THE INFLUENCE OF PHENOLIC COMPOUNDS FROM MEMBRANE SEPTUM ON THE PHISICAL-CHEMICAL PARAMETERS OF THE WALNUT OIL-ENRICHED EMULSION

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Abstract: *In the present study it was evaluated the possibility to incorporate the walnut oil in food emulsions recipe. It was elaborated obtaining technology of mayonnaise type emulsions based on mixture of sunflower oil and walnut oil in combination with phenolic compounds from membrane septum extract. Therefore were obtained emulsions with 50% fat, containing different concentrations of walnut oil (25, 50, 75, and 100%). The microstructure of emulsions was determined using an optical microscope, of digital model «Motic DMB 5-5». The lipid oxidation was assessed by measuring peroxide value (PV), acid value (AV), conjugated dienes content (CD), and 2-thiobarbituric acid value (TBA). It was shown the feasibility of walnut oil utilization to increase the biological value and physical-chemical parameters of food emulsion as compared with the traditional recipe.*

Keywords: *food emulsion, walnut oil, membrane septum, primary and secondary oxidation products.*

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1. Introduction

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. As a consequence, interest in the theory and practice of food emulsions has been increasing. Scientific studies are oriented more and more toward different aspects of the characteristics, formation, behavior, and application of these food emulsions. Regarding oils, a wide variety of different types of oils have traditionally been used in food emulsions, including soybean, corn, canola, olive, safflower, and sunflower oils [6].

The trend has been to replace traditional oils with more health-promoting oils, such as polyunsaturated lipids. Walnut oil (*Junglas regia* L.) is one of these beneficial oils. Walnut oil is high-quality oil due to its important physical and biochemical properties. In addition, walnut oil has significant economical value and medicinal importance for human health because of its essential composition of polyunsaturated fatty acids, especially linoleic (18:2) and linolenic (18:3) acids, bioactive minor components, such as tocopherols and phytosterols and is appreciated as specialty oil also because of its characteristic flavor and aroma [10].

But on the other side high levels of polyunsaturated fatty acids make walnut oil prone to oxidation. A major goal in walnut production is to find an appropriate method to stabilize walnut lipids. The oxidative stabilization of walnut oil is imperative to determine the feasibility of bringing it into commercial production.

Interest in the development of processes for the production or extraction of bioactive compounds from by-products sources has increased in recent years due to the potential applications of these compounds in food, chemical, and pharmaceutical industries. In the present study walnut membrane septum as a potential alternative source of bioactive compounds for food emulsion stabilization are evaluated.

The purpose of this study is to develop a new kind of food emulsion with a high biological value, contributing to improve the nutritional status of the population. In this regard, the possibility to incorporate the walnut oil in food emulsions recipe was evaluated.

To decrease the intensity of possible oxidative transformations of the investigated emulsion, the task was posed to obtain walnut oil-enriched emulsion with increased antioxidant properties at the expense of incorporating into its composition natural phenolic compounds from membrane septum, namely, antioxidative components.

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2. Materials and methods

2.1. Materials

As components for obtaining experimental samples of food emulsions sunflower oil, walnut oil, sugar, mustard powder, milk powder, vinegar, salt, emulsifier and natural extract from walnut membrane septum were used. All foodstuff used correspond to requirements for quality of the specifications and technical documentation.

2.2. Technology of samples preparation

Ten experimental samples of food emulsions were prepared for researching which differ by the content of walnut oil and membrane septum extract. To obtain samples of food emulsions with a high biological value 25, 50, 75 and 100% of sunflower oil was replaced by walnut oil. The figure 1 shows the technological scheme for producing the stabilized walnut oil-enriched emulsion at the expense of membrane septum extract. The obtained emulsion samples were placed in sterile plastic food containers with sealable lids and stored for 24 hours at 4 ^{0}C, then corresponding analyses were carried out.

2.3. Chemicals

2-thiobarbituric acid (4,6-dihydroxy-2-mercaptopyrimidine) was obtained from Alfa Aesar. 1,1-Diphenyl-2-picrylhydrazyl (DPPH˙) as free radical form (90% purity) was supplied by Sigma-Aldrich. Ethanol (99.9%), chloroform, 1-butanol, glacial acetic acid, potassium hydroxide, phenolphthalein, potassium iodide, sodium thiosulfate ($Na_2S_2O_3 \times 5H_2O$) and starch were supplied by Eco-Chimie (Chisinau, Moldova). All the chemicals used were of HPLC or analytical grade. Distilled water was used throughout.

