THE QUALITY AND STABILITY OF WALNUT OIL UNDER THE INFLUENCE OF STORAGE CONDITIONS

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Abstract

This study aims at determining the influence of various storage conditions on peroxid index value and colour in walnut oil.

We assessed the quality and stability of the extracted oil during storage at temperatures of +4°C and + 20-22 °C for six months of storage. We analyzed the following physical and chemical parameters of the walnut oil: acidity index, oil density, viscosity, iodine value and peroxide value. After six months of storage, we observed variations of the peroxide values (PV) ranging from 9.12 to 15.32 meq O_2 /kg walnut oil in samples stored at +4 °C, while the storage color parameters L a* b* of walnut oils, have not changed significantly.*

These observations are important because the walnut oil has a rich, nutty flavor that is perfect for salad dressings, to flavor fish and steaks and to sass with pasta.

Key words: walnut, total oil, stability, peroxide value, chromatic ordinates

INTRODUCTION

Walnut (*nux juglandes*) is harvested from walnut tree (*Juglans regia*) and is the most popular nut ingredient from Romania, known as common walnut. It is known to be the oldest tree, whose fruits are edible. The consumption of walnuts and walnut oil is beneficial for the health because it keeps the cholesterol level constant, the body weight within the range, it significantly reduces the risk of the coronary heart disease, it decreases the blood pressure, it prevents the installation of cancerous diseases and neurological disorders.

With a very high content of polyunsaturated fatty acids (73-84%), linoleic acid, linolenic, oleic and few saturated fatty acids (palmitic and stearic), walnuts oil ranks first among unsaturated oils before soybean oil (50-60%) and corn oil (40-50%).

The walnut oil is recommended in the treatment of cardio vascular diseases and in the diet of people with intellectual and strenuous activities due to its high content of polyunsaturated fatty acids.

In one study, the supplementation of a background diet with 68 g of walnut/day reduced the total and low-density lipoprotein cholesterol by 5 and 9 % respectively, and it was suggested that these reductions would have some positive effects in lowering the risk of coronary heart disease [5].

The absence fatty acids in the diet can cause health problems such as slow growth, the change of functions at the cellular level, endocrine disruptions, visible negative effects on the skin and mucous membranes [18].

The proteins from nut contain one of the essential amino acids, arginine, which participates in many biochemical processes in the human body, such as detoxification, secretion of hormones and the stimulation of the immune system.

The nut oil is used in food, in salads, in the preparation of mayonnaises and in frying. However it is recommended not to use walnut oil in frying because high temperatures may form toxic compounds and may lose its nutritional qualities. The oil-in-water (O/W) food emulsions are the basis of many food products and their properties define food quality to a great extent [7].

The oil is used frequently in medicines and cosmetic creams that can be applied directly

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on the skin or in various hair treatments. The nut oil is used as anthelmintic agent, as a treatment for menstrual problems and has the ability to moisturize the skin.

The most commonly used method for the extraction of nuts oil is Soxlet, the extraction with various solvents (chloride, chloroform and methanol, hexane), and the simplest method for the oil extractions is pressing.

The oil extracted by the pressing method has a low content of phospholipids, acids and peroxides. This shows that oil can be consumed without prior refining. However, there is a drawback with the oil obtained by pressing because it contains unsaturated fatty acids which directly the oxidative stability and reduce the self life [13].

The extraction of lipids with supercritical liquid with carbon dioxide is a relatively new method which allows obtaining a natural oil from a wide variety of plants that contains biologically active compounds [10, 11].

The polyunsaturated fatty acids from walnut oil has a high potential of decomposition by the auto-oxidation process, regardless of whether they are found in free form or in the structure of other compounds. The oxidation of lipids from the raw materials or oil can be accelerated by some external factors such as light, oxygen, temperature, storage and the ways of processing the raw material prior to being exposed to the oil extraction process. The auto-oxidation is the first process that occurs in the presence of light or oxygen. The auto-oxidation produces hydroperoxides what does not change the product from the point of view of the sensory appeal, but their degradation eliminates compounds (aldehydes, ketones) which strongly affect the smell and taste [14].

The antioxidants from walnuts and implicitly from walnut oil are vitamins of the B group, vitamin E, the phosphatides, copper from the minerals and the phytosterols, polyphenols and carotenoids from the phytonutritiens [2].

Phytosterols or plant sterols have a structure similar to cholesterol. This class of compounds has the ability to reduce the cholesterol from blood, can prevent certain cancers and can improve immunity [17]. Azadmard Damirchi, et al., observed that the total concentration of phytosterols found in different species of nuts are in the same proportion as those in olive oil, peanut butter and peanuts [2].

