Influence of Roasting on Oil Content, Bioactive Components of Different Walnut Kernel

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Abstract: A study was carried out to evaluate oil contents, fatty acid composition and tocopherol contents of several walnut types in relation to roasting process. The major fatty acid identified was linoleic acid in both roasted and unroasted walnut oils. Linoleic acid contents of unroasted walnut oil varied from 46.44 (Type 9) and 63.59% (Type 7), while the linoleic acid contents of roasted walnut oils at 120°C/h ranged from 55.95% (Type 3) to 64.86% (Type 10). Interestingly, linolenic acid contents of both roasted and unroasted oils changed between 9.43 (Type 10) and 16.29% (Type 8) to 9.64 (Type 10) and 16.58% (Type 8), respectively and were significant (p < 0.05) different. γ-tocopherol content of unroasted walnut oils varied between 6.3 (Type 3) and 11.4 mg/100g (Type 1) and γ-tocopherol contents of roasted walnut oils ranged between 28.1 (Type 8) and 38.2 mg/100g (Type 3). The oil could be useful for industrial applications owing to good physicochemical properties. Fatty acid values for oil obtained from roasted walnut were slightly higher than those reported for unroasted walnut oils.

Key words: walnut kernel, roasting, oil, fatty acid, tocopherol, GC, HPLC

1 Introduction

Walnut (Juglans regia L.) belongs to Juglandaceae family, and Turkey plays an important role in walnut production in the world1−4. Nuts are rich in protein, carbohydrate, unsaturated fatty acid, vitamin and minerals5−8. In several studies, the oil present in walnut kernels varied between 52 and 70%2,4,7,8. According to5,8,9, linoleic, linolenic and oleic fatty acids are the prominent fatty acids present in walnut kernel. Roasting is an important operation in nuts processing and majority of physicochemicals observed in nuts result from roasting operation10. Heat treatments including roasting are now commonly used in many food processing operations such as baking, sterilization, drying, cooking, tempering etc11,12. In addition, traditional method of heating often transfer heat slowly from the surface of products to the center and some also have undesirable effects on products quality13. Roasting operations have been shown to have desirable effects on the flavour, colour, fatty acid profile and bioactive components of kernel and seeds14,15. The normal temperature range used for roasting of edible nut ranges from 100-180°C for 5-60 min and the usual industrial procedure used in roasting in hot air method although different new techniques are also being applied depending on the intended final use16. Roasted nuts are being consumed as snacks with or without any additives and spices beside being important industrial raw material for preparing different baked, confectionary and other food products. The roasting process for nuts is indeed for certain desirable changes however, due to high polyunsaturated fatty acids contents, Malcolm roasting may require mild roasting temperature to avoid oxidation reaction of fatty acids17.

The aim of this study was to determine the effects of the roasting process (mild temperature of 120°C for 30 min) on the oil and tocopherol contents and the fatty acid profile of different types of walnut kernels and their oils. Results were also compared with those of raw walnut kernels.

2 Materials and Methods

2.1 Material

Walnut samples were provided from Ermenek (Karaman) distinct in Turkey. They walnuts were dried in oven at 70°C and the kernels were then separated from the hulls. The kernels were thereafter cleaned and kept at 4°C in a poly-
propylene bag for analysis.

2.1.1 Reagents

All reagents used in this present study were of analytical grade. Petroleum ether, HPLC grade tert-butyl methyl ether and heptanes were obtained from Merck, Darmstadt, Germany. Tocopherol and tocotrienol standards used were procured from CalBiochem (Darmstadt, Germany).

2.2 Methods

2.2.1 Roasting

Walnut kernels were roasted at 120°C for 30 min on an oven. The heating was completed when color of kernels was dark brown, and cooled.

2.2.2 Oil extraction

Walnut oil was extracted from ground walnut kernel using light petroleum ether in a Soxhlet apparatus for 5 h. Rotary vacuum evaporator was used to recover the remaining oil at 50°C. The walnut oil obtained was kept in colored glass bottles at −18°C for analysis.