2.4. Determination of the basic quality properties

Acidity of the food emulsion samples were determined by potassium hydroxide titration as described in AOCS Official Method Cd 3d-63 (AOCS, 1999) [1]. Peroxide value was determined according to AOCS Official Method Cd 8-53 (AOCS, 2003) [2]. Conjugated dienes were detected by a spectral method of analysis (λ=232 nm) according to the AOCS Official method Ti la 64 (AOCS, 1993) [3]. The formation of the secondary oxidation products accumulation in the investigated emulsion samples were characterized by the 2-thiobarbituric acid value in accordance with AOCS Official Method Cd 19-90 (AOCS, 2009) [4].

2.5. Definition of a microstructure and the sizes of oil droplets

By using an optical microscope of digital model "Motic DMB 5-5" (China) the microstructure of food emulsions was determined. For this purpose a drop of the investigated sample of emulsion was placed on the subject glass, covered with its integumentary glass and then established in a microscope.

2.6. Statistical analysis

Variance analysis of the results was carried out by least square method with application of coefficient Student and Microsoft Office Excel program. Differences were considered statistically significant if probability was greater than 95% (p-value <0.05). All assays were performed by triplicate at room temperature 20 ± 1 ^{0}C. Experimental results are expressed as average ± SD (standard deviation).

3. Results and discussion

Food emulsion represents difficult dispersed, stable fatty emulsion of direct type in which the disperse phase is distributed in the form of the smallest droplets in the dispersive medium, differentiated by an interface [9]. Actual trend of the oil industry is to produce food emulsion based on mixture of vegetable oils of different types according to their fatty acid composition. Walnut oil was chosen as a fortifier due to high content of polyunsaturated fatty acids and natural antioxidants.

Particular attention is paid to the possible impact of insertion ingredients on quality parameters on enriched products. As in technological process of obtaining food emulsion there is an interaction of various systems, a regrouping of making substances from products. Thus the disperse system finds certain structure properties.

The incorporation in composition of investigated samples of emulsion walnut oil was accompanied by a change of structure characteristics, such as perimeter, radius and area. The degree of change in these indicators depends on quantity of input walnut oil and the gradient speed of shift of a product. Results of researches of structure characteristics for compared samples of food emulsion are shown in table 1.

