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THERMO-OXIDATIVE STABILITY OF COLD-PRESSED WALNUT OIL

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Abstract: Walnut oil has many health benefits due to uniqe chemical composition: the desirable ratio of ω-3:ω-6 fatty acids and many compound present in a small amount. But, polyunsaturated fatty acids cause the weak oil stability. The aim of this research was to examine the thermo-oxidative stability of cold-pressed walnut oil at 180°C during 2 h. Significant sensory and chemical changes were observed. Specific absorbances at 232 nm and 270 nm increased during thermal treatment. Refractive index and peroxide value increased also. An acceleration of secondary oxidation products formation increase was recorded during 2 h of heating. After 2 h at 180°C a peroxide value indicated that the oil was no longer edible.

Keywords: walnut oil, cold pressing, peroxide value, specific absorbances

Introduction

Edible oils and fats provide energy, but also nutrients necessary for the proper functioning of the body such as essential fatty acids, phospholipids, vitamins, precursors of steroid hormones etc. Fats have and a protective role as thermal insulator and shield from mechanical injurie. However, the oils can have beneficial or harmful effects on human health depending on the type and amount of oil taken, but also depending on the oil producing way and oil processing. The oils can be obtained mechanically (by pressing with screw or hydraulic press) and by extraction. Cold-pressing is environmentally friendly, require less energy than organic solvent for extraction, and enables the production of oils that retain the components from oilseeds in a natural and mostly unchanged form.

In Serbia, the use of refined sunflower oil has dominated for decades. With the development of consumer awareness of the health benefits from cold-pressed oils, the demand for them has been growing in recent years. Oils from

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plants that are traditionally grown in our country, such as walnut, are insufficiently used for oil production although they have a very high nutritional value (Radovanović et al., 2022).

Cold-pressed walnut oil is golden yellow with mild pleasant taste of walnut. This oil contains the desired ratio of omega 3 and 6 fatty acids, which is important in the prevention of many diseases (Ros et al, 2018; Sánchez-González et al, 2017). Song et al. (2022) noted a large number of scientific papers that confirm that walnut oil showed anti-inflammatory, antitumor, antioxidant, immunomodulatory, neuroprotective, cardioprotective, antidiabetic, and antihyperlipidemic activities. Chauhan and Chauhan (2020) reported that long-term supplementation with walnuts in the diet can significantly improve memory, learning skills, motor coordination and anxiety-related behaviour, and connection with beneficial effects in maintaining cognitive function and protecting against age-related cognitive decline. So, cold pressed walnut oil is used as an addition to foods as salads and cold dressings, in cosmetics and the pharmaceutical industry. Walnut oil contains a high amount of polyunsaturated fatty acids (PUFA), that are easily change due to oxidation which causes poor shelf life of walnut oil.

During food preparation, oils are often expose at a high temperature. This generally reduces the quality of the oil, but the level of deterioration depends on the applied process parameters (Gao et al., 2022). It was shown that the a short-term thermal treatment (24 min at 180 °C) of the hazelnut kernels has an effect on minor changes in cold-pressed oil (Radovanović et al., 2024). It is interesting that heating of hazelnuts before and during pressing did not immediately significantly affect the oxidative changes, but reduced the stability of the oil during oil storage (Radovanović et al., 2021).

The changes in oil due to heating can be monitor by peroxide value (PV), main oil quality parameter defined by the rulebook. PV indicates the formation of peroxides and hydroperoxides as primary oxidation products. However, these products can easily decompose to secondary oxidation products, and PV can decrease even though the oxidation process has progressed. Specific absorbances can give additional insight into the oxidative changes.

In order to prevent unwanted thermo-oxidative changes in edible oils, it is necessary to understand the effect of certain process parameters on oil stability. The aim of this research was to analyze the oxidative stability of cold-pressed walnut oil during thermal treatment at 180°C.

Materials and methods

Obtaining cold-pressed walnut oil

Walnut kernels (2024 season) freed from the shell and impurities were used to obtaine oil, according to the procedure shown in Figure 1. Slightly crushing kernels were pressed in electric srew press OP 650 W (Gorenje, Slovenia) at the temperatres below 50°C. In order to free the oil from the sediment, centrifugation during 5 minutes at 3000 rpm (LC 320, Tehnica –Železnik, Slovenia) and decantation were performed.

