

The effect of heat treatment on phenolic compounds and fatty acid composition of Brazilian nut and hazelnut

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Abstract Brazilian peanut oil content increased with oven heating (65.08%) and decreased with microwave heating process (61.00%). While the phenolic content of untreated Brazilian nut was the highest of 68.97 mg GAE/100 g. Hazelnut (Sivri) contained the highest antioxidant activity (86.52%, untreated). Results reflected significantly differences between the antioxidant effect and total phenol contents of Brazilian nut and hazelnut (Sivri) kernels heated in the oven and microwave. Microwave heating caused a decrease in antioxidant activity of hazelnut. Gallic acid, 3,4-dihydroxybenzoic acid and (+)- and catechin were the main phenolic compounds of raw Brazilian nut with the value of 5.33, 4.33 and 4.88 mg/100 g, respectively, while the dominant phenolics of raw hazelnut (Sivri) kernels were gallic acid (4.81 mg/100 g), 3,4-dihydroxybenzoic acid (4.61 mg/100 g), (+)-catechin (6.96 mg/100 g) and 1,2-dihydroxybenzene (4.14 mg/100 g). Both conventional and microwave heating caused minor reduction in phenolic compounds. The main fatty acids of Brazilian nut oil were linoleic (44.39–48.18%), oleic (27.74–31.74%), palmitic (13.09–13.70%) and stearic (8.20–8.91%) acids, while the dominant fatty acids of hazelnut (Sivri) oil were oleic acid (80.84%), respectively.

The heating process caused noticeable change in fatty acid compositions of both nut oils.

Keywords Hazelnuts · Brazilian nut · Oil · Antioxidant activity · Total phenol · Fatty acid composition · Phenolic compounds · Roasting

Introduction

Hazelnut (*Corylus avellana* L.) is a significant and healthy nut because of its valuable nutrients. Turkey, especially coast of the Black Sea region, is the most important producer of hazelnut, contributing about 70.3% of the total world production (Alasalvar et al. 2010; Jakopic et al. 2011). The quality and fatty acid composition of hazelnut can be affected by climatic conditions, variety, location and cultural practices (Alasalvar et al. 2010; Ciarmiello et al. 2013). Hazelnut are rich source of essentials minerals, sterols, fatty acids, free phenolic acids, organic acids and phenolic compounds (gallic acid etc.) (Cristofori et al. 2008; Alasalvar et al. 2010; Jakopic et al. 2011; Ciarmiello et al. 2013). Due to their high polyphenol contents, hazelnuts are recognised as a good source of natural antioxidants (Solar and Stampar 2011). Among the species due to diversification of its culture and fruits, hazelnut and Brazilian nuts would constitute an excellent option as a food source. The Brazilian nut belonging to the family Lecythidaceae, is one of the most important extractive Amazonian species (Silva et al. 2016). Due to its pleasant taste and high nutritional value, the Brazil nut called as “vegetable meat” has become a very popular food worldwide. The Brazilian nut (*Bertholletia excelsa*) produces a fruit in which the seed kernel possesses nutritive potential due to its high lipid content (Costa et al. 2010). The

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Brazilian nut is one important plant of the Amazon tropical forest (Muller 1981). Roasting is one of the main operations that applied nuts, that can lead to various physico-chemical changes. Microwave energy and conventional heating are currently being used for several food processing operations, including cooking, drying, tempering, baking, pasteurization and sterilization (Rosenberg and Bogl 1987; Megahed 2001). Microwave process can offer several advantages (operation, energy savings, precise process control, faster start up and shut-down times) when compared to conventional heat processes (Decareau 1992; Megahed 2001). The roasting conditions have significant influences on color, flavor, fatty acid profile and bioactive compounds of kernel and seeds (Yoshida and Kajimoto 1994; Kim et al. 2002). Microwave energy differs from conventional treatment due to accomplished by means of electromagnetic waves, which penetrate deeply and heat rapidly (Schlegel 1992). Whereas, conventional heating methods transfer thermal energy from product-surfaces toward center 10–20 times more slowly as the microwaves heated product (Mudgett 1989). The aim of the study was to investigate the effect of heating on oil yield, bioactive properties, phenolic compounds and fatty acid composition of Brazilian nut and hazelnut (Sivri) kernel and oils.

Materials and methods

Materials

About 3 kg raw Brazilian nut was provided from market in Vilnius in Lithuania in 2016. Hazelnut (Sivri) (about 3 kg) was collected by hand in Giresun province, Turkey in 2016. Nuts were cleaned in an air condition, and then stored in polypropylene bags at room temperature.

Methods

Heat treatment

Each sample was heated as without the shell in microwave and oven. Brazilian nut and hazelnut (Sivri) kernels were heated in commercial electrical ovens at 130 °C for 20 min, and in a microwave oven at 720 W for 5 min. The heated samples were ground into powder using a grinder before analysis.

