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Volatile Compounds and Fatty Acid Composition of Crude and Refined Hazelnut Oils

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ABSTRACT: The volatile compounds, as well as fatty acid composition of crude and refined hazelnut oils, which are produced by different brands in Turkey, were analyzed by GC/MS, using a solid phase microextraction and GC/FID. Free fatty acid and peroxide value of samples were also determined. In crude hazelnut oils, there were significant differences between brands, in terms of propanoic acid, hexanoic acid, 1-octanol, heptanal, octanal, nonanal, cyclopentane and heptane. In contrast, only a few volatile compounds were determined in refined oil samples. In refined samples, major differences have been detected in terms of nonanal, trans-2-decenal and 2-octyl furan. The refining process usually decreased the amount and counts of volatile compounds. The industrial refining of the oils did not cause any significant changes in the fatty acid composition of the samples. However, the refining process caused a decrease in the free fatty acid content and the peroxide value of hazelnut oils.

Keywords: Fatty acid composition, Hazelnut oil, Volatile compound

Ham ve Rafine Fındık Yağlarının Uçucu Bileşikleri ve Yağ Asidi Kompozisyonu

ÖZ: Türkiye'deki farklı firmalar tarafından üretilen ham ve rafine edilmiş fındık yağlarının yağ asidi bileşiminin yanı sıra uçucu bileşikleri katı faz mikro ekstraksiyon kullanılarak GC/MS ve GC/FID ile analiz edilmiştir. Örneklerin serbest yağ asidi içeriği ve peroksit değerleri de belirlenmiştir. Ham fındık yağlarında, firmalar arasında propanoik asit, heksanoik asit, 1-oktanol, heptanal, oktanal, nonanal, siklopentan ve heptan açısından önemli farklılıklar olmuştur. Buna karşılık, rafine yağ örneklerinde sadece birkaç uçucu bileşik belirlenmiştir. Rafine örneklerde, nonanal, trans-2-dekenal ve 2-oktil furan açısından önemli farklılıklar tespit edilmiştir. Rafinasyon işlemi genellikle uçucu bileşiklerin miktarını ve sayısını azaltmıştır. Yağların endüstriyel rafinasyonu, örneklerin yağ asidi bileşiminde önemli bir değişikliğe neden olmamıştır. Bununla birlikte, rafinasyon işlemi fındık yağlarının serbest yağ asidi içeriği ve peroksit değerinde bir azalmaya neden olmuştur.

Anahtar kelimeler: Yağ asidi kompozisyonu, fındık yağı, uçucu bileşikler

INTRODUCTION

Hazelnut is mainly produced in Turkey, Italy, Spain and the USA. 675000 tones of hazelnut were produced in Turkey in 2017, which approximately makes up 70% of the world's hazelnut production (Anonymous, 2017). Hazelnut is considered an excellent source due to its nutritional value, as well as fatty acid composition (Özdemir and Akinci 2004; Crews *et al.,* 2005; Karabulut *et al.,* 2005). Besides, hazelnut oil is also a good source of phytonutrients and natural antioxidants such as alpha-tocopherol (Alasalvar *et al.,* 2003; Bacchetta *et al.,* 2013). Another important component in hazelnut oil is *sterol*. In sterol-based hazelnut oils, β-sitosterol is a major component followed by campesterol, Δ5-avenasterol and stigmasterol (Parcerisa *et al.,* 1998). The total content of sterols in crude and refined hazelnut oils ranges from 1057 ppm to 1832 ppm (Parcerisa *et al.,* 1998; Alasalvar *et al.,* 2003; Benitez-Sanchez *et al.,* 2003; Bada *et al.,* 2004; Crews *et al.,* 2005).

