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ORIGINAL ARTICLE

STUDY OF QUALITY INDICES OF FUNCTIONAL VEGETAL OIL MIXTURE*

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Solution of the problem of alimentation structure improvement is related to creation of functional food-stuff with a balanced content of the major nutrient materials enriched in missing micronutrients and, at the same time, being daily products. Multicomponent structure of vegetable oils provides ample opportunities for developing of products preventing deficiency in essential fatty acids, vitamins and other physiologically functional ingredients.
Grape-seed oil is of high bioavailability determined by a complex of biologically active substances, bioflavanoids, a group of vitamins, being the most important of them. Physiological effect of grape-seed oil includes anti-cholesterol property preventing cardio-vascular diseases.
The thesis covers studies of vegetable oil mixtures made on the basis of sunflower and grape-seed oils. The study covers oxidative stability of vegetable oil mixture, based on determination of intensity of primary and secondary oxidation products formation.

Keywords: sunflower oil, grape-seed oil, vegetable oil mixture, primary and secondary oxidation products, functional food-stuff.

1. Introduction

Nowadays the tendency of the development of the fat-and-oil industry represents the acquisition of vegetable oils for functional area distinguished by high biological value, improved by physicochemical and organoleptical indices of quality, oxidizing stability.

In accordance with the data published in *Statistical Yearbook of the Republic of Moldova (2007)* it is wort to be mentioned that the part of the sunflower oil is related to 85% of the general discharged capacity of vegetable oils in the Republic of Moldova (STAS 1129 – 93).

It is known that the wine-making sector in the Republic of Moldova is processing 300-350 thousand tons of grapes per year. There of this quantity except the basic production acquires 60-75 thousand tons of secondary products, namely seeds. The content of the seeds in a ton of grapes represents almost 7% of the mass. That is why it is necessary to use technological procedures for the secondary wine-making processing with the aim to acquire a varied range of valuable products with specific proprieties: paratartaric acid, vitamin E, seed oils (Statistical Yearbook of the Republic of Moldova, 2007).

The grape seed oil has a biologically active composition that differs from the other extracts through an increased content of vitamin E and F as well as mineral substances: zinc, copper, selenium. The most important compounds are protianidines that are 50 times more powerful as antioxidant agents than vitamin E and 20 times more powerful than vitamin C (SM 95:1996; Skurihin and Volgareva, 1987)

The aim of this work consists in the receipt of a two-component mixture of vegetable oils sunflower and grape seeds oil and for the further study of the physicochemical changes indices of the quality of the received oil mixture of the storing process.

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2. Materials and methods

1.1. Research materials

As research materials have been three patterns of twice refined and deodorized vegetable oils: sunflower (STAS 1129-93) (Snedecor, and Cochran, 1989), grape seeds (Sherwin, 2007), as well as a two-component mixture of the given oils in an equal ratio 80:20 (v/v) correspondingly.

1.2. Laboratory equipment

The laboratory equipment used in this work: Carl Zeiss Jena IR-spectrophotometer, "SPECORD M-85": 4000…400 cm^{-1}, Hamburg, Germany, UV/VIS -spectrophotometer, "HACH LANGE DR-5000" 190…1100 nm, Düsseldorf, Germany; Laboratory Glass Burette.

1.3. Methods of research

The methods of analysis used are represented in Table 2.

Table 2. The used methods of analysis

No	The method of analysis	The determined physicochemical indices
1.	IR-spectroscopy	- The analysis of infrared spectra of the researched vegetable oils and their (Mironov and Iancovskii, 1985; Pretsch *et al.*, 2006)
2.	UV/VIS -spectroscopy	- The analysis UV/VIS- spectra of the researched models of oils (Mironov and Iancovskii, 1985; Pretsch *et al.*, 2006) -p-aniside value, c.u. (IUPAC, 1987)
3.	Titrimetric analysis	- Acid value, mg KOH/g oil (GOST 11254-81, 1987) - Peroxide value, meq/kg oil (GOST 26593-85, 1985)

1.4. Determinations of errors and statistical analysis of obtained results

Investigations carried out in triplicates and statistically processed statistically by the method of those small square with application of Student coefficient and interval determination of investigation (Skurihin and Volgareva, 1987).

