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Comparative characteristics of sunflower oil with supplement of traditional Bulgarian herbs

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Sunflower oil produced by Pearl Ltd Veliko Tarnovo, with addition of Bulgarian herbs (oregano, thyme and pine cones) has been studied. The starting sunflower oil is a linoleic type containing predominantly linoleic acid ($C_{18:2}$ = 521 g.kg^{-1}), followed by oleic ($C_{18:1}$ = 344 g.kg^{-1}) and palmitic ($C_{16:0}$ = 115 g.kg^{-1}) acid. Upon the examination of fatty acid composition of sunflower oil with various herbs supplements an increase of the oleic acid from 344 g.kg^{-1} in the control to 422 ÷ 441 g.kg^{-1} in the extracts has been found. Oleic / linoleic acid ratio varies between 0.95 and 1.10 in the extracts, whereas in pure sunflower oil it is about 0.66. This ratio indicates a better balanced composition in terms of the nutritional value of the tested samples. Adding herbs to the oil reduces the content of tocopherols (from 721 mg.kg^{-1} to 388-459 mg.kg^{-1}), which has an impact on its oxidative stability. Adding pine cones to sunflower oil reduces its oxidative stability about 3 times (from 10.8 h to 3.5 h), while the addition of oregano and thyme to the oil leads to minor change in oxidative stability (from 10.8 h to 7.6h). Therefore, sunflower oil with addition of herbs is inappropriate for heat treatment, but can be used for sauces, dressings, mayonnaise, and creams with exception of the sample with addition of the pine cones. Color parameters of oils in SIELab colorimetric system have been studied. It was found that the addition of oregano and thyme does not influence significantly the brightness of the samples and leads to an increase in their green components, which is associated with an increase in chlorophyll content from 0.003 ppm for pure sunflower oil to 0.094 ppm - 0.117 ppm for samples with oregano and thyme. The addition of both recent herbs result in double increase the content of β- carotene, respectively from 2.76 ppm for the control to 4.92÷ 5.77 ppm for the oil samples with oregano and thyme.

Keywords: thyme, oregano, pine cones, fatty acid composition, tocopherols, oxidative stability, color

List of abbreviation:
TLC-Thin-layer chromatography;
FAME –Fatty acid methyl esters;
GC-Gas chromatography;
HPLC- High performance liquid chromatography;
FA - Fatty acids;
IP-Induction period;
1 – Oil extract of oregano; 2 - Oil extract of pine cones; 3 - Oil extract of thyme ; 4 -Sunflower oil

INTRODUCTION

Sunflower oil is lipid product typical for Bulgaria with large application in cookery and food industry. Its consumer qualities depend mainly on its fatty acid composition, the content of tocopherols (vitamin E), and of the possibilities to be stable during long term storage and thermal treatment. The main component of triacylglycerol fraction in conventional sunflower varieties is linoleic acid - 500 – 800 g.kg^{-1}, which belongs to the essential fatty acids that are vital for the human body. Due to its unsaturated nature, it is easily amenable to oxidation processes under the influence of light and oxygen from the air, a result of which the sunflower oil relatively quickly loses its consumer properties. Numerous attempts to increase its oxidative stability by the addition thereto of various natural and synthetic antioxidants have been made.

Bulgaria is reach in great variety of herbs that contain a high percentage of biologically active substances. They are rich in various compounds: alkaloids, glycosides, saponins, polysaccharides, tannins, flavonoids, lignans, coumarins, essential oils, vitamins, trace elements etc. In this regard, it is interesting to carried out investigations on the composition and stability of sunflower oil when adding thereto of various kinds of herbs Bulgar.

The main objective of presented study is the examination of fatty acid and tocopherol

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composition, oxidative stability and color parameters of oil extracts from Bulgarian herbs (oregano, thyme and pine cones) with a view to their application in salads, sauces and other food products.

EXPERIMENTAL

Sunflower oil, production of Pearl Ltd Veliko Tarnovo, is used for conducting surveys. The oil extracts were prepared in a ratio of 1:5 (herb / sunflower oil), and were kept under refrigerated conditions (0°C-4°C) for 6 months.

