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

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

21   **Keywords:** vegetable oils; emulsifiers; triglycerides; FAME; epoxidized fatty acids; glycerol;
22   polyglycerol; PGPR; renewable raw materials.
23

24   **1. Introduction**

25   Vegetable oils are considered as one of the most important renewable raw materials in the
26   manufacturing of surfactants for various purposes, biofuels, chemical reagents, etc. The cleavage of
27   the triglycerides **1** included in their composition by different nucleophilic reagents is the major
28   chemical basis of the technologies for processing them in fatty acids **2**, their salts, esters **3**, amides **4**
29   [1-7] (Scheme 1).
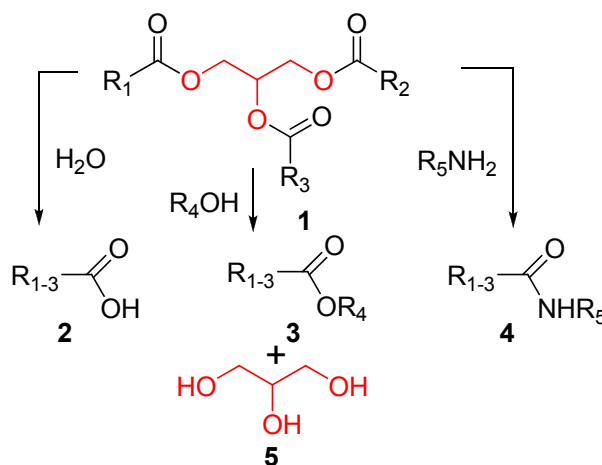
30
31   **Scheme 1**. Cleavage of vegetable oil triglycerides by nucleophilic reagents.

32   A common feature of the above mentioned reactions is the formation of glycerin **5** – the
33   compound, also of green chemistry interest, as a safe, renewable solvent and reagent [9-13].
34   Synthetic transformation of unsaturated fatty acid hydrocarbon radicals is also given great
35   attention [1,3,4,6,7,14]. Among the most commonly used in oleochemistry vegetable oils,
36   triglycerides of which contain fragments of unsaturated fatty acids, are sunflower, soybean,
37   rapeseed, castor, etc. In particular, oleic and linoleic acids are the main components of the fatty acid
38   composition of sunflower and soybean oils (Table 1) [6,15].

39   **Table 1.** Fatty acid composition of some vegetable oils.

Oil	16:0 [1]	18:0	18:1	18:2	18:3
Sunflower	7 [2]	4	18	71	0
Soybean	12	3	23	55	7

40   [1] 16:0 – palmitic acid, 18:0 – stearic acid, 18:1 – oleic acid, 18:1 – linoleic acid, 18:3 – linolenic acid,. [2] wt %.

41
42   A significant number of examples of structural and functional modification of unsaturated fatty
43   acids on multiple bonds are known, but the most interesting are epoxidation reactions of both the
44   acids themselves and their derivatives [1,3,4,7,14-27] (Scheme 2).

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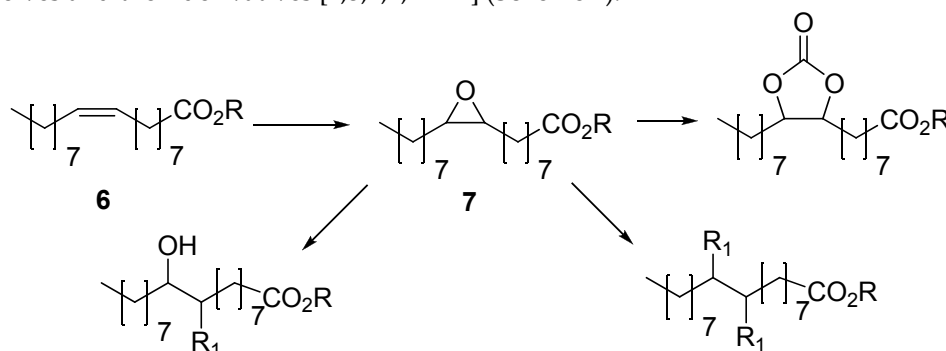
46   **Scheme 2**. Epoxidation of unsaturated acids of vegetable oils and some directions for the oxirane
47   cycle opening (on the example of oleic acid **6** and its epoxide **7**; R = H, Alk; R_1 = HO, R_2O, R_3COO,
48   NHR_4).