Furthermore, hazelnut oil is used for culinary purposes, especially as salad oil due to having high concentrations of oleic acid and desirable taste. Additionally, hazelnut oil is also used in cosmetics as a skin moisturizer (Bail *et al.,* 2009). The nutritional and sensory values of hazelnut oil depend on the geographical origin, hazelnut variety and the extraction process (Parcerisa *et al.,* 1993, 1994; Benitez-Sanchez *et al.,* 2003). In addition, the fatty acid composition of hazelnut oil is very similar to that of olive oil (Bacchetta *et al.,* 2013). The percentage of oleic acid found in crude and refined hazelnut oils varies between 72.8% and 83.5%, while the linoleic, linolenic and palmitic acids change from 7.6% to 16.6%, 0.1% to 0.13%, 4.4% to 8.3%, respectively (Parcerisa *et al.,* 1998; Özdemir *et al.,* 2001; Alasalvar *et al.,* 2003; Benitez-Sanchez *et al.,* 2003). According to the Turkish Food Codex Communiqué, hazelnut oil must contain 71-91% of oleic acid, 5.70–22.20% of linoleic acid and 4.32–8.89% of palmitic acid (Anonymous, 2012).

The characteristic flavor of hazelnut oil can be affected by roasting prior to the pressing stage. Hazelnut oil is marketed commercially in different forms: crude products from roasted or unroasted nuts, refined oils from unroasted nuts, or a mixture of both (Crews *et al.,* 2005). Several studies have been conducted on fatty acid composition along with some other properties of hazelnut oils (Bernardo-Gil *et al.,* 2002; Benitez-Sanchez *et al.,* 2003; Crews *et al.,* 2005; Azadmard-Demirchi and Dutta 2007; Miraliakbari and Shahidi 2008). However, there is very little information on the volatile profile of hazelnut oil (Caja *et al.,* 2000; Mildner-Szkudlarz and Jelen 2008; Bail *et al.,* 2009). The purpose of this study was to determinate the volatile compounds, fatty acid composition and other qualitative characteristics of crude and refined hazelnut oils.

MATERIALS AND METHODS

Materials

In research, crude (unrefined) and refined oil (including degumming, neutralizing, bleaching, winterizing and deodorizing stages) samples were taken from 5 different brands (A, B, C, D, E) as 15 crude and 15 refined, including 3 crude and 3 refined oil sample from each brand. Oil samples were stored in brown glass bottle at -20 °C until analyzed.

Free fatty acid content and peroxide value

Free fatty acid content and peroxide value of samples were determined according to the official methods (AOCS, 1998 a,b) described by American Oil Chemist's Society.

Fatty acid composition

Fatty acid methyl esters were prepared from hazelnut oil according to the method described by (Metcalfe and Schmitz, 1961) and determined by gas chromatography (GC, Agilent Technologies 6890N) with FID dedector. GC system was equipped with a capillary column (DB23, 60 m×250 μm×0.15 μm). The oven temperature was increased from 100 to 200 °C with rate of 5 °C min^{-1} and from 200 to 250 °C with a rate of 4 °C min^{-1}. The injection block and dedector temperatures were 250 and 280 °C, respectively. Helium was used as a carrier gas with a 1.2 mL min^{-1} flow rate.

Volatile composition

The volatile compounds of hazelnut oils were extracted by Solid Phase Microextraction (SPME) and analyzed by gas chromatography–mass spectrometry (GC/MS) according to (Cavalli *et al.,* 2004). 50/30 μm divinylbenzene/ carboxen/ polydimethylsiloxane (DVB/CAR/PDMS) fiber was used for the extraction of the volatile compounds. 20 g of hazelnut oil sample were placed into a 40 mL SPME vial (Supelco, Bellefonte, PA, USA) closed with a PTFE-faced silicone septum (Supelco, Bellefonte, PA, USA). The vial was placed in a thermo block (Supelco, Bellefonte, PA, USA) and waited for 90 minutes at 45 °C with magnetic stirring. The fiber was thermally desorbed into the injection port of the gas chromatography for 6 minutes. The enjector was set at 250 °C with splitless mode. The GC analysis were carried out with a mass selective dedector (MS, Agilent Technologies 5973). The gas chromatography was equipped with HP-1 (Agilent, 50m, 0.2 mm i.d., 0.55μm film) column. Helium was used as a carrier gas with a 1 ml/min flow rate. Oven temperature programmes were the following; held for 1 min at 45 °C, from 45°C to 230°C with a rate of 3°C min^{-1}, held for 5 min at 230 °C. Dedector and GC-MS interface temperatures were 250 and 280 °C, respectively. Mass spectra were obtained by electron impact at 70 ev. Data was acquired across the range 30-400 amu. The compounds were determined by comparing the results with mass spectra from a database developed by NIST and WILEY or standards molecules (for calculating Kovats Index, Supelco 44585-U, Bellefonte PA, USA).