Analysis of fatty acids. The fatty acid composition of oils was determined by gas chromatography (GC) after transmethylation of the respective sample with 20 $g.kg^{-1}$ H_2SO_4 in absolute CH_3OH at 50°C[1]. FAME were purified by TLC on 20x20 cm plates covered with 0.2 mm silica gel 60 G (Merck, Darmstadt, Germany) layer with mobile phase n-hexane:diethyl ether (97:3, v/v). GC was performed on a HP 5890 series II (Hewlett Packard GesmbH, Vienna, Austria) gas chromatograph equipped with a 60 m x 0.25 mm x 25 μm capillary DB - 23 column (Agilent J&W advanced, Agilent Technology, USA) and a flame ionization detector. The column temperature was programmed from 130 °C (1 min), at 6.5 °C/min to 170°C, at 3.0 °C/min to 215°C (9 min), at 40°C/min to 230°C (1 min); injector and detector temperatures were kept at 270 °C and 280 °C. Hydrogen was the carrier gas at a flow rate 0.8 mL/min; split was 1:50. Identification of fatty acids was performed by comparison of retention times with those of a standard mixture of fatty acids subjected to GC under identical experimental conditions[2].

Analysis of tocopherols. Tocopherols were determined directly in the oil by HPLC on a "Merck-Hitachi" (Merck, Darmstadt, Germany) instrument equipped with 250 mm x 4 mm Nucleosil Si 50-5 column (Merck, Darmstadt, Germany) and fluorescent detector "Merck-Hitachi" F 1000. The operating conditions were as follows: mobile phase of n-hexane: dioxan 96:4 (by volume), flow rate 1.0 ml/min, excitation 295 nm, and emission 330 nm[3] 20 μL 10 $g.kg^{-1}$ solution of oil in hexane were injected. Tocopherols were identified by comparing the retention times with those of authentic individual tocopherols. The tocopherol content was calculated on the basis of tocopherol peak areas in the sample versus tocopherol peak area of standard α-tocopherol solution.

Oxidative stability. Oxidative stability of oils was determined by measuring of IP, using conductometric detection of volatile acids. Rancimat apparatus Methrom 679 (Methrom, Herisau, Switzerland) was used at 100°C and an air flow rate 20 l/h[4].

***Color parameters*:** SIELab coordinates have been measured directly with spectrophotometer (Trintometer Lovibond PFX 195, UK). In mentioned colorimetric system L* is the brightness and it takes values from 0 (black) to 100 (white), a* is red-green axis, and b* is yellow-green axis[5]. The content of β-carotene and chlorophyll is defined using special software.

RESULTS AND DISCUSSION

Fatty acid composition of the studied oil extracts is listed in Table 1. Fatty acid composition is one of the main indicators characterizing the nutritional value of the oils and their oxidative stability during storage and heat treatment. The used sunflower oil has predominantly linoleic acid content (521$g.kg^{-1}$), followed by oleic (344$g.kg^{-1}$) and palmitic (115$g.kg^{-1}$), which associates it with the oils of linoleic acid in the range of, where the linoleic acid[6] quantity varies in range 480-740$g.kg^{-1}$, and the oleic one – 140-390$g.kg^{-1}$. It does not differ significantly from previously studied linoleic type oils in Bulgaria, and its composition is closest to that already obtained from Bulgarian sunflower variety "Musala"[6]. The ratio oleic/linoleic acid for oil extracts varies between 0.95 and 1.10, while for control sample it is around 0.66. Last ratio evidences better balance of fatty acid content, which is determining for the nutritive value of the tested samples. Comparatively high content of linoleic acid indicates good nutritive value of oil extracts, because this acid belongs to human body essential fatty acids. The content of oleic acid in oil extracts is higher with 80 – 100$g.kg^{-1}$ compared to the control.

Data about total tocopherol content and composition of oils are presented in Table 2.

Control sample has the highest content of tocopherols (721 $mg.kg^{-1}$), while in the oil extracts its content decreases (388 - 459 $mg.kg^{-1}$**)**. In the oil extracts mainly saturated derivates α- and β - tocopherols are identified. Basic representative of tocopherols in these oil extracts is α- tocopherol (945 – 961$g.kg^{-1}$).

The results from the investigation of oxidative stability of oil extracts are presented on Figure 1.