3. Results and discussions

In accordance with the experimental data of the researcher Uritu D. the content of the oil in grape seeds depends on the area where the grapes grow and varies from 9,5 to 20,0% on the whole territory of Moldova (Figure 1) (Statistical Yearbook of the Republic of Moldova, 2007).

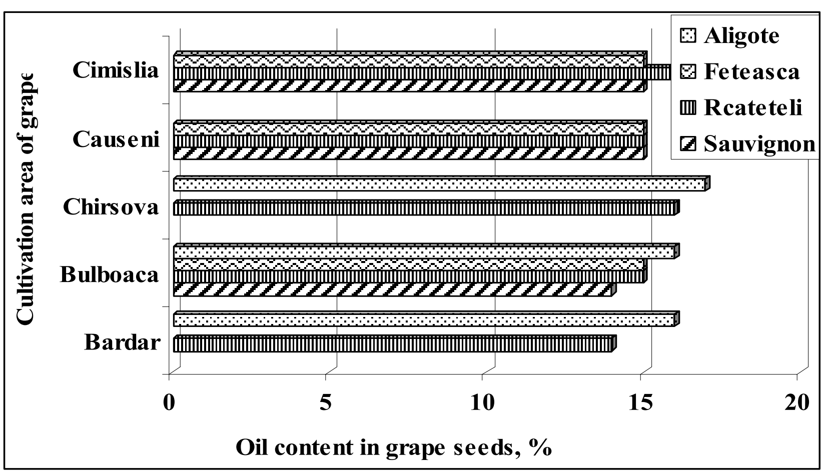

Figure 1. The content of the oil in the grape seeds related to the area of cultivation in the Republic of Moldova

It is known that the oil from the grape seeds represents a valuable product from the nutritional point of view, first of all due to the increased content of vitamin E (127-135 mg/100g oil) and the composition in fatty acids (Figure 2)

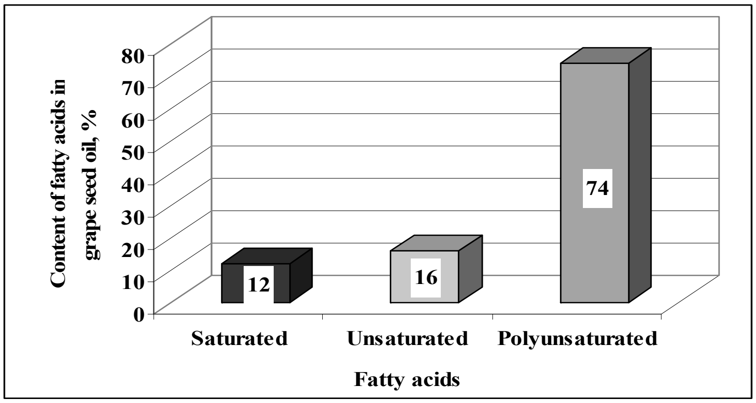

Figure 2. The content of the fatty acids in the grape seeds

The comparative chemical composition of the fatty acids from of the used sunflower oil and grape seeds oil respectively is indicated in Table 3.

