

QUALITY STUDY OF WALNUT OIL JUGLANS REGIA L

*Sandulachi Elisaveta, Tatarov Pavel

Technical University of Moldova – Chişinău, Moldova

*Sandulachi Elisaveta, luiza_sandulachi@yahoo.com

Abstract: Insufficient scientific information on the quality of walnuts grown in Moldova and the composition of their oils necessitates carry out a systematic study of the most representative varieties of national production in order to contribute with scientific arguments and establish a major potential for walnut oil production at industrial level. The main objectives of the study were to find out solutions in order to obtain walnut oil relatively stable during storage. This paper presents an argumentation of the factors that determine the quality of walnut oil. It presents the chemical composition of oil from walnuts Juglans regia L according to a research conducted in recent years.

Key words: walnut oil, stability, peroxide value, acid value, enzyme activity, Pirson correlation.

1. INTRODUCTION

Walnuts Juglans regia L. are known as relevant sources of oil beneficial to health. Although walnut oil is not described by the current Committee on Fats and Oils of the Codex Alimentarius, small amounts are produced and commercialized in countries such as France, Spain, Chile and Argentina. The oil is used directly (without refining) for edible purposes, mainly as a salad dressing. It is also used in the cosmetic industry as a component of dry skin creams and wrinkle and anti-aging products [10]. The oil content in commercial walnut varieties ranges from 620 to 740g /kg kernel [10]. Prasad [14] reported a mean value of 690g/kg in walnuts from different varieties and geographic origins.

Insufficient scientific information on the quality of walnuts grown in Moldova and the composition of their oils necessitates carry out a systematic study of the most representative varieties of national production in order to contribute with scientific arguments and establish a major potential for walnut oil production at industrial level. Being rich in mono and polyunsaturated walnut oil is unstable during storage. It is important to know the factors which determine the quality of walnut oil.

2. MATERIALS AND METHODS

2.1. Samples

Served as a subject:

A - Industrial walnut oil, sold in Moldova; B –Walnut oil, cold pressed (press screw laboratory, Technical University of Moldova, Chisinau); C - Walnut oil, cold pressed (B), without setting.

The presses have used varieties walnuts grown in Moldova. Oil samples were stored at 25-30°C.

2.2. Analytical methods

The regress of lipid oxidation was assessed by measuring Peroxide Value (PV), Acid Value (AV), Activity Polifenoloxidase (A PPO).

The traditional method of determining PV, expressed as mill equivalents of active oxygen per kilogram of oil (meqO₂/kg), involves a titration of the oil contains potassium iodide in a chloroform-acetic acid mixture. The hydro peroxides oxidase the iodide to iodine, which can be determined by titration with sodium thiosulphate (AOAC official method 965.33).

3. RESULTS AND DISCUSSION

Worldwide there are various studies aimed at oil stability during storage. In the reference study conducted found that the stability of walnut *Juglans regia* L. oil it is determined by several factors such as: chemical composition of walnuts (oil), oil extraction method, packaging, storage parameters etc. The oil content in walnut kernel is determined by the genotype but may also be influenced by environmental conditions and irrigation rate [14]. Minor differences were observed in crop year effects [9]. Oil content in different varieties of walnut *Juglans regia* L. reported in various studies it is within 570 ... 710 g/kg [5-10]. The major components of walnut oil are triacylglycerols (TAGs; up to 980 g kg⁻¹ oil), in which monounsaturated Fas (mainly oleic acid) and polyunsaturated FAS (PUFAS; linoleic and α -linolenic acids) are present in high amounts (Table 1), [2, 4, 5, 9, 14]. Nine TAG species have been characterized, of which trilinolein is the most abundant (\approx 37.7%), followed by dilinoleoyl-oleoyl-glycerol (18.5%) and dilinoleoyl-linolenoyl-glycerol (18.4%) [10]. The FA composition of walnut oil has been extensively reported for several cultivars from different geographic origins, including Argentina, [4, 13] the USA, [2] New Zealand, [1] Portugal, [12, 13] Turkey, [9, 11] Greece [18], and Germany [10] and Moldova [3, 15].