The walnuts contain a significant amount of tocopherols, but the walnut oil presents certain variations of this vitamin, because it can be very easily influenced by the way the oil is extracted and storage conditions. Walnuts are a rich source of phenols, which have a very high antioxidant potential. The phenolic acid and condensed tannins are prevailing in nuts, followed by resveratrol and gallic acid [8].

Toasting the nuts before entering into the extraction can decrease the percentage of certain constituents with antioxidant characteristics. Vaidya et Eun, 2013 found after determining and comparing the antioxidants from the walnut oil obtained from fresh fruit and from the oil obtained after roasting the fruits that the percentage of tocopherols was lower in the oil obtained after roasting the fruits. But during storage at a temperature of 60°C, in the dark, the researchers observed that the degradation tocopherols was lower in the case of the oil from roasted nuts, than that of fresh walnuts. This demonstrates that the retention of tocopherols is higher in oil extracted from walnuts [21].

Torres and Maestri studied the influence of packaging and its protection against oxidative processes and found that the glass containers wrapped in a layer of aluminum is the closest to the ideal packaging, protecting the product against photo-oxidation and the rancidity process [20].

According to Marcela L. Martínez et al., 2013 walnut oil kept in dark warehouses and at ambient temperature has a greater shelf life and a significant reduction in lipid oxidation, if synthetic antioxidants are added into the oil [14].

This study evaluates the correlations established between peroxide value and shelf life storage.

MATERIAL AND METHODS

Samples and storage conditions

The samples of the walnuts (200 g) used in this work were gathered in September

2012 and 2013 from three areas (north, west, south) of Suceava, a region in Romania.

Proximate characteristics of walnuts

The three different walnut samples were selected according to their reputation in the region in terms of their sensory and size quality characteristics.

For the chemical analysis, each group of walnuts was homogenized thoroughly and then analyzed to determine moisture (by drying the ground nuts at 103°C to a constant weight), fat (as an extractable component in Soxhlet apparatus) and protein (as crude nitrogen x 6.25), using standard methods (AOAC, 1995), ash (after dry 105°C, and carbonizing first at 250°C, then gradually ramping up the temperature to 600°C overnight) [9].

Table 1 shows the macronutrient distribution of the different walnuts samples. Moisture of walnuts presented the lower values. Walnut has high nutritional value, It is rich in proteins (14.51-15.59 %), Typically, the order of the total oil content follows the pattern S3 > S2 > S1 for year 2012 and similar for 2013.

Physical analysis

Oil density indicates how much mass has a determined volume in a certain temperature. Oil density was determined by pycnometry method, according to STAS 145 – 67.

$\rho = m/v$

Table 1 Preliminary physico-chemical indicators of samples used in analysis

		Moisture %	Ash %	Brute protein %	Total oil %
2012	S1-north	3.77	2.1	15.59	54.85
	S2 -west	3.85	2.2	14.81	55.5
	S3-south	4.58	2.05	15.26	66.1
2013	S4- north	3.96	2	15.28	54.1
	S5- west	4.23	1.9	14.51	56.9
	S6 - south	4.33	2.6	15.37	68.1

All analyses were carried out in duplicate

Viscosity describes the internal resistance that the fluid has to flow. It determines, in essence, the loss of thickness of oil layer due to friction. Viscosity measurements were carried out on the oil samples at ambient temperature (25°C), with a Brookfield viscometer (Brookfield Engineering Inc, Model RV- DV II Pro+) at 0.5rot/min; rpm with RV spindle. The unit of viscosity measured by a Brookfield viscometer DV-II + is in cP or mPa.S [4].

Chemical analysis

Peroxide Value (PV). PV was evaluated following the methods. It consists of the reaction in darkness of a mixture of oil and chloroform/acetic acid 2:3 (v/v) with a saturated potassium iodide solution. The free iodine released was titrated with a sodium thiosulfate solution until its yellow color disappeared. In this state, 0.5 ml starch solution (1% w/w) was added and titration was continued until the blue disappeared. The Peroxide value is expressed in mill equivalents of peroxide oxygen per kilogram of oil and calculated by the following equation:

peroxide value=V*N*1000/W

where: V is volume of applied sodium thiosulfate, N is the normality of thiosulfate and W is the oil weight.

Peroxide value was evaluated after 2, 4 and 6 months.

Iodine value was performed by Hannus method, according to STAS 145 / 19-67.

Free acidity was determined by titration of the dissolved oil in a mixture of alcohol-ether (1:2) with an aqueous solution of sodium or potassium hydroxide (Standard EN ISO 660)

All chemicals used in this study were supplied by Merck companies.

