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Evaluation of oxidative stability of emulsifiers of acylglicerol origin †

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Abstract: Obtaining new harmless to human health and the environment emulsifiers of acylglycerol origin based on sunflower oil with unsaturated fatty acids is relevant. The authors of this study obtained such emulsifiers under mild conditions (35–40°C) by the transesterification reaction of triacylglycerols of sunflower oil. Changes in the UV spectra of 0.02% solutions in isooctane were studied in the range from 200 to 285 nm depending on the storage duration and storage temperature of emulsifiers and oils. The results showed that in the process of storage new emulsifiers showed higher resistance to oxidation compared to oil.

Keywords: emulsifiers of acylglycerol origin; sunflower oil; ultraviolet (UV) spectroscopy; oxidative stability

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1. Introduction

Every day there is a growing demand for high-quality healthy food products manufactured applying the latest technologies using absolutely safe additives based on natural local raw materials [1]. Such additives are the additives of acylglycerol origin E471 – mono- and diacylglycerols (MAG and DAG) of fatty acids. They are safe, have the status of GRAS (Generally Regarded As Safe) and are used without restrictions. MAG and DAG are surfactants with a hydrophilic-lipophilic balance index of 3–4 [2], p. 79–80, and are widely used as lipophilic nonionic emulsifiers, emulsion stabilizers, leavening agents, and structurants. Their significant advantages are noted in the literature; that is related to their ability to improve the consistency and appearance of finished products, to increase their yield after heat treatment [1].

E471 emulsifiers are represented by a wide range of products on the modern market of ingredients. However, their composition and properties have significant drawbacks due to the harsh conditions of synthesis [2], p. 390. There are two chemical processes in the basis of technologies for obtaining acylglycerol emulsifiers: glycerolysis of fats (transesterification with glycerol) and esterification of glycerol with high molecular weight fatty acids. In industry, processes are carried out at temperatures of 220–260°C. Such harsh conditions lead to the intensification of thermal oxidation and thermopolymerization processes in emulsifiers [2], p. 441. New technologies for obtaining emulsifiers also have similar disadvantages and require the technological process to be carried out at temperatures not lower than 120°C [3].

As a rule, E471 emulsifiers are made by glycerololysis of palm oil and do not contain polyunsaturated fatty acids [3]. In our previous works [4] the technology of food emulsifiers of acylglycerol origin (EAGO) based on refined sunflower oil was substantiated. EAGO were

obtained under mild conditions (35–40°C), which ensured the preservation of essential biologically active components in them (in particular, 59.7% w-6 polyunsaturated linoleic acid).

The study of a new emulsifier must necessarily include experiments to determine its stability during storage which depends on the interaction activity of its acylglycerol components with oxygen [2]. The study of the oxidative stability of EAGO is an urgent task. The purpose of this work is to analyze the results of spectroscopic studies on the oxidative stability of acylglycerol emulsifiers obtained from sunflower oil under mild conditions, and to study their ability to stabilize the oxidative destruction of lipids.

2. Materials and Methods

2.1. Materials

The current study deals with emulsifiers of acylglycerine origin (EAGO) obtained with using the laboratory equipment under the mild conditions according to the authors' developed technology of transesterification of the refined sunflower oil [4].

A refined deodorized sunflower oil "Oleyna Traditional" (SE Suntrade, Dnipro, Ukraine) was a main raw material for the production of emulsifiers of acylglycerol origin (EAGO). This oil is a vegetable oil of the linoleic-oleic group.

2.2. Study of ultraviolet absorption spectra

Qualitative determination of polyunsaturated fatty acids, products of positional isomerism in a refined sunflower oil and EAGO was carried out by spectrophotometry in the ultraviolet (UV) region of the spectrum on a SF-46 spectrophotometer. Optical density data for samples of 0.02% solutions of EAGO in isooctane and 0.02% solutions of refined deodorized sunflower oil in isooctane was obtained in the spectrum from 200 nm to 290 nm. The spectra were measured for freshly prepared samples, as well as for samples stored at temperatures of 20±1°C, 50±1°C, 100±1°C for up to 100 days.