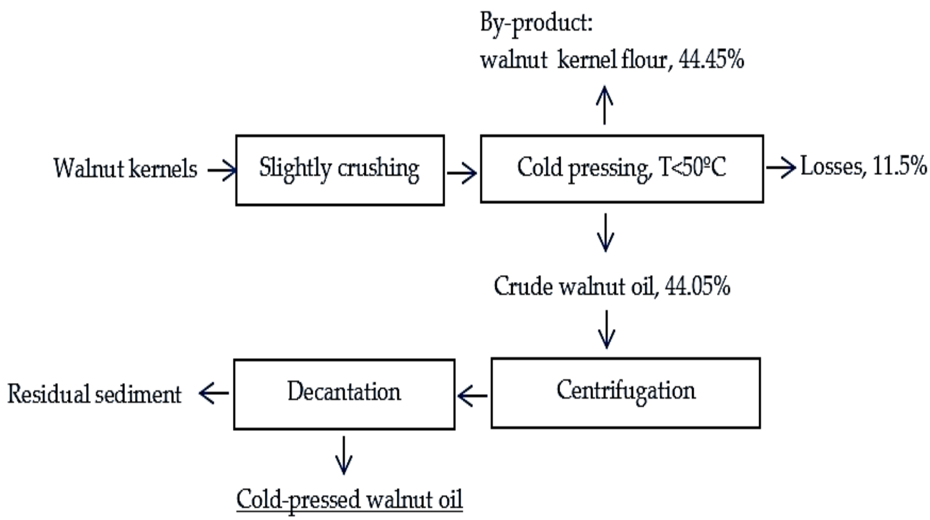


Fig.1. The process of obtaining cold-pressed walnut oil

Thermal treatment

Thermo-oxidative stability of the obtained cold-pressed walnut oil was monitored by measuring the peroxide value, specific absorbances and refractive index. The oil was thermally treated at 180 °C for 1 and 2 hours. All chemicals were p.a.

Determination of peroxide value

Peroxide value (PV) was determined by modified Wheeler's method (Dimić and Turkulov, 2000; Wheeler, 1932). 1 g ± 0.001 g of the sample was dissolved in

10 ml of a mixture of glacial acetic acid and chloroform (3:2, v/v). In this mixture it was added 0.2 ml of saturated potassium iodide solution (3.5 g KJ with 2.5 mL boiled and cooled destiled water) and mixed for exactly 1 min. After 1 min, the reaction was stopped by adding 20 ml of distilled water. A few drops of starch indicator (1%) were added and the liberated iodine was titrated with standard 0.01 M sodium thiosulphate solution. The end of the titration was the disappearance of the blue color. The PV is the amount of active oxygen in the lipids that corresponds to the amount of iodine released from KJ during titration. The PV was calculated according to equation (1) and expressed in mmol O_2 per kg of oil.

$$PV\ (mmol/kg) = \frac{(V_1 - V_0) \cdot f \cdot 5}{m} \qquad (1)$$

where V_1 is volume of titrant used for sample, in mL; V_0 volume of titrant used for blank; f is factor for exact concentration of sodium thiosulphate solution and m-weight of oil in g.

Determination of specific absdorbances

Specfic absorbances, K_{232} and K_{270}, measured by standard method (Dimić and Turkulov, 2000; ISO 3656, 1989) spectrophotometrically at 232 nm and 270 nm (Cary 300 UV/Vis, Agilent, USA). The oil sample dissolved with n-hexane as 1% (m/v). Absorbances were measured at the indicated wavelengths with n-hexane (HPLC grade) as a blank. 0.1 g ± 0.001 g was dissolved in 10 ml n-hexan. Specific absorbances calculated according to equation (2):

$$K_\lambda = \frac{A_\lambda}{c} \qquad (2)$$

where A_λ was measured absorbances at certain wavelength (232 nm or 270 nm), c- concentration of sample (g/100 ml)

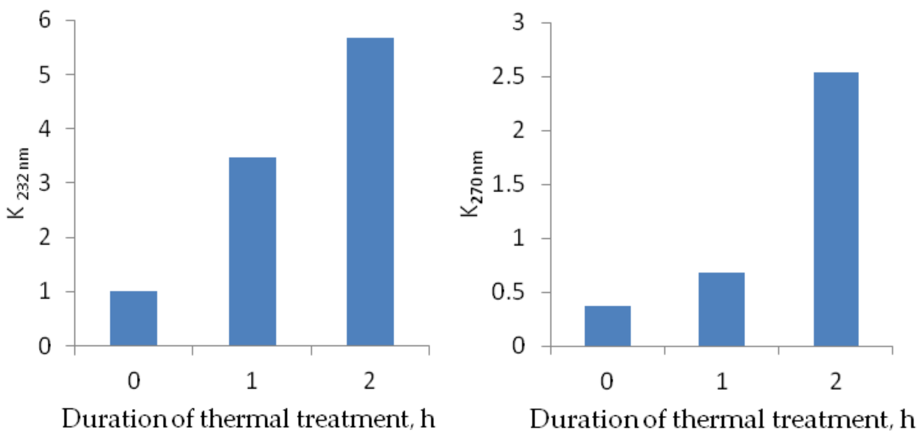
Determination of refractive index

The refractive index (RI) of cold-pressed walnut oil was measured by Abbe refractometer (A. Krüss-Optronic, Germany), with range 1.3000–1.7000 ±0.0001, and a monochromatic Na light (589.6 nm) at 25 °C.