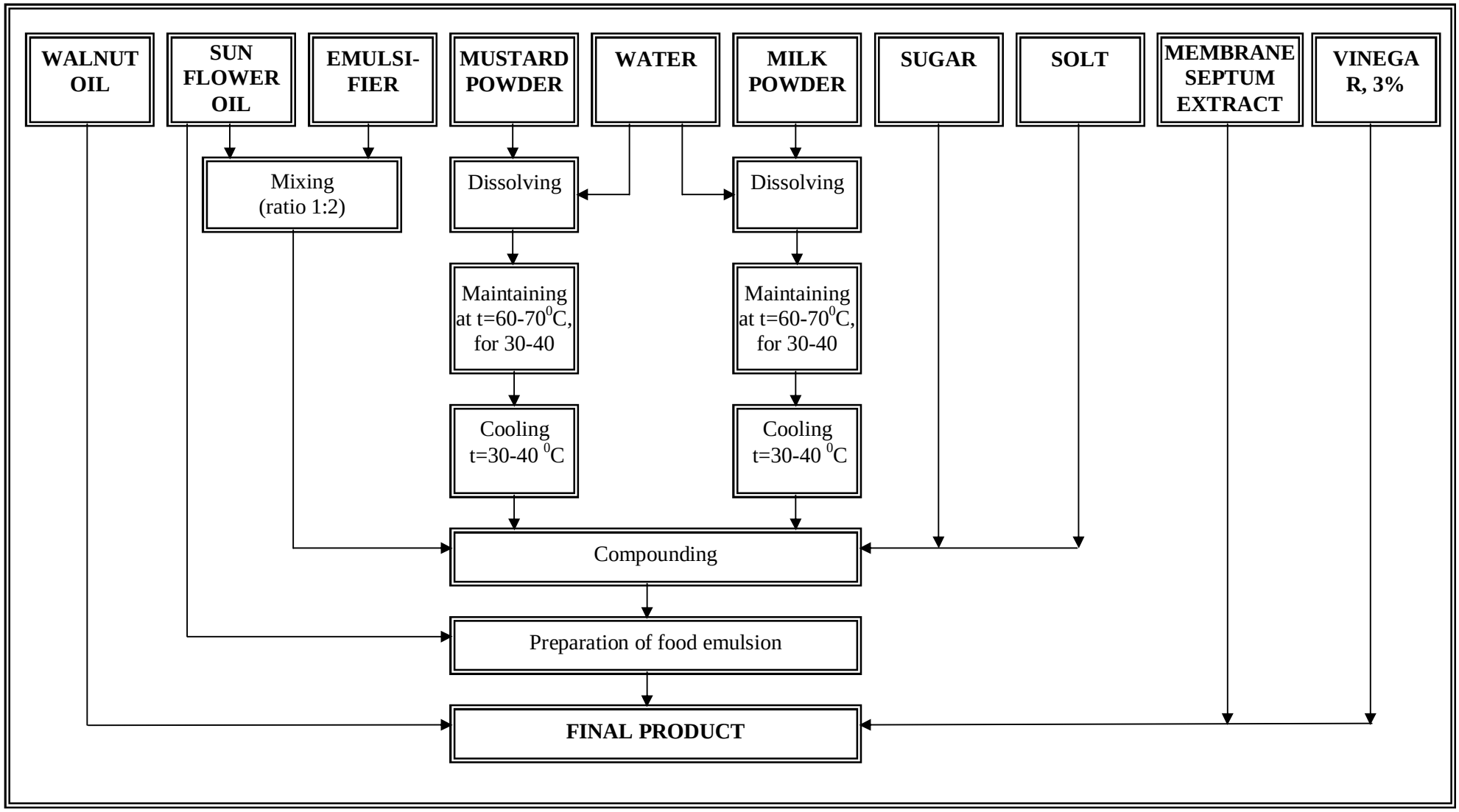

Fig. 1. *The main technological processes of producing stabilized walnut oil-enriched emulsion.*

Table 1. *The main oil droplets parameters of compared food emulsions*

No	Sample of food emulsion	Parameters of oil droplets		
		Perimeter, [µm]	Radius, [µm]	Area, [µm^2]
1	Mayonnaise sample (100% sunflower oil)	5.71±0.02	35.95±0.02	141.4±0.02
2	Mayonnaise sample (25% walnut oil)	7.85±0.03	49.32±0.03	272.23±0.03
3	Mayonnaise sample (50% walnut oil)	9.27±0.01	58.31±0.01	427.46±0.01
4	Mayonnaise sample (75% walnut oil)	12.44±0.03	78.24±0.03	770.06±0.03
5	Mayonnaise sample (100% walnut oil)	10.76±0.02	44.17±0.02	724.77±0.02

In compared samples of emulsions under the number 1 – 5 show the effect of input walnut oil (25, 50, 75 and 100%) on quality parameters of the microstructure of food emulsions compared with the control sample. It was notice that the most dense spherical and uniform arrangement of oil droplets is typical for samples of mayonnaise emulsions numbered 2 and 3, moreover, the oil droplets of this emulsions differ by the smallest sizes. Increasing the size of fat droplets in sample number 4 and 5 leads to a larger contact surface areas of spheres and, consequently, to reduce the viscosity of the food emulsion.

Walnut membrane septum is considered a source of bioactive compounds and have been widely used in traditional medicine. Antiradical and antibacterial activities have also been described for different *Juglans regia* cultivars. Walnut membrane septum is a by-product of the walnut production, being formed in large amounts. Probably due to its scarce utilization, this matrix is very little studied.

Walnut membrane septum extract was analyzed in our previous studies for total polyphenol content (TPC) and antioxidant activity. The TPC was determined using the Folin-Ciocalteu method. The antioxidant activity of the extracts was determined using 2,2 diphenyl-1-picrylhydrazyl radical DPPH•. Experimental results on the antioxidant activity of the bioactive compounds from walnut membrane septum allowed to make the assumption about possibility of their incorporation into food emulsions to prevent negative oxidation process [8].

Oxidative and hydrolytic decomposition is observed in the process of preparation food emulsion. The presence and depth of the process of oxidation and hydrolysis is characterized by the content of free fatty acids, i.e., the acid value (AV). The growth of the acid value or intensity in the formation of free fatty acids in the compared emulsion samples has a linear character (Fig. 2).

