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Proceeding Paper

Evaluation of the Oxidative Stability of Emulsifiers of an Acylglicerol Origin †

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Abstract: Obtaining new environmentally friendly emulsifiers of an acylglycerol origin based on sunflower oil with unsaturated fatty acids that are harmless to human health is relevant. The authors of this study obtained such emulsifiers under mild conditions (35–40 °C) by the transesterification reaction of triacylglycerols obtained from 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 the emulsifiers and oils. The results showed that, in the process of storage, the new emulsifiers showed a higher resistance to oxidation compared to oil.

Keywords: emulsifiers of an 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 by applying the latest technologies using absolutely safe additives based on natural local raw materials [1]. Additives of an acylglycerol origin, namely E471—mono- and diacylglycerols (MAG and DAG) of fatty acids—are such additives. 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, and are related to their ability to improve the consistency and appearance of finished products and 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 their harsh conditions of synthesis [2] (p. 390). There are two chemical processes used on the basis of technologies for obtaining acylglycerol emulsifiers, namely the glycerolysis of fats (transesterification with glycerol) and the esterification of glycerol with high-molecular-weight fatty acids. In industry, these processes are carried out at temperatures from 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 their technological processes to be carried out at temperatures not lower than 120 °C [3].

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

substantiated. EAGO were obtained under mild conditions (35–40 °C), which ensured the preservation of their essential biologically active components (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 was 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 dealt with emulsifiers of an acylglycerine origin (EAGO) obtained with using laboratory equipment under mild conditions according to the authors' developed technology of the transesterification of refined sunflower oil [4].

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

2.2. Study of Ultraviolet Absorption Spectra

The qualitative determination of polyunsaturated fatty acids, products of positional isomerism in the refined sunflower oil and EAGO was carried out by spectrophotometry in the ultraviolet (UV) region of the spectrum on a SF-46 spectrophotometer. The optical density data for the samples of 0.02% solutions of EAGO in isooctane and 0.02% solutions of refined deodorized sunflower oil in isooctane were obtained in the spectrum from 200 nm to 290 nm. The spectra were measured for the freshly prepared samples as well as for samples stored at temperatures of 20 ± 1 °C, 50 ± 1 °C and 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 the EAGO and sunflower oil samples, the value of specific absorption $E^{1\%}_{1cm}$ at 232 nm was determined using the formula:

$$E^{1\%}_{1cm}(232\ \text{nm}) = A_{232}/W, \quad (1)$$

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

2.4. Study of the Primary Products of the Oxidation of Lipids

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

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

2.5. Statistical Analysis

For the objective judgment about the degree of confidence of the data obtained, mathematical treatment of the obtained results was conducted. 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 the corresponding $(n - 1)$ degrees of freedom.

3. Results and Discussion

3.1. Study of Ultraviolet Absorption Spectra of EAGO and Sunflower Oil Samples

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

In Figures 1 and 2, the UV spectra of the 0.02% EAGO solution in isooctane and 0.02% solution of sunflower oil in isooctane are displayed correspondingly.

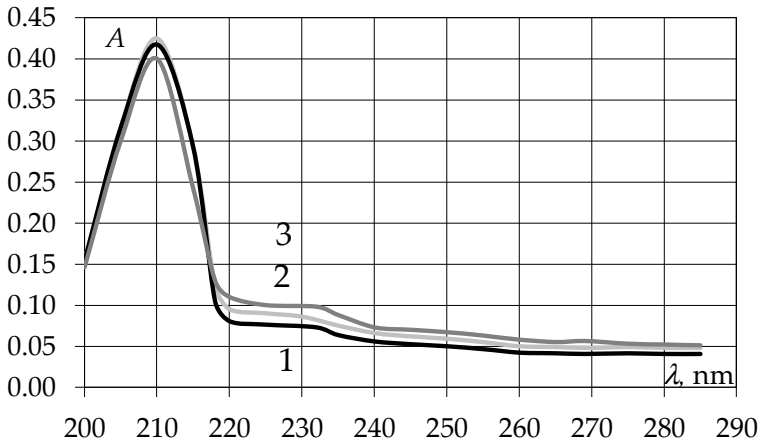

Figure 1. UV spectra of 0.02% isooctane solutions of EAHP samples, which were stored at a temperature of 20 ± 1 °C for: 1—0 days; 2—60 days and 3—100 days.