Data on the change and accumulation of conjugated diene and triene structures which are formed by positional isomerism and accompany the oxidation of EAGO and sunflower oil were analyzed in the spectrum region at wavelengths of 232 nm and 268 nm, respectively [5].

2.3. Determination of the specific absorption coefficient

Based on the optical density data of EAGO and sunflower oil samples, the value of specific absorption $E_{1cm}^{1\%}$ at 232 nm was determined using the formula:

$$E_{1cm}^{1\%}(232 \text{ нм}) = A_{232} / W, \quad (1)$$

where – A_{232} is the optical density of the investigated solution at 232 nm; W – is the mass fraction of the investigated solution.

2.4. Study of the primary products of the oxidation of lipids

Accumulation of oxidation products in EAGO and sunflower oil samples was evaluated by peroxide value [6]. The peroxide value (PV) in mmol 1/2 O/kg was calculated as a number of millimoles of active oxygen (1/2 O) which is equivalent to I_2 released from potassium iodide in glacial acetic acid by peroxides and hydroperoxides found in 1 kg of fat.

The data was obtained for the freshly prepared samples, as well as for the samples stored at temperatures of 20±1°C, 50±1°C for up to 100 days.

2.5. Statistical Analysis

For an objective judgment about the degree of confidence of the data obtained the mathematical treatment of the obtained results was made. The reliability of the results obtained was determined with the help of Student's coefficients for the taken significance level of $p < 0.05$ and corresponding (n-1) degrees of freedom.

3. Results and Discussions

3.1. Study of ultraviolet absorption spectra of EAGO and sunflower oil samples

To assess the oxidative stability of EAGO the kinetics of accumulation of products accompanying oxidation in EAGO was studied. For comparison, the oxidative stability of sunflower oil, from which emulsifiers were obtained, was also studied. Changes in the ultraviolet absorption spectra (UV spectra) of EAGO and sunflower oil depending on their storage duration (up to 100 days) and storage temperature (20±1°C, 50±1°C, 100±1°C) were studied.

In the Figures 1, 2 there are UV-spectra of 0,02% EAGO solution in isooctane and 0,02% solution of sunflower oil in isooctane, correspondingly.

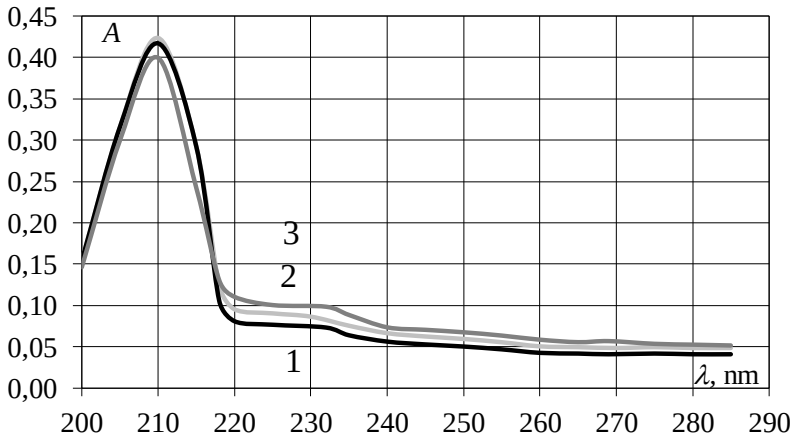

Figure 1. UV spectra of 0.02% isooctane solutions of EAHP samples, which were stored at a temperature of 20±1°C for: 1 – 0; 2 – 60 days; 3 – 100 days

