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Impact of roasting level on fatty acid composition, oil and polycyclic aromatic hydrocarbon contents of various dried nuts

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Abstract: Herein, the effects of roasting levels (rare, medium, and well) on the fatty acid composition, oil and polycyclic aromatic hydrocarbon (PAH) contents of various dried nuts (almonds, hazelnuts, peanuts, and cashews) were investigated. The roasting level affected the moisture and total oil contents, as well as the fatty acid composition. The roasting level had no significant effect ($P > 0.05$) on saturated fatty acid (SFA), monounsaturated fatty acid (MUFA) contents of the dried nuts, while it had a significant effect ($P < 0.05$) on polyunsaturated fatty acid (PUFA). In raw and dry roasted nut, the most common SFA, MUFA, and PUFA were palmitic, oleic, and linoleic acid, respectively. The amounts of linoleic acid and ∑PUFA, as well as ∑PUFA/∑SFA ratio were the lowest in the well roasted samples. Additionally, the types of dried nut had a significant effect ($P < 0.01$) on the amounts of total oil and fatty acid compositions. The highest total oil amount (62.15%) was found in hazelnuts, while the lowest PUFA content (7.54%) was also determined in hazelnuts. From the nutritional perspective of view, the highest ∑PUFA / ∑SFA ratio (2.40) belonged to almonds. Although the recovery rates of PAH standards varied between 70.14%–85.10%, none of the heavy PAH compounds could be detected in raw and roasted samples.

Key words: Almonds, hazelnuts, peanuts, cashews, roasting, fatty acid composition, polycyclic aromatic hydrocarbons

1. Introduction

Dried nuts are well known and consumed widely for their health benefits and unique sensory features. They also play a vital role in the domestic and foreign trade of Turkey. Turkey is one of the leading countries in the production, export and consumption of some types of dried nuts, especially hazelnuts (Erdogan, 2018). Dried nuts, such as almonds, hazelnuts, peanuts, and cashews are mainly consumed as a snack food (raw or roasted) or as ingredients in confectionery and bakery products. Dried nuts are rich sources of oil (46%–70%), most of which are low in saturated fatty acids and rich in unsaturated fatty acids, especially monounsaturated fatty acids (MUFAs). Oleic acid and linoleic acid are the most abundant MUFAs and polyunsaturated fatty acids (PUFAs) in dried nuts, respectively. Oleic acid contents were approximately 66%, 80%, 40%, and 61% of total fatty acids, in almonds, hazelnuts, peanuts and cashews, respectively (Köksal et al., 2006; Venkatachalam and Sathe, 2006; Ros, 2010; Schlörmann et al., 2015; Guo et al., 2020). Dried nuts are also a great source of protein (approximately 26% of energy), carbohydrate, minerals (phosphorus, copper), vitamins (E, folic acid, and niacin), and dietary fibers (Blomhoff et al., 2006; Brufau et al., 2006; Kornsteiner et al., 2006; Salas-Salvadó et al., 2006; Alasalvar and Shahidi, 2008; Ros, 2010; Özcan et al., 2011). Furthermore, dried nuts contain essential micronutrients, such as phytosterols and polyphenols (Ros, 2010).

Owing to the unique nutrient profile of dried nuts, especially their fatty acid compositions, frequent dried nut consumption may have some distinctive health benefits. For instance, it was reported that nut consumption can improve lipid profile in the blood by lowering plasma triglyceride levels in addition to the total and low-density lipoprotein (LDL) cholesterol with a parallel increase in the levels of high-density lipoprotein (HDL) cholesterol (Hyson et al., 2002; Lopes et al., 2011). Moreover, it was stated that the consumption of dried nuts would reduce the risk of coronary heart disease and inflammation (Higgs, 2003; Sabaté et al., 2010; Vinson and Cai, 2011). As well, they play an active role in the prevention of cancer, diabetes, hyperlipidemia, and obesity (Alper and Mattes, 2002). Some studies have shown the protective effects of nuts on hypertension and Alzheimer disease (Alasalvar et al., 2003; Higgs, 2003).

