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Proceeding Paper

Instrumental Evaluation of Selected Properties of Oil Extracted from Walnuts before and after the Roasting Process †

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Abstract: Walnuts (*Juglans regia*) are characterized by a high fat content of approximately 73%. The oil contained in the nuts is rich in unsaturated fatty acids, including monounsaturated oleic acid and polyunsaturated fatty acids, both of the n-3 and n-6 family. One important thermal process for nuts is roasting, which significantly increases their palatability. Technically, roasting is a drying process at high temperatures. The purpose of roasting is to reveal new flavor and aroma properties of the raw material. The aim of the current study was to determine and compare the fatty acid composition and oxidative and hydrolytic stability of oils extracted from both roasted and raw walnuts.

Keywords: walnut oil; acid value; peroxide value; oxidative stability; fatty acid composition

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1. Introduction

Nowadays, consumers are increasingly looking for alternatives to animal fats. Fats are a source of energy for the body, in addition to being a source of essential fatty acids (EFAs). The composition of the fatty acids determines the nutritional value of the fat. Walnut (*Juglans regia*) is characterized by high fat content, which is about 73% [1]. The fat contained in nuts is rich in unsaturated fatty acids, including monounsaturated oleic acid (C18:1, n-9), which contains a double bond at the n-9 position. In addition to monounsaturated fatty acids (MUFAs), walnut oil also contains significant amounts of polyunsaturated fatty acids (PUFAs), which have more than one double bond and, depending on the location of the first one, counting from the methyl end of the chain, are divided into two main groups: n-3 and n-6. Walnut oil also contains a small amount of saturated fatty acids, which is very beneficial from a nutritional point of view [2]. The fatty acids found mainly in walnut oil are oleic acid (C18:1), linoleic acid (C18:2) and α-linolenic acid (C18:3) [3].

Nutritional studies of walnut oil have focused primarily on the effects of walnut oil on gastrointestinal diseases [4]. Because it has strong anti-aging effects and can increase antioxidant capacity, walnut oil is a well-known product in the functional food market for the treatment of inflammatory bowel disease, and ulcerative colitis [5].

The world production of walnuts exceeds almost 1,500,000 tonnes. China, the United States, and Iran are the largest producers of walnuts in the world. In these countries, the production of walnuts amounts to approximately 25%, 20% and 11% of the total world production of this raw material, respectively. Currently, production in the above-mentioned countries is growing rapidly. According to data published by APEDA (Agricultural and Processed Food Products Export Development Authority), India exported 1069.70 tonnes of walnuts worth—USD 3.97 million, in the summer of 2021–2022 [6].

One important thermal process for nuts is roasting, which significantly increases their palatability. Technically, roasting is a drying process at high temperatures. The purpose of roasting is to reveal new flavor and aroma properties of the raw material. This process also

modifies the phenolic compounds profile, and in some cases, it improves the health benefit effects by enhancing their antioxidant capacity [7].

The aim of the current study was to determine and compare the fatty acid composition and oxidative and hydrolytic stability of oils extracted from both roasted and raw walnuts. The walnuts, which were purchased from the Polish market, were roasted at 100 and 160 °C for 9 and 60 min (four sets of conditions in total). The roasting of whole shelled nuts was carried out in a laboratory convection chamber dryer and repeated twice under each condition. Each batch contained several nuts. Before and after roasting, the nut oil was extracted with hexane.

2. Methods

2.1. Fatty Acid Composition

The fatty acid composition of unroasted and roasted nut oil was determined by gas chromatography. For this purpose, oil samples were esterified with methanol in accordance with the EN ISO 5509:2000 [8] standard to obtain fatty acid methyl esters (FAMEs). The previously prepared esters were introduced to the BPX-70 capillary column (60 m long, 0.25 mm internal diameter, 0.25 µm film thickness) of a Clarity YL6100 GC gas chromatograph, in which the mobile phase was nitrogen. The FAME separation conditions were as follows: an initial temperature of 60 °C was maintained for 5 min; the increment of temperature rise was 10 °C/1 min within the range from 60 °C to 180 °C; then, the increment of temperature rise was 3 °C/1 min within the range from 180 °C to 230 °C; the end temperature of 230 °C was maintained for 15 min; the temperatures of the detector and injector were 250 °C and 225 °C, respectively. The fatty acid composition was presented as a percentage of the total amount of fatty acids contained in the obtained oil. The determination was carried out according to the procedure described by Bryś et al. [9].