The oils were placed in bottles and stored in the refrigerator (+ 4^0 C, in dark) and others

at +20-22ºC (in dark), until the analysis commenced the following day.

Color evaluation

The color of the walnuts oil samples was determined using a reflectance colorimeter based on the chromatic ordinates L^*, a^* and b^* values, of the absorption spectrum.

The color parameters corresponding to the uniform color space CIELAB were obtained directly from the apparatus. Within the uniform space CIELAB, two color coordinates, a* and b*, as well as a psychometric index of lightness, L*, are defined. In this system, a* takes positive values for reddish colors and negative values for greenish ones, whereas b* takes positive values for yellowish colors and negative values for bluish ones. L* is an approximate measurement of luminosity, which is the property according to which each color can be considered as equivalent to a member of the grey scale, between black and white, taking values within the range of 0-100. Chroma (C*) is the attribute that allows the determination of the degree of difference to be determined in comparison with a grey color with the same lightness for each hue, so it is considered to be the quantitative attribute of colorfulness. Hue angle (H*) is the attribute according to which colors have been traditionally defined as reddish, greenish, etc., [12].

The calculation of the results of *the total color difference* (ΔE^*) between the two colors is given in terms of L*, a*, b* by the CIE 1976 formula [6]:

$$\Delta E* = \sqrt{Da*^2 + Db*^2 + DL*^2} \quad (1)$$

The white index represents the white color from food and can indicate the degree of discoloration during thermal processing or storage. Thus, the levels of *the white index (WI)* are obtained as follows:

$$WI = \sqrt{(100 - L*^2) + a*^2 + b*^2} \quad (2)$$

The yellow index(YI) chararcterizes the products that were degraded by light. The formula for the determination of the yellow (YI) is as follows:

$$YI = \frac{142{,}86 \cdot b*}{L*} \quad (3)$$

RESULTS AND DISCUSSIONS

Table 1 shows the values obtained for physico-chemical characteristics of the oil samples.

The density and viscosity ranged from 945 to 970 kg/m^3 respectively 74.2 to 65.7 mP.S (table 2). The analysis indicated that all of the six walnut oil samples showed a rheological as Newtonian fluid.

Table 2 Physical and chemical quality parameters of oil extracted from analyzed walnut samples

oil characteristics	Samples of oil walnuts					
	2012			2013		
	S1	S2	S3	S4	S5	S6
Density at 25°C (kg/m^3)	955	945	966	970	965	953
Viscosity mPa*s	74.2	65.7	67.4	68.9	66.5	66.9
Acidity (% oleic acid)	0.23	0.20	0.25	0.24	0.24	0.20

Values represent means of duplicate value

The iodine values on the three samples of the walnut oil in 2012 and 2013 are shown in Figure 1. The S3 oil has the highset value of the iodine index for 2012 and 2013 respectevly, with a value of 155 gI/100 g, and for 2014, the amount is 157 gI/100 g. Also, the vallues of the iodine index for S3 denotes that the oil obtained has the highest the degree of unsaturation. The lowest values of the iodine index have been registered for S2, both for 2012 and 2013.

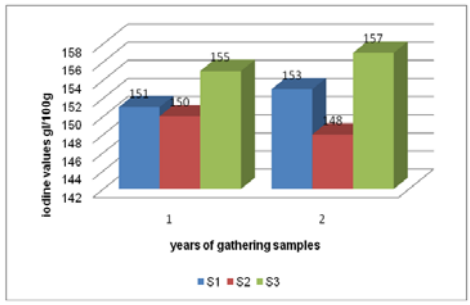

Figure 1 The iodine values of the oil samples (1-year 2012; 2-year 2013)

Crews&Hough, *et al.*, 2005 evaluated the composition of walnut oils obtained from nuts collected from seven countries, values for iodine value varied from 151.4÷156.8 (China) to 159.1÷164.4 (USA) [3]. However, the results obtained for iodine value were in accordance with previous studies.

Peroxide value

The effects of storage temperature on oxidative stability of walnuts oil were studied over a six months storage period. The peroxide index indicates the oxidation degree of lipids by means of oxygen, temperature and light actions [1].

At six months of storage in different conditions of storage, the peroxide index values of walnuts oil has also registered different values, depending on samples. The initial PV of fresh walnuts was very low (0.4 meq O2/kg walnut oil).

Changes in PV of the walnut oil samples stored at +4°C are given in Fig. 2.