Statistical analysis

The research was designed according to randomized complete block design. Sampling was conducted in 3 different times from 5 different brands. Results from cured and refined hazelnut oils were subjected to statistical analyses seperately. Differences between means were evaluated by Duncan's multiple range test using the IBM SPSS Statistics (Version 20) software (SPSS, Inc., Chicago, USA).

RESULTS AND DISCUSSION

Free fatty acid content and peroxide value

The results of the free fatty acid content of crude and refined hazelnut oils were given in Table 1. The free fatty acid content ranged between 0.87–1.10% in crude hazelnut oil samples (Table 1). In contrast, a high percentage of 2.096% of free fatty acid content in crude hazelnut oil was found by Karabulut *et al.,* (2005). In crude oils, free fatty acid content is an important indicator determining product quality. This value provides information about storage conditions prior to processing. Free fatty acid content shows an increase with lipase activity in unsuitable conditions (Akoh and Min, 2002).

In refined hazelnut oil samples, free fatty acid content ranged between 0.10–0.22%. These values were in accordance with the Turkish Food Codex Communiqué (Anonymous, 2012). The lowest free fatty acid content was determined in *Brand A* for crude oils and *Brand E* for refined oils. The decrease in free fatty acid content is thought to be caused by the neutralization process carried out during refining (Akoh and Min, 2002; Bhosle and Subramanian, 2005). Similar results were also observed in another study, where free fatty acid content of crude oil, neutralized oil and final product were found to be 2.096%, 0.087% and 0.051%, respectively (Karabulut *et al.,* 2005).

Table 1. The free fatty acid content and peroxide value of crude and refined hazelnut oils from different brands

	Brand	Free fatty acid (oleic acid%)	Peroxide value (meq O_2 kg^{-1} oil)
CRUDE	A_C	0.87±0.01a	10.97±0.06e
	B_C	0.92±0.01b	9.20±0.05b
	C_C	1.08±0.01d	9.90±0.12c
	D_C	1.05±0.01c	10.46±0.15d
	E_C	1.10±0.01e	8.13±0.13a
REFINED	A_R	0.16±0.01d	5.61±0.06c
	B_R	0.13±0.01b	6.55±0.06d
	C_R	0.15±0.01c	4.66±0.05a
	D_R	0.22±0.01e	8.86±0.11e
	E_R	0.10±0.01a	5.18±0.10b

Means ± SD, a-e: Any two means in the same column having the same letters in the same section are not significantly different ($P < 0.05$), SD; standard deviation

The peroxide values of both crude and refined hazelnut oil varies between 8.13 and 10.97 meq O_2 kg^{-1} oil, 4.66 and 8.86 meq O_2 kg^{-1} oil, respectively (Table 1). The peroxide value, which is an important quality criterion, is an indicator of peroxides resulting from auto-oxidation (Akoh and Min, 2002; Anonymous, 2006). Moreover, it was found that Brand E in crude oils and Brand C in refined oils showed the lowest average peroxide value. Also, Caponio *et al.*, (2011) and Kesen *et al.*, (2016) indicated that refining process causes a decrease in peroxide value.

According to Turkish standards, there must be a maximum of 10 meqO_2 kg^{-1} oil peroxide value in refined oils. All results in refined oils were in accordance with these standards.

Fatty acid composition

Oleic acid was the major fatty acid in the fatty acid composition of both crude and refined hazelnut oils, ranging between 78.97–to 84.79% in crude oils, and 75.83%–84.86% in refined ones (Table 2, 3). According to Turkish standards, the ratio of oleic acid can ranged between 71% and 91%. Among brands, significant differences were observed in both crude and refined oils, according to statistical analyses. In crude hazelnut oils, the differences among *Brands B, C* and *D* were not significant. In refined hazelnut oils, the lowest linoleic acid ratio (75.83±2.5%) was detected in samples taken from Brand E. This brand showed the highest linolenic acid content (18.70±1.83%).