Dried nuts are usually consumed as roasted. Roasting is an important process, which is necessarily responsible

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for certain sensory attributes (such as retain nuts flavor, color, and favorable crunchy texture) (Saklar et al., 2001). In addition, roasting reduces the dried nuts' bacterial and aflatoxin-producing fungi load (Ostadrahimi et al., 2014). However, roasting can affect the nutritive value of dried nuts, leading to changes in microstructural and chemical composition (Amaral et al., 2006). Many articles have reported changes in fatty acid composition, peptides, proteins, vitamins, phytosterols, phenolic compounds and consequently antioxidant activities during the roasting process (Amaral et al., 2006; Alamprese et al., 2009; Alasalvar et al., 2010; Chandrasekara and Shahidi, 2011; Vinson and Cai, 2011). On the other hand, some hazardous chemicals that might have negative impact on human health will also come off during roasting (Schlörmann et al., 2015; Guo et al., 2020).

Polycyclic aromatic hydrocarbons (PAHs), categorized as persistent organic pollutants, are consisting of two or more fused aromatic rings (Sun et al., 2019). They have mutagenic and/or carcinogenic effects, and produced during incomplete combustion or pyrolysis of organic materials (McGrath et al., 2007; Hu et al., 2015). Although they are found in air, water, soil, sediments, and smoke (Martorell et al., 2010); food processing techniques, such as smoking, barbecuing, and roasting may lead to the formation of PAHs (Jägerstad and Skog, 2005; Farhadian et al., 2010; Duedahl-Olesen, 2013; Moazzen et al., 2013). Roasting is one of the most common methods of thermal processing used to improve the sensory attributes through changes in color, retain the characteristic taste or aroma, as well as improving the texture (Kita and Figiel, 2007). Roasting can affect the formation of PAHs, depending on the roasting conditions, such as applied time and temperature parameters (Duedahl-Olesen, 2013). Food categories, such as oils, seafood, processed meat products, bakery products, fruits, vegetables, and dried nuts may contain varying amounts of PAHs (Singh et al., 2016; Sun et al., 2019; Oz, 2020). According to EFSA (2008), 18% dietary exposure of European consumers to BaP (an indicator of PAHs) could be attributed to vegetables, dried nuts, and pulses.

Several studies have investigated the physicochemical properties and nutritional values of different dry nuts. On the other hand, the information on PAH is scarce and to the best of the author's knowledge, there was only one study that examined the PAH levels in nuts purchased from Hong Kong markets (Qin et al., 2011). In addition, it is assumed that there is a need to investigate the effects of roasting process and levels on oil contents and fatty acid compositions of dried nuts. Therefore, the target of the present study was to determine and compare the moisture, total oil contents and fatty acid compositions of almonds (*Prunus dulcis*), hazelnuts (*Corylus avellana* L.), peanuts (*Arachis hypogaea* L.), and cashews (*Anacardium occidentale*) roasted at different levels (rare, medium, and well). We therefore, investigated the presence and/or formation of PAHs in dried nuts during the roasting process.

2. Material and methods

2.1. Raw materials

Dried nuts (almonds, hazelnuts, peanuts, and cashews) were obtained as raw from a local dried nuts seller in Erzurum, Turkey.

2.2. Reagents and standards

All chemicals were of high-performance liquid chromatography (HPLC), gas chromatography (GC) and/or analytical grade. All solutions, except HPLC- or GC-grade used for analysis of fatty acid compositions and PAHs, were passed through membrane filters (PTFE) with 0.45 μm pore size (Milex, Massachusetts, USA). Purified water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA). Supelco 37 component FAME mix was obtained from Merck (Darmstadt, Germany). Standard PAH mixture was procured from Supelco (Bellefonte, PA, USA). It consists of 10 μg naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Ac), fluorene (Flu), phenanthrene (Phe), anthracene (AnT), fluoranthene (FluA), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chry), benzo[b] fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (Bghip) and indeno [1,2,3-cd] pyrene (IncdP) in 1 mL acetonitrile. The stock standard solutions were prepared according to Oz and Yuzer (2016). Q-sep Q150 QuEChERS extraction salts (6 g MgSO4, 1.5 g NaOAc, 50 mL, Cat No # 26237) and Q-sep Q351 QuEChERS d-SPE (1200 mg MgSO4, 400 mg PSA, 400 mg C18, 15 ml, Cat No # 26221) were acquired from Restek Corporation (Bellefonte, PA, USA).

