Epoxidized methyl esters and triglycerides of vegetable oils unsaturated fatty acids as new reagents for the preparation of emulsifiers based on glycerol and its oligomers

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Abstract: Oligo- and polyesters of polyglycerol and polyricinoleic acid are widely used as emulsifiers in various industries. Based on the condensation of glycerol and its oligomers with epoxidized derivatives of vegetable oils, new promising emulsifiers for oil-water systems were obtained. Complex structural and functional spectral analysis of synthesized substances showed that the main reactions leading to the formation of the desired products were the opening of epoxide cycles, the transesterification of esters and the condensation of fatty acid derivatives. The new combination of renewable raw materials is of undoubted interest for deeper vegetable oils chemical processing.

Keywords: vegetable oils; emulsifiers; triglycerides; FAME; epoxidized fatty acids; glycerol; polyglycerol; PGPR; renewable raw materials.

1. Introduction

Vegetable oils are considered as one of the most important renewable raw materials in the manufacturing of surfactants for various purposes, biofuels, chemical reagents, etc. The cleavage of the triglycerides 1 included in their composition by different nucleophilic reagents is the major chemical basis of the technologies for processing them in fatty acids 2, their salts, esters 3, amides 4 [1-7] (Scheme 1).
A common feature of the above mentioned reactions is the formation of glycerin 5 – the compound, also of green chemistry interest, as a safe, renewable solvent and reagent [9-13].

Synthetic transformation of unsaturated fatty acid hydrocarbon radicals is also given great attention [1,3,4,6,7,14]. Among the most commonly used in oleochemistry vegetable oils, triglycerides of which contain fragments of unsaturated fatty acids, are sunflower, soybean, rapeseed, castor, etc. In particular, oleic and linoleic acids are the main components of the fatty acid composition of sunflower and soybean oils (Table 1) [6,15].

A significant number of examples of structural and functional modification of unsaturated fatty acids on multiple bonds are known, but the most interesting are epoxidation reactions of both the acids themselves and their derivatives [1,3,4,7,14-27] (Scheme 2).

Epoxidized vegetable oils are used as components of polyurethane compositions [17], plasticizers of polymers [18], etc.

One of the many directions of industrial chemical transformation of glycerin 5 is its oligomerization, leading to the formation of polyglycerols 8 - a mixture of oligomeric polyols [9,12] (Scheme 3), which are used in various ways as independent substances [28], and as synthetic blocks in processes of polycondensation, for example, in the preparation of polyglycerol polyricinoleate (PGPR). PGPR is widely used in the food industry as a safe emulsifier (E-476) in water-in-oil emulsions, in particular in the production of chocolate. The manufacturing of PGPR is based on polycondensation of polyglycerol 8 with polyricinoleic acid 10, which in turn is the product of condensation of ricinoleic acid 9, derived from castor oil triglycerides [29-35] (Scheme 3).
However, castor oil, as an oleochemical natural resource, is less available than, for example, sunflower or soybean oils. Therefore, epoxidized derivatives of unsaturated acids of these oils can be considered as new renewable raw materials analogues of ricinoleic acid due to easy opening of oxirane rings to form hydroxyl or ester groups.

In the course of our work on the search for new environmentally friendly emulsifiers in the series of polyglycerol esters [36], in this paper we present the results of studies on the synthesis and emulsifying properties of new polyglycerol polyricinoleate analogs based on the products of interaction of glycerol and polyglycerol with epoxidized methyl esters or triglycerides of unsaturated fatty acids from sunflower and soybean oils.

2. Results and discussion

2.1. Epoxidation of triglycerides and methyl esters of sunflower (soybean) oils unsaturated fatty acids

The availability of sunflower and soybean oil causes their widespread use in the oleochemical industry, in particular, in the production of biofuel (biodiesel) through the transesterification of triglycerides in their composition with methanol [1]. In our work, the preparation of fatty acids methyl esters (FAME) was carried out in the presence of sodium methoxide (Scheme 4).

![Scheme 4. Methanolysis of sunflower (soybean) oils triglycerides](image)

Today, a large number of methods exist for the epoxidation of vegetable oils and their derivatives [17-19,21-24,38]. However, many of them require the use of rare and / or expensive catalysts, sometimes additional costs are required for the isolation and purification of the final product. The most effective and simple method is the performic acid using as an epoxidizing reagent, which is formed in situ from hydrogen peroxide and formic acid [17,21,38].

In preliminary experiments it was found that the optimum molar ratio of the reagents was 0.55 (oil, or 1.65 moles FAME) : 1.10 (HCOOH) : 3.00 (H₂O₂). Hydrogen peroxide was added in four doses at 60 °C. The degree of conversion of unsaturated fatty acid derivatives was controlled by iodine values and oxirane oxygen content. After 15 h from the start of epoxidation (on the example of sunflower oil 11a or its ester 12a), oxirane oxygen content was maximum, while the iodine value was minimal and no further significant changes were occurred (Table 2). Thus, under these conditions, the maximum conversion of oil or ether over multiple bonds was achieved.
Table 2. Reaction time optimization for the epoxidation of sunflower oil 11a and its FAME 12a.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reaction time, h</th>
<th>Oxirane oxygen content, mass %</th>
<th>Iodine value, g I2/100 g</th>
<th>Oxirane oxygen content, mass %</th>
<th>Iodine value, g I2/100 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>-</td>
<td>158.9</td>
<td>-</td>
<td>153.7</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>1.6</td>
<td>116.8</td>
<td>1.8</td>
<td>120.1</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>3.8</td>
<td>78.5</td>
<td>3.5</td>
<td>98.3</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>4.5</td>
<td>50.1</td>
<td>4.7</td>
<td>75.3</td>
</tr>
<tr>
<td>5</td>
<td>12</td>
<td>6.5</td>
<td>40.7</td>
<td>5.3</td>
<td>54.2</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
<td>7.1</td>
<td>21.5</td>
<td>7.0</td>
<td>30.6</td>
</tr>
<tr>
<td>7</td>
<td>18</td>
<td>7.0</td>
<td>20.3</td>
<td>6.5</td>
<td>29.5</td>
</tr>
</tbody>
</table>

Gas chromatography analysis with mass spectrometric detection (GC-MS) of epoxidation products (on the example of sunflower oil FAME 12a) showed that the composition of their mixture was rather complicated. The main components were the methyl esters of hydroxy- and epoxy-derivatives of octadecanoic (I-IV) and, in part, octadec-12-enoic (V) acids (~ 82 wt%), along with methyl esters of saturated fatty acids, which did not oxidize under these conditions (~ 16 wt%) and unidentifiable substances (~ 2 wt%) (Figure 1, Table 3).

