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Optical properties of oil extracts of Bulgarian herbs

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We have studied oil extracts form oregano, thyme and pine cone in sunflower oil in 1:5 ratio (herb extract/sunflower oil). The fluorescence spectra have been obtained by using Light emitting diods (LEDs) working at wavelengths of $\lambda = 370$ nm, $\lambda = 395$ nm, $\lambda = 425$ nm and $\lambda = 450$ nm have been obtained. The oxidation processes have been studied using UV spectroscopy. The content of chlorophyll and β-carotene has been studied with the objective of finding correlation between them and the intensity of the fluorescence peak. It has been shown that the most informative spectra are those obtained for excitation at $\lambda = 425$ nm. They contain three fluorescence maxima related to the oxidation processes ($\lambda = 500$ nm) and chlorophyll ($\lambda = 675$ nm). Linear dependencies between the full content of tocopherols (Y) and absorption at 270 nm (A_{270}) and 232 nm (A_{232}) have been obtained $Y = -717.15A_{232} + 1830$, $R^2 = 0.924$, $Y = -1599A_{270} + 1549$, $R^2 = 0.947$.

Key words: UV-spectroscopy, fluorescence, sunflower oil with herbs, oxidation product, tocopherols

INTRODUCTION

Sunflower oil is a 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. Bulgaria is rich in a 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 fluorescence spectra and content of oxidation product of sunflower oil when adding thereto of various kinds of Bulgarian herbs.

The objective of the present work is to establish the relations between the physical and chemical parameters of oil extracts of sunflower oils enriched with Bulgarian herbs in analogy with commercially available the salad olive oils.

MATERIALS AND METHODS

Sunflower oil, production of Pearl Ltd, Veliko Tarnovo, is used for conducting the surveys. The oil extracts were prepared from authors in a ratio of 1:5 (herb / sunflower oil) 40 grams from oregano, thyme and pine cone were added in 200 ml sunflower oil and were kept under refrigerated conditions (0°C-4°C) for 6 months. After that extracts were filtered and their optical properties were investigated.

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 [1] 20 mL 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 a-tocopherol solution.

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 [2]. The chlorophyll and β-carotene are calculated using the transmission spectra in the visible region and values for color parameters by software program developed specially for Lovibond PFX 880 from the producer.

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The sources used to measure the fluorescence spectra are 370 nm, 395 nm, 425 nm LEDs. A fiber optic spectrometer (AvaSpec-2038, Avantes) with sensitivity in the (200-1100) nm range and a resolution of about 8 nm was used to measure the fluorescence spectra. The oil samples were placed in a cuvette 10 mm x 10 mm and irradiated by laser diodes (LDs) or light emitting diodes (LEDs).

RESULTS AND DISCUSSION

The fluorescence spectra were measured at 370 nm, 395 nm, 425 nm. It is evident that the good ratio between excitation and emission intensity there is for wavelength 425 nm and 450 nm. The results are present on the Fig. 1.

Two fluorescence peaks are clearly discernible.

i The first (500-525 nm), is related to oxidation products. Similar fluorescence maxima are observed for extra virgin olive oil between 500 nm and 520 nm [3].

ii The second (680-690 nm) is related to chlorophyll content in the studied oil samples. Similar fluorescence maxima have been observed for other vegetable oils such as rape seed, soy bean etc. [4].

The optical properties of sunflower oil extracts of traditional Bulgarian herbs were investigated similarly to herbs extracts from olive oil because sunflower salad oil is the most widely used in Bulgaria. The addition of herbs leads to a considerable increase of the chlorophyll content of the extract. In Fig. 1 the intensity of the second fluorescence peak related to chlorophyll increases.

Quantitative relations between the intensities of the indicated fluorescence peaks and parameters have been established. A specialized software to the Lovibond PFX 195 (UK) titrometer was used to determine the content of β-carotene by the color parameter data from the samples. The data is presented in Table 1.

The addition of herbs leads to a substantial increase of the content of β-carotene and pigments. The higher content of β-carotene correlates with the absorption in the UV range at 232 nm and 270 nm. Using the latter two parameters the degree of oxidation of the samples was estimated by determining the primary products of the oxidation (peroxides) by the UV absorption spectroscopy of the conjugated dien structures. The addition of herbs leads to a comparatively fast oxidation of the oil extracts which shows that they can be used n salads, dressings and sauces, but are not suitable for heat treatment. Dependencies between the chlorophyll content and that of β-carotene using the intensities of the fluorescence peaks were tested. With the increase of the absorption a 232 nm, the intensity of the fluorescence peak around 500 nm decreases. A linear dependence of the type $I_{676} = 76349.clorolophhyl + 9738.1$ between the chlorophyll and the second fluorescence peak with a high correlation R^2=0.96 is established.