49
50   Epoxidized vegetable oils are used as components of polyurethane compositions [17],
51   plasticizers of polymers [18], etc.
52   One of the many directions of industrial chemical transformation of glycerin **5** is its
53   oligomerization, leading to the formation of polyglycerols **8** - a mixture of oligomeric polyols [9,12]
54   (Scheme 3), which are used in various ways as independent substances [28], and as synthetic blocks
55   in processes of polycondensation, for example, in the preparation of polyglycerol polyricinoleate
56   (PGPR). PGPR is widely used in the food industry as a safe emulsifier (E-476) in water-in-oil
57   emulsions, in particular in the production of chocolate. The manufacturing of PGPR is based on
58   polycondensation of polyglycerol **8** with polyricinoleic acid **10**, which in turn is the product of
59   condensation of ricinoleic acid **9**, derived from castor oil triglycerides [29-35] (Scheme 3).

60
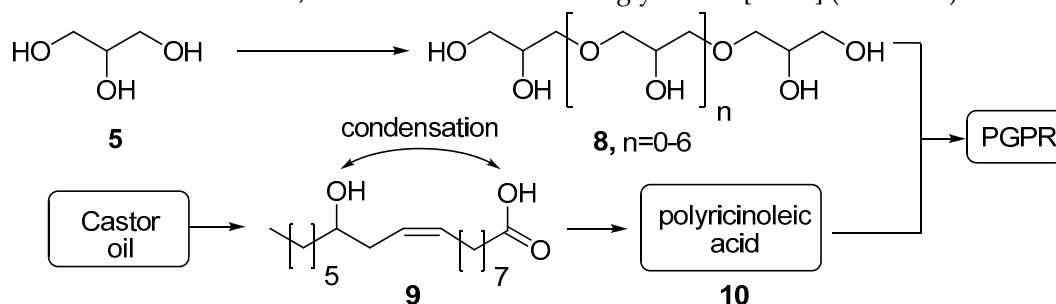
61   **Scheme 3.** The synthesis of polyglycerol polyricinoleate.

62   However, castor oil, as an oleochemical natural resource, is less available than, for example,
63   sunflower or soybean oils. Therefore, epoxidized derivatives of unsaturated acids of these oils can be
64   considered as new renewable raw materials analogues of ricinoleic acid due to easy opening of
65   oxirane rings to form hydroxyl or ester groups.
66   In the course of our work on the search for new environmentally friendly emulsifiers in the
67   series of polyglycerol esters [36], in this paper we present the results of studies on the synthesis and
68   emulsifying properties of new polyglycerol polyricionoleate analogs based on the products of
69   interaction of glycerol and polyglycerol with epoxidized methyl esters or triglycerides of
70   unsaturated fatty acids from sunflower and soybean oils.
71

72   **2. Results and discussion**

73   *2.1. Epoxidation of triglycerides and methyl esters of sunflower (soybean) oils unsaturated fatty acids*

74
75   The availability of sunflower and soybean oil causes their widespread use in the oleochemical
76   industry, in particular, in the production of biofuel (biodiesel) through the transesterification of
77   triglycerides in their composition with methanol [1]. In our work, the preparation of fatty acids
78   methyl esters (FAME) was carried out in the presence of sodium methoxide (Scheme 4).

11a,b

MeOH / MeONa   -   HO OH
                          OH

12a,b
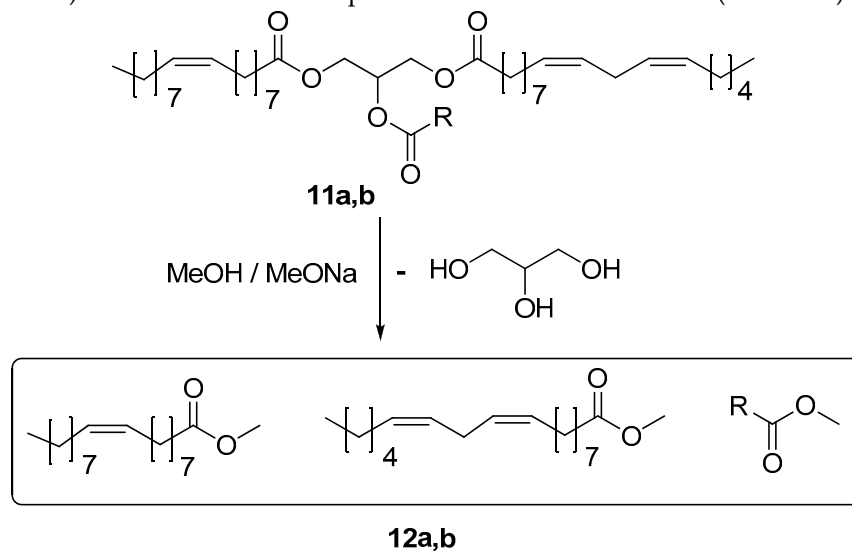
79   **a** - sunflower oil; **b** - soybean oil; R - saturated radicals

