STUDY OF THE LIGHT INFLUENCE ON THE WALNUTS OIL QUALITY

Abstract

This paper represents a statistical processing of experimental studies on the influence of light on the quality of nut oil (Juglans regia L). The conformity of nut oil Calaras and Kogalniceanu, harvested in 2013 and 2015, was analyzed in the Republic of Moldova. The objective of this study was to determine effect of storage conditions (stored at light and dark) on the stability of walnut oil during storage by measuring the Peroxide Values (PV), Acid values (AV), Kinetic Study of Lypid Peroxidation A (PV), Reichert Meissl Number, Polenske Number, Specific Gravity and Refractive Index. The nut oil was obtained by cold pressing in the Department of Food Technology, TUM scientific laboratory, the storage time of nut oil samples in the dark and the light was 6 months, tempering 20-22°C. The monitoring of the physicochemical indicators was carried out for 2 years in the Institutional project no. 11.817.04.40 Elaboration of methods for the walnut lipids protection (Juglans regia L.) of oxidative degradation, 2012-2014 and project no. 15.817.02.30A Methodological and technical elaboration for the modernization of the walnut processing technology (*Juglansregia L.*) with the use of biologically active components in functional food «NUCALIM-PROBIO» 2015-2018. It has been established that light is a determining factor in the quality of walnut oil at storage.

Keywords: *walnut oil, stored at linght, stored at dark, Peroxide Value, Lypid Peroxidation*

1. INTRODUCTION

Walnut oil is ~~high~~rich in omega-3 fats, which have been linked to a variety of health benefits, including reducing the risk of dementia and heart disease [16]. Medical studies show that it is a rich source of ellagic acid, an antioxidant that is known to detoxify elements that could trigger cancer. Walnut oil is also rich in melatonin, copper and manganese - all of which are key elements in regulating our body's metabolism [15, 16]. The problem associated with incorporating polyunsaturated lipids into food is their high susceptibility to oxidation [18, 21].

Lipid oxidation has received a great deal of attention because its implications are undesirable for human health and it contributes to a decrease in the nutritional value of food. Lipid oxidation is well known as the main cause of quality deterioration during the processing or storage of lipid-rich food [4,7, 26].

There are few published studies on the stability of walnut oil during storage [30], although there have been studies about the oxidative stability of other edible oils such as olive oil. Stability in these other oils are affected by the fatty acid composition and the anti-oxidant content [1, 26, 27].

Lipid oxidation causes rancidity that leads to loss of shelf life, product nutrition, and ultimately, saleable product and profits [26, 23, 32]. Strategies to postpone lipid oxidation are needed for both economic and consumer health, particularly because the healthier unsaturated fats are at greater risk for oxidation then saturated fats [8]. Degradation of the unstable primary oxidation products, hydroperoxides, leads to the formation of a variety of volatile compounds, such as aldehydes, ketones, hydrocarbons, alcohols, acid compounds and furans. Formed secondary products with low threshold values are responsible for the off-flavors development [14, 35].

2. MATERIALS AND METODES

> Comment [MGN1]: Review number sequence.

2.1. Sample and storage condition

The walnuts oil has been obtained by cold pressing (T=18…20°C) of walnuts varieties Calaras and Kogâlniceanu, harvested in 2013 and 2015. Procedures of walnut oil obtaining in laboratory conditions were following: *crushing the walnuts → kernels elimination → kernels grinding → pressing→ oil separation → oil packing and storage.*

The storage conditions for walnut oil were at light and at dark, ambient temperature (25°C).

2.2. Physical analysis

Oil density was determined by pycnometry method, according to STAS 145-67. Refractive index –

Peroxide value (*PV*)

Peroxide value was determined by official method Cd 8-53 and recommended practices of the American Oil Chemists Society (AOAC, 1997). This method determines iodine liberated from potassium iodide by the peroxides present in the oil:

$$PV(meg/kg) = \frac{(S-B) \times N \times 1000}{m} \quad (1)$$

where: B is the volume (mL) of titrant for blank, S is the volume (mL) of titrant for sample, N is the normality of $Na_2S_2O_3$ solution (0.1mol equi/L), and m is the weight (g) of oil sample.

Results were expressed as milliequivalents of oxygen per kilograme of oil (meq. Oxigen/kg of oil).

