Short note

The effect of microwave and roasted processing on the fatty acid composition of oils extracted from stone pine *(Pinus pinea)* nuts

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Crude oil, crude ash, crude protein and crude fibre contents of pine (*Pinus pinea*) nuts were determined as 50.8% and 48.7%; 3.1% and 2.7%; 24.8% and 23.3%; and 7.6% and 8.8%, respectively. In addition, peroxide values, acidity, density and refractive index values of both samples were established as 1.21 meqO_2/kg and 1.87 meqO_2/kg; 1.47% and 1.33% (oleic acid); 0.924 g/cm^3 and 0.921 g/cm^3; and 1.471 and 1.463, respectively.
Mineral contents of pine nuts were determined by *Inductively Coupled Plasma Atomic Emission Spectroscopy* (ICP-AES). Among the minor elements determined, Ni, Cd and Pb were found in lower concentrations. Macronutrient mineral contents of pine nuts were determined as Ca, K, Mg and P. The potassium contents of the nuts were found to be 7987.6 mg/kg and 8067.7 mg/kg for Balikesir and Kahramanmaras pine nuts, respectively, and were followed by P, Mg and Ca elements. Pinus nut oils are rich in unsaturated fatty acids.
The oleic acid contents of microwave roasted pine nuts samples ranged from 50.53% to 52.78% for Kahramanmaras and Balikesir provinces, respectively, corresponding to linoleic contents ranging from 38.48% to 38.50%.
However, pine nuts roasted by conventional heating contained 52.05% and 53.29% oleic acid and 38.83% and 37.59% linoleic acids. Oleic acid content of Balikesir pine nuts roasted by microwave heating was found to be lower compared with conventional heating.
Key words: stone pine, oil, roasting, microwave, chemical properties, minerals, fatty acid composition

Effetto del riscaldamento a microonde e della tostatura sulla composizione in acidi grassi di oli estratti dai pinoli (*Pinus pinea*).
I contenuti di olio grezzo, ceneri grezze, proteina grezza e fibra grezza dei pinoli (*Pinus pinea*) sono stati determinati rispettivamente come 50,8% e 48,7%; 3,1% e 2,7%; 24,8% e 23,3%; 7,6% e 8,8%.
Inoltre, i valori dei perossidi, dell'acidità, della densità e dell'indice di rifrazione di entrambi i campioni sono stati stabiliti rispettivamente come 1,21 meqO_2/kg e 1,87 meqO_2/kg; 1,47% e 1,33% (acido oleico); 0,924 g/cm^3 e 0,921 g/cm^3; 1,471 e 1,463.
Sono stati determinati i contenuti dei minerali nei pinoli mediante spettroscopia di emissione atomica al plasma accoppiato induttivamente (ICP-AES). Tra i microelementi determinati, Ni, Cd e Pb sono stati trovati in concentrazioni più basse. I contenuti dei macronutrienti nei pinoli erano determinati come Ca, K, Mg e P. I contenuti di potassio erano rispettivamente 7987,6 mg/kg e 8067,7 mg/kg per i pinoli Balikesir e Kahramanmaras, seguiti dagli elementi P, Mg e Ca. Gli oli dei semi di pinolo sono ricchi di acidi grassi insaturi.
I contenuti di acido oleico dei campioni di pinoli tostati nel microonde variavano rispettivamente dallo 50,53% al 52,78% per i pinoli provenienti dalle province Kahramanmaras e Balikesir, corrispondenti ad un contenuto di acido linoleico che variava dal 38,48% al 38,50%.
Tuttavia i pinoli tostati con il riscaldamento convenzionale contenevano 52,05% e 53,29% di acido oleico e 38,83% e 37,59% di acido linoleico. Il contenuto di acido oleico dei pinoli di Balikesir tostati mediante il riscaldamento a microonde è stato trovato più basso se confrontato con il riscaldamento convenzionale.
Parole chiave: pino domestico, olio, torrefazione, forno a microonde, proprietà chimiche, minerali, composizione in acidi grassi.