2.2.3 Fatty acid analysis

A gas chromatographic procedure was used to study the fatty acid profile of oil from walnut kernels. Walnut oil drop was added to n-heptane (1 mL) in a tube followed by which 50 μg sodium methylate was added. The tube was mixed thoroughly for 1 min at room temperature. Centrifugation 4500 × g for 10 min was carried out after adding 100 μL of water followed by removal of lower aqueous phase. HCL (50 μL) and 1 mol methyl orange was mixed and afterwards the lower aqueous phase was discarded. To the reaction mixture, 20 mg of sodium hydrogen sulphate was added and centrifugation was carried out at 4500 × g for 10 min. The upper phase in n-heptane was injected into a gas chromatography (Varian 5890) having a capillary column [CP-Sil 88 (100 m long, 0.25 mm ID, film thickness 0.2 μm)]. The analysis was closely monitored to ensure that injection block and detector temperature was constant at 260°C. Nitrogen served as the mobile phase at a flow rate and tocopherol content was determined accordingly. The heating was completed when color of kernels revealed that roasting significantly affected the oil content of walnut kernels. The oil content of the raw unroasted and roasted walnut kernels increased from 23.5% (Type 1) and 34.5% (Type 9) to 25.0% (Type 1) and 38.4% (Type 9), respectively. The oil content of roasted walnut kernels increased compared to unroasted walnut kernels. The increase in oil content may be attributed to evaporation of water from the walnut during the roasting. Consequently, significant differences was observed between raw and roasted walnut samples (p < 0.05).

With respect to the fatty acids in walnut oil samples, palmitic, oleic and linoleic acids were major fatty acids of walnut oils. Linoleic acid was the key fatty acid for both unroasted and roasted walnut oils. The linoleic acid contents of unroasted walnut oil change between 46.44% (Type 9) and 63.59% (Type 7) and roasted at 120°C/h also changed the linoleic acid contents of the oil from 55.95% (Type 3) to 64.86% (Type 10). Interestingly, the linolenic acid contents of raw and roasted walnut kernel oils changed from 9.43% (Type 10) to 16.29% (Type 8) and 9.64% (Type 10) to 16.58% (Type 8). Additionally, significant (p < 0.05) statistical difference was observed in the oleic acid present in roasted walnut oil as the values changed from 14.22% (Type 8) to 23.53% (Type 3).

3 Results and Discussion

The effect of roasting on fatty acid composition and oil yield of walnut kernels are shown on Table 1. The result revealed that the fatty acids in walnut oil samples, palmitic, oleic and linoleic acids were major fatty acids of walnut oils. Linoleic acid was the key fatty acid for both unroasted and roasted walnut oils.

The linoleic acid contents of unroasted walnut oil change between 46.44% (Type 9) and 63.59% (Type 7) and roasted at 120°C/h also changed the linoleic acid contents of the oil from 55.95% (Type 3) to 64.86% (Type 10). Interestingly, the linolenic acid contents of raw and roasted walnut kernel oils changed from 9.43% (Type 10) to 16.29% (Type 8) and 9.64% (Type 10) to 16.58% (Type 8). Additionally, significant (p < 0.05) statistical difference was observed in the oleic acid present in roasted walnut oil as the values changed from 14.22% (Type 8) to 23.53% (Type 3). However, no significant (p > 0.05) difference was observed in Type 1, 2, 4 and 6. As shown in Table 1, 80% of fatty acids in walnut samples were polyunsaturated fatty acids. The fatty acids identified in the walnut oil are palmitic (6.88-7.64%), stearic (2.32-3.40%), oleic (14.99%-22.72%), linoleic (57.24%-60.88%) and linolenic acids (5.31-12.13%) 4. The oleic, linoleic and linolenic acid contents of walnut oil changed between 15.9 and 23.7%, 57.2 and 65.1%, and 9.1-13.6%, respectively 3. Oil contents of walnut kernels can change between 50% and 70% depending on the agronomic conditions 4. These values are in good agreement with previous researches 1, 7. While our results related to unroasted walnut kernel are found partly similar compared to literature values, the results of roasted walnut fatty acids showed partly differences com-
Table 1  Oil content of fatty acid composition of unroasted (raw) and roasted walnut (Type 1-10) kernels (%).