Extraction of Brazilian nut and hazelnut kernels

For phenolic compounds and antioxidants, Brazilian nut and hazelnut kernels were extracted according to Jakopic et al. (2011) with some modifications. About 5 g of each samples were added to 15 ml of methanol. The mixture

was sonicated for 1 h, followed by centrifugation at 6000 rpm for 10 min and the supernatants were collected. The 10 ml of *n*-hexane was added and mixed using a vortex apparatus. The methanol and hexan layer were separated in separating funnel. These steps were repeated twice. After the extract was concentrated at 50 °C in a rotary evaporator, and after the dried extracts were dissolved in 1.5 ml of methanol, it was and injected to HPLC.

Total phenolic content

Total phenol contents were determined by Folin–Ciaccuetau (FC) reagent according to Yoo et al. (2004). About 10 mL of Na₂CO₃ solution tubes and 1 ml of Folin–Ciaccuetau were mixed, and was completed with 25 ml deionised water. After 1 h, total phenol content was measured 750 nm in a spectrophotometer. The results were given as mg gallic acid equivalent/100 g (dw).

Antioxidant activity

The free radical scavenging activity of sample was determined using DPPH (1,1-diphenyl-2-picrylhydrazyl) according to Lee et al. (1998). The extract was mixed with 2 ml methanolic solution of DPPH. The mixture was shaken vigorously and allowed to stand at room temperature for 30 min. And the absorbance was recorded at 517 nm by using a spectrophotometer.

Phenolic compounds

Phenolic compounds were determined by Shimadzu-HPLC equipped with PDA detector and Inertsil ODS-3 (5 µm; 4.6 × 250 mm) column. As mobile phases, the 0.05% acetic acid in water (A) and acetonitrile (B) mixture were used. The flow rate of the mobile phase and the injection volume were 1 ml/min at 30 °C and 20 µl, respectively. The peak records were carried out at 280 and 330 nm. The total running time for each sample was 60 min.

Oil content

Oil content of samples was determined according to AOAC (1990) method. Total oil content of hazelnut was extracted with petroleum benzene in Soxhlet Apparatus for 5 h and the solvent was removed with a rotary vacuum evaporator at 50 °C.

Fatty acid composition

Nut oils were esterificated according to ISO-5509 (1978) method, and analysed gas chromatography (Shimadzu GC-2010) equipped with flame-ionization detector (FID) and

capillary column (Tecnocroma TR-CN100, 60 m × 0.25 mm, film thickness: 0.20 µm). The temperature of injection block and detector was 260 °C. Mobile phase was nitrogen with 1.51 ml/min flow rate. Total flow rate was 80 ml/min and split rate was also 1/40. Column temperature was programmed 120 °C for 5 min and increased 240 °C at 4 °C/min and held 25 min at 240 °C (AOAC 1990).

Statistical analyses

A complete randomized split plot block design was used, and analysis of variance (ANOVA) was performed by using JMP version 9.0 (SAS Inst. Inc., Cary, N.C.U.S.A). All analyses were carried out three times and the results are mean ± standard deviation (MSTAT C) of independent Brazilian nut and hazelnut (Sivri) samples (Püskülcü and İköz 1989).

Results and discussion

Antioxidant activity, total phenol and oil contents of Brazilian and hazelnut kernels are presented in Table 1. The antioxidant activities and total phenolic contents of untreated samples were higher than heat-processed nut kernels. While the phenolic content of untreated Brazilian nut showed the highest total phenol content 68.97 mg GAE/100 g while hazelnut (Sivri) contained the highest antioxidant activity (86.52%, untreated). It was observed significantly differences between the antioxidant effect and total phenol contents of Brazilian nut and hazelnut (Sivri) kernels heated in the oven and microwave ($p < 0.05$). Both total phenolic content and antioxidant activity of Brazilian nut and hazelnut kernels were affected by heating process. Microwave heating caused a decrease in antioxidant activity in hazelnut (76.33%). Similarly, antioxidant activity of Brazilian nut was decreased from 81.77 to 34.60% after heating treatment. Concerning total phenolic content, the maximum reduction (from 68.97 to 25.88 mg

GAE/100 g) was observed in Brazilian nut when heated in microwave oven. Additionally, the decrease in antioxidant activity and total phenolic content of Brazilian nut was higher than hazelnut (Sivri). Brazilian peanut oil content increased with oven heating (65.08%), while it has decreased with microwave process (61.00%).