Table 2. Fatty acid composition of crude hazelnut oils

Fatty Acid	Brand				
	A_C	B_C	C_C	D_C	E_C
$C_{14:0}$	0.02±0.02a	0.02±0.02a	0.03±0.01a	0.02±0.00a	0.02±0.02a
$C_{16:0}$	4.16±0.80a	3.62±1.78a	5.09±0.10a	4.69±0.19a	4.81±0.27a
$C_{16:1}$	0.07±0.03a	0.04±0.01a	0.08±0.01a	0.07±0.01a	0.10±0.03a
$C_{18:1n9c}$	78.97±0.49a	84.07±1.65b	84.79±0.30b	83.39±0.29b	79.73±0.45a
$C_{18:2n6c}$	15.55±0.98c	11.63±0.62b	9.56±0.40a	11.26±0.09b	14.69±0.19c
$C_{20:0}$	0.06±0.07a	0.05±0.04a	0.09±0.00a	0.10±0.00a	0.11±0.08a
$C_{18:3n6}$	0.05±0.04a	0.09±0.05a	0.09±0.02a	0.09±0.01a	0.09±0.01a
$C_{20:1}$	0.13±0.05a	0.17±0.01a	0.12±0.03a	0.15±0.01a	0.15±0.02a
$C_{18:3n3}$	0.04±0.05a	0.02±0.01a	0.00±0.01a	0.03±0.02a	0.03±0.02a
$C_{20:3n6}$	0.02±0.02a	0.02±0.01a	0.01±0.01a	0.00±0.00a	0.02±0.02a
$C_{20:3n3}$	0.01±0.01a	0.01±0.01a	0.01±0.00a	0.01±0.01a	0.02±0.00a
$C_{23:0}$	0.01±0.00ab	0.04±0.02c	0.01±0.00a	0.03±0.02bc	0.03±0.00bc
$C_{24:0}$	0.00±0.00a	0.01±0.00a	0.03±0.00b	0.03±0.00b	0.03±0.01b
Σ SFA	4.25±0.83a	3.73±1.77a	5.25±0.09a	4.89±0.18a	5.01±0.38a
Σ USFA	94.78±0.40a	96.05±1.83a	94.65±0.11a	94.99±0.17a	94.84±0.29a
Σ PUFA	15.67±0.92c	11.76±0.67b	9.67±0.38a	11.39±0.11b	14.86±0.18c
Σ MUFA	79.11±0.52a	84.28±1.65b	84.98±0.33b	83.60±0.28b	79.98±0.45a

Means ± SD, a-e: Any two means in the same column having the same letters in the same section are not significantly different ($P < 0.05$), SD; standard deviation

Table 3. Fatty acid composition of refined hazelnut oils

Fatty Acid	**Brand**				
	A_C	**B_C**	**C_C**	**D_C**	**E_C**
$C_{14:0}$	0.01±0.02a	0.03±0.00a	0.01±0.01a	0.02±0.02a	0.02±0.02a
$C_{16:0}$	5.06±0.03a	2.44±2.21a	4.17±1.53a	3.47±1.34a	4.75±0.61a
$C_{16:1}$	0.18±0.02a	0.09±0.06a	0.11±0.03a	0.11±0.05a	0.11±0.06a
$C_{18:1n9c}$	82.19±0.13b	84.86±3.97b	81.76±2.08b	81,49±2,74b	75,83±2,50a
$C_{18:2n6c}$	11.99±0.18a	11.95±1.91a	13.55±0.60a	13,42±1,11a	18,70±1,83b
$C_{20:0}$	0.10±0.01a	0.09±0.06a	0.11±0.01a	0,14±0,00a	0,13±0,10a
$C_{18:3n6}$	0.06±0.02a	0.11±0.04a	0.07±0.04a	0,04±0,04a	0,08±0,06a
$C_{20:1}$	0.13±0.01a	0.10±0.07a	0.13±0.04a	0,13±0,01a	0,15±0,06a
$C_{18:3n3}$	0.02±0.03a	0.02±0.01a	0.01±0.02a	0,02±0,02a	0,02±0,01a
$C_{20:3n6}$	0.04±0.02a	0.02±0.01a	0.01±0.02a	0,02±0,02a	0,02±0,02a
$C_{20:3n3}$	0.00±0.00a	0.02±0.02a	0.00±0.00a	0,01±0,01a	0,01±0,00a
$C_{23:0}$	0.01±0.01a	0.02±0.01ab	0.00±0.01a	0,04±0,02c	0,01±0,00a
$C_{24:0}$	0.05±0.04a	0.01±0.01a	0.02±0.01a	0,02±0,00a	0,01±0,01a
Σ SFA	5.24±0.04a	2.60±2.25a	4.30±1.53a	3,69±1,34a	4,93±0,71a
Σ USFA	94.62±0.13a	97.16±2.17a	95.62±1.54a	95,24±1,96a	94,92±0,71a
Σ PUFA	12.12±0.19a	12.11±1.87a	13.63±0.59a	13,50±1,14a	18,84±1,80b
Σ MUFA	82.50±0.12b	85.05±3.89b	81.99±2.10b	81,73±2,70b	76,08±2,50a