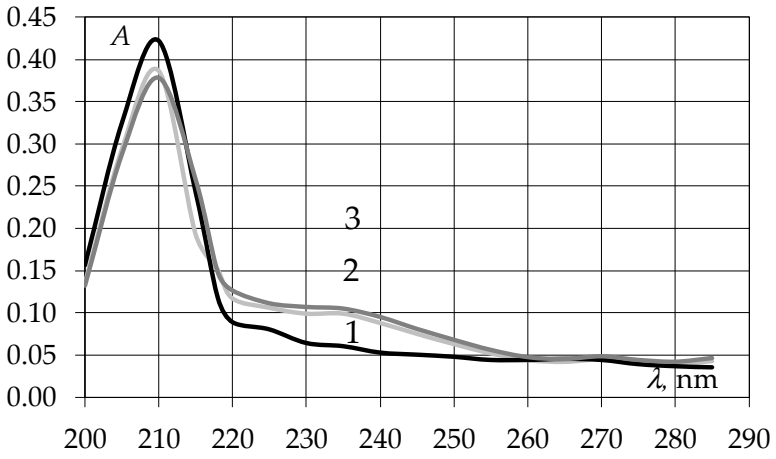

Figure 2. UV spectra 0.02% isooctane solutions of sunflower oil samples, which were stored at a temperature of 20 ± 1 °C for: 1—0 days; 2—60 days and 3—100 days.

In the absorption spectra of the freshly prepared EAGO samples (Figure 1, curve 1) and sunflower oil (Figure 2, curve 1) an intense band at 210 nm was detected, which corresponded to $\pi \rightarrow \pi^*$ transitions for isolated unsaturated bonds. This confirmed the high content of polyunsaturated acids in the triacylglycerols of the EAGO and sunflower oil from which they were 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 was up to 60 days), an absorption had almost the same intensity. In sample 3 (where the EAGO storage duration was up to 100 days), a slight decrease in the intensity of this band (210 nm) was observed compared to samples 1 and 2 due to the decrease in the proportion of fatty acids with isolated double bonds, which was due to of autoxidation. In Figure 2, a similar decrease in the absorption intensity at a wavelength of 210 nm can be noted for the sunflower oil samples 2 and 3, which were stored for 60 and 100 days, respectively.

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

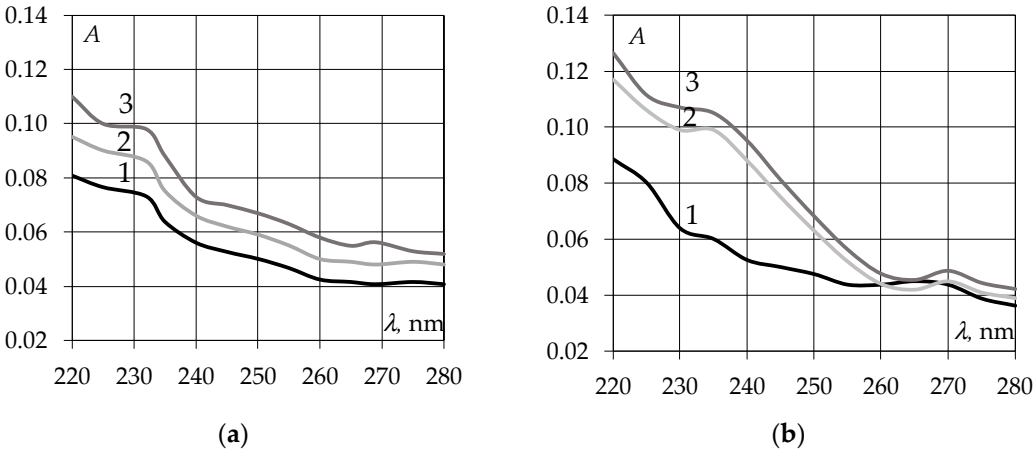

Figure 3. Changes in the UV spectra of 0.02% isooctane solutions at 232 nm and 268 nm during storage of EAGO (**a**) and sunflower oil (**b**) at a temperature of 20 ± 1 °C for: 1—0 days; 2—60 days and 3—100 days.