Linear dependencies between the full content of tocopherols (Y), absorption at 270 nm (A_{270}) and absorption at 232 nm (A_{232}) and the have been obtained $Y = -717.15A_{232} + 1830$, $R^2 = 0.924$, $Y = -1599A_{270} + 1549$, $R^2 = 0.947$.

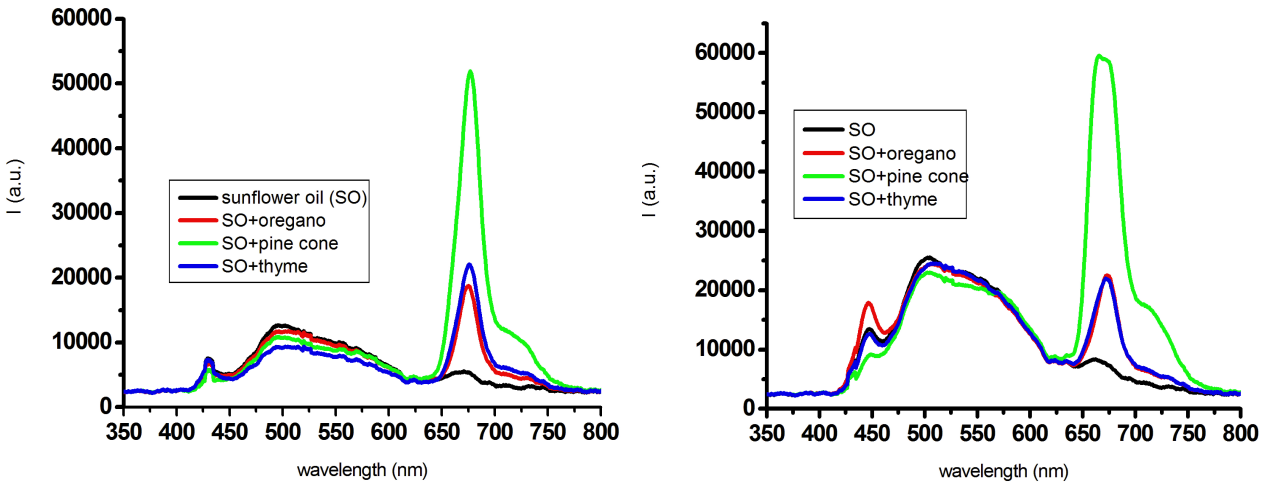

Fig. 1. Fluorescence spectra for sunflower oil extracts with herbs.

Table 1. Data for the absorption in the UV range, chlorophyll, β-carotene and total contetne of tocopherols in oil herb extracts

Type of oil extract	Clorophyll, ppm	β-carotene, ppm	Absorption at 232 nm (A_{232})	Absorption at 270 nm (A_{270})	Total content of tocopherols, mg/kg
Sunflower oil	0.003	2.76	1.554	0.523	721
Oil extract of thyme	0.094	5.57	1.983	0.709	459
Oil extract of oregano	0.117	4.92	1.898	0.661	458
Oil extract of pine cones	0.564	7.09	1.946	0.715	388

CONCLUSIONS

1. The addition of herbs to sunflower enriches it in pigments and vitamins.
2. The oily herbal extracts have a smaller oxidation stability and a lower general solution of tocopherols, which makes them inappropriate for thermal treatment.
3. There is a relation between the chemical parameters and the optical properties – the chlorophyll content and the fluorescence as well as UV absorption, and the general tocopherol content.
4. The combination of optical with chemical methods provides an accurate idea of the properties of modified food products.

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ОПТИЧНИ СВОЙСВА НА МАСЛЕНИ ЕКСТРАКТИ ОТ БЪЛГАРСКИ БИЛКИ

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(Резюме)

Изследвани са маслени екстракти от риган, мащерка и борова шишарка в слънчогледово олио в съотношение 1:5 (билка/слънчогледово олио). Получени са спектрите на флуоресценция при дължини на вълните съответно $\lambda = 370$ nm, $\lambda = 395$ nm, $\lambda = 425$ nm и $\lambda = 450$ nm. Проследени са окислителните процеси чрез ултравиолетова спектроскопия. Изследвано е съдържанието на хлорофил и β-каротен с цел откриване на корелация между тях и интензитета на пика на излъчване при флуоресцентните спектри. Показано е, че най-информативни са спектрите при $\lambda = 425$ nm. Те съдържат три флуоресцентни максимума, свързани с окислителните продукти около $\lambda = 500$ nm, с хлорофила около $\lambda = 675$ nm и с β-каротена около $\lambda = 429$ nm. Установени са линейни регресионни зависимости между пълното съдържание на токоферолите и адсорбцията при 270 nm и 232 nm от типа

$$Y = -717,15A_{232} + 1830, \qquad R^2 = 0,924; \qquad Y = -1599A_{270} + 1549, \qquad R^2 = 0,947.$$

където Y е пълното съдържание на токоферолите, а A_{232} и A_{270} са адсорбциите при 232 nm и 270 nm.