Table 1. Fatty acid composition of oil extracts with Bulgarian herbs

FA, g.kg^{-1}		1	2	3	4
C 12:0	lauric	3	4	3	2
C 14:0	myristic	3	2	2	2
C 16:0	palmitic	138	118	132	115
C 16:1	palmitoleic	2	1	2	2
C 17:0	margaric	1	1	1	1
C 18:0	stearic	6	6	8	10
C 18:1	oleic	441	422	435	344
C 18:2	linoleic	402	442	410	521
C 20:0	arachidic	2	2	3	1
C 20:1	gadoleic	1	1	3	1
C 22:0	behenic	1	1	1	1
saturated FA		**154**	**134**	**150**	**132**
unsaturated FA		**846**	**866**	**850**	**868**
monounsaturated FA		**444**	**424**	**440**	**347**
polyunsaturated FA		**402**	**442**	**410**	**521**

Table 2. Total tocopherol content and composition oil extracts with Bulgarian herbs

Tocopherols	*1*	*2*	*3*	*4*
α - tocopherol, g.kg^{-1}	946	961	961	945
β - tocopherol, g.kg^{-1}	54	39	39	55
Total tocopherol content, mg.kg^{-1}	458	388	459	721

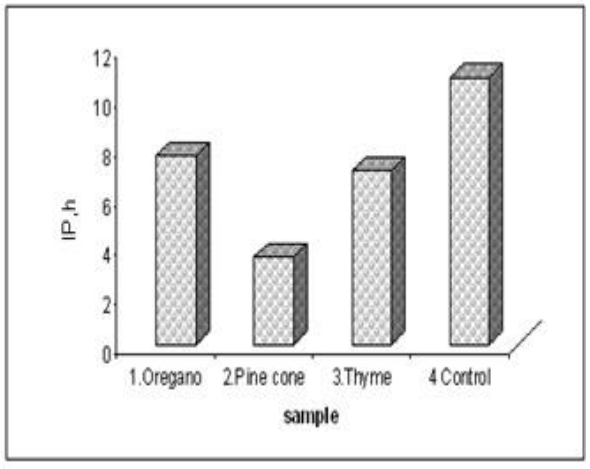

Fig 1. Oxidative stability of oil extracts

Oil extracts of oregano and thyme have lower oxidative stability (with about 3 hours) compared to the control, while the stability of the extract of pine cones is about three times lower than this of the control sample. Therefore, the last extract is not suitable for flavoring sunflower oil, as it leads to rapid oxidation and the oil is unsuitable for use in salads, sauces and more culinary products. Sunflower oil with added oregano and thyme is unsuitable for heat treatment, but due to its well-balanced nutritional value is useful for consumption in salads and sauces. The oil with oregano and thyme oxidative stability is comparable with that of cold-pressed walnut oil, which is used as a delicacy oil dressings for salads, sauces and meals[7].

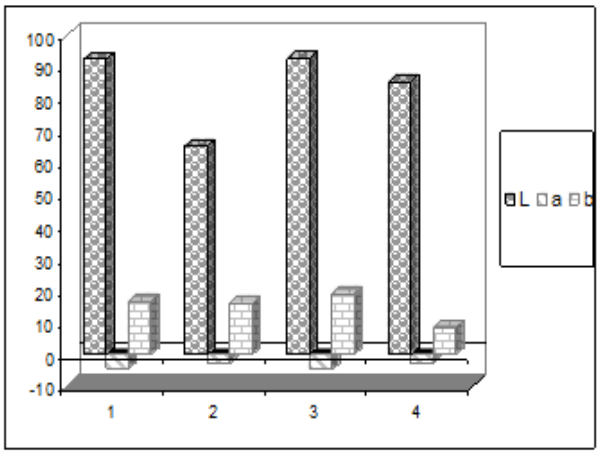

Fig. 2. Basic color coordinates of oil extracts from Bulgarian herbs in SIELab colorimetric system

The data for color parameters in SIELab colorimetric system allows calculating the color difference (ΔE) with respect the basic sample (sunflower oil). The biggest color difference is obtained for the extract of pine cones (ΔE = 21.6), while the color differences for those of oregano and thyme with control samples are compatible, being

respectively 10.9 and 13.0. The brightness of the extract of pine cone (65.14) has highest difference with the one of control sample (85.30). For the rest of the samples the change is not significant. Basic color coordinates are presented on Figure 2.