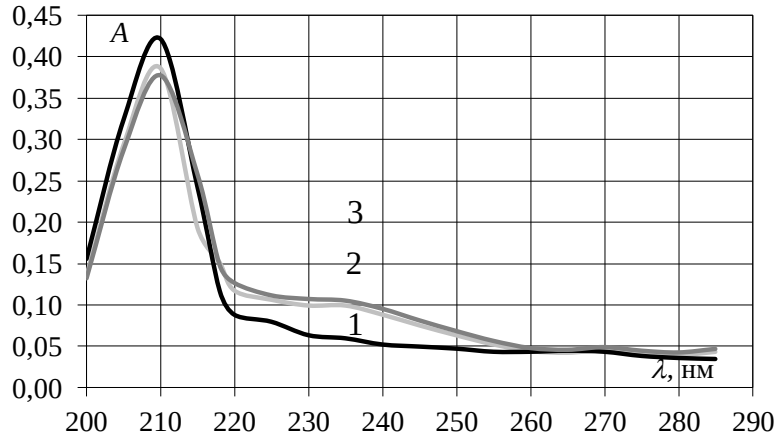

Figure. 2. UV spectra 0,02% isooctane solutions of sunflower oil samples, which were stored at a temperature of 20±1°C during: 1 – 0; 2 – 60 days; 3 – 100 days

In the absorption spectra of freshly prepared EAGO samples (Figure 1, curve 1) and sunflower oil (Figure 2, curve 1) an intense band at 210 nm was detected, which corresponds to $\pi \rightarrow \pi^*$ transitions for isolated unsaturated bonds. This confirms the high content of polyunsaturated acids in triacylglycerols of EAGO and sunflower oil from which they are made.

Certain qualitative changes took place under the influence of autooxidation. In Figure 1 in the area from 200 to 220 nm for spectra 1 and 2 (the duration of storage of EAGO is up to 60 days) an absorption has almost the same intensity. In the sample 3 (EAGO storage duration is up to 100 days) a slight decrease in the intensity of this band (210 nm)

is observed compared to samples 1, 2 due to a decrease in the proportion of fatty acids with isolated double bonds because of autoxidation. In Figure 2 the similar decrease in absorption intensity at a wavelength of 210 nm can be noted for sunflower oil samples 2 and 3 which were stored for 60 and 100 days.

Bands of $\pi \rightarrow \pi^*$ transitions in the conjugated diene (232 nm) and triene (268 nm) structures are formed by positional isomerism accompanying the autoxidation of EAGO and sunflower oil and are detected in the absorption spectra shown in Figure 3. The band at 232 nm (Figure 3 a) for sample 1 of freshly prepared EAGO and samples 2 and 3, that were stored at a temperature of 20°C for 60 days and 100 days, appears as a bend in the 210 nm band and is characterized by a slight increase in the conjugated diene structures, which were formed during a sufficiently long storage, and an increase in the value of specific absorption.

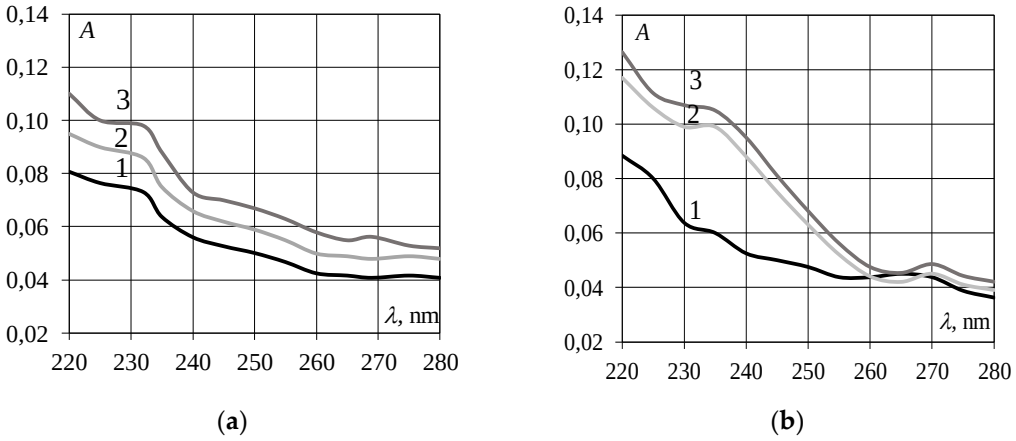

Figure 3. Changes in the UV spectra of 0.02% isooctane solutions at 232 nm and 268 nm during storage of EAGO (a) and sunflower oil (b) at a temperature of 20±1°C: 1 – 0; 2 – 60 days; 3 – 100 days

