Impact of roasting and frying on fatty acids, and other valuable compounds present in peanuts

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Peanuts contain reasonable levels of antioxidant, monounsaturated and essential polyunsaturated fatty acids that are known to have favourable impacts on human health. Processing conditions affect these favourable contents, e.g. roasting and frying. In this study, we experimented with raw and roasted peanuts as they are sold at Jordanian public stores. Our studies also include fried peanuts according to Jordanian local frying method. Our studies showed that roasting and frying peanuts significantly increased their levels of essential fatty acids EFA (alpha-linolenic acid to linoleic acid LA and ALA *p.value* 0.008 and 0.001 respectively). 1,1-Diphenyl-2-picryl-hydrazyl DPPH and bioactive compounds (*p.value* 0.01) were increased in fried and roasted peanuts which reduce the negative effects accompanied with the increasing in peroxide value. Our work presented in this paper shows how peanuts can be considered a good source of natural antioxidant and healthy fatty acids even after roasting or frying.

Keywords: DPPH; Essential Fatty Acids; Frying; Flavonoids; Peanuts; Peroxide Value; Phenolic; Roasting

1. INTRODUCTION

Peanuts are plant based foods that their consumption is associated inversely with several chronic diseases such as cardiovascular diseases (CVD), diabetes, some forms of cancer [1, 2], lower occurrence of coronary heart disease (CHD) [3], obesity, inflammation, hyperlipidaemia, and glucose intolerance which were thoroughly presented by many epidemiological evidences [4]. Several research works demonstrated the significant contribution of peanuts as an antioxidant, anti-inflammatory due their composition of phytochemical monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA) and fibre contents [1]. Therefore, peanuts are added to the recommended dietary guidelines by United States Food and Drug Administration (FDA) [5].
The oxidation of fat and fat containing foods is responsible for the deterioration in the food quality and nutritive value. In addition, the oxidation of PUFA in food may be related to diseases such as atherosclerosis, diabetes, and cancer [6]. These antioxidants occur in all higher plants and in all parts of the plant and seeds is one of richest source [7]. This beneficial effect of plants was related to presences of bioactive compounds that act as antioxidants (such as phenolics and flavonoids), free radical scavengers and metal chelating. Flavonoids intake has been demonstrated to decrease the risk of several chronic diseases due to their attributes of antioxidant, anti-inflammatory and anti-proliferation [1]. The ability of the samples to trap determined the antioxidant activity of peanuts 1,1-Diphenyl-2-picryl-hydrazyl DPPH radical to evaluate the antioxidant activity of extracts and pure substances [8].

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Peanuts as part of nuts are considered as one of the richest natural plant foods in fat, after vegetable oil. They account of around 50% of their weight as fat [9]. Luckily for us human beings, this fat is made of unsaturated fatty acids (USFA). Therefore; it is recommended to replace the fatty foods with nuts to obtain the beneficial effect of decreasing chronic diseases [2]. The high percentage of USFA and polyunsaturated fatty acids PUFA are very sensitive to the oxidation alternation due to frying/roasting treatments [10]. Peanuts contain a high level of Linoleic acid (LA) and reasonable levels of α-linolenic acid (ALA) which act as an anti-inflammatory agent [2]. Peanuts are rich in oleic acids (OL), which contains the most abundant monounsaturated fatty acids MUFA. The chief MUFA in peanuts is oleic acid (C18:1) while the main essential polyunsaturated fatty acids EFA are ALA and LA. Such composition explains the beneficial effects of peanuts in relation to decreasing the aforementioned set diseases risk. A diet rich in MUFA improves blood lipid profile due to decreasing low density lipoprotein (LDLs) and enhancing cholesterol: high density lipoprotein Chol:HDL ratio [11].

Peanuts are widely accepted and are convenient to eat [3]. Peanuts can be present in a wide range of foods whether as whole nuts or hidden/processed in items like confectionery, bakery, cereals, sweets, and biscuits etc. Roasted peanuts without any additives or spices have become popular snacks, as they are liked by children and well accepted as a healthy snack [12].