Oil extracts with oregano and thyme have high content of β-carotene and chlorophyll. The extract of pine cone also demonstrates essential rise of these parameters, but it worsens the gustatory qualities of the sunflower oil and nevertheless it enriches the oil, it makes the oil inapplicable for using in salads, sauces and other food products. The result is shown on Figure 3.

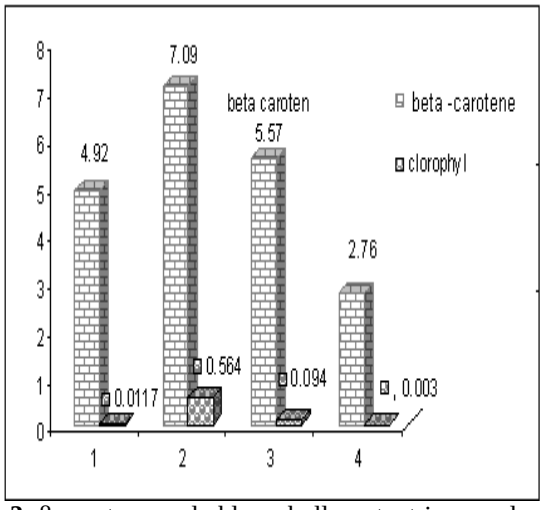

Fig. 3. β-carotene and chlorophyll content in samples of sunflower oil with addition of herbs.

CONCLUSION

Comparatively high content of linoleic acid and tocopherols in studied oil extracts shows their balanced nutritional value. Bulgarian herbs (oregano, thyme and pine corns) added to sunflower oil have prooxidative effect and the obtained oil extracts are inconvenient for thermal treatment. Due to the higher ratio oleic/linoleic acid the oil extracts of oregano and thyme can be used as delicacy dressings for salads, sauces and meals. Oil extracts of oregano and thyme have unchanged brightness and increased contents of chlorophyll and β - carotene, while the extract of pine corn has decreased brightness and increased color difference to the control.

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СРАВНИТЕЛНИ ХАРАКТЕРИСТИКИ НА СЛЪНЧОГЛЕДОВО ОЛИО С ДОБАВКА НА БЪЛГАРСКИ БИЛКИ

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(Резюме)

Слънчогледово олио с добавка на Български билки (риган, мащерка и шишарка),произведено от Pearl Ltd Veliko Tarnovo е изследвано. Посоченото олио е линоленов тип с доминиращо съдържание линоленова киселина ($C_{18:\ 2}$ = 521 $g.kg^{-1}$), следвана от олеинова ($C_{18:\ 1}$ = 344 $g.kg^{-1}$) и палмитинова ($C_{18:\ 2}$ = 521 $g.kg^{-1}$), киселини.Отношението на олеинова към линоленова варира между 0.95 и 1.10 в екстрактите, докато в чистото слънчогледово олио е около 0.66. Това отношение показва добре балансиран състав откъм хранителна стойност в тестваните образци. Добавянето на билки в слънчогледовото олио намалява съдържанието на токофероли (от 721 $mg.kg^{-1}$ до 388-459 $mg.kg^{-1}$), което влияе върху оксидантната стабилност. Добавянето на шишарка в слънчогледовото олио намалява оксидантната стабилност 3 пъти (от 10.8 часа до 3.5 часа), докато добавянето на риган и мащерка водят до минимална промяна в оксидантната стабилност (от 10.8 до 7.6 часа). Следователно слънчогледовото олио с добавка на билки е неподходящо за термична обработка, но може да бъде използвано за сосове, дресинги, майонези и други, с изключение на образеца с добавянето на шишарка.

Изучени са цветовите характеристики на олиото в SIELab колориметрична система. Добавянето на риган и мащерка не влияят на светлостта на образците и водят до нарастване на тяхната зелена компонента, което се свързва с нарастването на хлорофилното съдържание от 0.003 ppm за чисто слънчогледово олио до 0.094 ppm-0.117 ppm за образци с риган и мащерка. Добавката на посочените две билки води до двойно нарастване на β- carotene от 2.76 ppm до 4.92-5.77 ppm за образците с риган и мащерка.