Table 3. The chemical composition of the fatty acids in the composition of the triglycerides of sunflower and grape seeds oil (SM 95:1996; Skurihin and Volgareva, 1987; Statistical Yearbook of the Republic of Moldova, 2007)

Fatty Acids	**The content of the fatty acids,%**	
	Sunflower oil	**Grape seeds oil**
Acid stubble, $C_{14:0}$	0.1	0.6
Palmitic acid, $C_{16:0}$	7.4	5.9
Stearic acid, $C_{18:0}$	4.3	3.2
Oleic acid, $C_{18:1}$	19.4	14.4
Linoleic acid, $C_{18:2}$	**65.8**	**72.5**
Linolenic acid, $C_{18:3}$	**-**	**0.6**
Erucic acid, $C_{20:1}$	0.2	-
Other undeterminated (elements)	2.8	2.8

The analysis of these data proves that the grape seeds oil is higher in polyunsaturated fatty acids content (omega 6–linoleic acid) and contains, unlike the sunflower oil, higher amount of linolenic acid (omega 3).

In the given work the basic qualities of the compared patterns of the vegetable oils and their mixtures were experimentally determined. The obtained data are presented in the Table 4.

Table 4. The physicochemical indices of the quality of the tested oils patterns

Quality index	**Twice refined and deodorized oil**		
	Sunflower oil	**Grape seeds oil**	**Two-component mixture**
Acid value, mg KOH/g, oil	0.23 ± 0.04	0.17 ± 0.04	0.22 ± 0.04
Peroxid value, meq/kg, oil	8.56 ± 0.06	8.02 ± 0.04	8.18 ± 0.01
Aniside value, c.u.	0.69 ± 0.01	0.91 ± 0.01	0.73 ± 0.03

We further studied infrared spectra of the tested vegetable oil patterns and their mixtures (Figure 3)

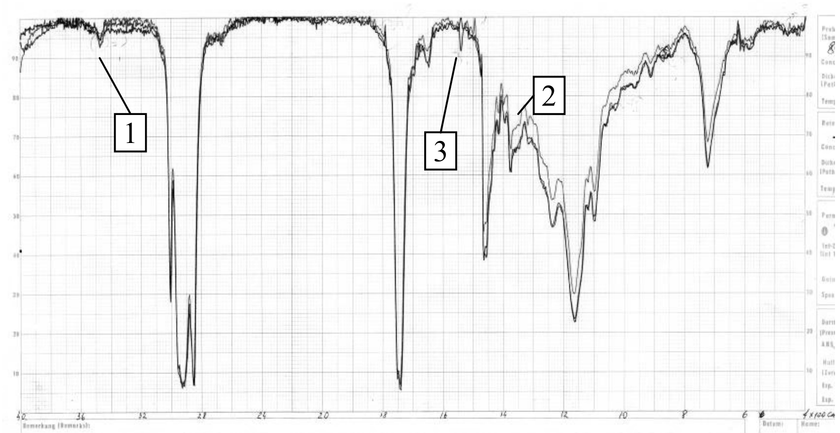

Figure 3. The spectra of the absorption in the case of sunflower oil (1), the grape seeds oil (2) and two-component mixture (3).

In the area of 1350-1500 cm^{-1} are registered the strips of the absorption (two) for the symmetrical and asymmetrical valence oscillation of the double links from the linoleic acid (9,12-octa-decadienoic). For the case of the grape seeds oil it is observed a relatively more reduced intensity in comparison with the sunflower oil (1500 cm^{-1}). At the same time the same time a weak absorption strip is observed at 1540-1550 cm^{-1}, characteristic for the presence of three double links in linolenic acid (9,12,15 –octa-deca-trienoic). This reduced intensity absorption strip is observed also in the mixture of the oils (80:20, v/v), fact that proves the biological added value of the oil mixture.

In this work, UV- oil spectra- for sunflower and grape seeds oils have been used (Figure 4)

