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VOLATILE AROMA COMPONENT OF NATURAL AND ROASTED HAZELNUT VARIETIES USING SOLID-PHASE MICROEXTRACTION GAS CHROMATOGRAPHY/MASS SPECTROMETRY

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ABSTRACT

Hazelnut is a very important nutrient in terms of human health. It is widely consumed as natural and roasted. Aromatic components could be used as marker for export criteria in hazelnut. Thus, this study aimed preliminary to compare the aroma profile of some hazelnut varieties and to determine the effect of roasting on aroma component in natural hazelnuts. Hazelnut varieties (18 Turkish and 2 foreign varieties) were obtained and then roasted at 135°C for 30 min. The volatile aroma components of hazelnuts were characterized via solid phase microextraction-gas chromatography-mass spectrometry (SPME/GC-MS). A total of 20 and 29 aroma compounds were detected by SPME/GC-MS in natural and roasted hazelnuts, respectively. Concerning natural hazelnut samples, the highest values among the Turkish and foreign varieties were obtained from nonanal in 'Kalınkara', 'Kan' and 'Negret-N9', which are mainly characterized by citrus, rosy, fatty flavor. In roasted samples, 2(3H)-furanone was determined in highest level in 'Cavcava', 'Mincane' and 'Negret-N9' and the flavor attributes of these varieties were oily-nut-like. In particular, Turkish hazelnut varieties such as 'Act' and 'Kalınkara' could be promising in terms of the highest amount of aromatic components in roasted hazelnuts.

Key words: Corylus avellana, aromatic component, hazelnut, SPME analyses, GC/MS

INTRODUCTION

Hazelnut is primarily grown in Turkey and produces 68% of the total production of world [Köksal 2019]. Hazelnut is an extremely important food product for human health and nutrition. Also, hazelnut include several compounds such as phytosterol (-sitosterol), flavonoids (catechin, quercetin, myricetin, and kaempferol), antioxidant phenolic compounds, as well as phenolic and hydroxycinnamic acids (gallic, caffeic, protocatechuic, vanillic, p-coumaric, ferulic and sinapic acids) [Köksal 2019].

Hazelnut consumed natural and roasted all over the world. Roasting process is provide to remove the inactivate enzymes, pellicles of kernels and decrease in water activity [Ozdemir et al. 2001]. In addition, this process improve the color, the crispy texture and the flavour of the product [Burdack-Freitag and Schieberle 2010]. Food industry utilized from roasted hazelnuts as chocolate, ice creams, cake, cereal bars, cookies, etc. [Marzocchi et al. 2017].

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Determination of aroma is very important in order to compare the odor and taste characteristics of food and that of its products [Morita et al. 2003]. The unique taste of fruit results from not only its acid and sugar content but also its unique aroma composition, many of which are defined as volatile aromas. Aroma is one of the most important quality criteria and it is essential to detect them clearly. Cemeroğlu et al. [2009] and Duan et al. [2014] reported that it is difficult to precisely determine the aroma compounds of fruit because aroma substances can change depending on many factors such as variety, climatic factors, ripeness degree, cultural practices, storage, harvest time and technical processing. The aroma of natural hazelnuts was described as the combination of some flavors such as fruity, nutty, green, citrus-like, earthy, flowery, malty, popcorn-like, potato-like, sour, and phenolic. These flavors are supplied by hexanal (green, grassy), octanal (soapy), acetic acid (sour), linalool (flowery), 2- and 3-methylbutanal (malty), 5-methyl-(E)-2-hepten-4-one (i.e. filbertone) and 5-methyl-(Z)-2-hepten-4-one (nutty, fruity), 2-acetyl-1-pirroline (popcorn-like), 3,6-dimethyl-2-ethyl pyrazine and 3,5-dimethyl-2-ethyl pyrazine (earthy, roasty), 2,3-butanedione and 2,3-pentanedione (buttery), and phenylacetaldehyde (honey, flowery) [Burdack-Freitag and Schieberle 2010, Alasalvar et al. 2012, Rosso et al. 2018].

Roasting of the hazelnut increases the concentrations of some components which can play an important role in the taste of the product. Roasting increases the amount of most ketones, among which 5-methyl-(E)-2-hepten-4-one (filbertone) contributes to the intense and characteristic odor (characteristic hazelnut smell and hazelnut-like flavor) in the roasted hazelnut and hazelnut oil. The most important characteristic odorant of roasted hazelnut is the filbertone [5-methyl-(E)-2-hepten-4-one], which is formed during the roasting process [Pfnuer et al. 1999, Langourieux et al. 2000]. Pyrazines, pyrroles, terpenes, acids ketones, aldehydes and furans, and pyrroles, which are flavoring substances, make hazelnuts as acceptable.

Previous reports also stated that ketones, aldehydes, furans and pyrroles, pyrazines also contribute to the aroma of the roasted hazelnut [Matsui et al. 1998, Pfnuer et al. 1999, Langourieux et al. 2000]. The vast majority of aldehydes are generally considered as lipid autoxidation products and contribute to green, oily, floral and fruity aroma in food. It has been stated that among aldehydes, 2-methylbutanal and 3-methylbutanal are responsible for malt, walnut and chocolate-like odors in the roasted hazelnut oil, and 2-methylpropanal is responsible for malt-like odors in the roasted hazelnut oil. Pyrazines provide the roasted hazelnut and hazelnut oil with the desired nut-like, roasted and sweet odors. Alcohols can give dark chocolate, crisp and sweet odors. The majority of the other alcohols detected can be formed by the decomposition of the hydroperoxides of fatty acids or the reduction of aldehydes.

Volatile compounds in hazelnut vary depending on variety, soil structure, climate, harvest time, cultivation method, drying methods, season, geographical origin, environmental factors, storage and maturity [Alasalvar et al. 2004].

Hazelnut is consumed both natural and roasted throughout world. Consumers mostly prefer the roasted hazelnut due to its desired taste, odor, crunchiness and crispiness. In previous studies on aroma compounds of hazelnuts, raw hazelnuts were generally examined. Whereas this study aimed to compare the differences of aroma components of many varieties in both raw and roasted hazelnuts, which were not examined in previous studies on the subject.

MATERIALS AND METHODS

Samples. Hazelnut Research Institute (Giresun, Turkey) provided (2 kg of each variety) Turkish hazelnut varieties ('Acı', 'Cavcava', 'Çakıldak', 'Foşa', 'İncekara', 'Kalınkara', 'Kara', 'Kan', 'Kuş', 'Kargalak', 'Yuvarlak', 'Yomra', 'Yassı, 'Uzun Musa', 'Tombul', 'Sivri', 'Palaz' and 'Mincane') at the beginning of the harvest season in 2019. 'Negret' and 'Tonda di Giffoni' were obtained (2 kg of each variety) from the IRTA Institute of Agrifood Research and Technology (Tarragona, Spain) in 2019. These Spanish varieties were chosen based on common varieties grown in European countries and also having desirable characteristics for international hazelnut trade. Hazelnuts were kept in a dark room at ambient temperature $15 \pm 3^{\circ}C$ in glass jar until analyzed. For determination of aroma components, nine samples from each of both natural and roasted hazelnuts (6 g each) were used.

Preparation and roasting of hazelnuts. All samples had the same caliber that is an average diameter of 9-10 mm. Hazelnuts had 5-6% initial moisture content. After the shell was broken, the inner hazelnut membrane of the raw and roasted hazelnut samples was separated and grounded before the analysis. Natural hazelnut samples were roasted from 130°C to 135°C temperature for 30 min [Ciemniewska-Zytkiewicz et al. 2014]. A stainless steel temperature-controlled roaster (Lewin, LW-100D, China) was used. Weight loss (accuracy of 0.01 g) values was perpetually recorded, in 1 min intervals. Each roasting processes was duplicate. Following roasting process, hazelnut samples were cooled at room conditions for 10 min and placed in glass jar then, kept at room temperature $(18 \pm 2^{\circ}C)$ until they were analysed. GC-MS analysis of samples was carried out in Ankara University Faculty of Engineering, Department of Food Engineering.