**Figure 1.** Structure of the major epoxidation products sunflower oil FAME 12a.
Table 3. Major products of sunflower oil FAME (12a) oxidation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>MW</th>
<th>Molecular ion peaks cluster, m/z (intensity, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>C_{19}H_{36}O_{3}</td>
<td>312.49</td>
<td>312 (100.0), 313 (21.1), 314 (2.6)</td>
</tr>
<tr>
<td>II</td>
<td>C_{19}H_{34}O_{4}</td>
<td>326.47</td>
<td>326 (100.0), 327 (21.1), 328 (2.9)</td>
</tr>
<tr>
<td>III</td>
<td>C_{19}H_{36}O_{4}</td>
<td>330.50</td>
<td>330 (100.0), 331 (21.1), 332 (2.9)</td>
</tr>
<tr>
<td>IV</td>
<td>C_{19}H_{36}O_{6}</td>
<td>362.50</td>
<td>362 (100.0), 363 (21.2), 364 (3.3)</td>
</tr>
<tr>
<td>V</td>
<td>C_{19}H_{36}O_{4}</td>
<td>328.49</td>
<td>328 (100.0), 329 (20.5), 330 (2.9)</td>
</tr>
</tbody>
</table>

Thus, in the epoxidation process partial opening of the oxirane rings was occurred simultaneously with the formation of diol fragments (Scheme 5,6).

Scheme 5. Epoxidation of vegetable oils triglycerides (11) and the structure of some products.

11a,b

- sunflower oil; b - soybean oil; R - saturated radicals
The formation of hydroxyl-containing compounds was not an undesirable process, since these substances are also formal synthetic equivalents of ricinoleic acid, like epoxy derivatives.

The structures of the substances, included in the epoxidized oils and FAME composition, were also confirmed by IR- and $^1$H NMR spectroscopy data. In the IR spectra of compounds 13a,b and 14a,b there are intensive bands of C=O bonds at 1750-1700 cm$^{-1}$ and ester fragments at 1225-1050 cm$^{-1}$. In comparison with the spectra of the initial oils and FAME, the characteristic bands for the epoxide cycle appeared in the region of 1240-1260 cm$^{-1}$ (the symmetric stretching vibrations of the ring) and 820-830 cm$^{-1}$ (asymmetric ones). The broadened band at 3550-3200 cm$^{-1}$ range corresponded to the hydroxyl groups formed as a result of certain oxirane cycle opening. The bands of the olefin moiety C-H bond at 725-721 cm$^{-1}$ are partially remained.

In $^1$H NMR spectra of epoxidized derivatives, there are signals sets of protons from alkyl groups of acyl residues, oxirane cycle(s), CH groups of diol fragments (in the products of the latter ring opening), and CH$_2$, CH$_3$ - glycerol protons for epoxidized triglycerides or a singlet the methoxycarbonyl group FAME. A set of triplets of terminal methyl groups was in the range of 0.81-0.89 ppm. The assignment of CH$_2$-groups multiplets was made on the basis of the literature data for such compounds [17,21,38]. The proton signals of acyl $\alpha$-methylene groups are observed at 2.19-2.29 ppm as a set of triplets, the multiplet of protons of $\beta$-methylene fragments was observed at 1.38-1.52 ppm. The proton signals of the methylene groups located next to the oxirane rings were in the range 1.24-1.45 ppm, and between them (for linolenic acid derivatives) - at 2.61-2.75 ppm. The proton multiplets of the other methylene units was observed at 1.13-1.30 ppm. The broadened singlet at 4.70 ppm was corresponded to the protons of OH-groups and indicated to the presence in the mixture of dihydroxy derivatives, formed during the opening of the epoxide cycle. Multiplets in the areas 3.98-4.28 and 5.15-5.21 ppm in the spectra of epoxidized oils were refered to protons of methylene and methine groups of glycerol. The singlet of the carbomethoxy group of epoxidized FAME was about 3.58 ppm. The proton signals of multiple bonds in the acyl residues of unsaturated fatty acids were also present in the spectra. Comparison of iodine values for epoxidized derivatives with the same of oils and FAME was indicated the conservation of 5-7% of unsaturated fatty acid residues (Table 4).
### Table 4. Some characteristics of vegetable oils, FAME and epoxidized derivatives.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Iodine value, g I₂/100g</th>
<th>Acid value, mg KOH/g</th>
<th>Saponification value, mg KOH/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sunflower oil (11a)</td>
<td>158.9</td>
<td>0.1</td>
<td>188.9</td>
</tr>
<tr>
<td>Soybean oil (11b)</td>
<td>172.3</td>
<td>0.3</td>
<td>192.3</td>
</tr>
<tr>
<td>Sunflower oil FAME (12a)</td>
<td>153.7</td>
<td>0.2</td>
<td>203.0</td>
</tr>
<tr>
<td>Soybean oil FAME (12b)</td>
<td>169.8</td>
<td>0.2</td>
<td>198.4</td>
</tr>
<tr>
<td>Epoxidized sunflower oil (13a)</td>
<td>15.5</td>
<td>0.4</td>
<td>197.3</td>
</tr>
<tr>
<td>Epoxidized soybean oil (13b)</td>
<td>15.0</td>
<td>0.2</td>
<td>196.0</td>
</tr>
<tr>
<td>Epoxidized sunflower oil FAME (14a)</td>
<td>13.0</td>
<td>0.4</td>
<td>199.1</td>
</tr>
<tr>
<td>Epoxidized soybean oil FAME (14b)</td>
<td>10.5</td>
<td>0.5</td>
<td>192.9</td>
</tr>
</tbody>
</table>

The saponification and acid values were changed insignificantly, so the hydrolysis of the ester groups did not occur under the epoxidation reaction conditions. The resulting epoxy derivatives without further purification were used in the synthesis of glycerol and polyglycerol esters.