Means ± SD, a-e: Any two means in the same column having the same letters in the same section are not significantly different ($P < 0.05$), SD; standard deviation.

There are significant differences between PUFA contents of brands, ranging from 9.67 %–15.67% in crude oils, and 12.11%–18.84% in refined ones. In addition, the unsaturated fatty acid ratio in total fatty acid composition ranged between 94.65%–96.05% in crude oils and 94.62%–97.16% in refined ones, with a slight difference. Saturated fatty acids were minor compounds in crude and refined hazelnut fatty acids, ranging from 3.73%–5.25% in crude oils and 2.60%–5.24% in refined ones. Similar results in hazelnut oils were found by Alasalvar *et al.* (2003), Parcerisa *et al.* (1998) and Benitez-Sanchez *et al.* (2003). In the present study, there are no statistically differences between brands in terms of saturated fatty acids in crude and refined oils as well (Table 2, 3). As shown in Table 3 and Table 4, the industrial refining of the oils did not cause any considerable changes in the fatty acid composition of hazelnut oils. For instance, oleic acid, which is a major fatty acid in hazelnut oils, ranged from 78.97%–84.79% in crude, and 75.83%–84.86% in refined ones. Similar results were also confirmed for other fatty acids.

Volatile composition

The volatile profile of crude hazelnut oils was provided in Table 4. A total of twenty-six volatile compounds from six different chemical groups, including aldehydes, ketones, acids, aromatic hydrocarbons, aliphatic hydrocarbons and alcohols were identified in the given samples. There are great differences between brands in terms of propanoic acid, hexanoic acid, 1-octanol, heptanal, octanal, nonanal, cyclopentane and heptane. Propanoic acid was only determined in Brand C. Within acids, acetic acid was generally found to be of the highest amounts. However, there were no substantial differences between brands. Hexanal, on the other hand, was detected as the major aldehyde in all brands. In aliphatic hydrocarbons, hexane was usually considered as a major compound. However, there were no major differences between brands in terms of this particular compound.