Table 1. Oil content and main fatty acids of some commercial walnut varieties from different origins [7-9, 11-13]

Variety	Oil content (g kg ⁻¹)	Fatty acids (mg g ⁻¹)				
		16 : 0	18:0	18:1 Ω 9	18:2 Ω 6	18:3 Ω 3
Chandler	695-725	66-69	15-17	161-178	565-589	165-186
Franquette	623-724	66-75	19-31	170-284	502-592	117-149
Lara	665-712	63-81	16-28	149-197	579-625	122-152
Mayette	665-732	59-70	18-27	161-223	554-575	130-176
Marbot	663-697	63-71	27-28	163-165	589-597	127-143
Mellanaise	630-697	63-70	26-28	145-171	587-616	125-145
Parisienne	631-715	62-63	24-29	174-195	577-624	96-132
Criolla	676-689	77-78	17-19	173-212	573-578	119-156
Hartley	710-714	68-81	9-13	167-179	584-592	146-160
Serr	711-728	66-67	18-19	167-179	167-179	584-592
Sorrento	716-739	72-76	15-17	172-191	589-593	129-150
Tulare	732-736	61-64	20-22	230-241	559-569	114-120

Fatty acid nomenclature: 16 : 0, hexadecanoic acid; 18 : 0, octadecanoic acid; 18 : 1n-9, cis-9-octadecenoic acid; 18 : 2n-6, cis-9,cis-12-octadecadienoic acid; 18 : 3n-3, cis-9,cis-12,cis-15-octadecatrienoic acid.

The high content of unsaturated fats can lead to oxidative stability and reduced shelf life of walnut oil. Although walnut kernels contain a diverse array of phenolic and polyphenol compounds with strong antioxidant and radical-scavenging properties, only minor amounts could be present in the extracted oils. Protection against oxidative

degradation seems to be limited mainly to tocopherol content. Other minor components characterized in walnut oil include phospholipids, sphingolipids, sterols (principally β -sitosterol), hydrocarbons (particularly C14–C20 n-alkanes) and volatile components [1].

The majority of the volatile components found in walnut oil are produced by oxidative breakdown of linoleic and linolenic acid hydro peroxides. Considering the sensory attributes characterizing such volatiles, they could adversely affect the sensory profile of the raw shelled walnut or its by-products (oil and flour) during handling and storage [10].

The formation of some volatiles (pentanal, 2-heptenal and 2-octenal) can be better explained by an enzymatic pathway, rather than chemical (non-enzymatic) [10]. In walnuts *Juglans regia* L may be present enzyme lipoxygenases (LOXs), which oxidases polyunsaturated fatty acids containing cis, cis-1,4-pentadiene fragments, such as linoleic and linolenic acids [6, 10]. The hydroperoxides produced by LOXs undergo cleavage to give short- and medium-chain hydrocarbons, aldehydes and alcohols (similar to those formed by non-enzymatic autoxidation) that contribute to the headspace volatile flavours [13]. In Figure 1 presents the reactions of autoxidation of linoleic acid and formation of major volatile compounds in walnut oil [10].

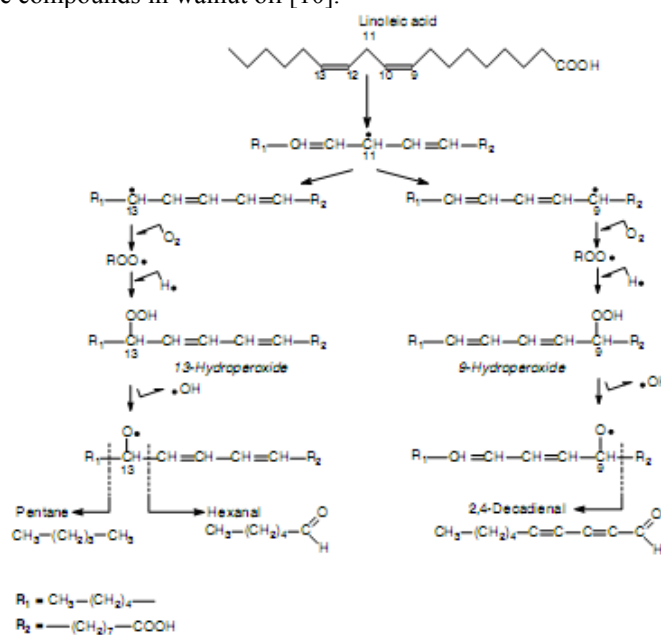


Fig. 1. Reactions of autoxidation of linoleic acid and formation of major volatile compounds in walnut oil [10]

Table 2 includes the experimental data across the physicochemical evolution of different indicators in walnut oil products in Moldova during storage. It was found that peroxide value (VP), acid value (VA) and activity PPO increase during storage. This phenomenon is observed in studies [16-19] attesting oxidative and enzymatic instability of walnuts and nut oil.