Roasting/frying are among the most common methods of peanuts thermal processing to improve the sensory properties. Although there are several commercial products prepared by dry roasting and frying, there is a lack of a scientific comparison of the differences in their nutrient. However, many studies examined the effects of food manufacturing treatments on peanut butter/paste but not enough work has been invested in the analysis on whole peanuts. Apart from the changing in the raw peanuts material, chemical changes take place due to roasting/frying. Those changes might be unfavourable and affect their health impacts. However, in Jordan, one of the common ways to present the local cuisine food (rice based) is to top rice with fried nuts; peanuts are one of them.

Due to their reasonable cost, peanuts are considered the most favourable snacks amongst Jordanians. This has motivated this study, focusing on peanuts as a whole nut and not as peanut butter or processed compositions that are not as popular in Jordan.

Several research studies either analysed peanuts' contents of special nutrients or tested the processing that takes place on the peanuts in laboratories. However, to the authors' best knowledge, very limited studies analysed the changing in the raw peanuts after going through the roasting or the frying according to the Jordanian eating style. In relevant studies, roasted peanuts were tested, but not fried peanuts. In this study, we tested the effects of roasting and frying that are applied and processed from 2 major stores in Amman, Jordan to examine how such treatments affect the total saturated fatty acids (SFA), MUFA oleic acid, EFA, oxidative stability presented by peroxide value, 1,1-Diphenyl-2-picryl-hydrazyl (DPPH) and bioactive compounds presented by flavonoids and phenolic. In this paper, we consider whole raw, roasted, and fried peanuts without shells. The treatment temperatures were not of our interest as we aimed to test the products that are commonly consumed by local people in Amman as they are sold.

2. MATERIALS AND METHODS

2.1. RAW AND ROASTED PEANUTS

Dehulled raw and commercially roasted peanuts (4 kg each) were purchased from the two major local nuts' stores in Amman. The samples were taken from the same batch that came from a single manufacture. Commercial peanut roasting was carried out using a roasting drum roaster at a temperature range of 100 - 120°C for 15-17 min. The raw and roasted peanuts were ground and sieved to obtain fine powder. The samples were then stored at –20°C until analysis.

2.2. PAN FRYING OF RAW PEANUTS

Pan frying of dehulled peanuts (100 g) was carried out at a temperature range of 170 - 180°C for 2.5 - 3 minutes using refined corn oil as heating medium. The heat medium was removed from the surface of the peanuts by tissues like the method used in households. Fried peanuts were ground, sieved and stored at –20°C until analysis. This process was carried out in three replicates.

2.3. FAT EXTRACTION

About 50 g of ground raw, roasted, or fried samples were soaked in petroleum ether for about 24 hours and then filtered. The petroleum ether phase was evaporated using a rotary evaporator under vacuum at a temperature not exceeding 40°C. The lipid fraction was stored at –20°C in a freezer for additional analysis.

2.4. EXTRACT PREPARATION

The powder raw, roasted, and fried peanut extraction was carried out according to the methods of Rizki et al. [13]: 10 g of each sample was suspended in 100 ml of 90% ethanol and shaken for 2 hours. After filtration, the samples were subjected to vacuum evaporation. The extract was recovered with 2 ml of

90% ethanol and assayed for its antioxidant activity, total phenolic compounds, and flavonoids.

2.5. TOTAL POLYPHENOLS CONTENT (TPC)

Total polyphenols content carried out according to the methods of Rizki et al. [13]**.** Samples of each extract (0.4 ml) were mixed with 2 ml of Folin-Ciocalteu (diluted 10 times). After 3 min, 1.6 ml of 7.5% sodium carbonate was added. The absorbance was read at 750 nm after 30 min of incubation at room temperature (26 ± 2°C). A standard curve was prepared using gallic acid and the results were expressed as mg gallic acid equivalent/g sample.