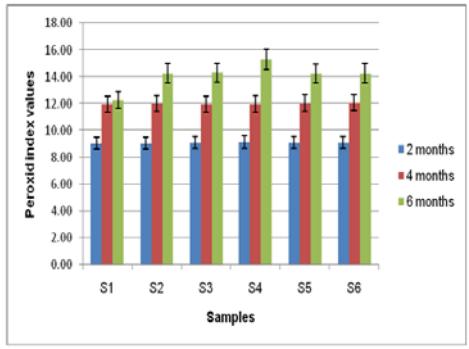

Figure 2 Changes in peroxide index value (PIV-meq O_2 /kg) of walnut oils as a function of storage time at **+4°C**

As seen in the Figure 2, the walnuts oil peroxide index values, determined at six months of storage at +4°C , have registered marked increase, especially in samples S3 (south of region) irrespective of the year of gathering.

Changes in PV at 6 months of storage at +20ºC - 22°C are shown in Figure 3.

After six months of storage, the walnut oil peroxide index values have raised more, as compared with the values registered after two months. The least values were registered in oil kept at +4°C, and the highest ones in oil samples kept at +20-22°C. Oils from walnuts did not change significantly in their PV until six months of storage at +20 - 22°C (figure 3).

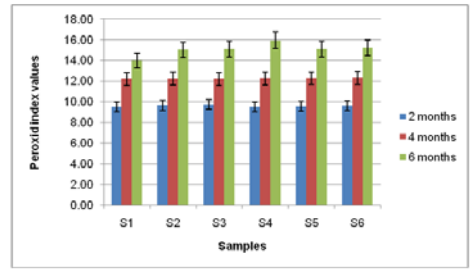

Figure 3 Changes in peroxide index value (PIV-meq O_2 /kg) of walnut oils as a function of storage time at +20°C - 22°C

A value of 25 meq O_2 /kg oil is considered as a maximum limit of acceptability for nuts [15]. In contrast, PV from samples stored at +20 - 22°C did not vary significantly along storage period and is were similar to the one obtained from the control sample stored at +4°C. The results described previously are in general in agreement with those reported by S.F. Mexis et al. (2009) who showed that raw shelled walnuts stored in PE pouches exposed to light after 12 months of storage had PV 31.4 meq O2/kg oil [15].

The walnut oil contains large amounts of vitamin E, which provides stability in time [22].

Colour

Table 3 shows that color parameters of cold-pressed walnut oils and the control sample. The color of walnut oil was

measured over a period of a year every six months and the analysis is performed only on walnut oil obtained by cold pressing.

The positive values of the index L * highlight the brightness of the product, the negative values of the index a* indicate that the product has a greenish color and negative values of the index b * indicate yellow coloring.

Thus, the color of the walnuts oils from the control sample is yellow-green, crystalline. The color is an important quality factor for consumer acceptance of walnut oil. A clear, light yellowish-green color of walnut oil is desirable for many food applications, especially for salad dressings [19].

Table 3 CIELAB L* a* b* of walnut oils

Proba de analizat	L*	a*	b*
Walnut oils	124.775	-14.25	-24,7
Walnut oils after 6 months stored at room temperature	39.2	-1.5	5.1

After a period of six months, the values have some modifications as follows: CIELAB L* a* b* of walnut oils are smaller as compared with control sample, and in this case, the index value of the index b* is positive.

The decrease of the L* values indicate that the walnut oil has lost its brightness. The values of a * and b * indicates a pale yellow-green color. After a storage period of six months at variations of temperature and light, it can be concluded that the oil has lost its color intensity.

Using the data in Table 3, three indexes were calculated: total color difference (ΔE *), white index (WI) and yellow index (YI), according with the equations (1), (2), (3).

The total color difference (ΔE *) is between 0.6 and 1.6. According with the literature, as long as the value of this parameter is less than or equal to 1.5, the product does not have major changes and is considered acceptable.

As for the white and the yellow indices, researchers say that there is a close correlation between them: if the white index (WI) increases, then the yellow (YI) must decrease for the product to be acceptable.

A possible increase of the yellow index (YI) may be due to the increased storage temperature[16].

CONCLUSIONS

This study indicated that there is considerable variation in the total composition of the oil from walnuts cultivated in Suceava county. It can be concluded that the lipid oxidation of the walnut oil occurred rapidly because of its content of polyunsaturated fatty acids.

The variation of the iodine values from the sample walnut oils was modest whereas the oxidation rate was highly dependent on storage period. There were observed linear correlations between parameters values versus storage time as well as the rate of parameter changes versus temperature.

Although there are changes in the color, these are not significant to assert that oxidative process of the oil started.

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