The phenolic compounds of Brazilian nut and hazelnut (Sivri) kernels are presented in Table 2. Gallic acid, 3,4-dihydroxybenzoic acid and (+)-catechin were the main phenolic compounds of raw Brazilian nut with the value of 5.33, 4.33 and 4.88 mg/100 g, respectively, while the dominant phenolics of raw hazelnut (Sivri) kernels were gallic acid (4.81 mg/100 g), 3,4-dihydroxybenzoic acid (4.61 mg/100 g), (+)-catechin (6.96 mg/100 g) and 1,2-dihydroxybenzene (4.14 mg/100 g). While statistically differences among Gallic Acid and 3,4-Dihydroxybenzoic acid contents of Brazilian nut and hazelnut (Sivri) treated with oven and microwave heating compared to control were observed, while no statistical differences among (+)-Catechin content of hazelnut (Sivri) treated between oven and microwave heating was observed. Generally, hazelnut (Sivri) kernels contained higher amounts of phenolic compounds than Brazilian nuts. Both conventional and microwave heating caused minor reduction in phenolic compounds. Additionally, less change in phenolics when samples were heated with conventional oven was observed.

The fatty acid composition of Brazilian nut and hazelnut (Sivri) samples is shown in Table 3. The main fatty acids of Brazilian nut oil were linoleic (44.39–48.18%), oleic (27.74–31.74%), palmitic (13.09–13.70%) and stearic (8.20–8.91%) acids, while the dominant fatty acids of hazelnut (Sivri) oil were oleic acid (80.84%), followed by linoleic and palmitic acids. The heating process caused noticeable change in fatty acid compositions of both nut oils. The highest oleic acid (82.21%) and the lowest linoleic acid (8.32%) content of hazelnut (Sivri) oil were observed when heated in conventional oven. Arachidonic acid was not found in hazelnut (Sivri) oil. When Brazilian nut was heated in microwave oven, oleic acid was decreased from 31.74 to 27.74%, linoleic acid content

Table 1 Antioxidant activity, total phenolic and oil contents of Brazilian nut and hazelnut samples

	Antioxidant activity (%)	Total phenol (mg/100 g)	Oil (%)
Control-B ¹	81.77 ± 0.00*a	68.97 ± 0.05a	63.04 ± 0.03b
C-B ²	40.66 ± 0.01b**	66.47 ± 0.05b	65.08 ± 0.07a
M-B ³	34.60 ± 0.00c	25.88 ± 0.00c	61.00 ± 0.05bc
Control-S ⁴	86.52 ± 0.00a	63.83 ± 0.02a	61.30 ± 0.11b
C-S	80.17 ± 0.00b	55.53 ± 0.02b	63.25 ± 0.05a
M-S	76.33 ± 0.01bc	46.75 ± 0.01c	62.94 ± 0.05bc

* Mean ± standard deviation (n:3)

** Values within each column followed by different letters are significantly different ($p < 0.05$)

¹Raw Brazilian hazelnut; ² conventional roasting; ³ microwave roasting; ⁴ raw Sivri hazelnut

Table 2 Phenolic compounds of Brazilian nut and hazelnut samples

Phenolic compounds (mg/100 g)	Control-B ¹	C-B ²	M-B ³	Control-S ⁴	C-S ²	M-S ³
Gallic acid	5.33 ± 0.80*a	5.14 ± 0.51b	3.38 ± 1.53c	4.81 ± 0.78a	2.71 ± 0.60b	2.50 ± 0.73c
3,4-Dihydroxybenzoic acid	4.33 ± 1.71a**	3.04 ± 1.16b	2.01 ± 0.01c	4.61 ± 1.93a	1.69 ± 0.47c	3.28 ± 1.96b
(+)-Catechin	4.88 ± 0.98a	3.52 ± 0.64b	3.37 ± 0.05c	6.96 ± 2.00a	4.22 ± 1.74c	5.52 ± 1.72c
1,2-Dihydroxybenzene	1.67 ± 0.50b	1.24 ± 0.10c	1.70 ± 0.22a	4.14 ± 0.66a	3.55 ± 0.16b	2.56 ± 0.89c
Syringic acid	0.73 ± 0.15a	0.35 ± 0.04b	0.64 ± 0.18c	1.58 ± 0.76b	1.67 ± 0.41a	1.42 ± 0.09c
Caffeic acid	0.64 ± 0.16a	0.51 ± 0.03b	0.30 ± 0.12c	0.27 ± 0.05c	1.34 ± 0.63a	0.64 ± 0.12b
Rutin trihydrate	0.53 ± 0.39a	0.48 ± 0.09b	0.37 ± 0.08c	1.39 ± 0.08a	0.54 ± 0.07c	0.79 ± 0.27b
<i>p</i> -Coumaric acid	0.05 ± 0.09a	0.04 ± 0.01b	0.04 ± 0.01b	0.22 ± 0.08a	0.21 ± 0.09ab	0.11 ± 0.01c
<i>Trans</i> -ferulic acid	0.32 ± 0.01a	0.32 ± 0.06a	0.24 ± 0.04b	0.41 ± 1.03c	0.48 ± 0.03b	0.65 ± 0.04a
Apigenin 7 glucoside	0.24 ± 0.05b	0.31 ± 0.10a	0.23 ± 0.07bc	0.60 ± 0.17c	0.77 ± 0.12b	0.82 ± 0.21a
Resveratrol	0.12 ± 0.07a	0.06 ± 0.01b	0.12 ± 0.03a	0.21 ± 0.09b	0.20 ± 0.08bc	0.26 ± 0.07a
Quercetin	0.20 ± 0.04b	0.18 ± 0.03bc	0.29 ± 0.11a	0.70 ± 0.09a	0.55 ± 0.07b	0.50 ± 0.04c
<i>Trans</i> -cinnamic acid	0.04 ± 0.01b	0.03 ± 0.01c	0.06 ± 0.01a	0.10 ± 0.03a	0.07 ± 0.03bc	0.08 ± 0.03b
Naringenin	0.66 ± 0.09a	0.13 ± 0.04c	0.20 ± 0.03b	0.70 ± 0.06a	0.38 ± 0.09b	0.34 ± 0.01c
Kaempferol	0.24 ± 0.02b	0.16 ± 0.07c	0.30 ± 0.03a	0.28 ± 0.00b	0.74 ± 0.16a	0.28 ± 0.05b
Isorhamnetin	0.32 ± 0.07a	0.17 ± 0.03c	0.26 ± 0.06b	0.49 ± 0.01ab	0.51 ± 0.04a	0.34 ± 0.05c