Results and discussion

During the pressing of walnut kernels, a crude oil yield of 44.05% and a walnut flour (by-product) yeald of 44.45% were achieved (Figure 1). The oil was cloudy and required a centrifugation to separate the clear walnut oil. Oil yield depends on the strength of the press, on the walnuts variety, on the degree of crushing, on the storage treatment that the walnut kernels had etc. Krulj et al (2021) obtained higher oil yield by semi-industry screw press: 54.89% primarily as a result of the higher power press used. It is inevitable that parts of the walnut kernel and oil remain on the press, which represents in this case a losses of 11%.

Thermal treatment resulted in oil quality deterioration, the degree of which depended on the duration of heating. The fresh clear cold pressed oil was golden yellow with a mild and pleasant walnut smell. Thermo-oxidative changes were observed by sensoricaly after 1 h of oil heating. The oil changed its color slightly, but the pleasant smell of walnuts intensified. However, after 2 hours of heat treatment, the oil turned dark brown and the rancid smell dominated. Specific absorbances at 232 nm indicate the formation of primary oxidation products and had a similar increasing trend during 2 h (Graph.1, a).

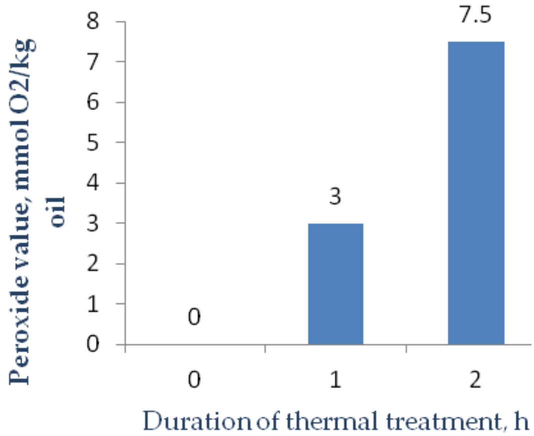


a) b)

Graph 1. Influence of thermal treatment duration at 180° C on the specific absorbances of cold-pressed walnut oil at 232 nm (a) and at 270 nm (b)

Specific absorbances at 270 nm indicate the formation of secondary oxidation products, thats increase was not linear and may indicate an accelerated formation of secondary products during thermal treatment (Graph.1, b).

Peroxide value (PV) is a quality oil parameter and indicates formation of peroxides and hydroperoxides. During heat treatment, oxidative changes was occurred in walnut oil, PV increased. (Graph 2).



Graph 2. Changes in the peroxide value (PV) of cold-pressed walnut oil during heat treatment at 180 °C

Fresh cold-pressed walnut oil had a good oxidation property, as the PV was zero. This indicates good quality of walnut kernels, stored in adequate conditions of optimal humidity, temperature and length of storaging, which prevented the oxidative processes. The maximum PV value for cold-pressed edible oils is 7.5 mmol O_2/kg oil (Official Gazette, 2013). Therefore, after 2 hours of exposure to a temperature of 180°C, cold-pressed walnut oil is no longer edible and should not be used in food.

The refractive index (RI) is identification parameter for oils, and depends on the chain length and saturation/unsaturation of fatty acids and for cold-pressed walnut oil was 1.4755 (Table 1).

Table 1. Refractive index changes during thermal treatment of cold pressed walnut oil at 180°C

Time, h	0	1	2
RI, 25°C	1,4755	1,4760	1,4760

RI for walnut oil can vary in a different range, from 1.4725 – 1.4745 (Đurović et al., 2024), 1.446 – 1.451 (Gharibzahedi et al., (2014) or 1.4777 – 1.4788 (Patraș and Dorobanțu, 2010). The RI increased slightly during the thermal treatment, with no difference after 1 and 2 h of heating the oil at 180 °C.

Conclusion

Fats and oils, as a basic foodstuff, can have a positive but also harmful effect on human health, depending on the type of fat, the way it is processed and used in the diet. Oils of high nutritional value are obtained by a mechanical process at low temperatures. Cold-pressed oils are characterized by mostly weak thermo-oxidative stability. Walnut oil has benefits to human health if it is as cold pressed and minimal thermally threated. The thermal treatment of this oil at 180°C during 2 h showed sensory and chemical changes. Specific absorbances, refractive index and peroxide value increased during thermal treatment. It was noticed a possible accelerated formation of secondary products with longer thermal treatment. After 2 h at 180°C a high peroxide value indicated that the oil was no longer edible.

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