|               | Oil % | C16:0 | C16:1 | C18:0 | C18:1 | C18:2 | C18:3 | C20:0 |
|---------------|-------|-------|-------|-------|-------|-------|-------|-------|
| Unroasted (Raw) |       |       |       |       |       |       |       |       |
| T1            | 23.5 ± 1.13* | 7.07 ± 0.17** | 0.14 ± 0.03b | 2.50 ± 0.13b | 14.29 ± 1.17f | 61.40 ± 1.42b | 14.47 ± 0.78c | 0.07 ± 0.01c |
| T2            | 34.1 ± 1.29a  | 6.27 ± 0.09b | 0.01 ± 0.00e  | 2.99 ± 0.11b | 15.73 ± 0.98e | 61.49 ± 1.67b | 13.45 ± 0.93d | 0.07 ± 0.01c |
| T3            | 27.9 ± 2.09d  | 5.65 ± 0.21c | 0.01 ± 0.00e  | 2.60 ± 0.09b | 20.19 ± 0.01b | 57.62 ± 1.34c | 13.85 ± 0.97d | 0.07 ± 0.01c |
| T4            | 26.5 ± 1.67e  | 6.45 ± 0.35b | 0.15 ± 0.01a  | 2.78 ± 0.17b | 14.72 ± 1.43f | 60.63 ± 1.56c | 13.88 ± 0.68d | 0.07 ± 0.01c |
| T5            | 30.0 ± 2.35c  | 6.49 ± 0.28b | 0.02 ± 0.01e  | 2.83 ± 0.19b | 15.78 ± 1.14e | 60.69 ± 1.73c | 15.02 ± 1.03b | 0.13 ± 0.03c |
| T6            | 29.3 ± 2.41c  | 6.26 ± 0.89b | 0.13 ± 0.03c  | 2.84 ± 0.21b | 15.18 ± 0.67e | 59.93 ± 1.39c | 15.04 ± 1.27b | 0.06 ± 0.02d |
| T7            | 32.5 ± 1.47b  | 6.31 ± 0.69b | 0.04 ± 0.01d  | 2.71 ± 0.09b | 14.96 ± 0.86f | 63.59 ± 1.68a | 12.00 ± 0.98e | 0.16 ± 0.03a |
| T8            | 33.4 ± 1.32b  | 6.01 ± 0.47b | 0.06 ± 0.01d  | 3.51 ± 0.16a | 33.99 ± 1.23a | 59.02 ± 1.91d | 16.29 ± 1.56a | 0.13 ± 0.01b |
| T9            | 34.5 ± 2.31a  | 5.10 ± 0.29c | 0.02 ± 0.01e  | 2.19 ± 0.13b | 17.68 ± 1.56c | 46.44 ± 0.68f | 12.09 ± 0.74f | 0.06 ± 0.01d |
| T10           | 27.2 ± 1.53d  | 6.74 ± 0.63b | 0.02 ± 0.01e  | 2.64 ± 0.17b | -       | -       | -      | -      |
| Roasted (Type 1-10) |     |      |       |       |       |       |       |       |
| T1            | 25.0 ± 1.45f | 37.1 ± 2.38a | 31.3 ± 2.57e | 28.8 ± 1.68 | 34.2 ± 1.77d | 34.3 ± 1.59d | 35.1 ± 1.61c | 36.2 ± 2.34ab |
| T2            | 7.13 ± 0.56a | 6.01 ± 0.93b | 5.61 ± 0.86c | 6.08 ± 0.89b | 6.47 ± 1.03b | 6.24 ± 1.13b | 6.16 ± 1.21b | 5.90 ± 0.94c |
| T3            | 0.15 ± 0.03a | 0.14 ± 0.03a | 0.13 ± 0.01b | 0.02 ± 0.01d | 0.07 ± 0.01c | 0.01 ± 0.01 | 0.11 ± 0.03b | 0.03 ± 0.01d |
| T4            | 2.57 ± 0.13b | 2.79 ± 0.09b | 2.46 ± 0.01b | 2.94 ± 0.32b | 2.80 ± 0.37b | 2.79 ± 0.27b | 2.66 ± 0.21b | 3.49 ± 0.46a |
| T5            | 15.11 ± 0.41c | 15.68 ± 0.49c | 23.53 ± 0.32a | 16.82 ± 1.24c | 14.46 ± 1.18d | 15.22 ± 1.31c | 14.90 ± 1.37d | 14.22 ± 1.29ab |
| T6            | 61.27 ± 2.17b | 61.70 ± 1.89b | 55.95 ± 1.56c | 60.26 ± 1.49c | 60.77 ± 2.40c | 60.81 ± 2.69c | 64.13 ± 1.58a | 59.57 ± 1.45d |
| T7            | 13.68 ± 0.98d | 13.67 ± 1.03d | 12.23 ± 1.16c | 13.67 ± 1.21d | 15.40 ± 1.53b | 14.00 ± 1.47c | 12.06 ± 1.32e | 16.58 ± 1.30a |
| T8            | 0.07 ± 0.01c | 0.06 ± 0.01cd | 0.07 ± 0.01c | 0.06 ± 0.01cd | 0.08 ± 0.01b | 0.07 ± 0.01c | 0.09 ± 0.03a | 0.09 ± 0.02a |
| T9            | -             | -             | -             | -             | -             | -             | -             | -             |
| T10           | -             | -             | -             | -             | -             | -             | -             | -             |