Fatty acid values (FFA)

FFA was analyzed by official method Ab 5-49 and recommended practices of the American Oil Chemists Society (AOAC, 1997). FFA was a quantitative determination of fatty acids in oil by titration against a standardized alkali solution (NaOH) as follows:

$$FFA \; (Oleic \; acid \; g/100g) = \frac{V \times N_1 \times 28,2}{m}; \quad (2)$$

where: V is the titration of sample (mL), and N_1 is the normality of NaOH solution.

Kinetic Study of Lypid Peroxidation of the walnuts oil

A change in the quality of lipids be mesured by the appearance or disapperance of one or more indices, symbolized by A (PV); the rate of apperance or disappearance of A can be represend by the Equation (3).

$$r_A = \frac{dA}{d\tau} = K[A]^m \quad (3)$$

Were K is the rate constant and m is the apparent order of reaction. The when m is 0,1 and 2 rate quation become in Equations (3) – (6) respectively.

Comment [MGN2]: Confuse. Revise the sentence.

$$A = A_0 - k_t, \qquad m = 0 \quad (4)$$

$$A = A_0 e^{-kt} \qquad m = 1 \quad (5)$$

$$\frac{1}{A} = \frac{1}{A_0} - K_t \qquad m = 2 \quad (6)$$

In order to establish the order of reaction, the value of A (PV) was plotted as a function of time [29], and is was obtained by linear regression the most useful mathematical model that represent the degradation kinetics of walnuts oil.

To estimate the shelf of walnuts oil, in terms of the appearance of hydroperoxides, it was proceeded to determine the parametres of the kinetic model that fit better the experimental data. Initially, the apparent order of reaction of the formation of these compounds was determined through a linear regression analysis.

Most of the reactions responsible for food quality loss have been classified as zero, first and second order [5]. These kinetic equations are specific for each food and for each temperature studied [29].

According to the coefficient of determination~~linear regression~~ (~~r~~R^2), the

kinetic model that adjusted the result from the degradation of walnuts oil correspond to a first order model Equation (7) for all (Control and Tested)

$$Ln(PV) = Ln(PV_0) - K_{pv} \times \tau \qquad (7)$$

Where *Kpv* is the rate constant for hydroperoxides formation, *t* is the reaction time and PV_o represents the peroxide value at time of reaction.

Reichert Meissl Number - is the number of milliliters of 0.1 N alkali (such as potassium hydroxide) required to neutralize the volatile water -soluble fatty acids in 5 g. of fat sample of fat. The Reichert Meissl test determines the amount of butyric and caproic acids which are readily soluble in water and the caprylic and capric acids which are slightly soluble.

$$Reichert - Meissl\ Value = (A - B) \times N \times 11 \quad (8)$$

where A – Volume in mlL of standard sodium hydroxide solution required for the test;
B – Volume in mLl in standard sodium hydroxide solution required for the blank; and
N - Normality of standard sodium hydroxide solution.

Polenske number - *i*s the number of milliliters of 0.1 N alkali necessary to neutralize the volatile, water –insoluble fatty acids which are present in 5 g of sample.

$$Polenske\ Value = 10 \times V \times N \quad (9)$$
Where,
V – Volume in ml of standard sodium hydroxide solution required for the test;
N - Normality of standard sodium hydroxide solution.

The optical index (I.O.) is a conditional indicator that determines the optical properties of the lipids, the refractive index and the absorption in the visible spectrum, λ 450nm. It is used for the qualitative analysis of the fat properties, as well as the determination of the unsaturation state.
Formula:

$$O.I = I\ ref_{50} + A_{450} \qquad (10)$$

Where: $I\ ref_{50}$- refractive index of the oil at 50 ° C;
A_{450} - the oil absorption value at the 450nm wave length.

   Photometric color index (PCI), Lovibond method approved by AOCS. This indicator allows us to compare quickly the influence of different processing methods and storage conditions of walnuts oils [20].

3. RESULTS AND DISCUSTSION
Being rich in mono and polyunsaturated acids, walnut oil is unstable during storage. It is important to know the factors which determine its quality [31-34]. Oil stability and quality depends on its chemical composition, especially the content of unsaturated fatty acids, as well as processing storage condition. During storage there are various physical, chemical and enzymatic changes that influence the quality of the walnut oil [13, 33].
Table 1 includes the average results of the chemical and physico-chemical indicators obtained in the testing of nut oil Calaraşi and Kogălniceanu, the harvest of the year 2013.