Table 2. Change indicators PV, VA and A PPO in oils produced from different varieties of nuts grown in Moldova during storage

Samples tested	Indicators tested	Term storage (days)					Allowable Values
		0	30	60	90	120	
A	PV	-	7,7	10	10	11	Government decision, Restriction technique
	VA	-	3.30	3.51	3.72	3.90	
	A PPO	-	-	0.6	0.72	0.1	
B	PV	8.0	9.3	12.6	15.2	28.1	VA - max.4, PV - max 10
	VA	3.21	3.36	3.62	3.74	4.03	
	A PPO	0.75	0.92	1.0	1.2	1.5	
C	PV	9.5	18.2	24.5	28.3	35.6	
	VA	3.2	4.7	5.1	5.7	6.0	
	A PPO	1.5	3.0	3.7	4.2	4.3	

PV- peroxide value, meg O₂/kg oil, VA - acid value, mg KOH/1g oil,
APPO – activity polifenoloxidase, units activity

In Figures 2, 3 and 4 presents the correlation between the peroxide value (PV), acid value (AV) and activity PPO of walnuts oil. Prisons coefficient was estimated and tested indicators.

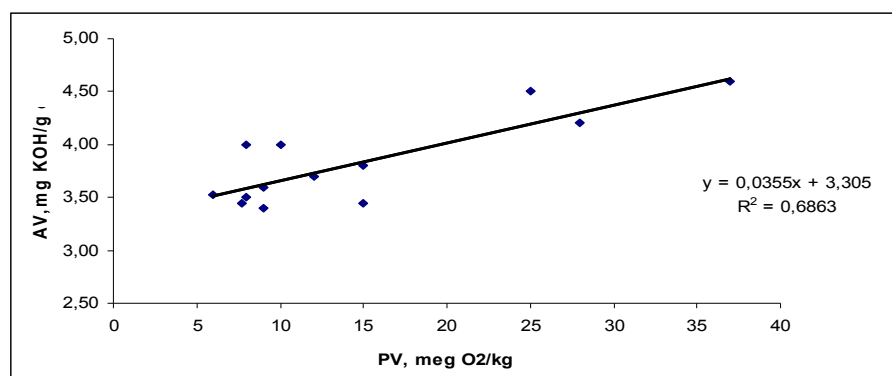


Fig. 2. Correlation between peroxide value and acid value of walnuts oil
Pirson correlation R (f = PV, AV) = 0.8284

High Pirson correlation (R (PV, A PPO) = 0.9622) was found between VA and activities PPO. Perhaps the correlation between VP and the activity of other enzymes, including the lipoxygenases is even more significant.

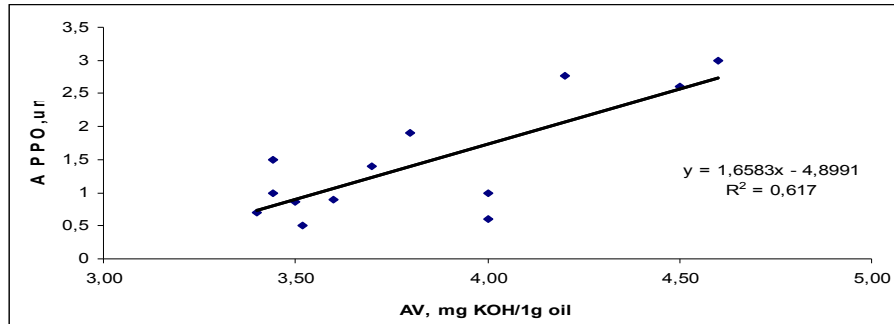


Fig.3. Correlation between activity PPO and acid value of walnuts oil
 Pirson correlation R (f = AV, APPO) = 0.7855

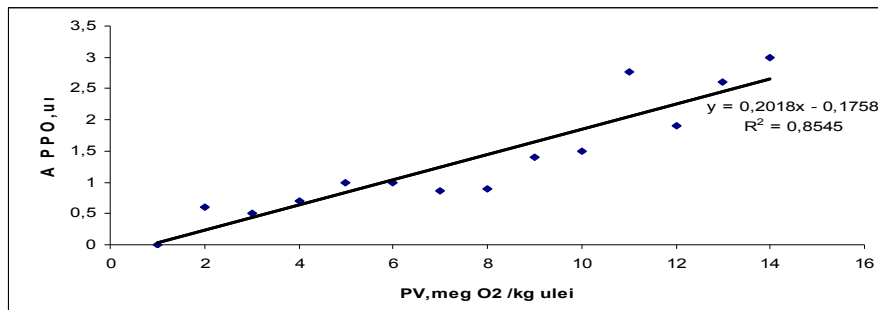


Fig.4. Correlation between activity PPO and peroxide value
 Pirson correlation R (f = PV, A PPO) = 0.9622

It is necessary to study and appreciate the factors that cause oxidative and enzymatic processes in walnuts and walnut oil to extend the oil storage. The oxidative stability is an important parameter in ascertaining the quality of oils, as it gives a good estimation of their susceptibility to oxidative degradation.