### 2.2. Condensation of vegetable oils epoxidized derivatives with glycerol and polyglycerol.

It was noted above that the preparation of PGPR generally includes the following steps: 1) synthesis of polyglycerol, 2) preparation of ricinoleic acid, 3) its polycondensation, 4) condensation of polyglycerol and polycricinoleic acid. A three-step process is known based on the polycondensation of ricinoleic acid in situ in the reaction with polyglycerol in the presence of alkaline catalysts in inert atmosphere at high temperatures [39]. These conditions were chosen as model in the study of the interaction of epoxidized triglycerides and methyl esters of unsaturated fatty acids with glycerol and polyglycerol. Earlier, we have obtained esters of fatty acids and polyglycerol by this method [36]. On the one hand, glycerol can polymerize into polyglycerol under these conditions, and, thus, the number of stages is reduced. On the other hand, the presence of polyglycerol fragments and fatty acid residues in the reaction products suggests appearance of emulsifying properties, as for PGPR.

Primarily, we have investigated the interaction of epoxidized triglycerides (13) and methyl esters (14) of sunflower (a) and soybean (b) oils fatty acids with glycerol at reagent molar ratio 1 : 1. The functionality of the major compounds, which were part of 13,14 (Figure 1), made it possible to suggest the following synthetic routes:

i) opening of oxirane rings resulting from the reaction of epoxy derivatives with glycerol or hydroxyl-containing triglycerides and FAME;
ii) transesterification of triglycerides or FAME with glycerol or hydroxyl-containing triglycerides and FAME;

iii) polycondensation of glycerol and similar reactions of polyglycerols in the directions (i) or (ii).

Gas chromatography analysis followed by electron impact mass-spectrometric detection was not possible due to the complex composition of the mixture and the presence of oligomeric compounds. The use of high-performance liquid chromatography was also inexpedient for the same reason. Therefore, to evaluate the qualitative composition of the products and confirm the proposed directions of epoxy derivatives interaction with glycerol, we used electrospray ionization high resolution mass spectrometry (ESI-HRMS) with direct input of samples, despite certain difficulties in the analysis of spectra. It should be noted that the fragmentation of molecular ions was very insignificant under these ionization conditions in comparison with electron impact.

In the mixture of products 15-16 dihydroxyoleic acid monoglyceride A was identified as a result of transesterification. The presence of polyglycerol esters B-E confirmed both the polymerization of glycerol and the subsequent transesterification. The formation of ester D also occurred as a result of the oxirane ring disclosure in epoxyderived linolenic acid (Scheme 7).

\[
\begin{align*}
13 & \quad a,b \quad + \quad \text{CH}_3\text{ONa} \quad \xrightarrow{220 \text{ } ^\circ \text{C}, \ 6-8 \text{ h}} \quad 15 \quad a,b \\
& \quad \text{A} \quad \xrightarrow{7} \quad \text{B} \quad \xrightarrow{7} \quad \text{C} \quad \xrightarrow{7} \quad \text{D} \quad \xrightarrow{7} \quad \text{E}
\end{align*}
\]

m/z\([M+H]^+ 389.2991/389.2902\)

m/z\([M+H]^+ 405.323/405.321\)

m/z\([M+H]^+ 703.570/703.572\)

m/z\([M+H]^+ 773.657/773.650\)

m/z\([M+H]^+ 1013.823/1013.823\)

\(15\): epoxidized sunflower oil (a), soybean oil (b)

\(16\): epoxidized sunflower oil FAME (a), soybean oil FAME (b)

R - residues of fatty acids and its derivatives

Scheme 7. Epoxidation of FAME (12) and the structure of some products

\(^1\) calculated for molecular formula+H\(^+\) \(2\)Founded by MS-ESI).

Similar processes occurred during the interaction of epoxidized derivatives 13-14 and polyglycerol. The reaction products of epoxidized soybean oil FAME with polyglycerol 18b-e were obtained at different molar ratios of the reagents in order to better assess their surfactant properties. The products composition in the reactions of the epoxy derivatives 13-14 with polyglycerol was also analyzed by ESI-HRMS (Scheme 8).
Thus, as a result of the transesterification reaction, monoesters of fatty acids and polyglycerol (F, G, H, I, J) with different degrees of polymerization were obtained. The presence of derivatives of hepta- (I) and nonaglycerol (J) indicated an increase in the degree of polymerization under the reaction conditions. Diesters of diglycerol (K), triglycerol (E), tetraglycerol (L) and pentaglycerol (M), as well as branched chain oligomers (D, N, O, P) also were found in the mixture.

Of course, based on the ESI-HRMS data, other ethers were also the products of the interaction of epoxidized derivatives 13-14 with glycerol or polyglycerol. Nevertheless, the selected identified compounds unambiguously characterized the directions of the proceeding reactions.

The qualitative structural and functional composition of products 15-18 was characterized by the position of absorption bands in IR spectra and signals in 1H NMR spectra. In the IR spectra of the
obtained substances, there were intense characteristic absorption bands of the ester fragment at 1750-1700 cm\(^{-1}\) (C = O) and 1240-1050 cm\(^{-1}\) (C-C(=O)-O, O-C-C). In the range 3550-3200 cm\(^{-1}\), there was an intense wide band associated with the stretching vibrations of the hydroxyl groups. Moreover, for the derivatives 17-18, obtained from polyglycerol, this band was more intense than for analogous derivatives 15-16, obtained from glycerol (Figure 2, example of soybean oil derivatives). The absence of absorption bands corresponding to oxirane cycles indicated their disclosure under the reaction conditions, as well as the value of the oxirane number not exceeding 0.1\% for all products 15-18.

Figure 2. IR spectra: (a) soybean oil FAME 12b; (b) epoxidized soybean oil FAME 14b; (c) esters from epoxidized soybean oil FAME and glycerol 16b; esters from the same epoxi-FAME and polyglycerol at various reagents ratio (d) 18b (1:1), (e) 18c (1:2), (f) 18d (1:3.5), (g) 18e (1:7).

In \(^1\text{H}\) NMR spectra of esters 15-18, proton signals of \(\alpha\) - and \(\beta\)-methylene groups (2.22-2.32 ppm and 1.51-1.53 ppm), the other methylene units (1.19-1.30 ppm), the set of triplets terminal methyl groups (0.82-0.86 ppm) were remained. The complex multiplet of polyglycerol protons were observed in the region 3.4-5.1 ppm. The presence of intense signals in the range 4.6-4.9 ppm, characteristic for PGPR oligomers [32], in the spectra of compounds 15-16 indicated to the polymerization of glycerol under esterification reaction conditions. In the product spectra, unlike the spectra of epoxidized derivatives, there were no signals of protons of oxirane rings in the region of 2.8-3.2 ppm, which also confirmed their disclosure.