2.3. Roasting process

Roasting level was chosen as a factor in the present study. Each type of dried nuts was divided into four equal parts. Five hundred grams of nuts were used for each repeat and roast level. A portion that was not subjected to roasting process in oven is considered as a control sample. Three different roasting levels, rare, medium and well, were applied to the other three portions. The roasting process was performed in a kitchen type oven (Arçelik, İstanbul, Turkey) set to 200 °C, which is a commonly used roasting temperature for dried nuts (Lin et al. 2016). As a result of pilot test, rare roasted dried nuts were roasted for 4 min, medium roasted nuts for 6 min, and well roasted nuts for 8 min. After all these roasting processes, it was paid attention that dried nuts can be consumed in terms of their color and aroma.

2.4. Determination of moisture and total oil contents

The moisture content was determined as weight loss of 10 g sample after drying at 102 °C for 24 h (Gökalp et al., 2010). The total oil contents of dried nuts were determined using ether extraction method, which is commonly used for the lipid extraction in dried nuts (AOAC 948.22; Venkatachalam and Sathe, 2006; Wang et al., 2018) The dried nuts were extracted for 8 h using diethyl ether (boiling point = 34.6 °C) as a solvent in Soxhlet extraction system. The total oil contents were determined gravimetrically.

2.5. Fatty acid compositions of the dried nuts

Fatty acid compositions were determined according to the fatty acid methyl ester (FAME) method (AOAC 996.01). To 0.1 g oil, 10 mL n-hexane and 0.5 mL 2 N methanolic KOH solution were added, shaken well (30 s), and then maintained at the dark for 1 h. Supernatant (100 µL) was injected directly into GC.

The FAME composition in oils was analyzed on a Shimadzu gas chromatograph (model QP2010 Plus) using a Restek RTX-2330 capillary column (60 m, 0.25 mm i.d., 0.1 µm film thickness, Restek Corporation Bellefonte, PA, USA) and a flame ionization detector (FID). After the column oven temperature was maintained at 100 °C for 3 min, it was ramped to 240 °C with an increase of 4 °C per min, maintained for 18 min at the last temperature value. The injection temperature was set at 250 °C and the detector temperature was set at 255 ° C. Helium was used as a carrier gas and the flow rate was set at 0.64 mL/min. The injection split ratio was at 1:80. The LabSolution computer program was used to control the GC/FID system and the FAME mix 37 standards (Supelco) were used as standard. FAME peaks were compared with retention times and chain lengths specified in the FAME standard (Ekiz and Oz, 2019).

2.6. Polycyclic aromatic hydrocarbon content of the dried nuts

The PAH analysis was carried out on both raw and dried nuts roasted at different levels using the quick, easy, cheap, effective, rugged and safe "QuEChERS" method (Özdemir et al., 2019) with minor modifications. Briefly, five grams dried nuts samples were weighted into 50 mL disposable polypropylene centrifuge tube to which 10 mL ultrapure water was added. The mixture was vortexed for 1 min. Afterward, 10 mL acetonitrile/1% acetic acid solution was added to the mixture and the tube was vortexed for 2 min. Next, Q150 QuEChERS extraction salt including 6 g $MgSO_4$ and 1.5 g NaOAc was weighed, added to the mixture, and then vortexed for 1 min. The tubes were centrifuged at 4000 rpm for 5 min and the whole supernatant was transferred to Q351 QuEChERS d-SPE tube containing 1200 mg MgS04, 400 mg PSA, and 400 mg C18. The tubes were vortexed for 1 min and then centrifuged at 4000 rpm for 5 min at room temperature. An aliquot of the final upper layer was the filtered using 0.45 µm syringe filter and stored in HPLC vials pending analysis.