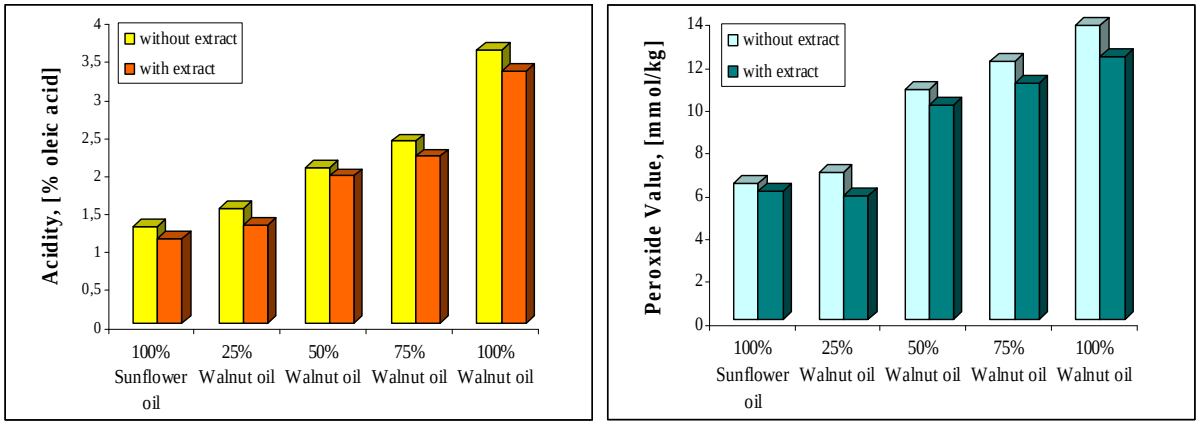

Fig. 2. *Effect of added walnut oil and membrane septum extract on the amount of acidity and peroxide values in compared mayonnaise samples*

The presence and quantity of peroxides in food emulsions are known to determine the level of the oil storage stability. Figure 2 shows the dynamics of the accumulation of these compounds in the compared emulsion samples during preparation. As the presented data show, the summary rate of oxidative reactions that lead to the formation of peroxides in the course of emulsion preparation is lower for the group of food emulsion with membrane septum extract.

Figure 3 shows the change in the intensity of the accumulation of conjugated dienes and malondialdehides (expressed by the amount of the 2-thiobarbituric acid value) in the compared food emulsions.

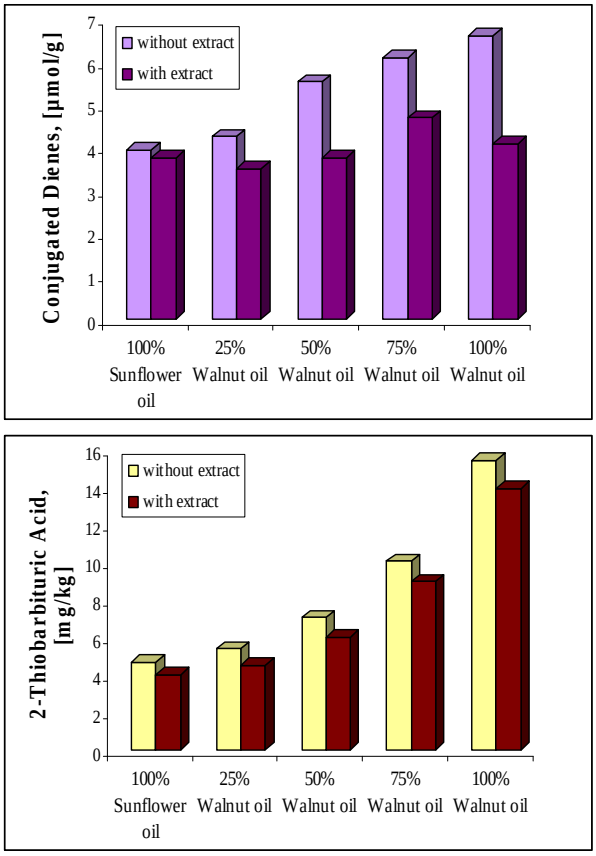

Fig. 3. *Effect of added walnut oil and membrane septum extract on the amount of conjugated dienes content and 2-thiobarbituric acid value in compared mayonnaise samples*

It was established that with increasing concentrations of walnut oil there had place the increase of the amount of primary and secondary products of lipid oxidation, such as peroxides and aldehides.

When comparing the antioxidative properties of the membrane septum extract incorporated into the emulsion samples, one should note that the antioxidative components of the extracts exert the significant influence on inhibiting the processes of walnut oil-enriched emulsion oxidation. This regularity is also traced for the acidity and peroxide values of the corresponding emulsion samples.

4. Conclusions

The effect of incorporated walnut oil on the structure characteristics of compared samples of food emulsions it is established that the sample containing walnut oil 25% is characterized by the most dense spherical and uniform arrangement of oil droplets of emulsion.

The composition of vegetable oils (sunflower and walnut) in a ratio of 3:1 used to create a food emulsion with a high biological value is the most optimal ratio of polyunsaturated fatty acids ω-3: ω-6, providing, in combination with phenolic compounds from membrane septum extract oxidation stability to the finished product.

This study demonstrates that natural extract such as walnut membrane septum could be used as alternative source of natural antioxidants in food industries, especially for food emulsion stabilization. The experimental results apparently indicated that walnut membrane septum extract exerts an effective influence on the processes of oil stabilization; i.e., they inhibit the intensity of the primary and secondary oxidation products accumulation.

5. Acknowledgements

This work was benefited from support through the 2817/16.04 project, "*Elaboration of methods to protect walnut lipids (Juglans regia L.) from oxidative degradation*", funded by the Academy of Science of Moldova and Moldavian Government.

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