Table 4. Volatile compounds of crude hazelnut oils

		Brand				
KI	**Compound**	**A_C**	**B_C**	**C_C**	**D_C**	**E_C**
	Acids					
570	Acetic acid	11,13±9,18a	nd	2,60±1,82a	3,98±3,93a	0,25±0,43a
887	Propanoic acid	nd	nd	0,50±0,45b	nd	nd
950	Hexanoic acid	1,70±1,58a	0,25±0,22a	0,44±0,58a	3,22±0,51b	1,49±0,23a
1142	Octanoic acid	0,44±0,29a	nd	0,20±0,20a	1,05±1,22a	0,20±0,07a
>1500	1,2-benzenedicarboxylic acid	1,19±1,30a	0,14±0,12a	2,60±1,45a	1,31±0,39a	0,54±0,50a
	Alcohols					
848	1-hexanol	1,17±2,03a	0,13±0,11a	0,13±0,22a	0,32±0,55a	0,46±0,41a
1052	1-Octanol	0,70±0,37b	0,08±0,07a	0,46±0,07ab	0,86±0,34b	0,52±0,16ab
	Ketones					
1071	2-nonanone	0,14±0,24a	0,02±0,03a	0,10±0,18a	0,20±0,18a	0,07±0,13a
1211	3-penten-2-one	0,20±0,09a	nd	0,30±0,15a	0,18±0,16a	0,19±0,06a
	Aldehydes					
773	Hexanal	4,99±4,69a	0,46±0,20a	1,33±0,19a	1,80±1,59a	1,49±0,26a
877	Heptanal	0,85±0,43b	nd	0,42±0,22ab	0,40±0,35ab	0,69±0,29b
929	Trans-2- heptanal	0,15±0,26a	nd	0,36±0,35a	0,57±0,49a	0,40±0,38a
980	Octanal	1,26±0,36cd	0,10±0,09a	0,73±0,30b	1,38±0,11d	0,92±0,19bc
1080	Nonanal	1,12±0,33b	0,10±0,09a	1,09±0,20b	1,49±0,43b	0,96±0,36b
1232	2-Decenal,(Z)	0,47±0,56a	0,10±0,10a	0,90±0,79a	1,03±1,38a	0,89±0,39a
1260	2,4-decadienal	nd	0,11±0,13a	0,21±0,20a	1,48±2,15a	0,10±0,09a
1323	2-dodecanal	nd	0,13±0,12a	0,80±0,65a	0,98±0,54a	0,42±0,37a
	Aromatic Hydrocarbons					
752	Toluene	nd	0,94±0,84a	0,55±0,95a	nd	Nd
	Alifatic Hydrocarbons					
500	Pentane	nd	7,12±6,35a	nd	nd	2,44±3,61a
600	Hexane	7,46±10,29a	15,10±11,44a	9,26±4,58a	nd	6,49±3,47a
625	Cyclopentane	0,08±0,14a	13,69±2,18c	0,98±1,70a	nd	9,84±3,01b
671	Cyclohexane	nd	2,70±0,19bc	2,95±1,83c	nd	1,11±0,83ab
700	Heptane	0,22±0,38a	nd	0,28±0,33a	nd	0,44±0,02a
710	2-pentene,2-methyl	1,17±1,06a	nd	0,23±0,39a	1,34±1,49a	0,93±0,28a
800	Octane	0,40±0,40a	0,14±0,12a	0,82±0,51a	0,32±0,55a	0,70±0,25a
1200	Dodecane	0,28±0,38a	nd	0,24±0,22a	0,07±0,13a	0,05±0,09a

Means ± SD, a-e: Any two means in the same column having the same letters in the same section are not significantly different ($P < 0.05$), SD; standard deviation, nd; not detectable. Results are expressed in Arbitrary Area Units ($x10^{-6}$) as means of 3 replicates of each samples. KI: Kovats index calculated for HP-1 capillary column (Agilent, 50m, 0.2 mm i.d., 0.55µm film) installed on a gas chromatograph equipped with a mass selective detector.

The volatile profile of refined hazelnut oils was given in Table 5. A total of eighteen volatile compounds from six different chemical groups, including aldehydes, ketones, acids, aliphatic hydrocarbons, furans and alcohols were identified in these samples. Results showed that a few volatile compounds were determined in refined hazelnut oil samples. The low concentration of the volatile compound or the absence of these compounds is considered to be an indicator of refining. It has been reported that the refining process reduced the number of volatile compounds in refined rapeseed and refined sunflower oil (Uriarte *et al.*, 2011).

1-octanol was determined as the only alcohol found in refined oils, while two types of alcohols were identified in crude oils (Table 4, 5). Alcohols are formed enzymatically from the lipoxygenase way of linoleic and linolenic acids (İlyasoğlu and Özçelik 2011). Acetic and octanoic acids were not determined in refined hazelnut oils. In contrast, different alcohols and acids were determined in previous studies on hazelnut and nut oils (Mildner-Szkudlarz and Jelen, 2008; Bail *et al.*, 2009).