Extraction. Determination of aroma components of hazelnuts were done based on Alasalvar [2003], Farinelli et al. [2009]'s methods with partial modifications. According to the methods, hazelnut samples were grinded and 10 g grinded samples were mixed with NaCl solution. The extraction for SPME technique was completed.

SPME technique. The solid phase microextraction (SPME) method was partially modified based on the Farinelli et al. [2009]. Hazelnuts (10 ± 0.01 g) were placed into a vial (40 mL) and kept in the hot plate at 60°C for 10 min. The volatile components were extracted with SPME fiber coated with polydimethylsiloxane/divinylbenzene (PDMS-DVB, 65 µm, Supelco, Bellefonte, PA, USA) [Doleschall et al. 2003]. Before analysis, the fibers were conditioned and thermally cleaned by inserting them into the GC system injector port at 250°C for 10 min in a stream of helium, and the aromatic compounds were absorbed by the SPME fiber in the headspace vial at 40°C for 40 min.

GC-MS analysis. Gas chromatography-mass spectrometry (GC-MS) method was appropriately modified based on the previous report of Farinelli et al. [2009]. GC-MS analysis of aroma components was performed using with a GC-MS instrument (GC-MS-QP2010, Shimadzu, Kyoto, Japan). The analysis was performed on a Restek RTX-5 capillary column (30 m \times 0.25 mm i.d. \times 0.25 µm film thickness) equipped with a mass detector. Helium (99.999% purity) with a flow rate of

1 mL/min was used as the carrier gas. Injection mode was splitless and both the injector and detector temperature was set at 250°C. The programmed sequence of coloumn was set at 50°C at 4 min initially. After the 4th minute, the temperature increased at 10°C/min to 200°C/min prior to being increased to 250°C at 20°C/ min and held at 200°C for 0.5 min. The mass detector was set in an ion mode (electron ionization) at an ionization voltage of 70 eV in the 50-500 amu (atomic mass unit) scan range for mass spectrum collection, and the ion source temperature was 280°C. The aroma components in hazelnuts were identified based on the reference of Choi et al. [2019]. The volatile aroma compounds were identified by searching WILEY and NIST spectrometry library considering mass spectra and retention time. Analysis of aroma components was achieved by peak area normalization [Zhang et al. 2020]. A sample of GC-MS chromatogram of the aroma components in natural and roasted hazelnut ('Tombul' variety) are shown in Figures 1 and 2. The volatile aroma components and relative contents are shown in Tables 1 and 2. Description of aroma components of natural and roasted hazelnut are also given in Table 3.

Statistical analysis. All analyses were made in triplicate. This experiment was set as randomized experimental design using ANOVA. Significant differences were checked by Duncan's Multiple Range Test in MSTAT-C at $p \le 0.05$ error level. Statistical analyses were performed using the Statistical Package for social sciences (SPSS 20.0) software. The results were expressed in peak area (%) as a mean value [Farinelli et al. 2009].

RESULTS AND DISCUSSION

Volatile aromatic components of natural and roasted samples are shown in Tables 1 and 2. Aroma components of hazelnuts were determined as 42 and 83 in natural and roasted, respectively. Among these, when except for their concentration below 1%, numbers of remaining aromatic components were 20 and 29 in natural and roasted samples, respectively. Almost all of the varieties contained a large part of the detected compounds (Tabs 1 and 2).

The number of aromatic components of the varieties were different. Turkish natural hazelnut varieties such as 'İncekara' (n = 20), 'Yomra' (n = 20), 'Uzun

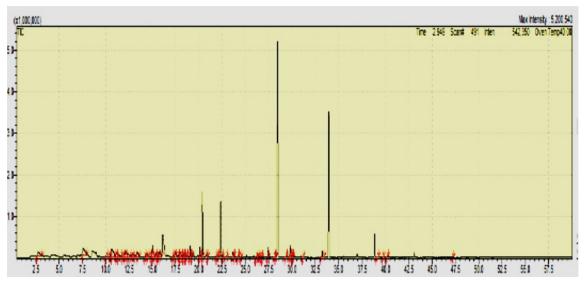


Fig. 1. GC-MS chromatogram of aromatic and volatile compounds of roasted hazelnut 'Tombul'

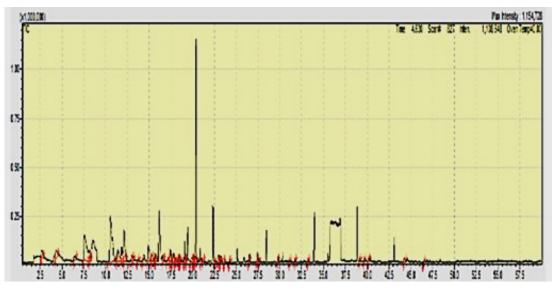


Fig. 2. GC-MS chromatogram of aromatic and volatile compounds of natural hazelnut 'Tombul'

Musa' (n = 20), 'Yuvarlak Badem' (n = 20), 'Tombul' (n = 20), 'Yassi Badem' (n = 19), 'Kalinkara' (n = 18), 'Kara' (n = 18) and 'Kuş' (n = 18) have more aromatic components than other varieties (n = 13 and 17) (Tab. 1). In addition, only 14 of the 20 aroma components were detected in the 'Tonda di Giffoni'. This was followed by 13 compounds at lowest in 'Foşa'. The number of compounds varied between 17 and 16 in other natural hazelnut varieties (Tab. 1). Although 2-pentanol and 4-heptanone were not found in the natural hazelnut of 'Negret-N9' and 'Tonda di Giffoni' varieties, they were detected in most of Turkish varieties. When each variety is evaluated individually; the differences between aromatic compounds were found statistically significant ($p \le 0.05$). When all varieties and components are evaluated together, the highest value (25.63%) was determined in the hexanal of the 'Kargalak' variety. This value is fol-