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

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

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

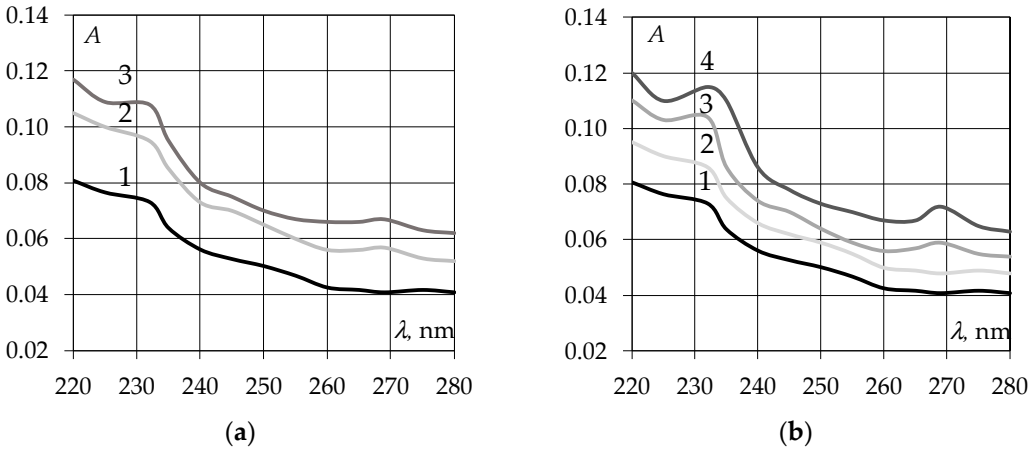

Figure 4. Changes in UV absorption spectra of 0.02% solutions in isooctane during storage of EAGO at a temperature of (**a**) 50 ± 1 °C for: 1—0 days; 2—40 days and 3—60 days; (**b**) 100 ± 1° C for: 1—0; 2—72 × 60^2 s; 3—124 × 60^2 s; 4—144 × 60^2 s.

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

So, summarizing the abovementioned, it is worth paying attention to the fact that the freshly prepared EAGO and sunflower oil had 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 turned into a band with an absorption maximum at 232 nm. The absorption also increased in the area with a maximum at 268 nm. This happened faster at higher temperatures. This trend was also confirmed by the 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 the thermally non-treated oils was related to the $\pi \rightarrow \pi^*$ electronic transition in conjugated hydroperoxides, since the value of specific absorption correlated with the peroxide value (PV), and both indicators increased with time in the same way [7]. Therefore, the change in the peroxide value of the EAGO and refined sunflower oil during their storage for 100 days was investigated (Table 1). The results of the statistical analysis of the experimental data showed that all the obtained peroxide values were significant, and the standard deviations from the average did not exceed 0.04 mmol 1/2O/kg.

The data in the Table 1 indicate a greater resistance to oxidation of the EAGO compared to oil. The maximum content of peroxides in the EAGO at a temperature of 20 ± 1 °C after 100 days was 5.01 mmol 1/2O/kg, and in the oil it was 5.67 mmol 1/2O/kg. A similar trend was observed during the storage of the samples for 60 days at a temperature of 50 ± 1 °C. The peroxide value of the EAGO samples (5.12 mmol 1/2O/kg) was 26.6% lower compared to that of the oil (6.98 mmol $\frac{1}{2}$O/kg).

The accumulation of peroxides during the storage of the EAGO and oil correlated with the obtained specific absorption rates.

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

4. Conclusions

According to the obtained results, in the process of storage of emulsifiers of an acylglycerol origin, they showed a higher resistance to oxidation compared to oil. The maximum content of peroxides in the samples after 100 days at 20 ± 1 °C was 5.01 mmol 1/2O/kg, and in the oil it was 5.67 mmol 1/2O/kg; at 50 ± 1 °C these values were 5.12 mmol 1/2O/kg and 6.98 mmol 1/2O/kg, respectively.

During the study of the oxidative stability of emulsifiers of an acylglycerol origin, it was found that they were able to influence the course the oxidation processes of lipids and reduce the rate of accumulation of oxidation products within them. Therefore, it can be predicted that in fats and fat-containing products, the processes of the oxidative destruction of lipids will also be inhibited under the influence of emulsifiers of an 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 an absolutely safe ingredient for stabilizing the quality of fats and fat-containing products that is perfectly compatible with lipids.

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