The PAHs content were determined using HPLC (Thermo Ultimate 3000; Thermo Scientific) with fluorescent detector (FLD-3000). A PAH column with a 3 µm particle size (150 mm × 2.1 mm) Hypersil TM Green PAH LC column (Hichrom, Reading, UK) was used for separation. Degassed ultrapure water and acetonitrile (HPLC-grade) were used as solvent A and B, respectively, and the flow rate of the elution was set at 0.6 mL/min. The column temperature was maintained at 25 °C and the injection volume was 20 µL (Oz, 2020).

2.7. Method validation for PAH analysis

The method performance was validated using the following parameters: the limit of detection (LOD), limit of quantification (LOQ), recovery, and precision (relative standard deviation, RSD%). The LOD and LOQ values were calculated according to the signal-to-noise ratios of PAH standards evaluated at concentrations ranged from 1–100 ng/g). A standard additional method was used to determine the recoveries of the PAHs.

2.8. Statistical analysis

The experiment was a completely randomized design. A Duncan multiple comparison test was used to determine the significance of the differences between the obtained values using the SPSS 13.0 statistical software package (SPSS Inc., Chicago, IL, USA).

3. Results and discussion

3.1. Moisture contents of the dried nuts

The effects of the dried nut types and roasting levels on the moisture content are shown in Table 1. As can be seen from the table, both dried nut types and roasting levels had a significant ($P < 0.01$) effect on the moisture content. Statistically, peanuts (3.53%) had the highest average moisture content followed by almonds (2.44%) > cashews (2.13%) = hazelnuts (1.96%). In this context, Demir and Cronin (2004) stated that even the same type of dried nuts showed variations in shape, size, and levels of maturity and moisture content. Cultivation conditions, such as geographical region, season, maturity level, harvesting time, soil type, and species diversity may affect the moisture content of dried nuts (Venkatachalam and Sathe, 2006; Schlörmann et al., 2015; Pelvan and Demirtaş, 2018).

As expected, the roasting process caused a significant decrease in moisture content of the dried nut samples. A significant decrease afforded by the increase of roasting level was also observed in our study. In this manner, Uysal et al. (2009) reported a moisture content 4.8% in raw hazelnuts samples, which is going to be decreased to 1.22%

Table 1. Effects of dried nut types and roasting levels on the content of moisture and total oil (%).

	n	Moisture (%)	Total oil (%)
Dried nuts (DN)			
Almonds	8	2.44 ± 1.53b	49.75 ± 5.83b
Hazelnuts	8	1.96 ± 1.84c	62.15 ± 3.05a
Peanuts	8	3.53 ± 2.79a	48.12 ± 3.49b
Cashews	8	2.13 ± 1.33c	48.30 ± 3.83b
Sign.		**	**
Roasting level (RL)			
Raw	8	5.03 ± 1.77a	47.43 ± 7.20c
Rare	8	2.94 ± 0.67b	51.79 ± 5.87b
Medium	8	1.58 ± 0.47c	53.95 ± 7.62ab
Well	8	0.52 ± 0.40d	55.16 ± 6.52a
Sign.		**	**
DN × RL		**	ns

Sign: significance, ns: not significant (P > 0.05). a–d: means with different letters in the same column and section are significantly different (P < 0.05), **P < 0.01.

after roasting at 150 °C for 20 min. Additionally, Tezer et al. (2015) found a significant reduction in moisture content of raw peanuts samples from 4.77 to 2.78% owing to roasting at 165 °C for 25 min. Furthermore, Liao et al. (2019) demonstrated that roasted cashew kernels in hot air oven at 140 °C for 33 min led to a decrease in the moisture content from 6.6% (raw samples) to 1.8% (roasted samples).