* Mean ± standard deviation (n:3)

** Values within each column followed by different letters are significantly different ($p < 0.05$)¹Raw Brazilian hazelnut; ² conventional roasting; ³ microwave roasting; ⁴ raw Sivri hazelnut**Table 3** Fatty acid compositions of Brazilian nut and hazelnut samples (%)

Fatty acids	Control-B ¹	C-B ²	M-B ³	Control-S ⁴	C-S ²	M-S ³
Palmitic	13.51 ± 0.01*b	13.09 ± 0.02c	13.70 ± 0.09a	5.57 ± 0.02bc	5.69 ± 0.033b	6.22 ± 0.01a
Stearic	8.91 ± 0.01a**	8.20 ± 0.01c	8.78 ± 0.04b	2.22 ± 0.01c	2.46 ± 0.00a	2.28 ± 0.00b
Oleic	31.74 ± 0.01a	31.19 ± 0.00a	27.74 ± 0.05b	80.84 ± 0.05b	82.21 ± 0.01a	80.88 ± 0.03b
Linoleic	44.39 ± 0.01c	46.19 ± 0.03b	48.18 ± 0.01a	10.02 ± 0.01a	8.32 ± 0.00c	9.26 ± 0.01b
Arachidic	0.23 ± 0.00b	0.22 ± 0.00bc	0.26 ± 0.00a	0.13 ± 0.00b	0.14 ± 0.00a	0.13 ± 0.00b
Linolenic	0.11 ± 0.00a	0.09 ± 0.03b	0.08 ± 0.03b	0.13 ± 0.00a	0.11 ± 0.00c	0.12 ± 0.00b
Arachidonic	0.19 ± 0.00c	0.21 ± 0.00a	0.20 ± 0.01b	–***	–	–

* Mean ± standard deviation (n:3)

** Values within each column followed by different letters are significantly different ($p < 0.05$)

*** Nondetection

¹Raw Brazilian hazelnut; ² conventional roasting; ³ microwave roasting; ⁴ raw Sivri hazelnut

increased from 44.39 to 48.18%. A significant difference between palmitic and linoleic acid content of Brazilian nut and hazelnut (Sivri) kernels heated in the oven and microwave was observed. Fatty acids of both nut oils were affected by heating process. Derewiaka et al. (2014) reported that Brazilian nut oil contained 17.9% palmitic, 9.9% stearic, 31.2% oleic and 38.8% linoleic acids. Roasting involves a number of physico-chemical changes including dehydration and chemical reactions (Ciarmiello et al. 2013). According to results, fatty acid composition and phenolic compounds were affected by conventional oven and microwave heating.

Conclusion

The antioxidant effect and total phenol contents of cashew nut extracts heated in the oven and microwave were reduced compared to the control. Gallic acid, 3,4-dihydroxybenzoic acid and (+)-catechin were the main phenolic compounds of Brazilian nut and hazelnut (Sivri) extracts heated at different microwave powers. It was not observed regular increase or decrease at fatty acid composition and phenolic compounds of Brazilian nut and hazelnut kernels associated with applied heating process. Therefore, antioxidant activity, total phenol, phenolic

compounds and fatty acid compositions of Brazilian nut and hazelnut (Sivri) were effected by heating treatment.

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