Some characteristics for a complex evaluation of the emulsifying ability were determined for products 15-18, obtained at 1 : 1 reagents molar ratio (Table 5). The known PGPR emulsifier Palsgaard 4125 was chosen as the reference sample.
Table 5. Characteristics of products 15-18, obtained at 1 : 1 reagents molar ratio.

<table>
<thead>
<tr>
<th>Comp</th>
<th>Iodine value, g I/100g</th>
<th>Acid value, mg KOH/g</th>
<th>Saponification value, mg KOH/g</th>
<th>Viscosity, mPa.s (25 °C)</th>
<th>Emulsifying effect (emulsion life half-period, min) 1</th>
<th>HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15a</td>
<td>5.3</td>
<td>0.7</td>
<td>173.2</td>
<td>61.1</td>
<td>5.8</td>
<td>10</td>
</tr>
<tr>
<td>15b</td>
<td>9.3</td>
<td>1.5</td>
<td>168.2</td>
<td>62.6</td>
<td>10.0</td>
<td>23</td>
</tr>
<tr>
<td>16a</td>
<td>6.7</td>
<td>0.5</td>
<td>161.6</td>
<td>56.2</td>
<td>8.6</td>
<td>44</td>
</tr>
<tr>
<td>16b</td>
<td>4.7</td>
<td>0.9</td>
<td>147.2</td>
<td>58.3</td>
<td>10.2</td>
<td>4</td>
</tr>
<tr>
<td>17a</td>
<td>9.0</td>
<td>1.4</td>
<td>129.8</td>
<td>54.0</td>
<td>5.9</td>
<td>46</td>
</tr>
<tr>
<td>17b</td>
<td>3.1</td>
<td>1.1</td>
<td>120.6</td>
<td>62.5</td>
<td>8.2</td>
<td>35</td>
</tr>
<tr>
<td>18a</td>
<td>4.6</td>
<td>0.6</td>
<td>83.6</td>
<td>62.1</td>
<td>5.3</td>
<td>58</td>
</tr>
<tr>
<td>18b</td>
<td>1.6</td>
<td>0.5</td>
<td>70.6</td>
<td>71.9</td>
<td>6.5</td>
<td>60</td>
</tr>
<tr>
<td>PGPR</td>
<td>100.3</td>
<td>2.0</td>
<td>156.2</td>
<td>81.5</td>
<td>48.4</td>
<td>120</td>
</tr>
</tbody>
</table>

1 For 1.0 % solution. 2 For 0.5% solution.

Compared with the starting epoxy derivatives 13-14, no significant changes in the iodine, acid and saponification values were observed except for decrease in the saponification value for polyglycerol based products 17,18, due to their less esterification. The emulsifying activity of the latter was higher than that of the analogous glycerol derivatives 15, 16. The most interesting was the esters 18b obtained by reaction of epoxidized FAME soybean oil 14b with polyglycerol 8. Therefore, we obtained products 18c-e with a molar ratio of 8 : 14b reagents equal to 1 : 2 (18c), 1 : 3.5 (18d) and 1 : 7 (18e). The use of a sevenfold excess of FAME 14b resulted in the formation of highly polymerized product 18e, insoluble in water and most organic solvents, which did not allow it to be characterized (Table 6).

Table 6. Characteristics of polyglycerol esters 18c,d.

<table>
<thead>
<tr>
<th>Comp (8 : 14b)</th>
<th>Iodine value, g I/100g</th>
<th>Acid value, mg KOH/g</th>
<th>Saponification value, mg KOH/g</th>
<th>Viscosity, mPa.s (25 °C)</th>
<th>Emulsifying effect (emulsion life half-period, min) 1</th>
<th>HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18c (1:2)</td>
<td>3.5</td>
<td>0.5</td>
<td>101.4</td>
<td>75.2</td>
<td>5.2</td>
<td>36</td>
</tr>
<tr>
<td>18d (1:3.5)</td>
<td>5.1</td>
<td>0.5</td>
<td>141.4</td>
<td>71.4</td>
<td>5.8</td>
<td>40</td>
</tr>
</tbody>
</table>

1 For 1.0 % solution.

In the IR spectra of esters 18c,d, decrease in the intensity of the hydroxyl groups absorption band was observed (Figure 2), which led to increase in the saponification value (Table 6). However, the decrease in emulsifying effect was occurred. Nevertheless, it was remained higher in comparison with glycerol derivatives.

2.3. Emulsifying ability of esters based on epoxidized vegetable oils derivatives.

HLB values were calculated for all synthesized compounds 15-18 [40]. The emulsifying ability and viscosity were determined for emulsions containing (v/v) 80% oil and 20% water (4: 1), as well as 50% oil and 50% (1 : 1) at test concentration 1% (Tables 5,6).
It was noted above that the emulsifying ability of products obtained from polyglycerol was higher than for glycerol analogues, and for epoxidized FAME polyglycerol esters, the emulsifying action is higher than for derivatives derived from epoxidized triglycerides. In the transition from an emulsion containing 20% water to an emulsion with higher water content (50%), the emulsifying action of the polyglycerol-based derivatives was reduced by about half, while for the glycerol derivatives this value were not decreased, but for compounds 15b and 16a was increased. Thus, the obtained esters, as well as PGPR, stabilized the emulsion with a high water content.

Despite the fact that esters 15-18 worse were stabilized emulsions than commercial PGPR Palsgaard 4125, nevertheless, the prospects of their research in this direction is not in doubt.

It is known [40] that from the HLB values of the surfactant molecules, their properties can be predicted. The values of HLB of the esters 15-18 shown in Table 5 were in a wide range. Thus, it could be assumed that all glycerol-based esters and epoxidized derivatives of vegetable oils would form a water-in-oil emulsion (w/o), while polyglycerol-based emulsions - an oil-in-water emulsion (o/w). However, with an increase in the degree of esterification, the type of emulsion formed might change. With a visual study of emulsions (an increase of x100), it was found that, for system containing 80% oil and 20% water (4 : 1), regardless of the ester type and difference in HLB, the emulsion w/o predominantly were formed. The images of emulsions of compounds 15b (HLB = 4.7) (a), 18d (HLB = 7.1) (b), 17b (HLB = 10.7) (c) and 18b (HLB = 13.7) (d) have been showed that the type the emulsion was the same (Figure 3).

![Figure 3. Images of emulsions at oil : water ratio 4 : 1 for compounds: (a) 15b; (b) 18d; (c) 17b; (d) 18b](image-url)
Figure 4. Images of emulsion at oil : water ratio 1 : 1 for compounds: (a) 15b; (b) 18d; (c) 17b; (d) 18b.