*mean ± standard deviation; ** Values within each row followed by different letters are significantly different (p < 0.05); ***nonidentified
Tocopherol contents of unroasted (raw) and roasted walnut (Type 1-10) kernel oils are shown in Table 2. While α-tocopherol contents of unroasted walnut oils changed from 3.9 mg/100 g (Type 5) to 6.1 mg/100 g (Type 7), α-tocopherol contents of roasted walnut oils ranged from 2.8 mg/100 g (Type 4) to 4.7 mg/100 g (Type 1). In addition, the highest β-tocopherol was found in unroasted walnut Type 3 oil (0.6 mg/100 g). Also, γ-tocopherol content of unroasted walnut oils varies between 6.3 mg/100 g (Type 3) and 11.4 mg/100 g (Type 1). Additionally, roasting significantly changed γ-tocopherol present in walnut oil from 28.1 mg/100 g (Type 8) and 38.2 mg/100 g (Type 3), while δ-tocopherol of oil prepared from raw walnut kernel changed from 6.3 mg/100 g (Type 3) to 11.4 mg/100 g (Type 1). The highest δ-tocopherol was found in roasted walnut Type 1 (10.7 mg/100 g). γ-Tocopherol dominates in tocopherol fraction for all tested oils followed by δ-tocopherol and α-tocopherol. The highest γ-tocopherol in raw and roasted walnut oils were found in oils extracted from Type 9 and Type 3, respectively. This has an impact on the increase in oxidative stability of the oils extracted from sample. β-Tocopherol was not found in the tested Type 2 and Type 8 walnut oils. Uzunova et al. reported that walnut oils growing at the different years contained 4.4-5.7% α-tocopherol, 0.0-0.2% β-tocopherol, 85.1-88.2% γ-tocopherol and 61.9-9.7% δ-tocopherol. β-Tocopherol was not found in the tested walnut oils, which is confirmed by other authors for different varieties of nuts. However, lower levels of β-tocopherol were found in walnut kernel used in this present study. Generally, tocopherol contents of roasted walnut oils partly decreased compared to tocopherol results of unroasted walnut oils. This decrease may be due to effect of heat applied during processing. The content of (γ + β)-tocopherol contents of oils extracted by the soxhlet method changed from 29.6 mg/100 g (Jupiter) to 38.4 mg/100 g (G. 139)10. Konsteiner et al.21 reported that cashew, hazelnut, peanut, pecan, pistachio and walnut kernel oils contained 0.3, 0.1, 1.8, 0.2, 0.5, and 3.8 mg/100 g δ-tocopherol, respectively. However, α-tocopherol present in raw walnut oil changed from 28.9 to 38.3 mg/100 g and this is comparable with values reported for walnut oil10, 24, 25, 26. The results obtained are in partly agreement with the previously published data although some differences. Tocopherol contents of unroasted and roasted walnut oils varied depending on walnut types. These changes may have been influenced by some climatic factors, walnut types, harvest time and analytical conditions. Hence it can be inferred that roasting treatments may affect certain physicochemical properties of walnut kernels and their oils while compared with the unroasted
ones. These properties were however, also noted to vary with the type of walnut cultivars. Hence, more studies may be carried out to monitor the effects of different roasting temperatures and times and hence optimum roasting conditions may be established for the walnut kernels.

4 Conclusion

All the kernel analysed exhibited differences in their oil content and fatty acid compositions and tocopherol contents depending on walnut types and roasting. The results of the experiment presented here show that walnut kernel oil have a distinctive fatty acid and tocopherol profiles. Especially, linoleic acid had dominant fatty acid for both processing. Generally, fatty acid values of roasted walnut oils were found partly high compared with unroasted results. The reason for this, fatty acids of walnut oils probably increased due to removing of the relative humidity during roasting of walnuts. Generally, tocopherol contents of roasted walnut oils partly decreased compared to tocopherol results of unroasted walnut oils. This decreasing can be probably due to heating process. The oil could be useful for industrial applications owing to good physicochemical properties. Unsaturated fatty acids and tocopherols have favorable effect and positive health benefit than saturated fatty acids.

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