80   **Scheme 4.** Methanolysis of sunflower (soybean) oils triglycerides . (Idealized ester structures, including only
81   the residues of unsaturated oleic and linoleic acids, are presented).

82   Today, a large number of methods exist for the epoxidation of vegetable oils and their
83   derivatives [17-19,21-24,38]. However, many of them require the use of rare and / or expensive
84   catalysts, sometimes additional costs are required for the isolation and purification of the final
85   product. The most effective and simple method is the performic acid using as an epoxidizing
86   reagent, which is formed in situ from hydrogen peroxide and formic acid [17,21,38].
87   In preliminary experiments it was found that the optimum molar ratio of the reagents was 0.55
88   (oil, or 1.65 moles FAME) : 1.10 (HCOOH) : 3.00 (H_2O_2). Hydrogen peroxide was added in four doses
89   at 60 ° C. The degree of conversion of unsaturated fatty acid derivatives was controlled by iodine
90   values and oxirane oxygen content. After 15 h from the start of epoxidation (on the example of
91   sunflower oil **11a** or its ester **12a**), oxirane oxygen content was maximum, while the iodine value was
92   minimal and no further significant changes were occurred (Table 2). Thus, under these conditions,
93   the maximum conversion of oil or ether over multiple bonds was achieved.
94

95   **Table 2.** Reaction time optimization for the epoxidation of sunflower oil **11a** and its FAME **12a**.

Entry	Reaction time, h	Epoxidation of 11a		Epoxidation of 12a	
		Oxirane oxygen content, mass %	Iodine value, g I$_2$/100 g	Oxirane oxygen content, mass %	Iodine value, g I$_2$/100 g
1	0	-	158.9	-	153.7
2	3	1.6	116.8	1.8	120.1
3	6	3.8	78.5	3.5	98.3
4	9	4.5	50.1	4.7	75.3
5	12	6.5	40.7	5.3	54.2
6	15	7.1	21.5	7.0	30.6
7	18	7.0	20.3	6.5	29.5

96

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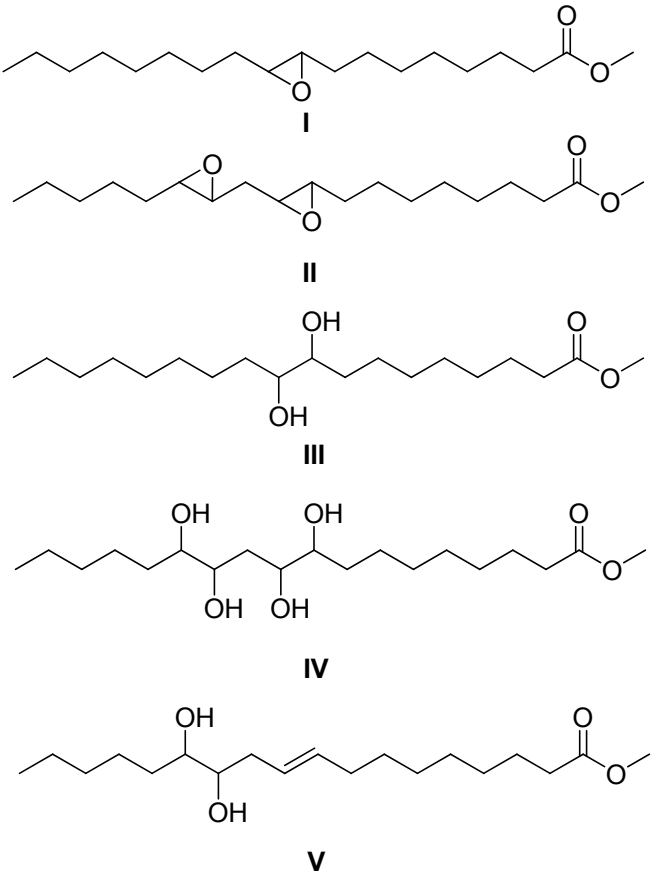

103
104   **Figure 1**. Structure of the major epoxidation products sunflower oil FAME **12a**.

