THE STUDY OF WALNUT OIL (*JUGLANS REGIA L.*) OXIDATIVE STABILIZATION BY SATURATED FATTY ACIDS

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Abstract. Walnut oil (*Juglans regia L*.) is a local lipid product rich in $\omega 3$ and $\omega 6$ polyunsaturated fatty acids, which are extremely subjected to oxidation. The mix of walnut oil with solid vegetable fats can stabilize the system. In order to save the biological potential of walnut oil, it was proposed to minimalize the content of saturated fatty acids in the stabilized mix by the use of a pure saturated fatty acid with a long carbon chain. Thus, the 15:85 is an optimal ratio of *Stearic acid: Walnut oil* mix so as to form a spreadable composition with a melting point similar to that of dairy fat.

Keywords: walnut oil, saturated and polyunsaturated fatty acids, oxidation, rancidity

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Introduction

Lipids are the essential food components that largely determine the nutritional qualities, biological, energy value and the taste of food. The main factor that characterizes the efficiency of dietary lipids assimilation in body is the balance ratio of fatty acids.

An important role belongs to polyunsaturated fatty acids and their excluding from the diet can affect the balance of vital processes [1]. The local lipid product rich in $\omega 3$ and $\omega 6$ polyunsaturated fatty acids is walnut oil (*Juglans regia L.*), which ratio of unsaturated fatty acids to saturated fatty acids is twice as high as the ratio in olive oil [2]. Therefore, the oxidative stability of a cold pressing walnut oil is lower than in the other types of local vegetable oils [3].

In view of the above, the scientific research has been planned in order to accumulate new data about oxidative stability of walnut oil, the possibility of its use to obtain new final products.

Materials and methods

The main research object was a virgin walnut oil (*Juglans regia L.*) obtained by a cold pressing method at the Technical University of Moldova.

The study of saturated fatty acids influence on the walnut oil oxidative stability and the potential of a new products obtaining was realized by the use of several solid vegetable fats (palm oil, cocoa butter) and a pure saturated fatty acid – stearic one. In order to obtain some comparative data, it was also used a monounsaturated fatty acid – oleic one.

The stability of mixes of walnut oil and saturated fatty acids was analyzed by Rancimat method using the 892 Professional Rancimat. The tests were carried out with 3g of the fat samples at temperature of 120°C and an airflow rate of 20 l/h. [4].

The measurement of fats melting point was realized by a standard capillary method [5].

Research results

Research started with a comparative analysis of chemical compositions of solid vegetable fats and virgin walnut oil (Table 1).

Fatty acid	Palm oil [6]	Cacao butter [7]	Walnut oil [8]
C8:0 (caprylic)		1,27	
C11:0 (undecanoic)		1,69	
C12: 0 (lauric)	0,1 - 0,4	19,68	
C14: 0 (myristic)	0,5 - 2,0		0,1
C16: 0 (palmitic)	39,0-46,8	28,16	2,9 - 7,0
C16: 1 (palmitoleic)	0,6		0,1
C18: 0 (stearic)	3,5 - 6,0	21,53	0,9 - 2,5
C18: 1 (oleic)	36,7 - 43,0	22,78	14,0 - 30,0
C18: 1 (trans-oleic)	≤ 1		
C18: 2 (linoleic)	6,5 – 12,0	4,88	53,0-70,0
C18:3 (linolenic)	0,5		9,8-13,0
C20: 0 (arachic)	1,0		
C20:1 (eicosenoic)			1,7
C22:1 (docosenoic)			3,8
Saturated	49,5	72,3	7,5
Monounsaturated	40,9	22,8	18,0
Polyunsaturated	9,6	4,9	74,5
Unsaturated / Saturated, ratio	1,02	0,77	12,33

Table 1. Fatty acid composition of vegetable fats (% of total fatty acids)

Presented data denotes that walnuts oils have a high content of polyunsaturated fatty acids, that are first of all oil components that are exposed to oxidation.

The rate of oxidation of fatty acids increases in relation to their degree of unsaturation [8]. The oxidative stability of walnut oil mixed in the proportion of 1:1 with cocoa butter and palm oil was analyzed (Table 2).

Vegetable fat	Induction time (IT), h	Stability time (ST), h	ST-IT, h
Cocoa butter [9]	915	-	-
Palm oil [9]	712	-	-
Walnut oil	1,92	2,56	0,64
Cocoa butter + Walnut oil (1:1)	2,33	3,34	1,01
Palm oil + Walnut oil (1:1)	3,14	3,84	0,7

Table 2. Induction period for vegetable fats at $120^{\circ}C$

According to presented data, even though the content of saturated fatty acids in cocoa butter is higher than in palm oil (Table 1), the induction time of Palm oil + Walnut oil mix is longer. But the period from the appearing of first volatile oxidation products to fat completely degradation is longer for Cocoa butter + Walnut oil mix.

Additionally, it was proposed to study the influence of oleic fatty acid on walnut oil oxidative stability (Figure 1). The content of this monounsaturated fatty acid in palm oil is almost twice as big as in cocoa butter (Table 1).



Fig.1. The oxidation stability of Oleic fatty acid + Walnut oil mix (1:1) at 120 °C

According to Fig.1, the presence of monounsaturated fatty acids in the mix on the contrary accelerates walnut oil oxidation. Thus, the stabilization potential of palm oil can be explicated by the "quality" of its saturated fatty acids and not by their quantity.

It has been assumed that the composition of palm oil essentially consists of saturated fatty acids with a longer carbon chain than in cacao butter. It has been made the calculations of carboxyl chain average length of unsaturated fatty acids (taking into account % fatty acid of total saturated fatty acids), that enter in the compositions of palm oil and cacao butter. In consequence, C_{lenght} (palm oil) = 16,16 and C_{lenght} (cacao butter) = 15,25.

In food industry solid vegetable fats are used in combinations with oils in order to obtain different kinds of spreadable products. The industrial transformation of vegetable fats – liquid at room temperature due to the concentration of unsaturated fatty acids – into spreadable fats is achieved by the crystallization of glycerides concomitantly with cooling and intensive mixing. One of the conditions necessary to carry out this process is that the melting point of vegetable fat should be similar to dairy butter t = 30 ± 5 °C [10], while the melting point of walnut oil is t = -18°C [11].

Solid vegetable fats balance the melting points of the vegetable oils mix due to the high concentration of saturated fatty acids. However, the composition of solid vegetable fats is complex and includes different types of saturated and unsaturated fatty acids, sometimes-even trans isomers (Table 1). Therefore, in order to optimize the mix of vegetable fats and minimize the concentration of saturated fatty acids, the use of a pure saturated fatty acid with a long carbon chain was proposed – stearic one.

In order to determine the optimal mix of walnut oil and stearic acid, the series of samples was made to obtain the Gibbs Roseboom Triangle (Figure 2), where an oleic acid was used as a monounsaturated fatty acid. The melting points of the samples were determined. The optimal zone of addition of stearic acid in walnut oil was established (~ 15% of total fat content) to form spreads based on walnut oil with a melting point similar to that of dairy fat.



Fig. 2. Diagram of Walnut oil / Monounsaturated fatty acid / Saturated fatty acid system

Conclusions

The oxidative stability of walnut oil is positive influenced by saturated fatty acids, especially with long carbon chains, and negative – by monounsaturated fatty acids. The mix of walnut oil and a pure saturated fatty acid has a research perspective in order

to obtain food emulsions with optimal melting point and increased oxidation stability.

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