Table 1. Aromatic con	nponents of natura	l hazelnuts (%)) 'İncekara'
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									Turkish haz	elnut varieti	es								0	n hazelnut rieties
Components	'Acı'	'Cavcava'	'Çakıldak'	'Foşa'	'İncekara'	'Kalın- kara'	'Kara'	'Kan'	'Kargalak'	'Kuş'	'Yuvarlak Badem'	'Yomra'	'Yassı Badem'	'Uzun- Musa'	'Tombul'	'Palaz'	'Sivri'	'Mincane'	'Negret- N9'	'Tonda di Giffoni'
Acetic acid	11.93 ±0.38 b*1	7.23 ±0.15 e	5.59 ±0.11 e	11.65 ±0.22 c	1.99 ±0.08 kl	1.45 ±0.271	1.63 ±0.091	6.06 ±0.51 d	1.57 ±0.08 j	1.96 ±0.31 j	11.87 ±0.12 a	8.67 ±0.41 b	2.84 ±0.70 gh	1.23 ±0.03 j	3.27 ±0.12 h	4.61 ±0.31 e	2.52 ±0.41 1	2.20 ±0.45 jkl	3.57 ±0.48 1	1.56 ±0.11 ıj
2-Pentanol	nd	nd	nd	nd	2.21 ±0.11 ikl	8.45 ±0.64 e	1.24 ±0.041	10.09 ±1.20 b	2.13 ±0.08 hij	4.62 ±0.56 g	1.27 ±0.091	1.76 ±0.18 1	8.56 ±0.38 c	1.54 ±0.70 j	1.73 ±0.107 iik	1.27 ±0.75 k	2.43 ±0.111	4.89 ±0.08 gh	nd	nd
1-Pentanol	9.05 ±0.15 d	12.23 ±0.39 a	4.94 ±0.56 f	2.29 ±0.70 h	3.92 ±0.12 g	1.42 ±0.401	8.91 ±0.75 c	9.58 ±0.80 b	1.87 ±0.26 j	2.71 ±0.101	3.40 ±0.16 g	1.84 ±0.07 1	13.97 ±0.98 a	1.65 ±0.46 j	1.89 ±0.47 ıj	13.16 ±0.43 b	1.99 ±0.761	nd	9.57 ±0.20 b	7.76 ±0.56 e
4-Heptanone	8.53 ±0.07 d	5.29 ±0.09 f	nd	nd	1.74 ±0.231	1.23 ±0.311	11.45 ±0.41 a	1.43 ±0.98 hij	2.56 ±0.05 hi	8.62 ±0.46 bc	3.24 ±0.20 g	1.87 ±0.21 1	1.45 ±0.08 j	7.56 ±0.18 de	1.65 ±0.60 iik	nd	nd	14.73 ±1.31 b	nd	nd
2-Heptanol	2.29 ±0.11 ij	2.97 ±0.18 hi	2.56 ±0.09 h	2.54 ±0.07 h	2.50 ±0.58 ijk	3.43 ±0.48 jk	11.01 ±1.75 a	3.45 ±0.11 f	1.76 ±0.03 j	3.57 ±0.09 h	5.89 ±0.41 de	2.14 ±0.12 hi	1.72 ±0.09 ij	2.67 ±0.321	3.56 ±0.18 gh	3.68 ±0.12 f	3.87 ±0.10 h	5.94 ±0.15 f	3.54 ±0.09 1	3.47 ±0.10 h
Heptanal	3.20 ±0.75 g	3.50 ±0.89 gh	2.20 ±0.27 h	8.54 ±0.09 e	3.54 ±0.39 gh	1.19 ±0.081	2.56 ±0.31 h	2.34 ±0.23 g	2.12 ±0.13 ij	3.32 ±0.07 hi	3.12 ±0.18 g	2.65 ±0.36 gh	3.32 ±0.87 fg	13.61 ±0.48 a	3.54 ±0.27 gh	4.01 ±0.22 ef	5.18 ±0.64 ef	7.18 ±0.18 e	5.64 ±0.18 g	9.01 ±0.22 d
Heptanol	9.85 ±0.23 c	7.43 ±0.04 e	7.22 ±0.07 d	7.27 ±0.27 f	13.26 ±0.09 a	3.34 ±0.28 jk	8.99 ±0.93 c	10.20 ±0.51 b	6.12 ±0.81 e	5.95 ±0.39 e	5.46 ±0.28 e	6.47 ±0.18 c	10.10 ±0.11 b	8.02 ±0.28 cd	8.45 ±0.36 cd	14.26 ±1.10 a	10.11 ±0.81 b	nd	8.17 ±0.07 cd	2.11 ±0.09 1
Hexanoic acid	16.50 ±0.08 a	9.00 ±0.58 b	3.87 ±0.23 g	nd	2.73 ±0.28 ii	12.37 ±0.58 b	7.08 ±0.31 d	7.93 ±0.88 c	2.64 ±0.07 hi	5.91 ±0.12 e	2.13 ±0.17 h	3.35 ±0.10 f	2.15 ±0.391	4.23 ±0.17 h	3.98 ±0.10 g	2.24 ±0.04 ij	2.27 ±0.101	1.16 ±0.21 m	nd	14.05 ±1.08 a
6-Methyl-5- -hepten-2-one	2.56 ±0.39 hi	7.20 ±0.81 e	2.16 ±0.58 h	6.00 ±0.05 g	6.67 ±0.05 e	10.01 ±0.76 c	3.13 ±0.04 gh	1.12 ±0.11 ij	4.86 ±0.10 f	1.81 ±0.11 j	5.45 ±0.08 e	11.65 ±0.58 a	9.96 ±0.23 b	7.59 ±0.52 de	7.95 ±0.98 d	nd	8.27 ±0.59 c	3.57 ±0.581	8.43 ±0.39 c	nd
Octanal	7.11 ±0.04 e	4.05 ±0.31 g	5.40 ±0.04 ef	14.95 ±0.41 b	8.89 ±0.12 c	1.11 ±0.011	7.47 ±0.92 d	nd	12.16 ±0.65 c	8.31 ±0.96 c	7.65 ±0.18 c	8.23 ±0.24 b	5.69 ±0.07 d	7.12 ±0.23 e	9.70 ±0.30 a	8.42 ±0.87 c	14.50 ±1.19 a	nd	7.67 ±0.24 de	10.95 ±0.82 c
1-Octanol	2.37 ±0.18 hij	1.55 ±0.11 j	2.43 ±0.13 h	9.99 ±0.22 d	7.69 ±0.04 d	4.13 ±0.38 hi	4.12 ±0.12 f	4.34 ±0.49 e	4.56 ±0.31 f	5.25 ±0.37 fg	5.34 ±0.07 e	5.14 ±0.32 d	5.87 ±0.46 d	8.45 ±0.52 bc	5.65 ±0.96 f	8.66 ±0.93 c	4.19 ±0.36 gh	17.67 ±1.11 a	4.62 ±0.52 h	nd
Heptanoic acid	1.87 ±0.15 jk	3.12 ±0.18 h	8.19 ±0.22 c	nd	2.32 ±0.15 jkl	7.52 ±0.16 f	1.87 ±0.23 1	4.32 ±0.13 e	2.56 ±0.14 hi	1.13 ±0.16 k	12.42 ±0.74 a	3.45 ±0.17 f	2.89 ±0.11 g	3.78 ±0.70 h	1.56 ±0.56 ik	2.54 ±0.77 hi	3.62 ±0.81 h	2.26 ±0.75 jk	2.41 ±0.61 jk	nd
2-Nonanone	8.91 ±0.28 d	nd	7.57 ±0.31 cd	1.06 ±0.141	4.71 ±0.16 f	3.81 ±0.107 ij	nd	1.93 ±0.06 gh	2.76 ±0.34 h	6.65 ±0.81 d	10.34 ±0.18 b	8.65 ±0.28 b	2.87 ±0.15 g	8.67 ±0.30 b	9.16 ±0.50 ab	3.04 ±0.10 gh	1.97 ±0.311	5.33 ±0.15 fg	2.01 ±0.10 kl	13.62 ±0.11 a
Nonanal	6.04 ±0.11 f	8.51 ±0.09 bc	7.91 ±0.49 c	7.38 ±0.18 f	6.44 ±0.13 e	16.06 ±1.15 a	3.45 ±0.38 g	23.29 ±1.75 a	6.87 ±0.91 d	6.35 ±0.22 de	6.12 ±0.18 d	4.87 ±0.36 d	5.86 ±0.81 d	4.89 ±0.07 g	8.79 ±0.16 bc	5.86 ±0.60 d	10.42 ±0.22 b	12.11 ±0.65 c	14.53 ±0.65 a	11.44 ±0.60 bc
Octanoic Acid	2.97 ±0.14 gi	8.14 ±0.49 cd	7.63 ±0.28 cd	nd	3.03 ±0.56 hi	nd	9.65 ±0.81 b	1.99 ±0.31 gh	13.54 ±0.88 b	3.41 ±0.04 h	3.56 ±0.14 g	2.98 ±0.15 fg	8.76 ±0.70 c	5.67 ±0.25 f	6.43 ±0.47 e	4.46 ±0.31 e	nd	1.14 ±0.38 m	6.48 ±0.47 f	1.33 ±0.14 j
Nonanoic acid	1.98 ±0.09 ijk	2.41 ±0.27 1	nd	nd	2.13 ±0.38 jkl	5.86 ±0.07 g	4.11 ±0.22 f	nd	nd	1.33 ±0.10 jk	1.95 ±0.16 h	2.12 ±0.10 hi	2.23 ±0.33 hi	2.67 ±0.321	3.42 ±0.09 gh	1.73 ±0.08 jk	2.46 ±0.13 1	2.57 ±0.11 j	2.82 ±0.35 j	1.64 ±0.25 ij
Hexanal	nd	7.59 ±0.13 de	8.16 ±0.31 c	6.18 ±0.39g	3.12 ±0.31 hi	9.21 ±0.10 d	1.45 ± 0.121	1.10 ±0.01 j	25.63 ±2.04 a	5.80 ±0.12 ef	4.34 ±0.23 f	5.34 ±0.34 d	4.38 ±0.23 e	2.45 ±0.371	3.74 ±0.28 gh	4.36 ±0.23 e	5.78 ±0.31 e	1.57 ±0.50 lm	6.79 ±0.15 f	nd
Decanal	1.44 ±0.56 kl	nd	12.46 ±0.80 a	20.08 $\pm 0.51 a$	10.41 ±0.80 b	1.55 ±0.161	nd	nd	nd	nd	2.12 ±0.19 h	2.54 ±0.13 gh	3.43 ±0.22 fg	2.76 ±0.04 1	3.56 ±0.20 gh	3.47 ±0.11 fg	nd	2.60 ±0.07 j	1.74 ±0.211	4.45 ±0.13 g
Formic acid, octyl ester	nd	7.22 ±0.22 e	nd	2.07 ±0.11 h	1.74 ±0.061	3.12 ±0.09 k	5.12 ±0.18 e	1.74 ±0.21 ghi	2.54 ±0.15 hi	nd	1.11 ±0.091	12.13 ±0.31 a	$\frac{-0.22}{3.95}$ ±0.18 ef	1.12 ±0.20 j	2.27 ±0.248 1	8.39 ±0.10 c	7.60 ±0.49 d	8.74 ±0.39 d	7.45 ±0.34 e	1.07 ±0.10 j
2-Pentyl-furan	3.40 ±0.31 g	2.56 ±0.07 1	11.71 ±0.75 b	nd	2.51 ±0.34 ijk	nd	1.78 ±0.261	5.69 ±0.39 d	nd	14.12 ±1.02 a	3.22 ±0.12 g	4.15 ±0.65 e	nd	4.32 ±0.70 gh	8.56 ±0.15 bcd	nd	8.06	4.47 ±0.10 h	4.56 ±0.38 h	5.47 ±0.32 f