105

106   **Table 3.**   Major products of sunflower oil FAME (**12a**) oxidation.

Compound	Formula	MW	Molecular ion peaks cluster, m/z (intensity, %)
I	$C_{19}H_{36}O_3$	312.49	312 (100.0), 313 (21.1), 314 (2.6)
II	$C_{19}H_{34}O_4$	326.47	326 (100.0), 327 (21.1), 328 (2.9)
III	$C_{19}H_{38}O_4$	330.50	330 (100.0), 331 (21.1), 332 (2.9)
IV	$C_{19}H_{38}O_6$	362.50	362 (100.0), 363 (21.2), 364 (3.3)
V	$C_{19}H_{36}O_4$	328.49	328 (100.0), 329 (20.5), 330 (2.9)

107
108   Thus, in the epoxidation process partial opening of the oxirane rings was occured
109   simultaneously with the formation of diol fragments (Scheme 5,6).
110
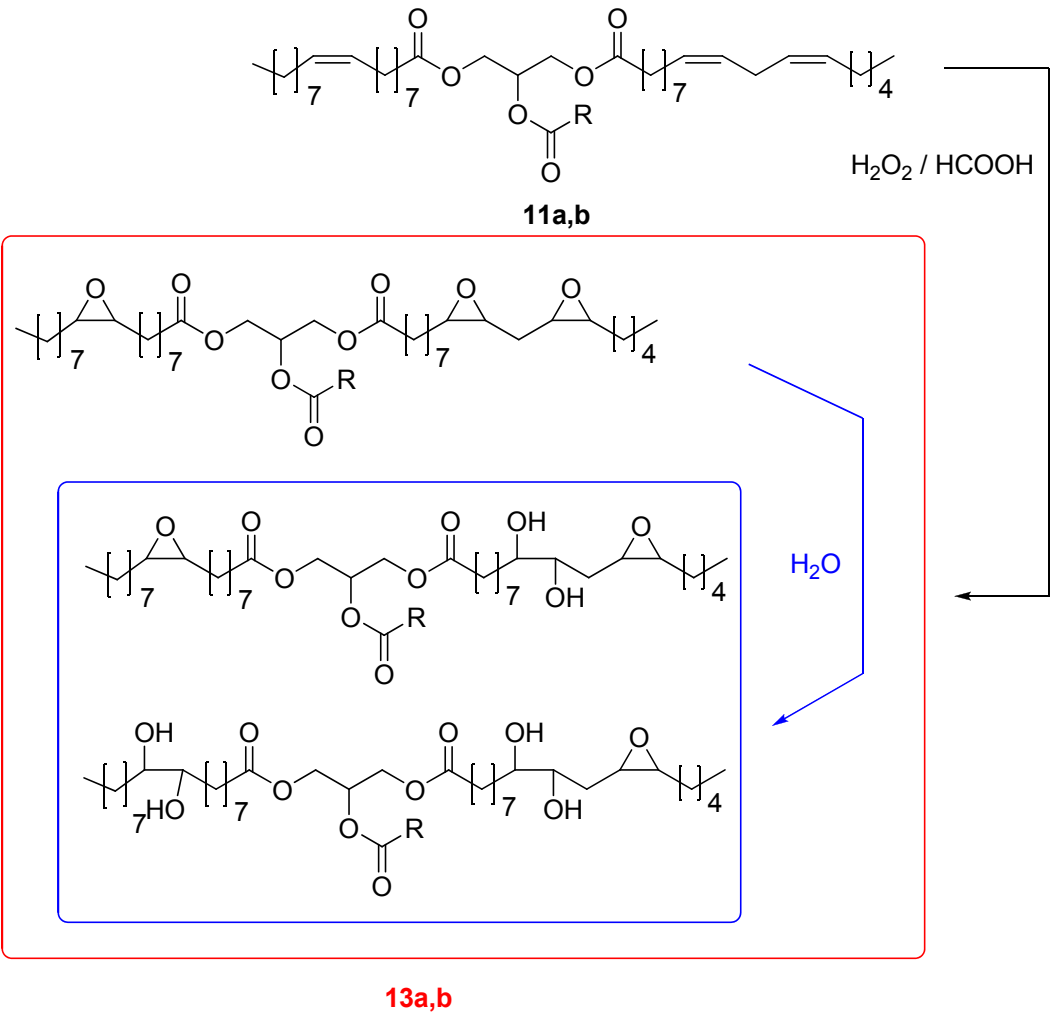
111   **a** - sunflower oil; **b** - soybean oil; R - saturated radicals