3.2. Total oil contents of the dried nuts

The effects of the dried nut types and roasting levels on the total oil contents are compiled in Table 1. As can be seen from the table, both dried nut types and roasting levels had a significant (P < 0.01) effect on the total oil contents. Statistically, hazelnuts (62.15%) had the highest average crude oil contents followed by almonds (49.75%) = cashews (48.30%) = peanuts (48.12%). In line to the present results, the total oil contents of hazelnuts, almonds, and cashews were found to be 61.6%, 50.1%, and 44.4%, respectively, as reported by Robbins et al. (2011). On the other hand, total oil contents in between 45.2% and 58.1% were reported by Kornsteiner-Krenn et al. (2013) in various nuts (cashews, peanuts, pistachios, almonds, and hazelnuts). As expected, a proportional increase has been observed in the total oil contents of the roasted nuts compared to the raw samples that could be attributed to moisture loss in dried nuts caused the roasting process. Well roasted nuts contained statistically higher levels of oil than raw or rare roasted nuts. In this context, Alasalvar et al. (2010) found that the oil contents of raw hazelnuts samples were in the range of 57.85%–68.31%, which ramped up to 61.37%–71.72% by roasting at 140 °C for 30 min. Similarly, Lin et al. (2006) asserted that increases in the roasting levels of almonds can cause an increase in oil contents.

3.3. Fatty acid compositions of the dried nuts

The effects of the dried nut types and roasting levels on the fatty acid composition are shown in Table 2. Dried nuts types had a significant effect (P < 0.01) on palmitic, stearic, oleic, and linoleic acids, ΣSFA, ΣMUFA, ΣPUFA, ΣPUFA/ΣSFA, ΣMUFA/ΣSFA, n-6, and n-9 fatty acids. In all of the dried nuts, the most common saturated fatty acids (SFAs) were palmitic and stearic acids. Similarly, it was declared that palmitic acid (ranged from 5.2% to 16.9%) was the predominated saturated fatty acid followed by stearic acid in various types of nut (Kornsteiner-Krenn et al., 2013).

Herein, the most common monounsaturated fatty acid (MUFA) was found to be oleic acid, whereas the most common polyunsaturated fatty acid (PUFA) was linoleic acid. Statistically, the highest ΣSFA content was recorded in cashews (17.65%) followed by peanuts (13.82%) > almonds (8.93%) = hazelnuts (8.44%). On the other hand, the highest ΣMUFA content was verified in hazelnuts (84.02%) followed by almonds (70.87%) > peanuts (65.66%) > cashews (62.15%). Furthermore, the highest ΣPUFA content was accomplished in peanuts (20.52%) = almonds (20.20%) = cashews (20.20%) followed by hazelnuts (7.54%). In this context, Kornsteiner-Krenn et al. (2013) stated that the total SFAs are only a small portion of total fatty acid contents estimated in ten different dried nuts with ratios varied between 7.9% and 18.3%. They also found that hazelnuts contain the highest total MUFA. In the present study, the total PUFA and linoleic acid contents in various dried nuts were similar to each other, except hazelnuts. In fact, the linoleic acid and total PUFA contents of hazelnuts were slightly lower than the values reported by others (Özdemir et al., 2001; Köksal et al., 2006; Kırbaşlar et al., 2012) and in line with those reported by Kornsteiner-Krenn et al. (2013). These differences could be correlated with genetic, morphologic, and environmental factors. In this respect, a method for determination of linoleic acid contents in 18 different types of hazelnuts was conducted by Alasalvar et al. (2010) and they found a range between 3.86%–13.77% and 4.92%–15.70%, before and after roasting, respectively. On the other hand, it was stated that the type of dietary fat intake would affect plasma cholesterol levels and MUFA and PUFA contents can counterbalance the unfavorable SFAs (Ros and Mataix, 2006; Sharma et al., 2016). It has to be noted that dried nuts examined in the present study may contain healthy oils.