2.2. Oxidative Stability

Thermal analysis was used to determine oxidative stability. Experiments using pressure differential scanning calorimetry (PDSC) were carried out with the help of a DSC Q20 (TA Instruments, New Castle, DE, USA) apparatus linked to a high-pressure chamber. Fat samples were placed in small aluminum pans in an oxygen atmosphere. The weight of the tested samples ranged from 3 to 4 mg, and the conditions under which the test was carried out were a constant temperature of 120 °C and a pressure inside the chamber of 1350–1400 kPa. From resulting PDSC curves, the times to reach the peak maximum were determined and used for the assessment of the oxidative stabilities of the samples. PDSC curves were analyzed using TA Universal Analysis 2000 software. The maximum oxidation time i.e., induction time (OIT) was determined based on the maximum rate of oxidation (maximum rate of heat flow). The determinations were made twice, and the result was taken as the arithmetic mean. The procedure for the determination of the oxidation induction time was described by Symoniuk et al. [10].

2.3. Acid Value

To determine the acid value by titration in correspondence with ISO standard 660: 2009 [11], the SI Analytics TL 7000 instrument was used. A 0.1 mol/L KOH solution in a titrator and a pH combination electrode for titrations in non-aqueous solutions were used for titration. The acid number is presented in mg KOH/g of sample.

2.4. Peroxide Value

The SI Analytics TL 7000 instrument was used to determine the peroxide value by iodometric titration, in correspondence with ISO standard 3960: 2007 [12]. A solution of 0.001 mol/L sodium thiosulfate in a titrator was used for titration, and a combined electrode with a platinum ring was used for oxidation–reduction potential measurements. The peroxide value is given in mEq peroxide/kg of sample.

3. Results and Discussion

The acid value is a measure of the amount of acidic substances in a fat or oil. It is a common parameter used in the fields of chemistry, food science, and lipid analysis to assess the quality and freshness of fats and oils. The acid value is typically expressed in milligrams of potassium hydroxide (KOH) required to neutralize the free acids present in 1 g of the fat or oil. The peroxide value is a measure of the extent to which fats and oils have undergone oxidation. It is a standard parameter used in the fields of chemistry, food science, and lipid analysis to evaluate the freshness and oxidative stability of fats and oils. The peroxide value is typically expressed in milliequivalents of active oxygen per kilogram of fat or oil. Both the acid value (AV) and the peroxide value (PV) are therefore the main factors of fat/oil quality. Depending on the values achieved, they may limit the use of oils in the food industry. The indicators discussed indicate hydrolytic and oxidative changes in fat [13].

Figure 1 shows the AV results for roasted and unroasted walnut oils. The use of different roasting conditions affects the AV of oil. The lowest AV can be observed when using a lower temperature and a shorter roasting time. However, the highest AV was obtained after 9 min of roasting at 160 °C and after 60 min of roasting at 100 °C. Similar observations were reported by Gao et al. [5], who examined the properties of oil obtained from walnuts by treating them with different temperatures at different time intervals. Their research shows a relationship in which the AV increases with increasing temperature and time of roasting. Therefore, generally increasing the roasting temperature and time, the AV of oils increases, but it can also be stated that individual temperatures and times have certain individual optima at which the AV reaches the lowest values for a given combination of time and temperature. Exceeding this optimal level is associated with an increase in the AV.