2.6. TOTAL FLAVONOID CONTENT

1 ml of the extract was added to 1 ml of aluminium trichloride (2% w/v). After 15 min of incubation, the absorbance was measured at 430 nm and the results were expressed as mg quercetin equivalents per mg extract Rizki et al. [13].

2.7. FREE RADICAL SCAVENGING ACTIVITY (DPPH)

The antioxidant activity of the sample extracts was evaluated following using 2, 2-diphenyl-1-1 picrylhydrayl (DPPH) radical according to the method of Sun and Ho [14]. An aliquot of 30 µl of the sample extracts was added to 0.5 ml of DPPH solution (25 mg/l) diluted to 5 ml of methanol. A control without extract was also prepared. The mixture was shaken vigorously and allowed to stand for 45 minutes in the dark and the absorbance was measured at 515 nm. The antioxidant activity of the extract was calculated using the formula:

$$\% \text{ Inhibition} = \frac{(\text{Absorbance sample} - \text{Absorbance control})}{\text{Absorbance control}} \times 100$$

2.8. VITAMIN *E.* DETERMINATION

Vitamin E was determined following the method used by [15]. The analysis of vitamin E was carried out using a Knauer HPLC System (Germany). The determination was carried out following the method of Gimeno et al. [15].

The oil sample of raw, roasted, and fried peanut was diluted in hexane (1:10). An aliquot of 200 µl was transferred to a test tube containing 600 µl of methanol and 200 µl of the internal standard solution (300 mg/ml of α-tocopherol acetate in ethanol). The mixtures were mixed, centrifuged at 3000 g for 5 min and then filtered through a 0.45 mm pore size filter. Fifty micrometres were directly injected into the Knaur HPLC system. The mobile phase was methanol-water (96:4, v/v) and the elution was performed at a flow-rate of 2 ml/min. The analytical column was Venusil XBP, C18 [2] (Agelant Technologies, USA) and was kept at 45°C. Detection was performed at 292 nm using Knauer UV detector (modle Smartline 2500, Germany).

2.9. DETERMINATION OF FATTY ACID PROFILE

Fatty acid methyl esters FAMEs of the peanuts samples were prepared according to Christopherson and Glass, 1969's method [16]. The prepared FAMEs were studied using capillary Gas Liquid Chromatography (GLC) analysis. The prepared methyl esters were analysed using capillary GLC column (Restek, Rtx-225, USA, cross-bond 90%-cyanopropylmethylpolysiloxane, 60 m and 0.25 µm df) immediately after esterification by injection 1 µl of the hexane layer through the injection port of the GLC (model GC-2010, shimadzu. Inc., Koyoto, Japan). The GLC condition was; initial column oven temperature was 165°C at 15°C/min and held at this temperature for 10 min., increased to 180°C at 1°C/min, then increased to 220°C at 3°C/min., and held at this temperature for 10 min. Injector temperature was 240°C, the flame ionization detector temperature was at 250°C, flow rate of He was 0.8 ml/min, and the split ratio used was 80:1. Fatty acid identification was carried out by injection standard fatty acids (Sigma, USA).

2.10. STATISTICAL ANALYSIS

Statistical analyses were performed using SPSS (Statistical Program for Social Sciences) version 17.0 for Windows. All analyses were conducted in triplicate, and data reported as means ± standard deviation (SD). Fatty acids' area [µV.s] from the chromatogram were completed and calculated by using Microsoft®Office Excel 2007 (12,0,4518,1014) MSO.