* The mean \pm standard error of the mean (n = 9). ¹ Different letters within rows shows significant differences in each column (p \leq 0.05); nd – not detecte

Table 2. Aromatic components of roasted hazelnut	; (%)	1
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									Turkish haz	elnut varieti	es								0	n hazelnut ieties
Components	'Acı'	'Cavcava	' 'Çakıldak	' 'Foşa'	'İncekara'	'Kalınkara	' 'Kara'	'Kan'	'Kargalak	' 'Kuş'	'Yuvarlak Badem'	'Yomra'	'Yassı Ba dem'	- 'Uzun- Musa'	'Tombul'	'Palaz'	'Sivri'	'Mincane'	'Negret-N9	, 'Tonda di Giffoni'
Acetic acid	4.34 ±0.04 e*1	2.87 ±0.31 g	5.16 ±0.44 f	2.36 ±0.09 g	3.90 ±0.07 f	12.19 ±1.07 c	10.49 ±0.254	1.08 ±0.31 k	4.81 ±0.14 f	1.91 ±0.11 j	2.35 ±0.07 jk	4.18 ±0.28 h	2.56 ±0.08 j	2.31 ±0.11 j	3.99 ±0.20 g	1.66 ±0.08 j	1.79 ±0.31 ıj	5.20 ±0.31 f	11.07 ±0.56 d	6.66 ±0.31 f
(E)-3-Penten- -2-one	11.92 ±0.89 b	1.53 ±0.09 h	2.12 ±0.29 hı	nd	nd	nd	8.62 ±0.58 c	2.22 ±0.44 ıj	nd	1.23 ±0.08 jk	nd	1.56 ±0.07 l	1.26 ±0.23 k	5.46 ±0.22 f	nd	nd	nd	1.38 ±0.21 1	nd	nd
1-Pentanol	2.85 ±0.70 gh	15.34 ±1.07 b	nd	12.73 ±0.79 a	4.39 ±0.21 f	1.70 ±0.07 ıjkl	nd	1.95 ±0.08 j	3.74 ±0.31 g	nd	nd	11.1 ±0.48 b	3.45 ±0.11 hı	7.34 ±0.41 e	nd	6.35 ±0.10 e	9.08 ±0.21 d	nd	7.44 ±0.21 e	nd
Hexanal	7.52 ±0.31 d	1.07 ±0.04 h	18.16 ±1.02 a	8.05 ±0.34 d	1.36 ±0.44 1	1.16 ±0.24 jkl	5.35 ±0.53 d	nd	nd	13.54 ±1.04 a	11.15 ±0.98 c	nd	1.57 ±0.147 k	9.22 ± 0.43 c	15.62 ±0.34 a	2.75 ±0.10 1	2.98 ±0.04 h	8.18 ±0.63 e	5.88 ±0.11 f	13.19 ±0.50 a
2-Heptanone	1.88 ±0.44 1	nd	nd	nd	nd	nd	nd	2.15 ±0.17 j	7.28 ±0.51 d	nd	nd	nd	2.56 ±0.21 j	1.51 ±0.071	2.15 ±0.14 1	nd	1.78 ±0.08 jk	nd	3.53 ±0.21 h	nd
Heptanal	2.19 ±0.23 1	3.45 ±0.28 g	1.57 ±0.04 1	1.82 ±0.31 hi	4.09 ±0.11 f	1.09 ±0.40 kl	1.39 ±0.14 ıj	2.88 ±0.31 hi	nd	1.87 ±0.18 jk	2.49 ±0.68 j	4.32 ±0.09 ghi	4.36 ±0.41 g	5.09 ±0.25 g	3.01 ±0.10 h	3.10 ±0.20 hi	1.78 ±0.09 jk	nd	3.13 ±0.21 h	nd
Benzaldehyde	3.33 ±0.76 fg	nd	1.99 ±0.05 hi	nd	nd	14.08 ±1.08 b	nd	nd	3.42 ±0.22 g	1.15 ±0.09 kl	1.78 ±0.07 kl	nd	10.62 ±0.42 b	nd	1.72 ±0.08 ıjk	nd	14.63 ±0.41 a	nd	nd	11.50 ±0.30 b
Heptanol	2.89 ±0.14 g	nd	nd	6.31 ±0.50 e	14.0 ±1.14 b	17.07 ±1.10 a	8.12 ±0.94 c	9.19 ±0.78 d	11.04 ±0.91 a	nd	nd	4.93 ±0.08 fg	7.23 ±0.44 d	3.36 ±0.16 h	1.05 ±0.09 k	14.64 ±0.87 a	4.53 ±0.21 g	12.00 ±0.51 c	1.79 ±0.08 1	2.11 ±0.09 1
Hexanoic acid	3.17 ±0.09 fg	14.37 ±0.97 c	1.63 ±0.11 1	nd	nd	1.88 ±0.09 1	3.18 ±0.25 e	nd	nd	4.40 ±0.64 gh	5.78 ±0.32 g	nd	nd	nd	1.79 ±0.08 ıj	7.57 ±0.25 d	5.38 ±0.30 f	1.70 ±0.08 1	1.91 ±0.09 1	4.05 ±0.21 h
Eucalyptol	1.02 ±0.14 j	nd	2.16 ±0.60 hi	1.45 ±0.09 hi	1.63 ±0.05 ghi	nd	nd	11.87 ±0.64 c	5.04 ±0.17 f	nd	14.87 ±1.01 a	4.05 ±0.28 hi	nd	2.16 ±0.21 j	2.24 ±0.41 1	5.53 ±0.20 f	nd	nd	2.29 ±0.11 1	nd
3-Methyl-2- cyclohexen- -1-one	2.24 ±0.04 hı	2.69 ±0.14 g	nd	nd	nd	1.63 ±0.10 ıj	2.14 ±0.30 gh	3.04 ±0.74 gh	nd	4.71 ±0.47 g	nd	14.78 ±0.77 a	5.87 ±0.35 ef	nd	nd	nd	nd	nd	nd	nd
1-Octanol	13.59 ±0.04 a	5.02 ±0.17 f	2.44 ±0.15 h	7.84 ±0.72 d	5.97 ±0.24 e	9.13 ±0.80 d	11.11 ±0.80 b	nd	4.69 ±0.57 f	3.80 ±0.32 h	8.11 ±0.85 e	nd	nd	2.15 ±0.08 j	8.86 ±0.24 c	7.87 ±0.30 d	5.20 ±0.20 fg	3.72 ±0.20 h	nd	nd
2-Nonanone	4.52 ±0.04 e	1.50 ±0.04 h	1.74 ±0.08 hı	1.04 ±0.01 1	13.62 ±1.18 b	nd	1.22 ±0.08 j	1.69 ±0.09 jk	nd	7.70 ±0.24 e	nd	2.99 ±0.14 j	1.33 ±0.14 k	1.26 ±0.10 m	nd	1.16 ±0.08 j	2.54 ±0.10 hi	14.61 ±1.10 b	nd	9.63 ±0.62 c
Nonanal	11.0 ±0.52 c	6.91 ±0.23 e	10.01 ±0.95 c	6.66 ±0.23 e	8.19 ±0.34 d	5.17 ±0.70 g	8.35 ±0.34 c	8.83 ±0.55 d	nd	6.63 ±0.33 f	4.74 ±0.24 h	2.50 ±0.18 jk	5.15 ±0.21 f	8.79 ±0.40 d	15.43 ±0.64 a	11.65 ±0.60 b	13.15 ±0.56 b	9.09 ±0.40 d	nd	11.44 ±0.54 b
Octanoic acid	3.57 ±0.33 f	3.01 ±0.09 g	nd	1.33 ±0.13 hı	nd	1.75 ±0.10 ıj	1.49 ±0.11 hı	3.75 ±0.24 g	8.67 ±0.21 c	12.51 ±0.98 b	nd	1.78 ±0.33 l	6.32 ±0.14 e	5.06 ±0.35 g	1.42 ±0.10 jk	nd	4.78 ±0.20 fg	nd	4.33 ±0.10 g	8.73 ±0.41 d
4-Methyl-5- hiazoleethanol	7.13 ±0.84 d	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	15.22 ±0.58 b	nd