For the samples 1–3, the values of specific absorption are 3.84; 4.53; 5.16, correspondingly, and are significantly lower than the results obtained for samples of sunflower oil stored for up to 100 days (3.71; 5.21; 6.63). The band at 268 nm (Figure 3 a) is absent in the EAGO samples 1 and 2; and has a negligible intensity in the sample 3; and the values of specific absorption are, respectively, 2.15; 2.53; 2.96 and do not exceed those ones for sunflower oil (2.32; 2.37; 3.06).

The UV spectra of EAGO samples stored for 60 days at a temperature of 50°C (Figure 4 a) look somewhat different, as well as the spectra of the samples that were exposed to heat at 100° C for 6 days ($144 \cdot 60^2$ s) (Figure 4 b). Thus, from the Figure 4 it can be seen that the samples 3 (a) and 3, 4 (b) have a clearly defined maximum at 232 nm.

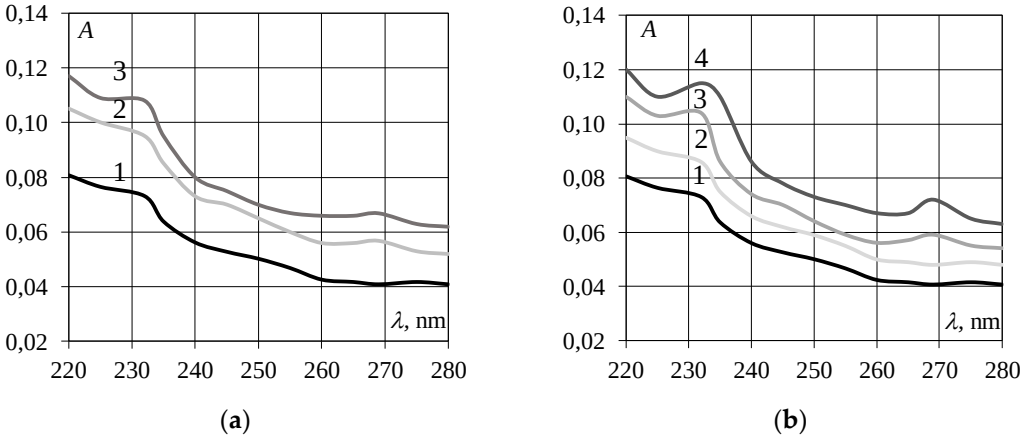

Figure 4. Changes in UV absorption spectra of 0.02% solutions in isooctane during storage of EAGO at a temperature of (a) 50±1°C: 1 – 0; 2 – 40 days; 3 – 60 days; (b) 100±1° C: 1 – 0; 2 – $72 \cdot 60^2$ s; 3 – $124 \cdot 60^2$ s; 4 – $144 \cdot 60^2$ s

This indicates on a significant increase in conjugated diene structures that were formed during the storage of EAGO samples from 40 days to 60 days at a temperature of 50°C (sample 3) and from 124·60² s to 144·60² s at a temperature of 100°C (samples 3, 4). The trend is confirmed by an increase in the value of specific absorption, which is 4.87 and 5.18 for the samples 2, 3 stored at a temperature of 50°C for 40 days and 60 days, respectively; and is 4.53, 5.20 and 5.75 for the samples 2–4 stored at a temperature of 100°C 72·60² s; 124·60² s; 144·60² s, respectively.

A comparison of the band at 268 nm with a negligible intensity in the UV spectra of EAGO samples (Figure 4) also indicates on a noticeable increase in conjugated triene structures in EAGO samples 2 and 3 (Figure 4 a) after 40 days, 60 days of storage at a temperature of 50°C. The value of specific absorption at 268 nm also increases from 3.16 to 3.52. For samples that were exposed to heat at 100°C for 5 days (120·60² s) and 6 days (144·60² s) (Figure 4 b), the specific absorption index increases from 2.95 to 3.6, respectively.