   Oil oxidation is an undesirable series of chemical reactions involving oxygen that degrades the quality of an oil. Oxidation eventually produces oil rancidity, with accompanying off flavours and smells. The entire oil is in a state of oxidation - you cannot stop it completely - but there are ways to reduce it. Therefore, attempts should be made to reduce oxidation at each stage of oil manufacture. Oxidation is not one single reaction, but a complex series of reactions.

When oil oxidises it produces a series of breakdown products in stages, starting with primary oxidation products (peroxides, dienes, free fatty acids), then secondary products (carbonyls, aldehydes, trienes) and finally tertiary products [6, 10, 32].

Table 1. Chemical and Physical characteristics of walnut oil

Type of oils	Storage time, days	Reichert-Meissl Value	Polenske Value	Specific Gravity at 25°C	Refractive index at 25°C
Walnuts oil, (Calaras), 2013					
Walnut oil, stored at light	control	0.380	1.76	921	1.4763
	3	0.396	0.11	921	1.4773
	7	0.440	0.17	919	1.4770
	10	0.451	0.12	920	1.4690
	15	0.453	0.14	920	1.4680
	30	0.420	0.14	925	1.4720
	60	0.432	0.16	919	1.4780
	90	0.450	0.18	921	1.4680
	120	0.455	0.18	924	1.4790
	150	0.442	0.20	930	1.4793
Walnuts oil, (Kogâlniceanu), 2013					
Walnut oil, stored at dark	control	0.380	1.76	921	1.4763
	3	0.561	0.19	921	1.4772
	7	0.682	0.18	921	1.4771
	10	0.429	0.14	919	1.4763
	15	0.435	0.17	922	1.4750
	30	0.440	0.20	920	1.4757
	60	0.550	0.23	927	1.4790
	90	0.560	0.30	930	1.4790
	120	0.620	0.27	928	1.4789
	150	0.680	0.36	933	1.4797

Table 2 includes the results obtained from the statistical processing of PV and IA indicators in nut oil stored under different dark and light conditions.

Table 2. Change PV and AI value during oil storing in light and dark

Test parameters, storage conditions	Storage time, days							Year
	0	**30**	**60**	**90**	**120**	**150**	**180**	
	PV, meqO$_2$/kg							
Cold pressed oil, unfiltered, t-20^{0}C dark	8.8±0.1	9.3±0.2	12.6±0.1	15.2±0.1	28.1±0.2	29.3±0.2	30.1±0.1	2013
Cold pressed oil, unfiltered, t-20^{0}C light	9.5±0.2	18.2±0.1	24.5±0.2	28.5±0.2	35.6±0.1	30.7±0.2	30.9±0.2	2013
Cold pressed oil dehydrated, t-20^{0}C, dark	0.96±0.1	2.95±0.2	7.9±0.2	10.6±0.2	48.8±0.05	50.9±0.02	46.56±0.1	2015
Cold pressed oil dehydrated, t-20^{0}C, light	0.96±0.1	8.45±0.2	15.8±0.1	30.3±0.1	148.3±0.2	223.4±0.2	173.4±0.2	2015
	Acidity indices, mgKOH/g							
Cold pressed oil, unfiltered, t-20^{0}C dark	3.21±0.1	3.36±0.2	3.62±0.2	3.74±0.1	4.03±0.1	5.5±0.2	6.2±0.1	2013
Cold pressed oil, unfiltered, t-20^{0}C light	3.2±0.2	4.7±0.1	5.1±0.1	5.7±0.1	6.0±0.2	6.8±0.2	7.6±0.1	2013
Cold pressed oil dehydrated, t-20^{0}C, dark	0.12±0.06	0.15±0.01	0.16±0.02	0.19±0.01	0.21±0.03	0.60±0.03	0.76±0.02	2015
Cold pressed oil dehydrated, t-20^{0}C, light	0.12±0.02	0.18±0.01	0.23±0.01	0.28±0.02	0.33±0.01	0.63±0.003	0.84±0.01	2015

During the early stages, lipid peroxidation starts at a slow rate, even more in the presence of antioxidants because they effectively quench most of the free radicals produced. ~~In~~As a consequenc~~e~~, the level of these compounds remains low until the antioxidant is almost consumed completely; once this happens, reaction rates increases exponentially until there are no more oxidizable substrates [11, 17].

In other studies [22, 25, 28], the temperature and light influence on the nut oil quality are presented. The influence of temperature and light on the stability of nut oil depends on the quality of the stored oil [23, 25].