nd	3.11 ±0.71 g	nd	9.72 ±0.54 c	2.22 ±0.84 g	5.08 ±0.32 g	1.98 ±0.26 gı	14.04 ±0.82 b	11.56 ±1.05 a	8.05 ±0.54 e	13.05 ±0.41 b	7.16 ±0.34 cd	11.04 ±0.68 b	2.66 ±0.15 1	11.11 ±0.27 b	12.12 ±0.80 b	nd	nd	nd	2.18 ±0.20 1
nd	nd	6.86 ±0.84 e	7.77 ±1.02 d	nd	nd	nd	7.08 ±0.43 e	nd	nd	nd	nd	nd	nd	nd	3.47 ±0.21 gh	nd	14.46 ±0.70 b	10.89 ±0.24 d	nd
1.63 ±0.231j	nd	nd	11.1 ±1.02 b	15.06 ±1.00 a	6.07 ±0.20 f	2.38 ±0.24 fg	nd	1.46 ±0.08 1	7.52 ±0.75 e	7.39 ±0.41 f	5.74 ±0.87 e	8.65 ±0.54 c	13.05 ±0.94 b	7.13 ±0.41 e	nd	10.82 ±0.31 c	nd	nd	10.95 ±0.31 b
nd	5.03 ±0.54 f	7.44 ±0.64 de	1.88 ±0.24 g	nd	1.81 ±0.09 ıj	nd	1.13 ±0.08 k	nd	nd	1.51 ±0.151	6.87 ±0.66 d	2.92 ±0.14 1j	14.61 ±1.10 a	1.07 ±0.09 jk	nd	nd	4.68 ±0.21 fg	nd	4.90 ±0.41 g
7.55 - ±0.64 d yl	nd	9.32 ±0.63 c	2.44 ±0.09 g	1.47 ±0.41 hı	2.87 ±0.40 h	11.07 ±0.87 b	1.02 ±0.11 k	4.72 ±0.11 f	1.13 ±0.071	nd	nd	nd	nd	nd	nd	1.07 ±0.11 k	nd	nd	nd
nd	11.11 ±1.01 d	6.74 ±0.52 e	5.03 ±0.85 f	nd	5.04 ±0.34 g	nd	5.06 ±0.22 f	8.75 ±0.41 c	11.47 ±0.97 c	7.14 ±0.22 f	4.31 ±0.64 ghi	7.36 ±0.21 d	9.18 ±0.85 c	nd	9.21 ±0.20 c	nd	nd	12.40 ±0.87c	nd
nd	5.09 ±0.21 f	nd	nd	1.54 ±0.08 ghi	nd	1.29 ±0.07 j	nd	nd	nd	nd	3.89 ±0.23 1	nd	nd	8.06 ±0.30 d	nd	nd	4.04 ±0.20 gh	nd	5.11 ±0.21 g
e nd	nd	11.51 ±0.82 b	nd	nd	1.04 ±0.05 l	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
nd	nd	nd	6.46 ±0.74 e	12.07 ±1.00 c	1.04 ±0.051	2.07 ±0.05 g	17.08 ±1.07 a	6.12 ±0.33 e	nd	6.93 ±0.51 f	7.74 ±0.35 c	12.07 ±0.87 a	3.17 ±0.41 h	5.74 ±0.21 f	nd	7.21 ±0.35 e	nd	nd	nd
7.58 ±0.74 d	1.04 ±0.04 h	nd	nd	2.07 ±0.37 gh	nd	17.45 ±1.07 a	nd	nd	3.05 ±0.22 1	nd	2.12 ±0.09 kl	nd	nd	nd	nd	nd	nd	nd	nd
nd	16.80 ±0.45 a	7.72 ±0.40 d	4.54 ±0.47 f	nd	nd	1.36 ±0.42 ıj	1.22 ±0.36 k	9.89 ±0.41 b	nd	8.96 ±0.44 d	4.70 ±0.33 fgh	1.55 ±0.09 k	1.91 ±0.08 k	7.44 ±0.21 de	8.91 ±0.31 c	nd	17.05 ±0.56 a	17.04 ±0.56a	7.52 ±0.11 e
1.08 ±0.16 j	nd	nd	nd	8.41 ±0.54 d	3.03 ±0.85 h	nd	4.72 ±0.24 f	6.25 ±0.28 e	nd	nd	nd	nd	nd	nd	nd	2.03 ±0.09 ıj	nd	nd	nd
nd -	nd	3.43 ±0.13 g	1.47 ±0.05 hi	nd	7.17 ±0.40 e	3.01 ±0.14 ef	nd	2.56 ±0.14 h	9.33 ±0.51 d	3.75 ±0.31 1	5.28 ±0.20 ef	4.13 ±0.21 gh	1.71 ±0.09 kl	2.17 ±0.02 1	4.01 ±0.20 g	11.25 ±0.56 c	3.89 ±0.20 h	3.08 ±0.20 h	2.03 ±0.09 1
	nd 1.63 $\pm 0.231j$ nd 7.55 $\pm 0.64 d$ nd nd nd e nd 7.58 $\pm 0.74 d$ nd 1.08 $\pm 0.16 j$	nd $\pm 0.71 \text{ g}$ nd nd 1.63 $\pm 0.231j$ nd nd 5.03 $\pm 0.54 \text{ f}$ nd 5.03 $\pm 0.54 \text{ f}$ 7.55 $\pm 0.64 \text{ d}$ nd nd 11.11 $\pm 1.01 \text{ d}$ nd 5.09 $\pm 0.21 \text{ f}$ e nd nd rd nd nd 5.09 $\pm 0.21 \text{ f}$ e nd nd nd nd f nd nd nd nd nd f nd nd nd f nd nd nd f nd f nd f 1.04 $\pm 0.04 \text{ h}$ nd 16.80 $\pm 0.45 \text{ a}$ f 1.08 $\pm 0.16 \text{ j}$ nd	nd $\pm 0.71 \text{ g}$ nd nd nd 6.86 $\pm 0.23 \text{ ij}$ nd nd nd 5.03 7.44 $\pm 0.54 \text{ f}$ 244 e nd 5.03 7.44 nd 5.03 7.44 $\pm 0.54 \text{ f}$ 240.64 de 7.55 nd 9.32 $\pm 0.64 \text{ de}$ 232 $\pm 0.64 \text{ de}$ 9.32 $\pm 0.63 \text{ c}$ a nd 11.11 6.74 $\pm 0.63 \text{ c}$ a nd 11.11 6.74 $\pm 0.21 \text{ f}$ nd 11.51 $\pm 0.82 \text{ b}$ a a a nd 11.51 $\pm 0.82 \text{ b}$ a a a nd a a a a a a a a a a a a a a a a a a a <td>nd $\pm 0.71 \text{ g}$ nd $\pm 0.54 \text{ c}$ nd nd 6.86 7.77 $\pm 0.23 \text{ ij}$ nd nd $\frac{11.1}{\pm 1.02 \text{ d}}$ nd 5.03 7.44 1.88 $\pm 0.54 \text{ f}$ $\pm 0.64 \text{ de}$ $\pm 0.24 \text{ g}$ nd 5.03 7.44 1.88 $\pm 0.54 \text{ f}$ $\pm 0.64 \text{ de}$ $\pm 0.24 \text{ g}$ -2.55 nd nd 9.32 2.44 $\pm 0.64 \text{ de}$ $\pm 0.24 \text{ g}$ $\pm 0.64 \text{ de}$ $\pm 0.24 \text{ g}$ -2.55 nd nd 9.32 2.44 $\pm 0.09 \text{ g}$ -40.64 d 11.11 6.74 $\pm 0.09 \text{ g}$ $\pm 0.85 \text{ f}$ nd 11.11 6.74 $\pm 0.09 \text{ g}$ $\pm 0.85 \text{ f}$ nd 11.01 d $\pm 0.52 \text{ e}$ $\pm 0.85 \text{ f}$ nd nd 11.51 nd nd e nd nd 11.63 nd nd e nd nd nd 14.74 $e^{-1.44} \text{ e}^{-1.44} \text{ e}^{-1.44} \text{ e}^{-1.44} \text{ e}^{-1.44} \text{ e}^{-1.44} \text{ e}^{-1.44} \text{ e}^{-$</td> <td>nd $\pm 0.71 \text{ g}$ nd $\pm 0.54 \text{ c}$ $\pm 0.84 \text{ g}$ nd nd $\frac{6.86}{\pm 0.84 \text{ e}}$ $\frac{7.77}{\pm 1.02 \text{ d}}$ nd 1.63 nd nd $\frac{11.1}{\pm 0.25 \text{ i}}$ $\frac{15.06}{\pm 1.00 \text{ a}}$ nd $\frac{5.03}{\pm 0.54 \text{ f}}$ $\frac{7.44}{\pm 0.64 \text{ de}}$ $\frac{1.88}{\pm 0.24 \text{ g}}$ nd nd $\frac{5.03}{\pm 0.54 \text{ f}}$ $\frac{7.44}{\pm 0.64 \text{ de}}$ $\frac{1.88}{\pm 0.24 \text{ g}}$ nd -$\frac{7.55}{\pm 0.64 \text{ d}}$ nd $\frac{9.32}{\pm 0.63 \text{ c}}$ $\frac{2.44}{\pm 0.09 \text{ g}}$ $\frac{1.47}{\pm 0.41 \text{ hn}}$ nd $\frac{11.11}{\pm 1.01 \text{ d}}$ $\frac{6.74}{\pm 0.52 \text{ e}}$ $\frac{5.03}{\pm 0.85 \text{ f}$ nd nd $\frac{11.01}{\pm 0.21 \text{ f}}$ nd nd $\frac{1.54}{\pm 0.08 \text{ ghn}}$ $\frac{1.54}{\pm 0.08 \text{ ghn}}$ e nd nd $\frac{11.51}{\pm 0.82 \text{ b}}$ nd nd $\frac{12.07}{\pm 0.37 \text{ gh}}$ $\frac{1.00 \text{ c}}{\pm 0.74 \text{ d}}$ $\frac{2.07}{\pm 0.37 \text{ gh}}$ $\frac{1.04}{\pm 0.40 \text{ d}}$ $\frac{10.42}{\pm 0.40 \text{ d}}$ $\frac{4.54}{\pm 0.47 \text{ f}}$ nd $\frac{8.41}{\pm 0.54 \text{ d}}$ nd $\frac{16.80}{\pm 0.45 \text{ a}}$ $\frac{7.72}{\pm 0.40 \text{ d}}$ $\frac{4.54}{\pm 0.40 \text{ d}}$ nd $\frac{8.41}{\pm 0.54 \text{ d}}$ $\frac{4.54}{\pm 0.54 \text{ d}}$</td> <td>nd$\pm 0.71 \text{ g}nd\pm 0.54 \text{ c}$$\pm 0.84 \text{ g}$$\pm 0.32 \text{ g}$ndnd$6.86$ $\pm 0.84 \text{ e}$$7.77$ $\pm 1.02 \text{ d}$ndndnd1.63 $\pm 0.23 \text{ ij}$ndnd11.1 $\pm 1.02 \text{ b}$$15.06$ $\pm 1.00 \text{ a}$$6.07$ $\pm 0.20 \text{ f}$nd5.03 $\pm 0.54 \text{ f}$$7.44$ $\pm 0.64 \text{ de}$$1.88$ $\pm 0.24 \text{ g}$nd1.81 $\pm 0.09 \text{ ij}$7.55 $\pm 20.64 \text{ d}$nd9.32 $\pm 0.63 \text{ c}$$2.44$ $\pm 0.09 \text{ g}$$1.47$ $\pm 0.40 \text{ h}$nd11.11 $\pm 1.01 \text{ d}$$6.74$ $\pm 0.52 \text{ e}$$5.03$ $\pm 0.85 \text{ f}$nd5.04 $\pm 0.34 \text{ g}$nd11.11 $\pm 1.01 \text{ d}$$6.74$ $\pm 0.52 \text{ e}$$5.03$ $\pm 0.85 \text{ f}$nd5.04 $\pm 0.34 \text{ g}$nd11.11 $\pm 0.21 \text{ f}$ndnd1.54 $\pm 0.085 \text{ gh}$ndnd11.11 $\pm 0.22 \text{ f}$nd1.04 $\pm 0.34 \text{ g}$ndnd11.51 $\pm 0.82 \text{ b}$ndnd1.04 ± 0.051ndnd1.04 $\pm 0.051$$7.58$ $\pm 0.74 \text{ d}$$1.04$ $\pm 0.40 \text{ h}$nd2.07 $\pm 0.37 \text{ gh}$ndnd16.80 $\pm 0.45 \text{ a}$ $\pm 0.40 \text{ d}$$4.54$ $\pm 0.47 \text{ f}$ndnd7.108ndndnd8.41 $\pm 0.351 \text{ d}$$3.03$ $\pm 0.85 \text{ h}$</td> <td>nd$\pm 0.71 \text{ g}$nd$\pm 0.54 \text{ c}$$\pm 0.84 \text{ g}$$\pm 0.32 \text{ g}$$\pm 0.26 \text{ gr}$ndnd$\frac{6.86}{\pm 0.84 \text{ e}}$$7.77$ $\pm 1.02 \text{ d}$ndndndnd1.63 $\pm 0.23 \text{ ij}$ndndnd11.1 $\pm 1.02 \text{ b}$$\pm 1.00 \text{ a}$$\pm 0.20 \text{ f}$$\pm 0.24 \text{ fg}nd5.03$ $\pm 0.54 \text{ f}$$7.44$ $\pm 0.64 \text{ de}$$\pm 0.24 \text{ g}nd1.81$ $\pm 0.24 \text{ g}$nd1.81 $\pm 0.09 \text{ gi}$nd7.55 $\pm 0.64 \text{ d}$nd9.32 $\pm 0.63 \text{ c}$$2.44$ $\pm 0.09 \text{ g}$$1.47$ $\pm 0.41 \text{ hi}$$2.87$ $\pm 0.40 \text{ h}$$11.07$ $\pm 0.87 \text{ b}$nd11.11 $\pm 1.01 \text{ d}$$6.74$ $\pm 0.52 \text{ e}$$5.03$ $\pm 0.85 \text{ f}$nd5.04 $\pm 0.34 \text{ g}$ndnd11.11 $\pm 1.01 \text{ d}$$6.74$ $\pm 0.52 \text{ e}$$5.03$ $\pm 0.85 \text{ f}$nd1.47 $\pm 0.34 \text{ g}$$1.29$ $\pm 0.34 \text{ g}$nd11.11 $\pm 1.01 \text{ d}$$6.74$ $\pm 0.52 \text{ e}$$5.03$ $\pm 0.85 \text{ f}$nd1.04 $\pm 0.34 \text{ g}$ndnd11.51 $\pm 0.021 \text{ f}$nd$nd$$1.29$ $\pm 0.085 \text{ g}$$1.04$ $\pm 0.085 \text{ h}$$1.04$ $\pm 0.051$$2.07$ $\pm 0.055 \text{ g}$$^{7.58}$ $\pm 0.74 \text{ d}$$1.04$ $\pm 0.04 \text{ h}$nd$nd$$2.07$ $\pm 0.37 \text{ gh}$$nd$$1.36$ $\pm 1.07 \text{ a}$nd16.80 $\pm 0.74 \text{ d}$$7.72$ $\pm 0.45 \text{ d}$$4.54$ $\pm 0.47 \text{ f}$$nd$$nd$$1.36$ $\pm 0.452 d$</td> <td>nd $\pm 0.71 \text{ g}$ nd $\pm 0.54 \text{ c}$ $\pm 0.32 \text{ g}$ $\pm 0.26 \text{ g}$ $\pm 0.82 \text{ b}$ nd nd nd $\frac{6.86}{\pm 0.84 \text{ e}}$ $\frac{7.77}{\pm 1.02 \text{ d}}$ nd nd nd $\frac{7.08}{\pm 0.43 \text{ e}}$ 1.63 $\pm 0.23 \text{ j}$ nd nd nd nd nd $\frac{7.08}{\pm 0.24 \text{ fg}}$ nd nd $\frac{5.03}{\pm 0.54 \text{ f}}$ $\frac{7.44}{\pm 0.64 \text{ de}}$ $\frac{1.88}{\pm 0.24 \text{ g}}$ nd $\frac{1.81}{\pm 0.09 \text{ j}}$ nd $\frac{1.13}{\pm 0.08 \text{ k}}$ 7.55 $\pm 0.64 \text{ d}$ nd 9.32 $\pm 0.63 \text{ c}$ 2.44 $\pm 0.09 \text{ g}$ $\frac{1.47}{\pm 0.41 \text{ hi}}$ 2.87 $\pm 0.41 \text{ hi}$ 1.02 $\pm 0.34 \text{ g}$ 1.02 $\pm 0.07 \text{ j}$ 1.02 $\pm 0.11 \text{ k}$ nd $\frac{11.11}{\pm 0.52 \text{ e}}$ $\frac{5.03}{\pm 0.32 \text{ g}}$ nd $\frac{5.04}{\pm 0.34 \text{ g}}$ nd $\frac{5.06}{\pm 0.22 \text{ f}}$ nd $\frac{11.51}{\pm 0.52 \text{ e}}$ $\frac{1.54}{\pm 0.88 \text{ bh}}$ nd $\frac{1.29}{\pm 0.07 \text{ j}}$ nd $\frac{1.29}{\pm 0.07 \text{ j}}$ nd end nd nd $\frac{1.64}{\pm 0.74 \text{ e}}$ $\frac{1.207}{\pm 1.00 \text{ c}}$ $\frac{1.04}{\pm 0.051}$ $\frac{2.07}{\pm 0.075 \text{ g}$ $\frac{17.08}{\pm 1.07 \text{ a}}$ $\frac{1.74}{\pm 1.07 \text{ a}$</td> <td>$\begin{array}{cccccccccccccccccccccccccccccccccccc$</td> <td>$\begin{array}{cccccccccccccccccccccccccccccccccccc$</td> <td>$\begin{array}{cccccccccccccccccccccccccccccccccccc$</td> <td>$\begin{array}{cccccccccccccccccccccccccccccccccccc$</td> 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* The mean \pm standard error of the mean (n = 9). ¹Different letters within rows shows significant differences in each column (p \leq 0.05); nd – not detected