Commercial PGPR Palsgaard 4125 with HLB = 9.5 formed an emulsion of the w/o type, regardless of the ratio of water: oil (Figure 5).

Figure 5. Images of PGPR Palsgaard 4125 emulsion at oil : water ratio: (a) 4 : 1; (b) 1 : 1.

It is known that PGPR is used not only as an effective emulsifier, but also as a viscosity regulator [32-35]. When 1% of esters 15-18 were added to the emulsion containing 80% oil and 20% water, the viscosity increased by 1.5 times compared to the viscosity of pure sunflower oil (Table 4,5). This index was maximally increased when using esters (18b-d) based on epoxidized soybean oil FAME and polyglycerol. For the emulsion containing 50% oil and 50% water, no significant increase in viscosity was observed (Figure 6).
Thus, the new polyglycerol esters obtained by condensing epoxidized derivatives of unsaturated fatty acids of sunflower and soybean oil with glycerol and its oligomers showed emulsifying activity against oil-water emulsions. Further optimization of the structural-functional composition of these esters will make it possible to improve their surface-active properties for practical use.

3. Materials and Methods

3.1. General.

Sunflower and soybean oils were provided by EFKO GC (Alekseevka, Belgorod region, Russia). Other reagents were purchased from commercial suppliers and used as received.

All synthetic procedures were carried out in a batch reactor UNIC -150-2 (Lenz Laborglas GmbH & Co. KG, Wertheim, Germany) with reaction vessel (volume 2 l, with thermostatic jacket and bottom discharge valve) which could be equipped with reflux condenser, dropping funnel, etc. Heating of the reaction mass was carried out with a circulation thermostat Huber CC – 202 with controller Pilot ONE, providing the temperature constancy 0.02 °C (Peter Huber Kältemaschinenbau AG, Offenburg, Germany). The reaction mixture was stirred using an overhead stirrer IKA – Werke Eurostar 40 digital with electronic speed control (Vacuuming was carried out usingchemistry pumping unit PC 3004 VARIO, capable fully solvent recovery, efficient recycling and active environmental protection (Vacuubrandt GmbH + Co. KG, Wertheim, Germany). NMR \(^1\)H spectra were registered on Bruker DRX 500 (500.13 MHz) spectrometer in DMSO-d<sub>6</sub>, internal standard was TMS. IR spectra were acquired using a Vertex 70 FTIR spectrometer with Platinum ATR (Bruker Ltd., Moscow, Russia). Refractive index measurements were carried out on an IRF-454 BM refractometer (KOMZ JSC, Kazan, Russia). The emulsion type was determined by a Biomed 6 microscope (Biomed Ltd., St. Petersburg, Russia) with a ToupCam digital camera (Hangzhou ToupTek Photonics Co. Ltd, Hangzhou, China). Viscosity was measured using sine-wave vibro viscometer SV-10A (A&D Company Ltd., Tokyo, Japan).

The acid, saponification, and hydroxyl values of products were calculated by the known techniques, the oxiran oxygen content (value) was determined according to the AOCS official method Cd 9-57 [37]. The molar mass of triglycerides was calculated from saponification value: M = 56000 x 3/SV, where M is the triglyceride molar mass g/mol, 56000 is the molar mass of KOH (mg/mol), 3 is the stoichiometric coefficient, SV is the saponification value of triglycerides (mg KOH/g).
Gas-chromato-mass spectrometric analysis (GC–MS) was carried out by an Agilent Technologies 7890B GC system with an Agilent Technologies mass selective detector 5977A MSD (Agilent Technologies, Santa Clara, CA, USA). Sample inlet temperature was 280 °C, analytic interface - 150/230 °C. Electron impact ionization energy was 70 eV. Separation was done on a HP-5ms UI capillary column (30 m x 0.250 mm x 0.25 μm, stationary phase - 5% phenylmethylpolysiloxane). The gas flow rate was 1.0 ml/min, with continuous flow. The sample volume was 1 μl; split injection - 20 : 1. Temperature regimes were as follows: isotherm 120 °C (2 min), heating at 10 °C/min to 180 °C (1 min), heating at 3 °C/ min to 270 °C (5 min), heating at 10 °C/ min to 300 °C (3 min). Signal registration was performed using total ion current (TIC) in a scanning region of 35 – 650 m/z. Polyglycerol was pre-silylated with BSFTA (Merck KGaA, Darmstadt, Germany) for 40 min at 70 °C.

High performance liquid chromatography with high resolution mass-spectrometric detection under electrospray ionization (HPLC-HRMS-ESI) in combination with UV detection was used to determine the molecular weight of the condensation products of epoxidized derivatives with glycerol and polyglycerol. The device consisted of liquid chromatograph — Agilent 1269 Infinity and time-of-flight high resolution mass detector — Agilent 6230 TOF LC/MS (Agilent Technologies, Santa Clara, CA, USA). Block ionization was double electrospray, detection mass range was from 50 to 2000 Dalton (positive ions mode). Capillary voltage was 4,0 kV, fragmentor + 191 V, skimmer + 66 V, OctRF 750 V. Column Poroshell 120 EC-C18 (4,6 x 50 mm; 2,7 mkm) was used. Gradient eluation: acetonitrile /water (0.1 % formic acid); flow rate: 0.4 mL/min. Software for collection and elaboration of research results was MassHunter Workstation/Data Acquisition V.06.00.

3.2. Synthesis

3.2.1. Polyglycerol 8.

Polyglycerol 8 (the refractive index 1.4890-1.4905 and the hydroxyl number 1169 mg KOH/g) was prepared according to the procedure described earlier [36]. The average molecular weight of polyglycerol (275 g/mol) was determined from the oligomer content based on the GC-MS and MS-ESI data analysis. Polyglycerol was consisted of glycerol (20 wt %), di- and triglycerol (30 wt %), penta- and hexaglycerol (50 wt %).

3.2.2. Fatty acids methyl esters (FAME) 12a,b.

FAME 12a,b were prepared according to a known procedure [21,41], modified for the batch reactor UNIC -150-2.

Methanol (3.75 mol, 210 g, 256 mL), sodium methoxide (0.035 mol, 1.89 g) and the corresponding vegetable oil 11a,b (1 mol) were placed in the reactor. The reaction mixture was refluxed for 2 h. After cooling, the mixture was left for ~ 2 h until completely separated into two layers. The lower, glycerol layer was removed through the bottom discharge valve. Crude FAME twice was washed with water (2 x 200 mL). After separating of water, the solvent residues are removed under reduced pressure and product was poured through the bottom discharge valve. Esters were used in epoxidation reactions without further purification.