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

113
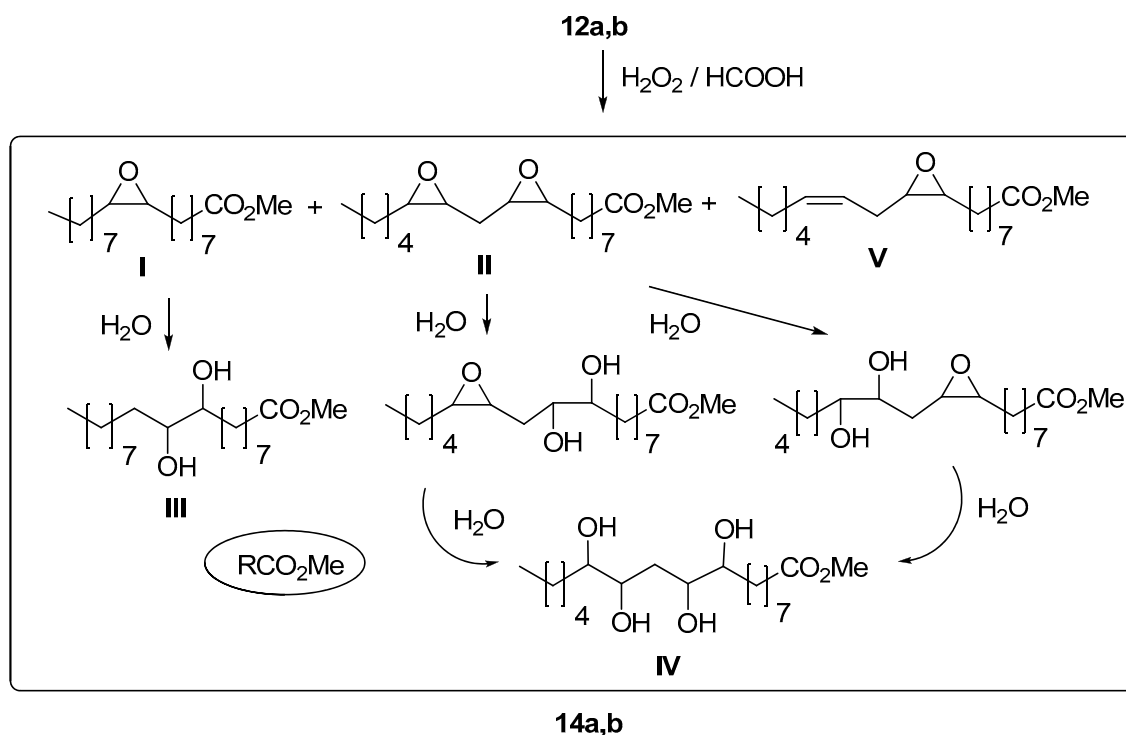
Scheme 6. Epoxidation of FAME (**12**) and the structure of some products.