Table 3. Description of aroma components of natural and roasted hazelnut

Components acids	Attributes
Acetic acid	strong, pungent vinegar
Hexanoic acid	unpleasant, cheesy, sweaty
Octanoic acid	colorless, oily liquid/slight, unpleasant odor
Formic acid	colorless, highly corrosive liquid/characteristic pungent odour
Alcohols	
Heptanol	colorless, oily liquid with a powerful, herbaceous odour
2-Heptanol	colorless, liquid with a fresh lemon-like, grass-herbaceous odour
1-Octanol	colorless, liquid/sharp fatty-citrus odor
2-Nonanol	colorless, liquid, fruity
2-Pentanol	colorless, liquid with a winey, ethereal odor
Terpenoids	
Eucalyptol	colorless, mobile liquid; camphor like aroma
Cyclohexene, 1-methyl-4-(1-methylethylidene)	
Aldehydes and ketones	
Heptanal	strong, pungent, fatty
Hexanal	vegetal, grassy, liquid; sweet green aroma
2-Heptanone	fruity, spicy odour
4-Heptanone	fruity and sweet or menthol-like odour
Benzaldehyde	sweet, strong almond
Nonanal	citrus, rosy, fatty
2-Pentyl-furan	fruity, green bean, vegetable
Benzene acetaldehyde	green, floral, sweet hyacinth
Decanal	fatty, floral, orange
1-Pentanol	cocoa odour
(E)-3-Penten-2-one	fruity and pungent odour
3-methyl-2-cyclohexen-1-one	mild cherry odour
2-Nonanone	fruity, floral, fatty, herbaceous odour
4-Methyl-5-thiazoleethanol	beefy, nutty odour
1-Pentanol,3 methyl methyl ethyl methyl- 3-methyl-1-pentanol	cocoa odour
Nonanoic acid	colorless to pale yellow liquid
Octanal	fatty-orange odour
2(3H)-Furanone, 5-heptyldihydroheptyldihydro-methyl	tropical fruit aroma
Formic acid octyl	characteristic pungent odour
5-Hepten-2-one, 6-methyl- 5-hepten-2-one	strong fatty, green citrus-like odour
Caryophyllene	warm moss-like, spicy aroma
2(3H)-Furanone, 5-butyldihydro-butyldihydro	oily-nut-like aroma
3-Octen-2-one	earthy, fruity blueberry note
3-Methyl-2-cyclohexen-1-one	clear liquid; medicinal, phenolic, mild cherry odour

lowed by nonanal (23.29%) in 'Kan' variety and decanal (20.08%) in 'Foşa' variety. Considering the total amount of aromatic components in all varieties; it has been determined that the dominant aroma components in natural hazelnut varieties were nonanal, heptanol and octanal, respectively. These components were followed by 1-pentanol and 1-octanol, respectively. The highest nonanal values among hazelnut varieties were obtained 'Kan' (23.29%), 'Kalınkara' (16.06%) and 'Negret-N9' (14.53%). The highest heptanol values were in 'Palaz' (14.26%), 'İncekara' (13.26%) and 'Kan' (10.20%), respectively. The highest octanal values were determined in 'Foşa' (14.95%), 'Sivri' (14.50%) and 'Kargalak' (12.16%) varieties. Nonanoic acid and 2-pentanol showed the lowest values according to the sum of their amounts in all varieties (Tab. 1). Both the number and quantities of the aroma compounds determined for the Turkish natural hazelnut varieties were found to be higher than the other hazelnut varieties.

A total of 83 components were found in roasted hazelnuts. When the aromatic and volatile compounds with concentrations below 1% were not taken into account, the number of components was reduced to 29 and this is seen in Table 2. It is important that the aroma components were determined in raw and roasted hazelnut samples were higher than the two Spanish hazelnut varieties.

A large number of aroma components were determined in roasted hazelnuts such as 'Aci' (n = 20), 'Kalınkara' (n = 20), 'Foşa' (n = 19), 'Kara' (n = 19), 'Kan' (n = 19), 'Yomra' (n = 19), 'Yassı Badem' (n = 19), and 'Uzun Musa' (n = 19). Low number of aromatic components (n = 13 and 14) were found in 'Mincane', 'Negret-N9' and 'Tonda di Giffoni', respectively (Tab. 2).

In particular, a large number of compounds that were not detected in the roasted samples of the foreign varieties were found at different concentrations among the Turkish varieties: 3-penten-2-one; 3-methyl-2-cyclohexen-1-one; 1-octanol; 2(3H)-furanone, 5-eptyldihydroheptyldihydro-methyl; caryophyllene; cyclohexene, 1-methyl-4-(1-methylethylidene); 1-heptanol and 3-octen-2-one (Tab. 2).