Sunflower oil (11a). IR (neat), ν (cm⁻¹): 2922, 2852 (CH), 1744 (C=O), 1196, 1161, 1095 (C–O), 723 (CH=); 1H-NMR (DMSO-d₆), δ (ppm): 0.82-0.89 (CH₃), 1.15-1.30 (CH₂acid), 1.43-1.52 (βCH₂acid), 1.90-2.05 (CH₂CH=CHacid), 2.10-2.30 (αCH₂acid), 2.61-2.75 (CH=CHCH₂CH=CHacid), 3.92-4.25 (CH₂glycerol), 5.15-5.35 (CH=CH+CHglycerol).

Soybean oil (11b). IR (neat), ν (cm⁻¹): 2922, 2852 (CH), 1744 (C=O), 1197, 1161, 1095 (C–O), 721 (CH=); 1H-NMR (DMSO-d₆), δ (ppm): 0.83-0.87 (CH₃), 1.15-1.30 (CH₂acid), 1.47-1.53 (CH₂acid), 1.99-2.02 (CH₂acid), 2.23-2.29 (αCH₂acid), 2.63-2.74 (CH=CHCH₂CH=CHacid), 3.94-4.28 (CH₂glycerol), 5.18-5.37 (CH=CH+CHglycerol).

Sunflower oil FAME (12a). Esters were synthesized from 889 g sunflower oil 11a. Colorless liquid. Yield 827 g (93 %, base on the amount of oil). IR (neat), ν (cm⁻¹): 2922, 2852 (CH), 1742 (C=O),
385 1195, 1170, 1095 (C=O), 725 (CH=); 1H-NMR (DMSO-d6), δ (ppm): 0.84-0.87 (CH3), 1.23-1.33 (CH2acid),
386 1.49-1.52 (βCH2acid), 1.96-2.03 (CH2CH=CHacid), 2.26-2.29 (αCH2acid), 2.72-2.75
387 (CH=CHCH=CHacid), 3.58 (CH3O), 5.27-5.35 (CH=CH).
388 Soybean oil FAME (12b). Esters were synthesized from 873 g soybean oil 11b. Colorless liquid.
389 Yield 825 g (94 %, base on the amount of oil). IR (neat), ν (cm⁻¹): 2922, 2852 (CH), 1742 (C=O), 1170,
390 1105 (C=O), 725 (CH=); 1H-NMR (DMSO-d6), δ (ppm): 0.84-0.87 (CH3), 1.23-1.33 (CH2acid),
391 1.49-1.52 (βCH2acid), 1.96-2.04 (CH2CH=CHacid), 2.26-2.29 (αCH2acid), 2.72-2.75
392 (CH=CHCH=CHacid), 3.58 (CH3O), 5.27-5.35 (CH=CH).
393 3.2.3. Epoxidation of vegetable oils (11) and fatty acid methyl esters (FAME) (12).
394 The oils and FAME solventless epoxidation was carried out by generated in situ performic acid
395 according to the modified for the batch reactor UNIC -150-2 procedure [17,38].
396 An oil (0.55 mol) or FAME (1.65 mol) was charged into reactor. The formic acid (1.1 mol, 60 g (50
397 mL) 85 wt % water solution) was added with stirring. Then the (1.32 mol, 150 g (135 mL) 30 wt %
398 water solution) was added drop wise with vigorous stirring. The reaction mixture was heated for 4 h
399 at 60 °C with vigorous agitation. After that another 68 mL (0.66 mol) of the hydrogen peroxide
400 solution was added drop wise and agitation was continued under the same conditions and the
401 procedure was repeated again. Then, another 68 mL (0.66 mol) of the hydrogen peroxide solution
402 was added and stirring was continued at the same temperature until completion of the reaction
403 (monitored by changing the oxirane oxygen content and the iodine value of the reaction mixture).
404 Further the reaction mixture was washed with 5 % solution NaHCO3 (2 x 500 mL) and then with
405 water (2 x 500 mL). Water residuals were removed with a chemistry pumping unit at 70 °C and
406 pressure 30 mBar for 30 min.
407 Epoxidized sunflower oil (13a) was obtained from 489 g 11a. Colorless liquid. Yield 435 g IR (neat),
408 ν (cm⁻¹): 3489 (OH), 2922, 2852 (CH), 1740 (C=O), 1244 (COC), 1153, 1095 (C–O), 824 (COC), 727
409 (CH=); 1H-NMR (DMSO-d6), δ (ppm): 0.82-0.89 (CH3), 1.17-1.30 (CH2acid), 1.32-1.47 (CH3COCHacid),
410 1.48-1.52 (βCH2acid), 1.89-2.03 (CH2CH=CHacid), 2.17-2.29 (αCH2acid), 2.61-2.75
411 (CHOCH2CHOCH2acid), 2.82-3.02 (CHOacid), 4.04-4.28 (CH2glycerol+OHal), 5.15-5.51
412 (CH=CH+CHglycerol).
413 Epoxidized soybean oil (13b) was obtained from 480 g 11b. Colorless liquid. Yield 439 g IR (neat),
414 ν (cm⁻¹): 3383 (OH), 2922, 2852 (CH), 1742 (C=O), 1246 (COC), 1153, 1095 (C–O), 824 (COC), 723
415 (CH=); 1H-NMR (DMSO-d6), δ (ppm): 0.85-0.88 (CH3), 1.23-1.32 (CH2acid), 1.36-1.44 (CH3COCHacid),
416 1.48-1.52 (βCH2acid), 1.93-2.03 (CH2CH=CHacid), 2.26-2.29 (αCH2acid), 2.71-2.75
417 (CHOCH2CHOCH2acid), 2.88-3.03 (CHOacid), 4.08-4.29 (CH2glycerol+OHal), 5.15-5.22
418 (CH=CH+CHglycerol).
419 Epoxidized sunflower oil FAME (14a) were obtained from 455 g esters 12a. Colorless liquid. Yield
420 419 g IR (neat), ν (cm⁻¹): 3464 (OH), 2922, 2852 (CH), 1742 (C=O), 1244 (COC), 1153, 1095 (C–O), 824
421 (COC), 725 (CH=); 1H-NMR (DMSO-d6), δ (ppm): 0.84-0.87 (CH3), 1.19-1.29 (CH2acid), 1.32-1.41
422 (CH3COCHacid), 1.48-1.52 (βCH2acid), 1.98-2.03 (CH2CH=CHacid), 2.26-2.29 (αCH2acid), 2.61-2.65
423 (CHOCH2CHOCH2acid), 3.07-3.17 (CHOacid), 3.58 (OCH3), 4.09 (OHal), 5.19-5.31 (CH=CH).
424 Epoxidized soybean oil FAME (14b) were obtained from 465 g esters 12b. Colorless liquid. Yield
425 422 g IR (neat), ν (cm⁻¹): 3464 (OH), 2922, 2852 (CH), 1738 (C=O), 1247 (COC), 1172, 1120 (C–O), 824
426 (COC), 725 (CH=); 1H-NMR (DMSO-d6), δ (ppm): 0.84-0.88 (CH3), 1.21-1.32 (CH2acid), 1.39-1.44
427 (CH3COCHacid), 1.48-1.52 (βCH2acid), 1.95-2.03 (CH2CH=CHacid), 2.26-2.30 (αCH2acid), 2.61-2.64
428 (CHOCH2CHOCH2acid), 2.80-3.05 (CHOacid), 3.58 (OCH3), 4.12 (OHal), 5.37-5.49 (CH=CH).
429 3.2.4. General procedure for synthesis of glycerol and polyglycerol esters (15-18).
430 A mixture of glycerin (5) (1 mole, 92 g) or polyglycerol (8) (1 mole, 275 g), sodium methoxide
431 (0.02 mole, 1.08 g in reactions with glycerol or 0.07 mole, 3.78 g in reactions with polyglycerol) and
432 epoxidized vegetable oil (13a,b) (1 mole) or its epoxidized FAME (14 a-b) was heated in argon flow
433 at 220 °C and agitation at 1500 rpm for 6-8 h. The methanol formed as a result of the FAME
transesterification was distilled off. The product was cooled to a temperature of 60 °C under an inert atmosphere, and then was poured through the bottom discharge valve into a storage container.