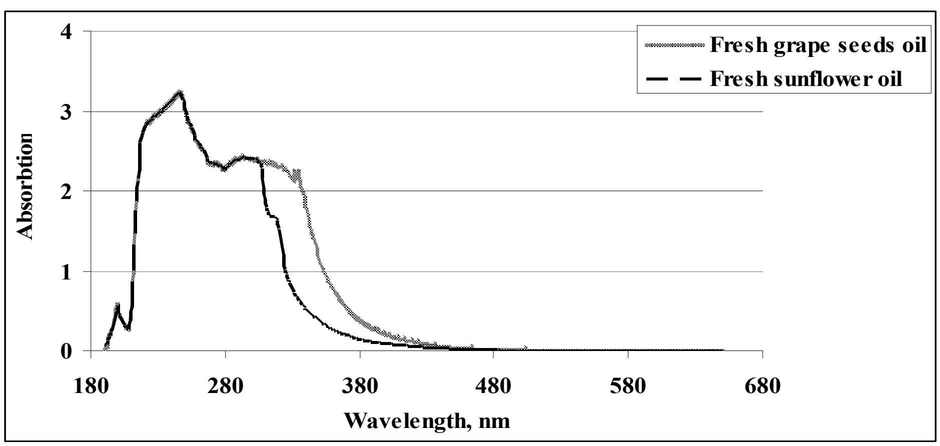

Figure 4. UV-spectra of the compared vegetable oil patterns: sunflower and grape seeds oils

It is known that in the process of the vegetable oils storing oxidizing and hydrolytic disintegration can appear. The presence and the level of the oxidation process and the oil hydrolysis are characterized by the content of the fatty acids, the level of the acid value (Akoh and, Min, 2008). The experimental data on the acid value change of compared vegetable oil patterns and their mixture during two months of storage are presented in Figure 5.

The importance of the acid value in fresh vegetable oils varies between 0.17 to 0.23 mg KOH/g of oil. The presence of the free fat acids in fresh patterns that are not exposed to the process of storage can be explained by the fact that free fat acids are a normal intermediate product for the exchange of fat material as well as for the possible hydrolytic transformations of the vegetable oils in the process of their apportionment (Neceaevet al., 2001).

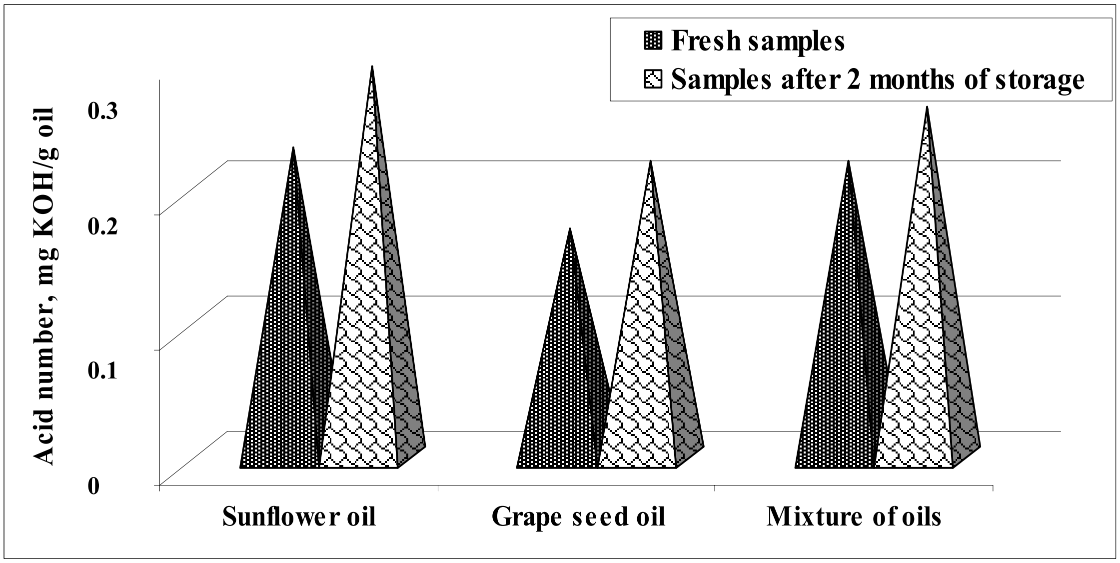

Figure 5. The evolution of the acid values of the compared vegetable oil patterns and their mixtures during two months of storage

It is known that the availability and the quantity of the peroxide and hydroperoxide in the vegetable oils conditions depends on the degree of the oils stability while storing (Uritu, 2007).

