasted hazelnuts, are not significantly different (p > 0.05). Ferulic + sinapic acids = coeluted peak.

Table 6. Contents of Free, Bound, and Total Phenolic Acids (mg/100 g) in Natural and Roasted Turkish Hazelnut Varieties[a]

	natural			roasted			
hazelnut variety	free phenolic acids	bound phenolic acids	total phenolic acids	free phenolic acids	bound phenolic acids	total phenolic acids	loss in roasted hazelnuts (%)
Çakıldak	1.56 ± 0.02 a	6.62 ± 0.10 a	8.18 ± 0.11 a	0.05 ± 0.01 a	3.70 ± 0.03 a	3.75 ± 0.03 a	54.2
Foşa	1.58 ± 0.05 ab	6.89 ± 0.06 b	8.47 ± 0.02 b	0.86 ± 0.01 b	4.29 ± 0.04 b	5.15 ± 0.05 b	39.2
Karafındık	1.66 ± 0.03 bc	7.36 ± 0.04 c	9.02 ± 0.07 c	1.22 ± 0.06 c	4.68 ± 0.10 c	5.90 ± 0.08 c	34.6
Mincane	1.69 ± 0.05 c	12.62 ± 0.05 d	14.31 ± 0.08 d	1.27 ± 0.02 c	9.95 ± 0.08 d	11.22 ± 0.09 d	21.6
Palaz	0.56 ± 0.01 d	8.42 ± 0.06 e	8.98 ± 0.05 c	0.21 ± 0.02 d	3.70 ± 0.05 a	3.91 ± 0.03 e	56.5
Sivri	0.40 ± 0.01 e	8.45 ± 0.05 e	8.85 ± 0.05 c	0.15 ± 0.00 d	4.97 ± 0.04 e	5.12 ± 0.05 b	42.1
Tombul	0.28 ± 0.00 f	5.93 ± 0.02 f	6.21 ± 0.02 e	0.04 ± 0.01 a	3.03 ± 0.04 f	3.07 ± 0.04 f	50.6

[a]Data are expressed as the mean ± SD (n = 3) on a fresh weight basis. Means ± SD followed by the same letter, within a column of natural and roasted hazelnuts, are not significantly different (p > 0.05). Average loss = 42.7%.

studies have found that phenolic compounds, including condensed tannins, are mainly located in the skin of the nut.[16,20,26−28] Hazelnut has been reported to contain the highest amount of condensed tannins among seven tree nuts (hazelnut, almond, cashew, chestnut, pecan, pistachio, and walnut).[29,30] Among almond, hazelnut, and walnut crude extracts, hazelnut crude extract was found to have the highest content of condensed tannins (using 80%, v/v, acetone) using the vanillin/HCl method.[31] Meanwhile, the highest amount of total tannins was detected in the hazelnut byproduct extracts with the highest amount of total phenols.[20]

Phenolic Acids. Free and bound phenolic acids were determined in seven varieties of natural and roasted hazelnuts (Tables 4−6). A total of five phenolic acids were tentatively identified in both natural and roasted hazelnuts, two of which were a hydroxylated derivative of benzoic acid (gallic and protocatechuic acids) and three of which were cinnamic acid derivatives (p-coumaric, ferulic, and sinapic acids). In addition, two phenolic acids (gallic and protocatechuic acids) in free form (Table 4) and five phenolic acids (gallic, protocatechuic, p-coumaric, and ferulic + sinapic acids) in bound form (Table 5) were detected.

Phenolic acids were mainly found in the bound form. Gallic, protocatechuic, p-coumaric, and ferulic + sinapic acids were present in all hazelnut varieties, albeit to different extents, and the first two were dominant (Table 5). The content of free and bound phenolic acids varied considerably among both natural and roasted hazelnut samples (Tables 4 and 5). Mincane had the highest amount of free and bound phenolic acids, whereas Tombul had the lowest (Table 6). Significant differences exist (p < 0.05) between natural and roasted hazelnut varieties. The content of total phenolic acids in natural hazelnuts ranged from 6.21 mg/100 g in Tombul to 14.31 mg/100 g in Mincane. Their corresponding values for roasted hazelnuts ranged from

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3.07 mg/100 g in Tombul to 11.22 mg/100 g in Mincane. The average loss of total phenolic acids was 42.7% because of skin removal after roasting. Several factors may affect the phenolic acid contents upon roasting, such as the content of phenolic acids in the skin, their thermal decomposition, and eventually their liberation from esters, glucosides, and bound forms. We did not control these processes, but we believe that the broad range of the phenolic acids lost in roasted hazelnuts could be caused by different contents of phenolic acids in the skin.

Recently, Schimitzer et al.[8] identified two hydroxybenzoic acid derivatives (gallic and protocatechuic acids) in natural hazelnut, natural hazelnut without skin, and roasted hazelnut. The highest content of protocatechuic acid was detected in natural hazelnut for all analyzed varieties and was decreased from 42 to as much as 91% when skin was removed. Roasting had an ambiguous effect on the content of protoctechuic acid compared to natural hazelnut without skin. Our present study was in good agreement with their findings.

Shahidi et al.[10] compared phenolic acids of hazelnut kernel and its byproducts (skin, hard shell, green leafy cover, and leaf) and found that skin contained approximately 1.4-fold greater phenolic acids than that of the hazelnut kernel. The order of total phenolic acid concentration was as follows: hazelnut hard shell > hazelnut green leafy cover > hazelnut tree leaf > hazelnut skin > hazelnut kernel. However, the dominance of each acid in the products depended upon its location in the samples examined. Among the identified phenolic acids (gallic, caffeic, *p*-coumaric, ferulic, and sinapic acids), *p*-coumaric acid was the most abundant in hazelnut kernel, hazelnut green leafy cover, and hazelnut tree leaf, whereas gallic acid was the most abundant in hazelnut skin and hazelnut hard shell, possibly implying the presence and perhaps the dominance of tannins in the latter samples.[10] Recently, Del Rio et al.[18] identified four phenolic acids in hazelnut skins, namely, gallic, protoctechuic, syringic, and coumaric acids. Protoctechuic acid has also been reported to be the predominant phenolic acid in hazelnut skin.[32]

The present work suggests that roasting has a significant effect on the loss of total phenolics, ORAC values, condensed tannins, and free and bound phenolic acids because of the removal of the brown skin. It is suggested to consume natural hazelnut with its brown skin to obtain the benefit from natural functional properties. Among roasted hazelnuts, Mincane had the highest content of total phenolics, ORAC values, condensed tannins, and total phenolic acids. The reason for this could be explained by the fact that some skin remained in roasted Mincane even upon roasting. In all other varieties, the skin was removed as a result of roasting. To investigate the effect of thermal processing instead of skin removal, further research is required to observe the effects of roasting on the antioxidant status and phenolic profiles of hazelnut with or without skin.

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