Table 5. Volatile compounds of refined hazelnut oils

		Brand				
KI	**Compound**	**A_R**	**B_R**	**C_R**	**D_R**	**E_R**
	Acids					
887	Propanoic acid	0,16±0,28a	nd	0,36±0,31a	0,13±0,23a	nd
950	Hexanoic acid	0,07±0,12a	0,19±0,18a	0,23±0,40a	0,44±0,18a	0,05±0,09a
>1500	1,2-benzenedicarboxylic acid	0,69±0,62a	0,69±0,10a	1,71±0,74a	0,78±0,13a	1,68±1,55a
	Alcohols					
1052	1-Octanol	0,24±0,22a	0,36±0,13a	0,24±0,21a	0,18±0,16a	0,33±0,30a
	Ketones					
1071	2-nonanone	nd	nd	0,11±0,19a	nd	0,10±0,09a
1211	3-penten-2-one	nd	nd	nd	nd	0,10±0,18a
	Aldehydes					
773	Hexanal	1,51±0,46a	1,42±0,09a	1,06±0,92a	2,07±0,10a	0,97±0,84a
877	Heptanal	0,74±0,24a	0,55±0,07a	0,88±0,19a	0,64±0,11a	0,49±0,43a
929	Trans-2- heptanal	0,55±0,48a	0,60±0,07a	0,50±0,49a	0,76±0,14a	0,47±0,41a
980	Octanal	1,10±0,09a	1,05±0,19a	1,15±0,21a	1,03±0,12a	1,37±0,03a
1080	Nonanal	1,77±0,09a	1,88±0,29a	2,22±0,47a	1,97±0,22a	3,27±0,71b
1232	2-Decenal,(Z)	nd	0,56±0,98a	3,44±2,22b	1,96±0,35ab	1,49±1,30ab
1260	2,4-decadienal	0,23±0,21a	0,30±0,05a	0,83±0,48a	0,36±0,05a	0,84±0,80a
1323	2-dodecanal	1,64±0,70a	1,74±0,49a	3,21±2,28a	1,90±0,45a	3,27±2,15a
	Furanes					
1272	2-octylfuran	nd	0,25±0,04b	0,20±0,18ab	0,34±0,04b	0,20±0,18ab
	Alifatic Hydrocarbons					
700	Heptane	0,59±0,57a	1,11±0,18a	1,17±1,03a	1,14±0,29a	0,73±0,71a
800	Octane	1,28±0,29a	1,35±0,17a	1,93±0,81a	1,34±0,17a	1,22±0,41a
1200	Dodecane	0,04±0,08a	0,07±0,13a	0,09±0,15a	0,18±0,06a	nd

Means ± SD, a-e: Any two means in the same column having the same letters in the same section are not significantly different ($P < 0.05$), SD; standard deviation, nd; not detectable. Results are expressed in Arbitrary Area Units ($x10^{-6}$) as means of 3 replicates of each samples. KI: Kovats index calculated for HP-1 capillary column (Agilent, 50m, 0.2 mm i.d., 0.55µm film) installed on a gas chromatograph equipped with a mass selective detector.

In refined hazelnut oil samples, considerable differences were found in terms of nonanal, trans-2-decenal and 2-octyl furan compounds. Hexanal and octane were found to be major compounds within aldehydes and aliphatic hydrocarbons, respectively. Hexanal has also been identified with high amounts in many other vegetable oils (Caja *et al.,* 2000; Mildner-Szkudlarz and Jelen 2008; Bail *et al.,* 2009; Uriarte *et al.,* 2011). Aldehydes such as hexanal and trans-2-hexanal are formed by the degradation of unsaturated fatty acids (Bail *et al.,* 2009). They cause an undesirable flavor and limit the shelf life (Fullana *et al.,* 2004).

Another important finding for refined oils was the presence of furans. This compound was detected in all brands, except Brand A. Furans are colorless, lipophilic, and highly volatile, low-molecular-weight compounds. Formation of furans from unsaturated fatty acids has been reported to be associated with lipid oxidation (Owczarek-Fendor *et al.,* 2010).

In crude hazelnut oil, toluene was determined as the only aromatic hydrocarbon; however, in the some samples, eight different aliphatic hydrocarbons were determined (Table 4). No aromatic hydrocarbon was observed after the refining process, and refining caused a significant decrease in the number of aliphatic hydrocarbons (Table 5). Two different ketones were determined in hazelnut oils in both (crude and refined), but the refining process has also led to a decrease in the levels of these compounds.

CONCLUSIONS

It was evident that free fatty acids and peroxide values of hazelnut oils were shown to be significantly reduced by industrial refining processes. Similarly, refining caused a reduction in the number and amounts of volatile compounds. Among the different brands, some differences have also arisen in terms of fatty acid composition. The industrial refining of the oils did not cause any significant changes in the fatty acid composition of hazelnut oils. Oleic acid, which was the major fatty acid, fluctuated between 78.97%–84.79% in crude oils and 75.83%–84.86% in refined ones. The refined hazelnut oils examined in this study were all in compliance with Turkish standards.

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