For esters (18b-e) molar ratio of polyglycerin (8) : epoxidized FAME soybean oil (14b) was varied.

Esters (15a) were obtained from glycerol and 851 g epoxidized sunflower oil (13a). Viscous yellow liquid. Yield 916 g. IR (neat), ν (cm⁻¹): 3452 (OH), 2922, 2852 (CH), 1731 (C=O), 1248, 1174, 1058 (C–O), 725 (CH₃); ¹H-NMR (DMSO-d₆), δ (ppm): 0.82-0.88 (CH₃), 1.17-1.32 (CH₂acid), 1.34-1.42 (CH₂CHOacid), 1.47-1.55 (βCH₂acid), 1.92-2.05 (CH₂CH=CHacid), 2.17-2.32 (αCH₂acid), 2.78-2.88 (OCH₃CHOacid), 3.44-5.50 (CH₂glycerol+OH+CH=CH+CH₂glycerol).

Esters (15b) were obtained from glycerol and 857 g epoxidized soybean oil (13b). Viscous yellow liquid. Yield 923 g. IR (neat), ν (cm⁻¹): 3395 (OH), 2922, 2852 (CH), 1732 (C=O), 1247, 1174, 1056 (C–O), 723 (CH₃); ¹H-NMR (DMSO-d₆), δ (ppm): 0.79-0.88 (CH₃), 1.16-1.29 (CH₂acid), 1.34-1.40 (CH₂CHOacid), 1.45-1.55 (βCH₂acid), 1.92-2.05 (CH₂CH=CHacid), 2.21-2.32 (αCH₂acid), 2.78-2.88 (OCH₃CHOacid), 3.44-5.55 (CH₂glycerol+OH+CH=CH+CH₂glycerol).

Esters (16a) were obtained from glycerol and 281 g epoxidized soybean oil FAME (14a). Viscous yellow liquid. Yield 308 g. IR (neat), ν (cm⁻¹): 3383 (OH), 2922, 2852 (CH), 1732 (C=O), 1247, 1120, 1047 (C–O), 723 (CH₃); ¹H-NMR (DMSO-d₆), δ (ppm): 0.80-0.89 (CH₃), 1.16-1.31 (CH₂acid), 1.34-1.40 (CH₂CHOacid), 1.45-1.55 (βCH₂acid), 1.92-2.05 (CH₂CH=CHacid), 2.21-2.32 (αCH₂acid), 2.70-2.78 (OCH₃CHOacid), 3.44-5.55 (CH₂glycerol+OH+CH=CH+CH₂glycerol).

Esters (16b) were obtained from glycerol and 290 g epoxidized soybean oil FAME (14b). Viscous yellow liquid. Yield 317 g. IR (neat), ν (cm⁻¹): 3382 (OH), 2922, 2852 (CH), 1731 (C=O), 1246, 1176, 1047 (C–O), 725 (CH₃); ¹H-NMR (DMSO-d₆), δ (ppm): 0.80-0.90 (CH₃), 1.16-1.31 (CH₂acid), 1.35-1.42 (CH₂CHOacid), 1.47-1.57 (βCH₂acid), 1.95-2.03 (CH₂CH=CHacid), 2.20-2.32 (αCH₂acid), 2.76-2.84 (OCH₃CHOacid), 3.44-5.45 (CH₂glycerol+OH+CH=CH+CH₂glycerol).

Esters (17a) were obtained from glycerol and 851 g epoxidized sunflower oil (13a). Viscous yellow liquid. Yield 1075 g. IR (neat), ν (cm⁻¹): 3346 (OH), 2922, 2852 (CH), 1733 (C=O), 1247, 1095, 1045 (C–O), 675 (CH₃); ¹H-NMR (DMSO-d₆), δ (ppm): 0.82-0.88 (CH₃), 1.17-1.32 (CH₂acid), 1.36-1.42 (CH₂CHOacid), 1.47-1.55 (βCH₂acid), 1.92-2.05 (CH₂CH=CHacid), 2.21-2.31 (αCH₂acid), 2.78-2.88 (OCH₃CHOacid), 3.44-5.54 (CH₂glycerol+OH+CH=CH+CH₂glycerol).