The Figure 6 represents the data about the changes of the peroacid value of the compared patterns of the vegetable oils and their mixtures depending on the period of storage.

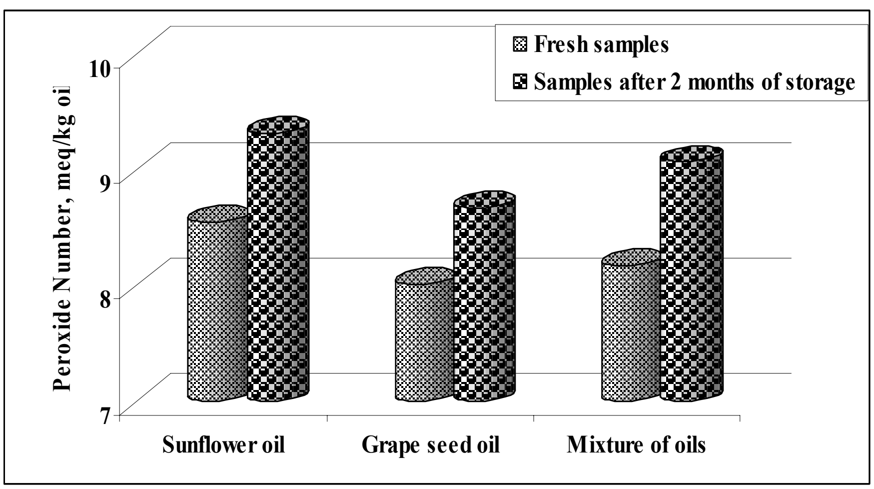

Figure 6. The change of the peroxide value of the compared vegetable oil patterns and their mixtures during two months of storage

The peroxide value of the vegetable oil patterns does not change too much after two months of storage and varies for the sunflower oil from 8.56 to 9.3 meq/kg oil, for the grape seeds oil from 8.02 to 8.68 meq/kg oil and for the two-component mixture from 8,18 to 9.08 meq/kg oil. Insignificant changes of the peroxide value for all the tested vegetable oil patterns can be explained by the short time of the storage period of the oil namely two months.

It is well-known that peroxide links are unstable to oxidation and in the process of storage they lead to the formation of the second oxidation products on the vegetal oils such as: aldehyde, ketons and their derivatives with different length of carbon chain (Frankel, 2005).

If peroxide does not influence the change of the organoleptic indices of the quality of the vegetable oils then the aldehyde and ketons, formed during the further stages of oxidation, will represent promoters of the unpleasant taste and smell of the oxidized vegetal oils (Keszler et al., 2000).

The other aims of the work was to accumulate secondary products of the oxidation of the tested vegetal oil patterns and their mixtures and to determine the p-aniside value during the storage period. The obtained experimental data are presented in Figure 7.