Although it is desirable that the amount of PUFA is high in the dried nuts due to the its positive effects on

Table 2. Effects of dried nut types and roasting levels on the fatty acid composition (%).

	n	Palmitic acid	Stearic acid	Oleic acid	Linoleic acid	∑SFA	∑MUFA	∑PUFA	∑PUFA/∑SFA	∑MUFA/∑SFA	n-6	n-9
Dried nuts (DN)												
Almonds	8	7.46 ± 1.32b	1.42 ± 0.27d	69.06 ± 1.32b	20.20 ± 4.71a	8.93 ± 1.66c	70.87 ± 3.09b	20.20 ± 4.71a	2.40 ± 0.85a	8.10 ± 1.00b	20.20 ± 4.71a	70.31 ± 3.10b
Hazelnuts	8	5.83 ± 0.14c	2.61 ± 0.07c	83.82 ± 0.23a	7.43 ± 0.26b	8.44 ± 0.18c	84.02 ± 0.23a	7.54 ± 0.29b	0.90 ± 0.05c	9.96 ± 0.20a	7.54 ± 0.29b	83.82 ± 0.23a
Peanuts	8	9.34 ± 0.30a	4.45 ± 1.49b	65.58 ± 2.04c	19.70 ± 0.62a	13.82 ± 1.79b	65.66 ± 1.88c	20.52 ± 0.56a	1.50 ± 0.16b	4.82 ± 0.60c	20.52 ± 0.56a	65.60 ± 12.00c
Cashews	8	9.80 ± 0.36a	7.78 ± 1.57a	61.69 ± 2.14d	19.96 ± 0.30a	17.65 ± 1.94a	62.15 ± 1.96d	20.20 ± 0.07a	1.16 ± 0.16bc	3.58 ± 0.65d	20.20 ± 0.07a	61.82 ± 2.09d
Sign.		**	**	**	**	**	**	**	**	**	**	**
Roasting level (RL)												
Raw	8	7.85 ± 1.85a	4.02 ± 2.92a	69.77 ± 9.05a	17.72 ± 6.51a	11.89 ± 4.59a	70.09 ± 8.95a	18.02 ± 6.54a	1.67 ± 0.92a	6.84 ± 2.91a	18.02 ± 6.54a	69.81 ± 9.01a
Rare	8	7.86 ± 1.87a	4.10 ± 2.95a	69.79 ± 9.20a	17.60 ± 6.47ab	11.99 ± 4.66a	70.11 ± 9.11a	17.89 ± 6.51a	1.63 ± 0.86ab	6.78 ± 2.90a	17.89 ± 6.51a	69.83 ± 9.16a
Medium	8	8.35 ± 1.83a	4.00 ± 2.63a	70.00 ± 9.06a	16.48 ± 6.05ab	12.38 ± 4.07a	70.85 ± 9.16a	16.78 ± 6.20ab	1.40 ± 0.59ab	6.47 ± 2.74a	16.78 ± 6.20ab	70.56 ± 9.16a
Well	8	8.37 ± 1.68a	4.14 ± 2.65a	70.58 ± 9.04a	15.50 ± 5.73b	12.57 ± 3.91a	71.65 ± 9.13a	15.78 ± 5.91b	1.26 ± 0.43b	6.37 ± 2.60a	15.78 ± 5.91b	71.35 ± 9.13a
Sign.		ns	ns	ns	*	ns	ns	*	*	ns	*	ns
DN × RL		ns	ns	ns	*	ns	ns	*	*	ns	*	ns

Sign: Significance, ns: not significant (P > 0.05), a–d: means with different letters in the same column and section are significantly different (P < 0.05), *P < 0.05, **P < 0.01

health, changes in fatty acid compositions of same type dried nuts can be varied depending on climate, season, and geographic area. Therefore, ΣPUFA/ΣSFA ratio is commonly used for evaluation of nutritional value of oil rich foods with a desirable ratio greater than 0.45 (Özogul and Özogul, 2007). In the present study, the ΣPUFA / ΣSFA ratio varied between 0.90 and 2.40, depending on the dried nut types. While the highest rate was found in almonds; ΣPUFA / ΣSFA ratio was higher than the recommended value (0.45) in all dried nuts. Although these results are crucial in terms of nutritional value, it should be noted that this may affect the shelf life, due to the fact that polyunsaturated fatty acid-rich foods are prone for lipid oxidation.