Esters (17b) were obtained from glycerol and 857 g epoxidized soybean oil (13b). Viscous yellow liquid. Yield 1093 g. IR (neat), ν (cm⁻¹): 3394 (OH), 2922, 2852 (CH), 1732 (C=O), 1247, 1145, 1047 (C–O), 725 (CH₃); ¹H-NMR (DMSO-d₆), δ (ppm): 0.82-0.90 (CH₃), 1.16-1.33 (CH₂acid), 1.35-1.42 (CH₂CHOacid), 1.45-1.56 (βCH₂acid), 1.95-2.05 (CH₂CH=CHacid), 2.21-2.34 (αCH₂acid), 2.72-2.76 (OCH₃CHOacid), 3.34-5.45 (CH₂glycerol+OH+CH=CH+CH₂glycerol).

Esters (18a) were obtained from glycerol and 281 g epoxidized soybean oil FAME (14a). Viscous dark yellow liquid. Yield 489 g. IR (neat), ν (cm⁻¹): 3334 (OH), 2922, 2852 (CH), 1732 (C=O), 1247, 1085, 1041 (C–O), 703 (CH₃); ¹H-NMR (DMSO-d₆), δ (ppm): 0.82-0.90 (CH₃), 1.16-1.33 (CH₂acid), 1.35-1.42 (CH₂CHOacid), 1.45-1.56 (βCH₂acid), 1.95-2.05 (CH₂CH=CHacid), 2.21-2.34 (αCH₂acid), 2.72-2.76 (OCH₃CHOacid), 3.34-5.45 (CH₂glycerol+OH+CH=CH+CH₂glycerol).

Esters (18b) were obtained from glycerol and 290 g epoxidized soybean oil FAME (14b). Viscous dark yellow liquid. Yield 496 g. IR (neat), ν (cm⁻¹): 3357 (OH), 2922, 2852 (CH), 1731 (C=O), 1247, 1091, 1043 (C–O), 723 (CH₃); ¹H-NMR (DMSO-d₆), δ (ppm): 0.82-0.91 (CH₃), 1.16-1.31 (CH₂acid), 1.35-1.42 (CH₂CHOacid), 1.47-1.56 (βCH₂acid), 1.95-2.05 (CH₂CH=CHacid), 2.21-2.32 (αCH₂acid), 2.72-2.76 (OCH₃CHOacid), 3.34-5.50 (CH₂glycerol+OH+CH=CH+CH₂glycerol).

Esters (18c) were obtained from glycerol 275 g (1 mol) and 580 g (2 mol) of epoxidized soybean oil FAME (14b). Viscous dark yellow liquid. Yield 715 g. IR (neat), ν (cm⁻¹): 3340 (OH), 2925, 2856 (CH), 1732 (C=O), 1242, 1089, 1053 (C–O), 723 (CH₃); ¹H-NMR (DMSO-d₆), δ (ppm): 0.80-0.90 (CH₃), 1.17-1.30 (CH₂acid), 1.33-1.44 (CH₃CHOacid), 1.45-1.53 (βCH₂acid), 1.95-2.05 (CH₂CH=CHacid), 2.21-2.32 (αCH₂acid), 2.70-2.75 (OCH₃CHOacid), 3.34-5.50 (CH₂glycerol+OH+CH=CH+CH₂glycerol).

Esters (18d) were obtained from glycerol 147.5 g (0.5 mol) and 507.5 g (1.75 mol) epoxidized soybean oil FAME (14b). Viscous dark yellow liquid. Yield 526 g. IR (neat), ν (cm⁻¹): 3357 (OH), 2922, 2852 (CH), 1731 (C=O), 1247, 1091, 1043 (C–O), 723 (CH₃); ¹H-NMR (DMSO-d₆), δ (ppm):
Esters (18) were obtained from polyglycerol 147.5 g (0.5 mol) and 1015 g (3.5 mol) epoxidized soybean oil FAME (14b). Viscous dark yellow liquid. Yield 963 g.

$\nu (\text{cm}^{-1})$: 3357 (OH), 2922, 2852 (CH), 1731 (C=O), 1247, 1091, 1043 (C–O), 723 (CH=); $\delta (\text{ppm})$:

- 0.81-0.92 ($\text{CH}_3$), 1.16-1.30 ($\text{CH}_{2\text{acid}}$), 1.35-1.42 ($\text{CH}_2\text{CHO}_{\text{acid}}$), 1.45-1.55 ($\beta\text{CH}_2\text{acid}$), 1.95-2.05 ($\text{CH}_2\text{CH=CH}_{\text{acid}}$), 2.21-2.32 ($\alpha\text{CH}_2\text{acid}$), 2.70-2.76 ($\text{OCHCH}_2\text{CHO}_{\text{acid}}$), 3.34-5.45 ($\text{CH}_2\text{glycerol} + \text{OH} + \text{CH=CH} + \text{CH}_{\text{glycerol}}$).

3.3. Emulsifying properties determination of esters (15-18)

The emulsification ability was evaluated visually in time of spontaneous stratification (destruction) of the emulsion column in a high vessel after emulsification [15,36,42]. The volume of the separated disperse phase was fixed at regular time intervals. For the stability measure of the emulsion, a “half-life” was accepted – this is the time during which 50% of the dispersed phase is separated.

In the described procedure, sunflower refined deodorized oil was a fat phase, the aqueous phase was distilled water. A sample of the emulsifier (1.2 g) was dissolved in 96 ml of oil at 60 °C and agitation at 700 rpm, then water (24 ml) was added and the mixture was held for 15 minutes. For 1:1 emulsions the volumes of oil and water were 60 ml.

A small amount of a neutral fat-soluble dye (1-(phenylazo)-naphtole-2) was added to 1 ml of the resulting emulsion and the type of emulsion was determined with a microscope at x100 magnification.

4. Conclusions

Herein, we presented the new combination of renewable raw materials based on vegetable oil derivatives in the synthesis of polyglycerol oligo- and polyesters. The qualitative spectral structural and functional analysis of the products, obtained by the interaction of glycerin, its oligomers with epoxy derivatives of triglycerides, methyl esters of unsaturated fatty acids, which are part of sunflower and soybean oil, showed that the main processes were the opening of epoxide cycles, transesterification of esters, and glycerol condensation. The greatest emulsifying activity was found for products derived from epoxidized soybean oil FAME and polyglycerol. These compounds also effectively regulated the viscosity of the oil-water emulsions. Thus, epoxy derivatives of vegetable oils are new functional analogues of ricinoleic acid in the preparation of emulsifiers in a series of polyglycerol esters. Further optimization of the latter composition will help improve their surface-active properties for practical use.

Supplementary Materials: The IR, $^1$H-NMR spectra, MS-analysis data of the obtained substances are available online at www.mdpi.com/link.

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


Sample Availability: Samples of the compounds 13-18 are available from the authors.