So, summarizing abovementioned it is worth to pay attention to the fact that freshly prepared EAGO and sunflower oil have a plateau in the UV spectrum at 220–240 nm and a very weak absorption in the region 270–285 nm. In the process of oxidation, the plateau at 220–240 nm turns into a band with an absorption maximum at 232 nm. The absorption also increases in the area with a maximum at 268 nm. This happens faster the higher is the temperature. This trend is also confirmed by literature data [7, 8].

3.2. Studying the primary products of the oxidation of lipids in EAGO and sunflower oil samples

The origin of the 232 nm band at the absorption maximum in the spectra of thermally non-treated oils is related to the $\pi \rightarrow \pi^*$ electronic transition in conjugated hydroperoxides, since the value of a specific absorption correlates with the peroxide value (PV), and both indicators increase with time is the same way [7]. Therefore, the change in the peroxide value of EAGO and refined sunflower oil during their storage for 100 days was investigated (Table 1). The results of statistical analysis of experimental data showed that all obtained peroxide values were significant, and the standard deviations from the average did not exceed 0.04 mmol 1/2O/kg.

Table 1. Changes in the peroxide value of EAGO and refined sunflower oil during their storage at temperature 20±1°C, 50±1°C

Duration, days	PV, mmol 1/2O/kg			
	20±1°C		50±1°C	
	EAGO	Sunflower oil	EAGO	Sunflower oil
0	3,34±0,01	3,30±0,01	3,34±0,01	3,30±0,01
10	3,35±0,01	3,39±0,01	3,40±0,02	3,67±0,02
20	3,36±0,02	3,57±0,02	3,65±0,02	4,28±0,03
30	3,39±0,02	3,73±0,03	3,86±0,03	4,94±0,03
40	3,61±0,02	4,28±0,03	4,67±0,02	5,65±0,02
60	4,06±0,03	5,00±0,04	5,12±0,03	6,98±0,04
80	4,56±0,04	5,26±0,03	–	–
100	5,01±0,03	5,67±0,03	–	–

The data in the Table 1 indicates on a greater resistance to oxidation of EAGO compared to oil. The maximum content of peroxides in EAGO at a temperature of 20±1°C after 100 days is 5.01 mmol 1/2O/kg, in oil – 5.67 mmol 1/2O/kg. A similar trend is observed during storage of the samples for 60 days at a temperature of 50±1°C. The peroxide value of EAGO samples (5.12 mmol 1/2O/kg) is 26.6% lower compared to the one for oil (6.98 mmol 1/2O/kg).

Accumulation of peroxides during the storage of EAGO and oil correlates with the obtained specific absorption rates.

4. Conclusions

According to the obtained results in the process of storage of emulsifiers of acylglycerol origin they showed higher resistance to oxidation compared to oil. The maximum content of peroxides in them after 100 days at (20±1)°C was 5.01 mmol 1/2O/kg, and in oil – 5.67 mmol 1/2O/kg, at (50±1)°C – 5.12 mmol1/2O/kg and 6.98 mmol 1/2O/kg, respectively.

During the study of the oxidative stability of emulsifiers of acylglycerol origin it was found that they are able to influence the course oxidation processes of lipids and reduce the rate of accumulation of oxidation products in them. Therefore, it can be predicted that in fats and fat-containing products the processes of oxidative destruction of lipids will also be inhibited under the influence of emulsifiers of acylglycerol origin.

Thus, the results of the study proved the ability of acylglycerol emulsifiers, obtained under mild conditions from sunflower oil, to stabilize the oxidative destruction of lipids, as well as the feasibility of their use as a perfectly compatible with lipids and absolutely safe ingredient for stabilizing the quality of fats and fat-containing products.

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Conflicts of Interest: The authors declare no conflict of interest.

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