1. INTRODUCTION

Stone pine (*Pinus pinea* L.) known as pine nuts, and are edible and highly nutritious [1-3]. It has been widely planted throughout the Mediterranean regions, mainly in Spain, Portugal, Italy, Greece, Albania, and Turkey. It is reported that the Turkish production of pine nut was about 1200-1300 tons/year for the year 2004 [1]. Pine nuts are consumed raw or roasted and used as an additive in many food preparations [4]. According to Savage [5], the daily consumption of nuts may lower the risk of coronary heart disease as well as non-fatal myocardial infraction.
The seed contains 45% lipids and 21% proteins on a dry weight basis [6]. The chemical composition of pine seeds is affected not only by the variety but also by the geographical and climatic factors [7].
Microwave energy is currently being used for several food processing operations, including cooking, drying, tempering, baking, pasteurization and sterilization [8,9]. The microwave process can offer several distinct advantages when compared to conventional heat processes. These advantages include speed of operation, energy savings, precise process control, faster start up and shut-down times [10]. The effect of microwave heating on nutrients depends on factors such as the size and shape of the food product, thickness and quality [11]. Some work was carried out on the physical and chemical properties of *Pinus pinea* kernels and oils [1-4,7; 12; 13]. However, the effect of microwave and oven roasted processing on fatty acid compositions of pine nut (*P. pinea* L.) oils was not carried out. Therefore, the aim of this study was to investigate the effect of microwave and oven roasted processing on fatty acid compositions of oils extracted from pine nuts growing Balikesir and Kahramanmaras provinces in Turkey.

2. MATERIAL AND METHODS

2.1. MATERIAL

The nuts of the *Pinus pinea* were used in this study. Pine nuts were harvested from plants cultivated in Balikesir and Kahramanmaras provinces in October 2011. After the harvest, the samples were immediately dried at 35°C till the moisture level was <6%. Following this, the nuts were packed in coloured glass bottles, transported to the laboratory. For the same physical properties of the harvested samples, seed length and width were determined. The shells of the nuts were removed before the analyses. The skinned meat samples were used for all the chemical analyses.

2.2. METHOD

Peroxide values, acidity, density, refractive index, iodine value and unsaponifiable matter were determined according to the standard AOAC [14] method. Protein content was established according to the Dupon method. Crude protein was calculated by using a nitrogen conversion factor of 6.25 [19]. Protein content was determined by the Dumas Nitrogen Analyzer (DNA) (Velp NDA 701-Italy). Protein was calculated using the general factor (6.25).

Working conditions of dna:
O_2 flow rate: 400 ml/min
He flow rate: 195 ml/min
Combustion reactor 1030°C
Reduction reactor: 650
Pressure (mbar): 881.0

2.2.1. Oven roasted

About 50 g of stone pine kernels were distributed uniformly as a thin layer on the trays, and roasted in an oven (Nüve FNO55, Ankara, Turkey) at 200°C for 10 min.

2.2.2. Microwave heating

A small microwave oven (Arcelik ARMD 580, Turkey) with a maximum output of 900 W and 2450 MHz was used for roasting experiments. The dimensions of the microwave cavity were 34,5×34,0×22,5 cm. Its roasting glass plate was 28 cm in diameter. The microwave oven was operated by a control terminal which could control the microwave power level and emission time. In addition to this, the glass plate rotated for 5/min and the direction of 360 degrees rotation could be changed by pressing the on/off button. Microwave heating was carried out at 900 W for five minutes.

2.2.3. Determination of fatty acids

Fatty acid compositions for pine nut oil were determined using a modified fatty acid methyl ester method as described by Hişil [15]. The oil was extracted three times for 2 g air-dried seed sample by homogenization with petrolium ether. The oil samples (50-100 mg) were converted to their fatty acid methyl esters (FAME). The methyl esters of the fatty acids (1μl) were analysed in a gas chromotography (Shimadzu GC-2010) equipped with a flame ionising detector (FID), a fused silica capillary column (60 m × 0.25 mm i.d.; film thickness 0.20 mikrometere). It was operated under the following conditions: oven temperature program. (90°C for 7 min. Raised to 240°C at a rate 5°C/min and then kept at 240°C for 15 min); injector and detector temperatures, 260 and 260°C; respectively, carrier gas. nitrogen at flow rate of 1.51 ml/min; split ratio. 1/50 μl/min. A standard fatty acid methyl ester mixture (Sigma Chemical Co.) was used to identify sample peaks. Commercial mixtures of fatty acid

methyl esters were used as a reference data for the relative retention times [14]. Quantitative analyses of the fatty acids were performed using the heptadecanoic acid methyl ester as an internal Standard.