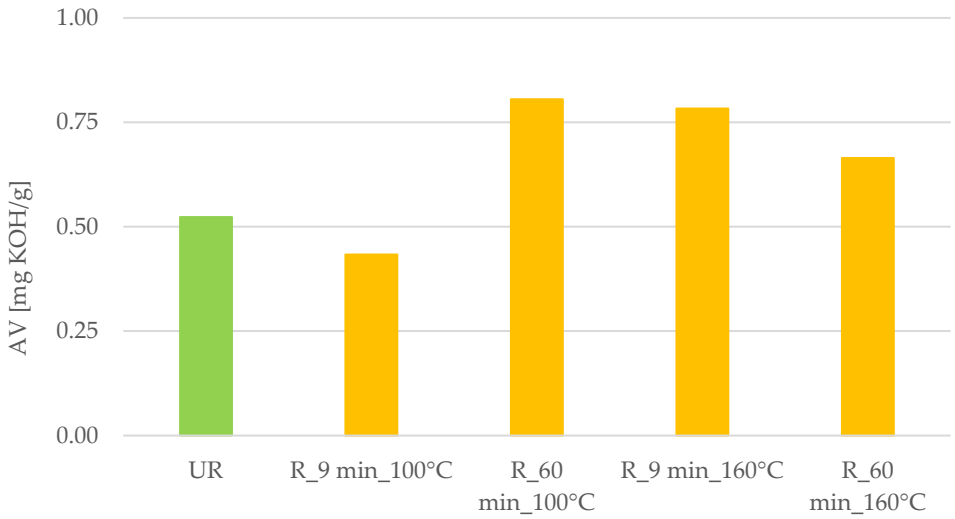

Figure 1. Acid value (AV) of oils from roasted (R) and unroasted (UR) walnuts.

Taking into account the obtained results regarding the peroxide value (PV), which is an indicator of the primary oxidation products, as well as the oxidation induction time (OIT) determined using differential pressure scanning calorimetry, it can be concluded that roasting does not affect the oxidative stability of the oil. Both samples before and after roasting are characterized by a similar PV as well as a similar OIT (Figure 2). The peroxide value values for each analyzed oil were below 0.01 mEq peroxide/kg. Comparing this oxidation stability with other oils, it can be concluded that walnut oil is characterized by a short OIT. This may be due to the high content of unsaturated fatty acids in its composition. Oxidative stability refers to the resistance of fats to undergoing oxidative reactions that can lead to rancidity and the formation of harmful compounds. It is a critical quality parameter for both dietary fats and fats used in various industrial applications. Oxidative stability

is influenced by several factors, including the chemical structure of the fatty acids, the presence of antioxidants, and the conditions under which the fats are stored and used.

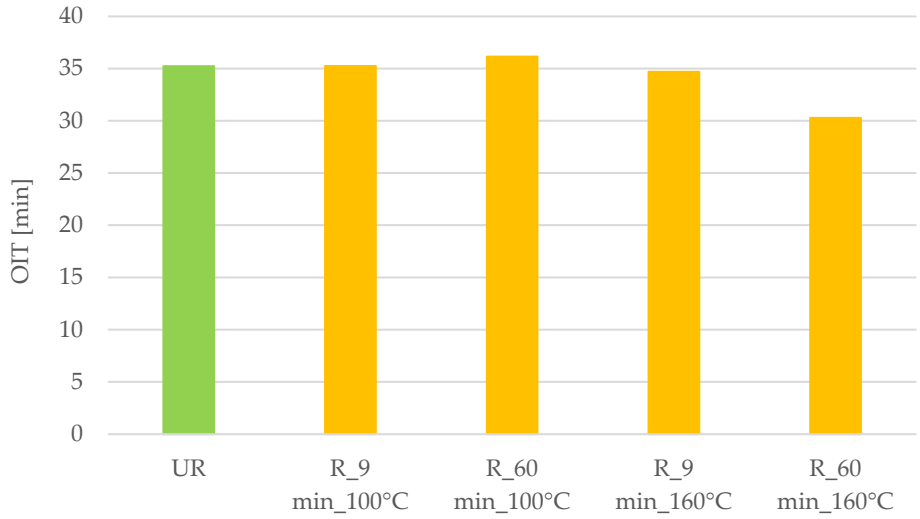

Figure 2. Oxidation induction time (OIT) of oils from roasted (R) and unroasted (UR) walnuts.

Based on the results obtained (Figure 3, Table 1), it can be unequivocally concluded that the fatty acids that dominate in walnut oil are polyunsaturated acids, i.e., linoleic acid (C18:2 n-6) and α-linolenic acid (C18:3 n-3). The oil contained in walnuts is also rich in monounsaturated fatty acids, including monounsaturated oleic acid (18:1). However, saturated fatty acids, i.e., hexadecanoic acid (16:0), heptadecanoic acid (17:0), octadecanoic acid (18:0), and eicosanoic acid (20:0), are found in the smallest amounts. Research by scientists confirms these results [3].