Oxidative processes of lipid fraction during prosessing and storage contribute food quality. They may change nutritional value of food because of impact on essential fatty acids, proteins and vitamins [5].

Figure 1 shows the modification of the peroxide index in walnut oil samples stored in the dark and light during the 3 months,

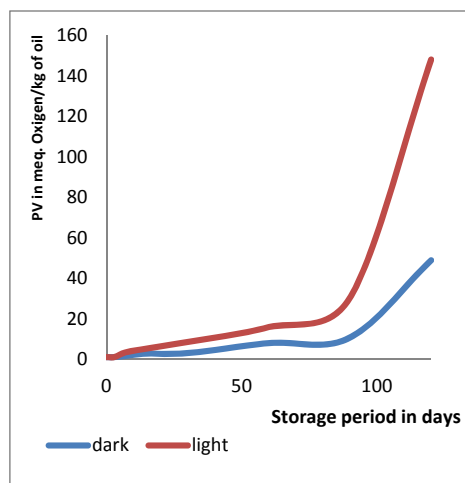harvest of 2015. Figure 2 shows the modification of index PCI.

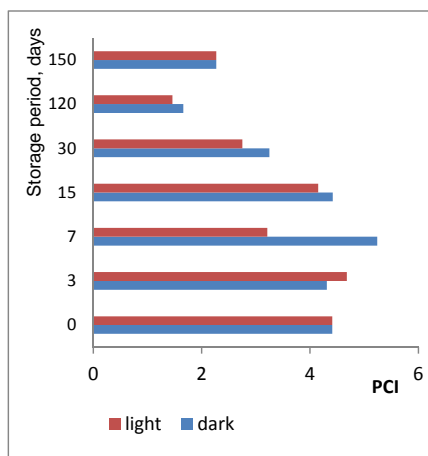**Figure 1.** Change of peroxide index during storage of nut oil under light and dark conditions

Figure 2. PCI index values for nut oil samples stored in light and dark

Degradation of the unstable primary of volatile compounds, such as aldehydes, ketones, hydrocarbons, alcohols, acid compounds and furans. Formed secondary products with low threshold values are responsible for the off-flavors development [12, 14].

Table 3 presents the results obtained from the statistical processing of the indicators tested in the Kogilniceanu nut oil, harvest of 2015.

Table 3. Changing the quality indicators of nut oil kept in the dark and light

Type of oils	Storage time, days	PCI, (average value)	Optic indeces (O.I)	A (PV)	Ln (VP)
Walnut oil, stored at light	0 (initial)	4,41 ±0,13	2,35± 0,01		
	3	4,68 ± 0,01	2,21± 0,02	0.04	-3.2189
	7	3,21 ± 0,04	1,83± 0,01	2.34	0.8501
	15	4,15 ± 0,07	1,60± 0,02	4.25	1.4469
	30	2,75± 0,03	1,05± 0,02	7.49	4.6973
	60	1,80 ± 0,01	0,45± 0,02	14.84	2.6973
	120	1,46 ± 0,04	0,00± 0,01	29.34	3.3790

	150	2,03 ± 0,03	0,00± 0,01	147.04	4.9904
	180	2,84 ± 0,05	0,00± 0,01	159.04	5.0689
Walnut oil, stored at dark	0 (initial)	4,41 ±0,13	2,35± 0,01		
	3	4,31 ± 0,12	2, 30± 0,02	0.04	-3.2189
	7	5,24 ± 0,07	2, 10± 0,02	0.64	-0.4463
	15	4,42 ± 0,12	1,89± 0,01	1.79	0.5822
	30	3, 25± 0,02	1,65± 0,02	1.99	0.6881
	60	2,10± 0,01	1,35± 0,02	6.94	1.9373
	120	1,66 ± 0,02	0,90± 0,01	9.64	3.8679
	150	0,97 ± 0,01	0,60± 0,02	47.84	3.8678
	180	2,27 ± 0,03	0,30± 0,02	64.04	4.1589

CONCLUSION

During storage, walnut oil is extremely unstable, subject to physical and chemical changes with the accumulation of primary and secondary oxidation compounds.

Based on the study we found that the main factors determining the quality and safety of nut oil are: the variety and chemical composition of the walnuts, the climatic conditions, the used agro-technics, the walnut quality and safety, the method of obtaining the oil, the oil storage conditions.

The stability of the oil depends on several factors, one of which is light. The bibliographic study indicates that there is little worldwide information on the impact of light on the quality and safety of nut oil.

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