3. RESULTS

3.1. TOTAL PHENOLIC (TPC) AND FLAVONOIDS CONTENT

The Folin-Ciocalteu reagent is not specific for phenolic compounds, since it can be reduced by several non-phenolic compounds. Although the exact reaction of this reagent with reducing species in not fully understandable, but it is considered that a complex is formed between phosphor molybdic tungstate and reducing species such as phenolate ion, changing colour from yellow to blue [13]. As shown in Table I, The TPC for the dehulled peanut was 1.16 mg/g that goes along with those of Fakhriya et al. [17] and slightly higher than those reported by Win et al. [18]. It is evident that roasting at 110-120°C for 15-17 min significantly increased TPC. The increase was about

64% of TPC in the raw peanut. Furthermore, pan frying showed higher increase in TPC when compared to those of raw or roasted samples. The increase in TPC after frying at 170°C for about 2.5 min was about 115.5% and 39% of the registered TPC for the raw and roasted peanut, respectively.

Table I - Effects of roasting and frying of peanut kernel on total phenolic content, total flavonoids and DPPH Radical scavenging activity

Parameters	Raw	Roasted	Fried
Flavonoid content (mg/g) as quercetin	1.2 ± 0.21^{a*}	2.2 ± 0.5^{b}	2.3 ± 0.5^{b}
Total phenolic content (mg/g) as gallic acid	1.16 ± 0.2^{b}	1.80 ± 0.25^{a}	2.5 ± 0.5^{a}
DPPH (%)	42.6 ± 5.4^{c}	55.6 ± 4.3^{b}	81.4 ± 6.2^{a}

* Values within the same row with different superscripts were significant differences (P <0.05) according to LSD.
^{a,b} indicate the group that significantly different from each other based on LSD test.

Similarly, flavonoids significantly increased in the roasted and fried peanut when compared to those of the raw one. However, no significant differences in flavonoids content between roasted and fried peanuts in flavonoid concentrations. These results agree with those of Win et al. [18] who reported that roasting of kernel peanut flour at 160°C for 10 min increased TPC from 0.92 to 1.17 mg/g sample. Similar results were reported by Talcott et al. [19] who reported that peanut kernel roasting at 170°C for 10 min increased from 0.913 mg/g kernel to 0.949 mg/g kernel.

3.2. FREE RADICAL SCAVENGING ACTIVITY (DPPH)

The antioxidant activity of the peanut extract products studied in this study was evaluated using DPPH radical. This radical is commonly used for the assessment of antioxidant activity *in vitro*. DPPH is a very stable organic free radical with deep violet colour that gives absorption maxima within 515-528 nm range. Upon receiving proton from any hydrogen donor, mainly from phenolics, it loses it chromophore and becomes yellow. As the concentration of phenolic compounds or degree of hydroxylation of the phenolic compounds increases their DPPH radical scavenging activity also increases, and can be defined as antioxidant activity [20]. In this study, the radical scavenging activity was in the order: fried > roasted > raw (Table I). The radical scavenging activity of the fried and roasted peanut extracts was about 1.9 and 1.3 greater than that of the raw extracts. The higher antioxidant activity of the fried and roasted extracts might be the liberation of phenolics that may be bound to peanut kernel components such as proteins or carbohydrates during roasting and frying.

Figure 1 shows a good correlation between TPC and Antioxidant activity measured by DPPH radical scavenging activity (r^2 = 0.979). A good correlation has been reported between TPC and DPPH radical scavenging activity for sweet potato leaves extracts (r^2 = 0.799) (20) for peanut hulls, raw and roasted peanut (r^2 = 0.8436) [18].

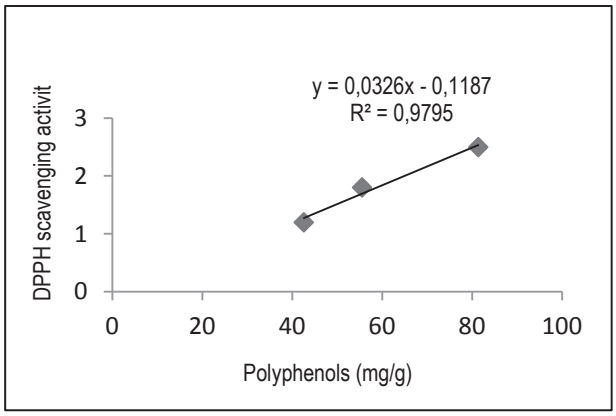

Figure 1 - Correlation of TPC and DPPH radical scavenging activity

3.3. EFFECT OF ROASTING AND FRYING ON OXIDATIVE RANCIDITY OF PEANUT OIL

The effect of peanut kernel roasting on the oxidative rancidity of its oil was evaluated by determining the peroxide value (PV) and main fatty acids and *trans* fatty acids.