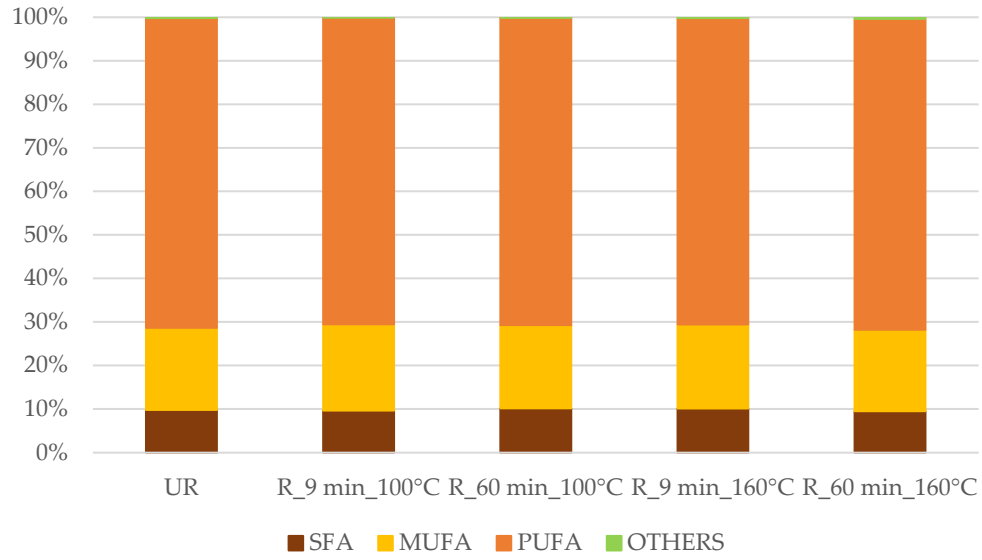

Figure 3. Percentage of fatty acids from the following groups: saturated fatty acids (SFAs), monounsaturated fatty acids (MUFAs), polyunsaturated fatty acids (PUFAs), and other fatty acids.

Walnut oil consists mainly of triacylglycerols, which constitute 83–95% of the total fraction of this oil. The triacylglycerols in question consist of tri-unsaturated and asymmetric di-unsaturated glycerides. As mentioned earlier, the fatty acids in walnut oil are mostly unsaturated. In the case of walnut oil, the largest amounts include linoleic acid and oleic acid. The 2-position of triacylglycerol is dominated by linoleic acid [6]. The only monounsaturated fatty acid found in walnut oil is oleic acid [14]. The roasting process did not affect the fatty acid composition of the analyzed oils.

Table 1. Fatty acid composition of oils from unroasted (UR) and roasted (R) walnuts.

Fatty Acid	UR	R 9 min_100 °C	R 60 min_100 °C	R 9 min_160 °C	R 60 min_160 °C
C16:0	7.50 ± 1.22	6.90 ± 0.37	7.55 ± 1.05	7.51 ± 0.61	6.96 ± 0.11
C16:1	0.12 ± 0.02	0.14 ± 0.06	0.13 ± 0.02	0.13 ± 0.03	0.12 ± 0.01
C17:0	0.07 ± 0.01	0.08 ± 0.01	0.09 ± 0.01	0.13 ± 0.06	0.08 ± 0.01
C17:1	0.05 ± 0.01	0.04 ± 0.01	0.05 ± 0.01	0.08 ± 0.05	0.07 ± 0.02
C18:0	2.15 ± 0.08	2.54 ± 0.05	2.42 ± 0.02	2.27 ± 0.11	2.34 ± 0.11
C18:1 n-9	18.52 ± 0.25	19.43 ± 0.03	18.70 ± 0.06	18.77 ± 0.35	18.21 ± 0.52
C18:2 n-6	59.01 ± 0.82	58.22 ± 0.18	58.43 ± 0.93	58.36 ± 0.08	58.93 ± 0.42
C18:3 n-3	12.12 ± 0.17	12.26 ± 0.01	12.21 ± 0.08	12.00 ± 0.68	12.51 ± 0.33
C20:0	0.09 ± 0.01	0.11 ± 0.01	0.10 ± 0.03	0.21 ± 0.14	0.14 ± 0.04
C20:1	0.18 ± 0.03	0.25 ± 0.04	0.28 ± 0.04	0.36 ± 0.13	0.31 ± 0.04

4. Conclusions

The results indicate that hydrolytic stability decreased after roasting, as a slight increase in acid value was recorded in the oil extracted from roasted walnuts. The oxidative stability of the walnut oil after roasting did not change significantly. Generally, the low oxidative stability of walnut oil may be related to the high content of polyunsaturated fatty acids (about 70%). The roasting process does not change the fatty acid composition of the analyzed oils.

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