CONCLUSION

Walnuts *Juglans regia* L are important sources of vegetable protein and polyunsaturated fatty acids. Nutmeg contains the optimum ratio of $\Omega 6$ and $\Omega 3$. Oxidative stability is an important criterion in ascertaining the quality of oils. The balance of ω -6/ ω -3 ratio (1:1 to 1:4) is also an important determinant in decreasing the risk for coronary. Quality and oil stability depends on its chemical composition, especially the content of unsaturated fatty acids, as well as processing and storage conditions.

During storage in walnut oil held various physicochemical and enzymatic changes that influence the quality.

There was a significant correlation between peroxide value, acid value and enzyme activity. Pirson correlation has the following meanings:

$$R (f = PV, AV) = 0.83; R (f = PV, A PPO) = 0.96; R (f = AV, APPO) = 0.79.$$

REFERENCE

1. Amaral, J.S. et al. Determination of sterol and fatty acid compositions, oxidative stability, and nutritional value of six walnut (*Juglans regia* L) cultivars grown in Portugal. *J Agric. Food Chem.* (51) 2003, pp.7698–7702
2. Caglarirmak, N. Biochemical and physical properties of some walnut genotypes (*Juglans regia* L). *Nahrung. Food* (47), 2003, pp. 28–32
3. Ciumac, J. et al. Composition in fatty acids of Moldavian walnuts (*Juglans regia* L). *Papers of the International Symposium Euro-aliment 2007*, Galati University Press, 2007, pp.32-34
4. Crews, C. et al. Study of the main constituents of some authentic walnut oils. *J Agric. Food Chem.* (53), 2005, pp. 4853–4860
5. Dogan, M. and Akgul, A. Fatty acid composition of some walnut (*Juglans regia* L) cultivars from east Anatolia. *Grasas Aceites* (56), 2005, 328–331
6. Frankel, E.N. *Lipid Oxidation*. PJ Barnes & Associates, Bridgewater, 2005, pp.67–98
7. Garcia, J.M. et al. Lipid characterization in kernels from different walnut cultivars. *Turk J Agric. Forest* (18), 1994, 195–198
8. Martinez, M.L. and Maestri, D.M. Oil chemical variation in walnut (*Juglans regia* L) genotypes grown in Argentina. *Eur. J Lipid Sci. Technol.* (110), 2008, pp. 1183–1189
9. Martinez, M.L. et al. Varietal and crop year effects on lipid composition of walnut (*Juglans regia*) genotypes. *J Am Oil Chem. Soc.* (83), 2006, pp. 791–796
10. Martinez, M. L. et al. Walnut (*Juglans regia* L) genetic resources, chemistry, by-products, Society of Chemical Industry. *J. Sci. Food Agric* (90), 2010, 1959-1967
11. Ozkan, G. and Koyuncu, M.A. Physical and chemical composition of some walnut (*Juglans regia* L) genotypes grown in Turkey. *Grasas Aceites* (56), 2005, 141–146
12. Pereira, J.A. et al. Bioactive properties and chemical composition of six walnut (*Juglans regia* L) cultivars, *Food Chem. Toxicol.* (46), 2008, pp. 2103–2111
13. Piccirillo, P. et al. Exploring the role of lipoxygenases on walnut quality and shelf-life. *Acta Hort.* (705), 2006, pp.543–545
14. Prasad, R.B.N. Walnuts and pecans, in *Encyclopedia of Food Science and Nutrition*, ed. by Caballero B, Trugo L and Finglas P. Acad. Press, London, 2003, pp. 6071–6079
15. Sandulachi, E. et al. Aprecierea indicatorilor fizico-chimici ai uleiului din miez de nucă produs în Republica Moldova, *Materialele conferinței studenților, doctoranzilor și colaboratorilor UTM*, 2011
16. Savage, G.P. Dutta, P.C. and McNeil D.L., Fatty acid and tocopherol contents and oxidative stability of walnut oils. *J Am Oil Chem. Soc* (76), 1999, pp.1059–1063
17. Sharma, O.C. and Sharma, S.D. Genetic divergence in seedling trees of Persian walnut (*Juglans regia* L.) for various metric nut and kernel characters in Himachal Pradesh. *Sci. Hort.* (88) 2001, pp.163–171
18. Tsamouris, G., Hatziantoniou, S. and Demetzos, C. Lipid analysis of Greek walnut oil (*Juglans regia* L). *J. Biosc.* (57), 2002, pp.51–56
19. Zeneli, G., Kola, H. and Dida, M. Phenotypic variation in native walnut populations of northern Albania. *Sci. Hort.* (105), 2005, 91–100