As shown in Table II, roasting and frying affected negatively the oxidative rancidity of peanut oil as pleasured by PV. However, the effect of roasting was more noticeable than frying (p.value ≤0.05). This could be due to the longer roasting time (15-17 min) when compared to frying (2-3 min) that affect the oxidation activity. This might be confirmed by the slight decrease in linoleic acid content of the roasted seeds oil. It is evident from the data in Table II that there was insignificant increase in *trans* fatty acids.

The data in Table II showed that the SFA in peanut oil was low (about 16%), while those of USFA were high (about 84%). It is evident that roasting and frying had little or no effect on the unsaturated fatty acids, particularly essential fatty acids and unsaturated/saturated fatty acids ratio.

4. DISCUSSION

The bioactive peanut compounds such as antioxidants, phenols, flavonoids, vitamin E and fatty acids are associated with numerous health benefits.

Flavonoids and phenols showed to be doubled in treated peanuts than raw ones. The increase in those

Table II - Effect of roasting and fraying of peanut kernel on oil oxidation, fatty acid composition and *trans* fatty acids

Parameters	Raw	Roasted	Fried
PV (Meq O_2/kg oil)	nd**	3.72 ± 1.30[b]	0.755 ± 0.134[a]
C16:0%	11.6 ± 1.0 [a]*	11.7 ± 0.9 [a]	11.1 ± 0.2 [a]
C18:0%	3.2 ± 0,02[a]	3.1 ± 0.01[a]	3.3 ± 0.001[a]
C18:1%	43.57 ± 2.06[a]	46.27 ± 1.65[a]	42.47 ± 2.17[a]
C18:2%	36.31 ± 1.55[a]	34.24 ± 0.52[b]	37.63 ± 1.16[a]
C18:3%	0.048 ± 0.001[a]	0.045 ± 0.001[a]	0.045 ± 0.01[a]
SFA %	16.90 ± 1.01[a]	16.31 ± 0.18[a]	16.70 ± 1.01[a]
Trans fatty acids%	0.029 ± 0.004[a]	0.032 ± 0.006 [a]	0.036 ± 0.005[a]

* Values within the same row with different superscripts were significant differences (P <0.05) according to LSD. ** nd: not detected.
[a, b] indicate the group that significantly different from each other based on LSD test.

compounds is thought to give the delicious taste in roasted and fried peanuts rather than the raw ones. It is worth to notice that peanuts have a similar quantity of total flavonoids like red apple at 15 mg/100g and apricot at 13 mg/100g [22]. This can motivate the idea of considering peanuts as a rich source of total flavonoids similarly to certain types of fruits and vegetables. Raw nuts are known to have a tart-like taste but once roasted or fried this taste is prone to decrease/vanish. One of the explanations stems from the increase in flavonoids and phenols. Our analysis shows that flavonoids (rutin acid) have been doubled in means (raw = 11.8, roasted = 21.8, and fried = 22.5) in treated peanuts with no significance in the p-value (0.07).

A similar increase has been noticed in phenolic acid (galic acid) with significant differences between treated peanuts and raw ones. However, fried peanuts doubled the phenolic amount than the raw ones. The increase of TPC because of roasting and frying could be due to the Maillard reaction that results in the formation of Maillard derivatives such as pyrols and furans that may react with Folin – Ciocalteu reagent [23].

The ability of the samples to trap determined the antioxidant activity of peanuts DPPH radical [8]. Peanuts are not a major source of dietary carotenoids [1]. It was not detected in our three sample pools. Therefore, most of the antioxidant capacity in peanuts applies on DPPH, flavonoids, and phenolic acids.