The aromatic compound concentrations in the roasted hazelnut varieties also different. The differences between the highest and lowest values are significant in all roasted hazelnut varieties ($p \le 0.05$). The highest value (17.45%) was determined in the 1-heptanol in the 'Kara' variety. This value is followed by cyclohexene, 1-methyl-4-(1-methylethylidene) (17.08%) in 'Kan' variety and heptanol (17.07%) in 'Kalınkara' variety. Considering total amount of all varieties for each component, it is seen that the dominant aromatic compound is nonanal. This compound is followed by hexanal and heptanol. The highest nonanal values are 'Tombul' (15.43%), 'Sivri' (13.15%) and 'Tonda di Giffoni' (11.44%); the highest hexanal values were determined in 'Çakıldak' (18.16%), 'Tombul' (15.62%) and 'Kuş' (13.54%) varieties. Heptanol was determined at highest level in 'Kalınkara' (17.07%), 'Palaz' (14.64%) and 'Incakara' (14.00%) in roasted samples. According to the sum of the amounts in all varieties, caryophyllene and 4-methyl-5-hiazoleethanol showed the lowest values (Tab. 2). When raw and roasted hazelnut aromatic compounds were evaluated comparatively, acetic acid; 1-pentanol; heptanal; heptanol; hexanoic acid; hexanal; octanal; 1-octanol; 2-nonanone; nonanal; octanoic acid and 2-pentyl-furan were determined in both natural and roasted hazelnuts. In addition, 2-pentanol; 4-heptanone; 2-heptanol; 6-methyl-5-hepten-2-one; heptanoic acid; nonanoic acid; decanal and formic acid, octyl ester were found in only natural hazelnut (Tabs 1 and 2). Analysis results show that roasting was very effective on the formation of some hazelnut aromatic compounds such as (E)-3-penten-2-one}; 2-heptanone; benzaldehyde; eucalyptol; 3-methyl-2-cyclohexen-1-one; 4-methyl-5-thiazoleethanol; 3-methyl-1-pentanol; benzene acetaldehyde; 2(3H)-furanone, 5-heptyldihydroheptyldihydro-methyl;, formic acid, octyl,; 2-nonanol; caryophyllene; cyclohexene; 1-methyl-4-(1-methylethylidene); 1-heptanol; 2(3H)-furanone; 3-octen-2-one; , 2-cyclohexen-1-one (Tabs 1 and 2). Similar findings were reported by Saklar et al. [1999], Langourieux et al. [2000], Wickland et al. [2001], Alasalvar et al. [2003] and Cemeroğlu et al. [2009], who stated also roasting process changed the volatile and aroma compounds of hazelnut varieties by providing different flavor, aroma and odor.

The desired taste of the roasted hazelnut is formed through the changes in the aromatic compounds, namely: 2-cylohexen-1-one; 1-octanol; heptanol and octanol, which are present in the natural hazelnut varieties

[Alasalvar et al. 2004]. Although 2-cylohexen-1-one and octanol are not found in the natural hazelnut samples in our study, the highest 1-octanol values were found in 'Mincane' (17.67%), 'Foşa' (9.99%), 'Palaz' (8.66%) and 'UzunMusa' (8.45%) varieties, respectively. However, this compound was not found in 'Tonda di Giffoni' variety. The highest heptanol values were found in 'Palaz' (14.26%), 'İncekara' (13.26%), 'Kan', 'Sivri' and 'Yassı Badem' varieties (10.20%, 10.11% and 10.10%, respectively). The lowest heptanol levels were in 'Tonda di Giffoni' (2.11%), 'Yuvarlak Badem' (5.46%) and 'Kuş' (5.95%) (Tab. 1).

According to the results, the aroma compound exhibited the highest and lowest values in different varieties. However, the highest values of all compounds in both natural and roasted hazelnut samples were determined in the Turkish hazelnut varieties. Apart from, the highest 2-nonanone value in natural 'Tonda di Giffoni' (13.62%) hazelnut variety, the highest octanoic acid value in roasted 'Tonda di Giffoni' (8.73%), the highest 4-methyl-5-hiazoleethanol and formic acid values were determined in roasted 'Negret-N9' variety (15.22% and 12.40%, respectively). This situation reveals Turkish hazelnut varieties are rich in volatile substances and aroma compounds rather than other Spanish varieties.

The description of aroma components of natural and roasted hazelnuts investigated in this study is summarized in Table 3. Aromatic components were classified depending on groups of acids, alcohols, terpenoids and aldehydes and ketones in the current study. It is suggested that hazelnut varieties can have an odor of their own depending on aromatic compounds and their threshold values. Our odor definitions of aroma compounds are consistent with previous studies and some of them reported them as: sweet, ethereal, and fruity for 2-pentanone; green and fresh grassy for hexanal; light green and fusel oil for 2-pentanol; fruity for 3-penten-2-one; dark chocolate-like, crisp, and sweet for 3-methyl-1-butanol; fruity, sweet, and oily for heptanal; rancid, burnt, wine-like, balsamic, slightly sweet, and ethereal for 1-pentanol; walnut and fresh hazelnut-like for 5-methyl-(E)-2-hepten-4-one; strong, sharp, and heavy for 6-methyl-5-hepten-2-one; green, oily, and straw-like for 1-hexanol; aldehyde-like, sweet, citrus, orange, and fruity for nonanal; woody and heavy for 1-heptanol; sweet, buttery, grassy, and green for 1-penten-3-ol; butter-like for 2,3-pentanedione; and fruity and spicy for 2-heptanone [Triqui and Guth 1997, Canturk et al. 2018, Langourieux et al. 2000, Siegmund and Pfannhauser 2000, Van Ruth and Roozen 2000].

When the findings were evaluated in general, it was seen that the natural and roasted hazelnut samples exhibited a complex volatile component profile and showed differences depending on variety. This indicates that not only certain compounds play a role in the formation of aroma and flavor, but also including different aroma-active ingredients for each variety. This situation is consistent with previous reports by Langourieux et al. [2000], Alasalvar et al. [2003], Alasalvar et al. [2004], Cordero et al. [2008], Cordero et al. [2010] and Burdack-Freitag and Schieberle [2010]. The authors stated that aroma-active compounds are responsible for unique taste of each variety. Also reported volatile and aroma compounds of hazelnut significantly vary depending on ecological conditions, maturity stage, harvest time, postharvest drying and storage.

CONCLUSION

Previous studies have examined fewer hazelnut varieties. In this study, it has been used almost all of the Turkish varieties and two Spanish varieties, which are very important for international trade. In addition, the contents of the aroma components in both natural and roasted forms of the same varieties were compared. Thus, the inclusion of the other important Turkish varieties whose aroma content has not been determined makes an important contribution to the literature.

Roasting of hazelnut is so important to fulfill the quality requirements and consumer acceptance of global and domestic markets. Aroma components are accepted as a main indicator in terms of hazelnut desirable flavor quality. It is well known that choosing the best cultivar in terms of high quality is crucial to provide sustainability. Therefore, in the current study, volatile aroma component of some hazelnut varieties was investigated.

Although the highest and lowest amounts of aromatic components showed important differences depending on varieties, the aromatic components detected in the roasted hazelnuts were more diverse

than those in the natural hazelnuts. In addition, both natural and roasted hazelnuts of Turkish varieties were found to have a higher number and diversity of aromatic compounds, and most were in higher quantities. Nonanal, heptanol and octanal in natural varieties; nonanal, hexanal and heptanol were the dominant components in roasted varieties. According to our results, the highest nonanal level was found in natural hazelnuts such as 'Kan', 'Kalınkara' and 'Negret-N9' and it was also found in roasted samples of 'Tombul', 'Sivri', 'Tonda di Giffoni'. Heptanol has the highest values in both natural and roasted samples of 'Palaz' and 'İncekara' varieties and also in 'Kan' for natural and in 'Kalınkara' for roasted. The highest values of octanal was found in natural 'Foşa' and 'Sivri'; hexanal was the highest for roasted samples of 'Çakıldak', 'Tombul' and 'Kuş' varieties.

Promising results were also observed in 'Aci' and 'Kalınkara' roasted hazelnut varieties thanks to having high level of aromatic compounds (n = 20). It can be concluded that these Turkish varieties could lead to increase of usage in both roasted hazelnut processing industry and world hazelnut trade.

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CONFLICT OF INTEREST

All authors declare that they have no conflicts of interest.

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