2.2.4. Determination of mineral contents

Collected samples were dried at 70°C in a drying cabinet with air-circulation until they reached a constant weight. After a dried and ground sample of about 0.5 g was digested by using 5ml of 65% HNO_3 and 2 ml of 35% H_2O_2 in a closed microwave system (Cem-MARS Xpress). The volumes of the digested samples were completed to 20 ml with ultra-deionized water and mineral concentrations which were determined by an inductively coupled plasma-optical emission spectroscopy (ICP AES; (Varian-Vista, Australia). Measurements of mineral concentrations were checked using the certified values of the related minerals in the reference samples received from the National Institute of Standards and Technology (NIST; Gaithersburg, MD, USA) [20].

Working conditions of ICP-AES:

Instrument:	ICP-AES (Varian-Vista)
RF Power:	0.7-1.5 kw (1.2-1.3 kw for Axial)
Plasma gas flow rate (Ar):	10.5-15 L/min. (radial) 15“ (axial)
Auxiliary gas flow rate (Ar):	1.5”
Viewing height:	5-12 mm
Copy and reading time:	1-5 s (max.60 s)
Copy time:	3 s (max. 100 s)

2.2.5. Statistical analyses

Results of the research were analysed for statistical significance by analysis of variance [16].

3. RESULTS AND DISCUSSION

The some physical and chemical properties of pine nuts and their oils harvested from *P.pinea* plants grown in Balikesir and Kahramanmara^{9} provinces of Turkey are presented in Table I.

Crude oil, crude ash, crude protein and crude fibre contents of nuts were determined as 50.8 and 48.7%, 3.1 and 2.7%, 24.8 and 23.3% and 7.6 and 8.8%, respectively. In addition, peroxide values, acidity, density and refractive index values of both samples were established as 1.21 and 1.87 meq O_2/kg, 1.47 and 1.33% oleic acid, 0.924 and 0.921 g/cm^3 and 1.471 and 1.463, respectively. Zadernowski et al. [3] reported that the peroxide value and total free fatty acid contents of *Pinus sibirica* cultivar harvested in Siberia were found 0.51 mMO_2/kg of oil and 2.40 mg KOH/g of oil, respectively. The peroxide value is 2-5 times lower than those reported by Amaral, Casal et al. [17] for oils obtained from six walnut cultivars. The chemical composition of pine nuts is effected not only by the variety but also by geographical and climatic factors [7].

Mineral contents of pine nuts were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Among the micronutrient elements determined Ni, Cd and Pb were found to be lower. Fe, Ni and Zn contents of samples collected from Balskesir and Kahramanmaras provinces were found.7-76.3 mg/Kg, 0.23-0.11 mg/Kg and 68.3-63.7 mg/Kg, respectively. Macronutrient mineral contents of pine nuts were determined as Ca, K, Mg and P. The potassium contents of nuts were found to be 7987.6 mg/kg and 8067.7 mg/Kg for Balikesir and Kahramanmaras pine nuts, respectively, followed by P, Mg and Ca elements (Table II). Nergiz & Dönmez [1],

Table I - Phsical and chemical properties of pine nut and their oils (n:3)

Properties	Locations	
	Balikesir	Kahramanmaras
Number of seeds /100g	141±1.3*	137±0.9
Weight (g)	0.229±0.011	0.232±0.008
Length (mm)	14.20±1.17	15.21±0.96
Width (mm)	5.44±0.98	5.26±0.51
Crude oil (%)	50.8±2.7	48.7±2.3
Moisture (%)	5.8±0.21	5.4±0.13
Crude ash (%)	3.1±0.28	2.7±0.17
Crude protein (%)	24.8±2.6	23.3±1.3
Crude fibre (%)	7.6±0.63	8.8±0.98
Proxide value (meq O_2/Kg)	1.21±0.11	1.87±0.03
Acidity (% oleic)	1.47±0.18	1.33±0.12
Density (g/cm^3)	0.924±0.011	0.921±0.014
Refractive Index (*n*20/D)	1.471±0.031	1.463±0.027

(*) mean±standard deviation

Table II - Mineral contents of pine nuts (mg/Kg) (n:3)