Evidences demonstrated the healthy impact of peanut consumption due to their composition. Around 62% of nuts energy is coming from fat [11]. The fatty acids composition of peanuts is beneficial because SFA is low (%) and the MUFA content is significantly higher than SFA in peanuts, which was shown in our findings (SFA = 16% while MUFA 46% of total fat). The type of dietary fat intake affects the plasma cholesterol level more than the total fat intake [11]. The high content of MUFAs and PUFAs are considered healthy fats and counterbalance the unfavourable effect of SFAs in the peanut oil content [9]. In our study, it has been shown that SFA concentrations were similar among the three sample pools suggesting that roasting and frying have no effects on the SFA in peanuts. Oleic acid in peanuts is predominant and doubled the SFA. Peanuts contain a high content of LA which is one of the essential fatty acids that can be converted to arachidonic acid and then metabolised into the n-6 eicosanoids. Conversely, the ALA content is low and has the pro-inflammatory actions of the n-6 eicosanoids [2]. Therefore; due to the balance of n-6 and n-3 PUFA in the diet and its critical effect on CVD, the peanut intake should be controlled, especially the raw and the roasted one. On the other hand; the fried peanut balance is better. Essential fatty acids are realistically present in peanuts. This strengthens their association to health benefits especially chronic diseases such as CHD and diabetes. Differences in the concentration were highly significant from raw and roasted on the one hand, and fried peanuts on the other, in LA and ALA (0.008 and 0.001, respectively). The type of dietary fat intake affects the plasma cholesterol level more than the total fat intake [11]. The high content of MUFAs and PUFAs are considered healthy fats, and counterbalance the unfavourable effect of SFAs in the peanut oil content [9].

Frying replaces parts of the peanuts' evaporated water therefore the fat can increase by around 5% [10]. In fried peanuts, the FA content of essential fatty acids increased and can be explained by the contribution of oil used in frying. One would recommend frying peanuts for healthy benefits as the concentration of SFA and MUFA (OL) were stable while the EFA increased significantly.

Nuts are considered one of the fat exchange foods in the exchange list that contains 5 grams of fat and 45 calories for each serving. A serving consists in 10 whole peanuts categorised under MUFA [24]. Although peanuts are listed under fat foods [24], eating peanuts did not increase the body composition or the body weight in a study done by Barbour et al. [4] justified their study due to incomplete nutrient absorption and energy utilization of the presence of OL as a predominant MUFA. However, the relatively high fat and protein content improved satiety along

with providing a healthy snack for the weight management of children [12]. The high OL fatty acid from peanuts improved the serum lipid and apolipoprotein profile in free-living postmenopausal hypercholesterolemic women who were at risk for cardiovascular disease benefited from a low in fat high in oleic acid peanuts diet and this diet resulted in an improved serum lipid and apolipoprotein profile [22]. MUFAs reduce bad cholesterol levels (LDL) and regulate blood sugar and insulin levels [9]; the richer the peanuts in MUFAs the healthier the dietary fat type.
The healthy nutrient compositions of peanuts motivate recommending them as "smart" snacks with zero empty calories [12].

5. CONCLUSION

Although PV was not detected in raw peanuts while it was detected in treated ones, the increase in DPPH, flavonoids and phenolic acids in the treated peanuts decrease the effect of PV and increase the antioxidant activity. Fatty acid profiles are seen to be better in fried peanuts, more than roasted and raw peanuts due to the increase in essential fatty acids while SFA and MUFA were stable. Our findings suggest that fried peanuts that are eaten widely amongst Jordanians do not have adverse effects. In fact, quite the contrary was shown when fried using unsaturated fatty acid oil (vegetable oil). This study showed that peanuts can be considered a good source of natural antioxidants even after roasting or frying due to the increase in PUFAs, phenolic acid and antioxidant capacity.

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