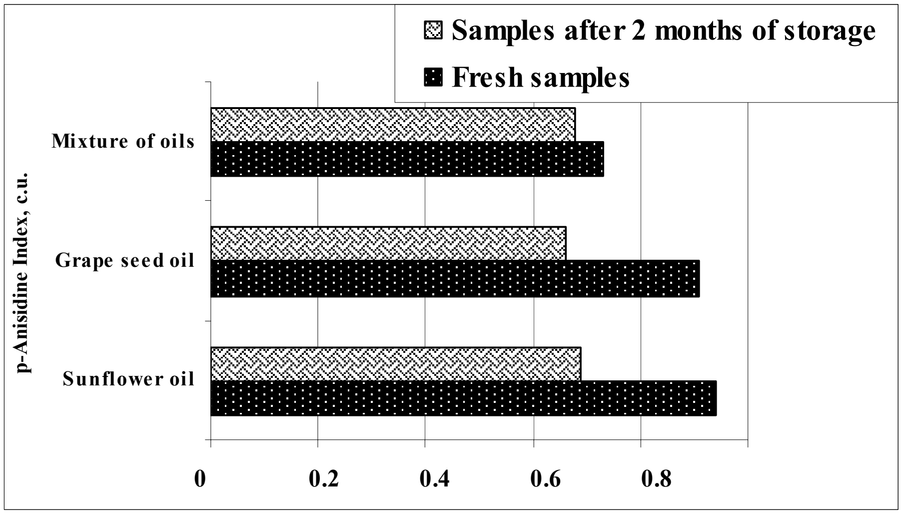

Figure 7. The evolution of the p-aniside value of the compared vegetable oil patterns and their mixtures during two months of storage

As we can observe in Figure 7, the formation of the two-component vegetable oil mixture renders effective influence on the processes of stabilization of the tested oils. So the level of the p-aniside value for the sunflower oil after two months of storage was 0.94 c.u. and for two-component mixture the given size varied from 0.66 to 0.91 c.u.

The positive difference in the level of p-aniside value is explained, probably, by the stable action of the antioxidizing properties of the two-component mixture of the tested oils in the processes of the formation of secondary products of the oxidation.

The study of UV- spectra showed that the tested oils have not been exposed to important changes after two weeks of storage (Figure 8).

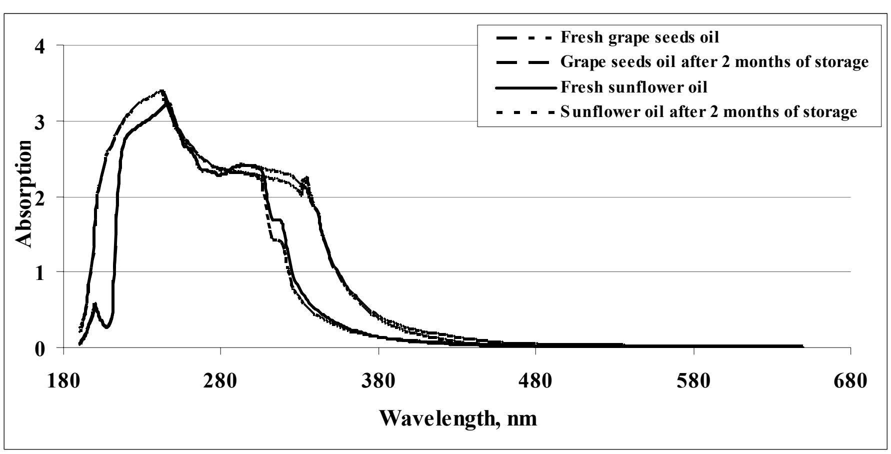

Figure 8. UV-spectra of the researched sunflower oil patterns and grape seeds

4. Conclusions

1. The comparative analysis of the fatty acids content of the triglyceride for the tested vegetal oils showed that the grape seeds oil differs through a higher content of polyunsatured fatty acids (6-linoleic acid), also in comparison with sunflower oil it contains a considerable quantity of linolenic acid (3) that allows us to speak about a high biological value of the two-component vegetal oil mixture.

2. It is demonstrated that the essential physicochemical indices of quality of the tested oil patterns-sunflower oil, grape seeds oil and two-component mixtures- are in limits of the provided technical documentation for the corresponding products.

3. The comparative analysis of IR-spectra of vegetal oils, showed that grape seeds oil and two-component mixture in comparison with sunflower oil differ in the content of linoleic acid and this is proved by the characteristic peak of 1540-1550 cm-1. This result allows us to speak about a high biological value of the two-component vegetable oil mixture.

4. On the basis of the acid, peroxide and p-aniside values evolution, it can be stated that two-component mixture of the tested vegetal oils differ providing a relatively high stability or a lower rate of accumulation of primary and secondary products of oxidation in the process of storage.

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