Properties	Locations	
	Balikesir	Kahramanmaras
Ca	147.8±3.6*	151.3±2.3
K	7987.6±17.1	8067.2±11.8
P	5678.3±10.8	6728.9±13.4
Mg	3987.6±8.3	4768.1±7.4
Fe	83.7±2.7	76.3±3.2
Ni	0.23±0.02	0.11±0.01
Pb	0.003±0.00	0.002±0.00
Zn	68.3±3.2	63.7±1.7
Cd	0.0096±0.0008	0.0114±0.0016

(*) mean±standard deviation

Table III - Fatty acid compositions of pine nut oils

Treatments	Fatty Acids (%)					
Kahramanmaras	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Arachidic
Microwave	6.34	2.36	50.53	38.48	1.11	1.13
Raw	6.44	0.59	51.69	39.18	0.89	1.18
Oven	6.40	0.58	52.05	38.83	0.90	1.16
Balikesir						
Microwave	6.64	1.27	51.78	38.50	0.34	1.22
Raw	6.52	0.80	52.16	38.31	1.16	1.02
Oven	6.65	0.57	53.29	37.59	1.23	1.22

reported that pine nut obtained from the private pine nut processing factory in Bergama-Izmir contained 5.1% moisture, 4.5% ash, 44.9% oil, 31.6% crude protein. In addition, sodium, potassium, calcium, magnesium, copper, zinc, iron, manganese and phosphorus of pine nuts were found to be 11.7 mg/100g, 713 mg/100g, 13.8 mg/100g, 325 mg/100g, 1.5 mg/100g, 6.4 mg/100g, 10.2 mg/100g, 6.9 mg/100g and 512 mg/100g [1]. Among all the *Pinus* varieties, the highest protein content (34%) was reported for *P. pinea* [18]. In previous studies, oil content of pine nuts changed from 31% to 68% [4]. Commercial pine nut samples (*P. pinea*) analysed in Italy contained oil 50.3% [13]. According to results, pinus nuts are rich in oils; their contents vary due to differences in species and environmental factors. In general, similar results were carried out by Nergiz & Dönmez [1] and Wolff & Bayard [4].

Fatty acid compositions of pine seeds roasted by conventional and microwave heating are recorded in Table III, which shows that oleic and linoleic acids account for more than 88% of the total fatty acids. *Pinus* nut oils are rich in unsaturated fatty acids. The oleic acid contents of microwave roasted pine seeds ranged from 50.53% to 51.78% for Kahramanmaras and Balikesir provinces, respectively, corresponding to linoleic contents ranging from 38.48% to 38.50%. However, pine nuts roasted by conventional heating contained 52.05% and 53.29% oleic acid and 38.83% and 37.59% linoleic acids. Palmitic acid contents of both samples were found to be similar, and was not effected from both microwave and conventional heating. Oleic acid content of Balikesir pine nuts roasted by microwave heating were found to be partly low compared with the conventional heating. However, stearic acid contents of nuts roasted by microwave were found to be at the partly high levels. Generally, linoleic and arachidic acids of pine nuts with both treatments were established at the level <1.5%. In raw materials, oleic and linoleic acids accounted for 51.69 and 39.18% to 52.16% and 38.31% for Kahramanmaras and Balikesir provinces, respectively. Previous studies showed that the oils of Pinus cultivars contained oleic and linoleic acids at relatively high levels [1,2,4,7]. Our results were found to be similar with the reported values. According to the results, we can state that pine seeds have high protein and oil, P, K and Mg contents. The seed lipids of the investigated samples were rich in linoleic acid. It has a beneficial effect on blood lipids, lowering blood pressure and serum cholesterol [1].

4. CONCLUSION

Pine seeds can be always roasted in these heating methods such as microwave and conventional heating. *Pinus* nut oils are rich in unsaturated fatty acids.

The oleic acid contents of microwave roasted pine seeds ranged from 50.53% to 51.78% for Kahramanmaras and Balikesir provinces, respectively, corresponding to linoleic contents ranging from 38.48% to 38.50%. However, pine nuts roasted by conventional heating contained 52.05% and 53.29% oleic acid and 38.83% and 37.59% linoleic acids.
Palmitic acid contents of both samples were found to be similar, and were not effected from both microwave and conventional heating. Oleic acid content of pine nuts roasted by microwave heating was found to be partly low compared to conventional heating. It can be concluded that microwave heating of pine nuts is recommended for short periods. Thus, the pine nuts are rich in source of many important nutrients such as oil, protein, minerals and fatty acids.

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