In the present study, the roasting process had a significant effect ($P < 0.05$) on linoleic acid, ΣPUFA, ΣPUFA / ΣSFA, and n-6 fatty acids. In raw as well as all roasted dried nuts, the most common SFAs were palmitic and stearic acids, oleic acid was the most common MUFA, whereas linoleic acid was the most common PUFA. It was demonstrated that roasting process may cause a significant reduction in the contents of linoleic acid, ΣPUFA, ΣPUFA/ ΣSFA, and n-6 fatty acids. Statistically, the lowest amounts of linoleic acid, ΣPUFA, and ΣPUFA/ΣSFA ratios were accomplished in well roasted samples. This finding could be attributed to the prolonged roasting process that would allow oxygen to reacts readily with unsaturated fatty acids. It was reported that fatty acids, especially unsaturated ones (such as linoleic and linolenic) are strongly oxidized at high temperatures (Stevenson et al., 1984; Kırbaşlar et al., 2012). However, in the current study, the ΣPUFA / ΣSFA ratios for all roasting levels were higher than the recommended value (0.45) in terms of nutritional value.

Roasting levels showed no statistically significant effect on total SFA and MUFA amounts ($P > 0.05$). This was assumed to be related to the fact that SFAs and MUFAs are more resistant to oxidation than PUFAs under thermal roasting process. In this context, O'Keefe et al. (1993) recorded the oxidation rates of fatty acids at 1:10:100:200 for stearic, oleic, linoleic and linolenic acids, respectively. On the other hand, no significant increases were observed in the total SFA amount of medium and well roasted nut samples. This could be correlated to the partial transformation of PUFAs into some saturated fatty acids as a result of oxidation. Generally, the fatty acid compositions of various nut types roasted at different levels are comparable to those reported by others (Özdemir et al., 2003; Durmaz and Gökmen 2011; Rodrigues et al., 2011; Schlörmann et al., 2015; Zhang et al., 2020).

3.4. Method validation values and PAH contents of the dried nuts

In the present study, eight heavy PAH compounds, including benzo[a]anthracene (BaA), chrysene (Chry), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (Bghip) and indeno[1,2,3-cd]pyrene (IncdP) were investigated. Figure 1 shows the HPLC chromatograms of PAH mix stock solutions. The limits of detection (LOD) and quantification (LOQ) were ranged between 0.027 and 0.125 ng/g and between 0.089 and 0.413 ng/g, respectively. The recovery rates were in between 70.14 and 85.10% with RSD ≤ 20%. In addition, the regression coefficients of the PAH standard curves (1–100 ng/g) were found to be > 0.999. These values were in good agreement with the values for European Commission. According to the European Commission Regulation No 836/2011 (European Commission, 2011), the LOD, LOQ and recovery rates for BaP, BaA, BbF and Chry should be ≤ 0.30 ng/g, ≤ 0.90 ng/g and 50%–120%, respectively.

In the present study, none of the analyzed PAHs were detected (below the LOD) either in raw or roasted samples. The result in the raw nuts is thought to be related to the low presence of environmental PAHs in the growing areas of nuts or to the nuts' shell acting as a barrier for PAHs. To the best of our knowledge, there was only one research

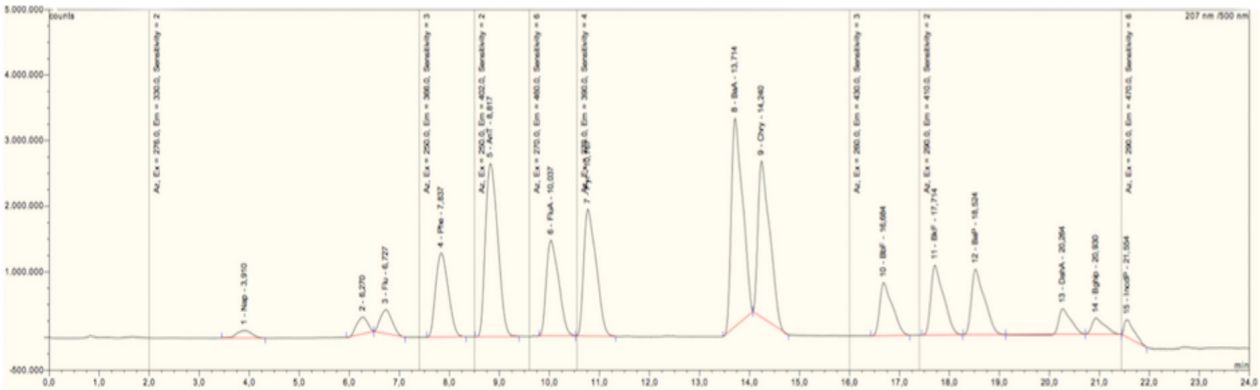

Figure 1. The HPLC chromatograms of PAH mix stock solutions (5 ng/g).

that report PAH content in roasted dried nuts. In that study, PAH contents of various dried nuts purchased from Hong Kong supermarkets were determined (Qin et al., 2011). They found that low molecular weight PAHs (such as, naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene) were the dominant PAHs quantified in dried nuts (almonds, peanuts, and cashews), however, high molecular weight PAHs (such as, benzo(b + k)fluoranthene, benzo(a)pyrene, indeno[1,2,3-c,d]pyrene, dibenz[a,h]anthracene, and benzo[g,h,i]perylene) were not detected. In this respect, Zakaria et al. (2002) stated that the low molecular weight PAHs was come primarily from petrogenic pollution. Herein, the absence of PAHs in the dried nut samples might be related to the investigated high molecular weights PAH. On the other hand, this result may have been influenced by the temperature/time combination applied through roasting process. Because high molecular weight PAHs are mainly of pyrogenic origin and the applied roasting temperature/time combination in the present study may not have caused the pyrolysis. Another reason could be the occurrence of new compounds with antioxidant properties through the Maillard reaction during roasting. Açar et al. (2009) have reported that the high antioxidant capacity of Maillard products is related to the formation of reductone-type structures and/or metal chelating properties of melanoidins. They also revealed that the increase in total antioxidant capacity (due to the formation of Maillard reaction products with antioxidant properties) could be attributed to roasting process in foods containing starch rich foods, such as cashews. The other reason could be due to tocopherol contents of nuts. Because it is known that nuts are also an important source of tocopherol isomers, which are considered as antioxidant active compounds (Robbins et al., 2011). Antioxidants may function as free radical scavengers (Britt et al., 1998). Janoszka (2011) has stated that antioxidants could prevent the oxidation and polymerization of hydrocarbons produced from decomposition of fatty acids and protein. Liskova et al. (2020) declared that β-carotene, retinol and tocopherols would reduce B[a]P-induced mutagenicity and oxidative stress in HepG2 cell line via modulation of xenobiotic-metabolizing enzymes. Therefore, it is highly recommended to include food rich in β-carotene, retinol and tocopherols into the diet in the areas of high PAHs pollution.

4. Conclusion

The results of the present study showed that the roasting level would affect the oil contents and fatty acid compositions, in particular polyunsaturated fatty acids content. The ∑PUFA/∑SFA ratio (an important parameter in terms of nutritional value and health benefits) was significantly decreased in well roasted samples. Thence, we may recommend the application of rare and medium roasting level to dry roasted nuts. Although the highest total oil content was noticed in hazelnuts, the highest ∑PUFA / ∑SFA ratio was observed in almonds. This result shows that not only the amount of oil but also the fatty acid compositions would affect the nutritional value. In refer to SFA and PUFA results; almonds are remarkable among the dried nuts in terms of nutrition and health perspective. On the other hand, we have shown that roasting level had no apparent influence on the formation of heavy PAHs levels. It is therefore recommended to investigate the effect of roasting level on light PAHs formation for further research works.

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