116   The formation of hydroxyl-containing compounds was not an undesirable process, since these
117   substances are also formal synthetic equivalents of ricinoleic acid, like epoxy derivatives.
118   The structures of the substances, included in the epoxidized oils and FAME composition, were
119   also confirmed by IR- and ^{1}H NMR spectroscopy data. In the IR spectra of compounds **13a,b** and
120   **14a,b** there are intensive bands of C = O bonds at 1750-1700 cm^{-1} and ester fragments at 1225-1050
121   cm^{-1}. In comparison with the spectra of the initial oils and FAME, the characteristic bands for the
122   epoxide cycle appeared in the region of 1240-1260 cm^{-1} (the symmetric stretching vibrations of the
123   ring) and 820-830 cm^{-1} (asymmetric ones). The broadened band at 3550-3200 cm^{-1} range
124   corresponded to the hydroxyl groups formed as a result of certain oxirane cycle opening. The bands
125   of the olefin moiety C-H bond at 725-721 cm^{-1} are partially remained.
126   In ^{1}H NMR spectra of epoxidized derivatives, there are signals sets of protons from alkyl
127   groups of acyl residues, oxirane cycle(s), CH groups of diol fragments (in the products of the latter
128   ring opening), and CH-, CH$_2$ - glycerol protons for epoxidized triglycerides or a singlet the
129   methoxycarbonyl group FAME. A set of triplets of terminal methyl groups was in the range of
130   0.81-0.89 ppm. The assignment of CH$_2$-groups multiplets was made on the basis of the literature data
131   for such compounds [17,21,38]. The proton signals of acyl α-methylene groups are observed at
132   2.19-2.29 ppm as a set of triplets, the multiplet of protons of β-methylene fragments was observed at
133   1.38-1.52 ppm. The proton signals of the methylene groups located next to the oxirane rings were in
134   the range 1.24-1.45 ppm, and between them (for linolenic acid derivatives) - at 2.61-2.75 ppm. The
135   proton multiplets of the other methylene units was observed at 1.13-1.30 ppm. The broadened
136   singlet at 4.70 ppm was corresponded to the protons of OH-groups and indicated to the presence in
137   the mixture of dihydroxy derivatives, formed during the opening of the epoxide cycle. Multiplets in
138   the areas 3.98-4.28 and 5.15-5.21 ppm in the spectra of epoxidized oils were refered to protons of
139   methylene and methine groups of glycerol. The singlet of the carbomethoxy group of epoxidized
140   FAME was about 3.58 ppm. The proton signals of multiple bonds in the acyl residues of unsaturated
141   fatty acids were also present in the spectra. Comparison of iodine values for epoxidized derivatives
142   with the same of oils and FAME was indicated the conservation of 5-7% of unsaturated fatty acid
143   residues (Table 4).

144

145   **Table 4.** Some characteristics of vegetable oils, FAME and epoxidized derivatives.

Compound	Iodine value, g I$_2$/100g	Acid value, mg KOH/g	Saponification value, mg KOH/g
Sunflower oil (**11a**)	158.9	0.1	188.9
Soybean oil (**11b**)	172.3	0.3	192.3
Sunflower oil FAME (**12a**)	153.7	0.2	203.0
Soybean oil FAME (**12b**)	169.8	0.2	198.4
Epoxidized sunflower oil (**13a**)	15.5	0.4	197.3
Epoxidized soybean oil (**13b**)	15.0	0.2	196.0
Epoxidized sunflower oil FAME (**14a**)	13.0	0.4	199.1
Epoxidized soybean oil FAME (**14b**)	10.5	0.5	192.9

146

147   The saponification and acid values were changed insignificantly, so the hydrolysis of the ester
148   groups did not occur under the epoxidation reaction conditions. The resulting epoxy derivatives
149   without further purification were used in the synthesis of glycerol and polyglycerol esters.
150

151   *2.2. Condensation of vegetable oils epoxidized derivatives with glycerol and polyglycerol.*

152
153   It was noted above that the preparation of PGPR generally includes the following steps: 1)
154   synthesis of polyglycerol, 2) preparation of ricinoleic acid, 3) its polycondensation, 4) condensation
155   of polyglycerol and polyricinoleic acid. A three-step process is known based on the
156   polycondensation of ricinoleic acid in situ in the reaction with polyglycerol in the presence of
157   alkaline catalysts in inert atmosphere at high temperatures [39]. These conditions were chosen as
158   model in the study of the interaction of epoxidized triglycerides and methyl esters of unsaturated
159   fatty acids with glycerol and polyglycerol. Earlier, we have obtained esters of fatty acids and
160   polyglycerol by this method [36]. On the one hand, glycerol can polymerize into polyglycerol under
161   these conditions, and, thus, the number of stages is reduced. On the other hand, the presence of
162   polyglycerol fragments and fatty acid residues in the reaction products suggests appearance of
163   emulsifying properties, as for PGPR.
164   Primarily, we have investigated the interaction of epoxidized triglycerides (**13**) and methyl
165   esters (**14**) of sunflower (**a**) and soybean (**b**) oils fatty acids with glycerol at reagent molar ratio 1 : 1.
166   The functionality of the major compounds, which were part of **13,14** (Figure 1), made it possible to
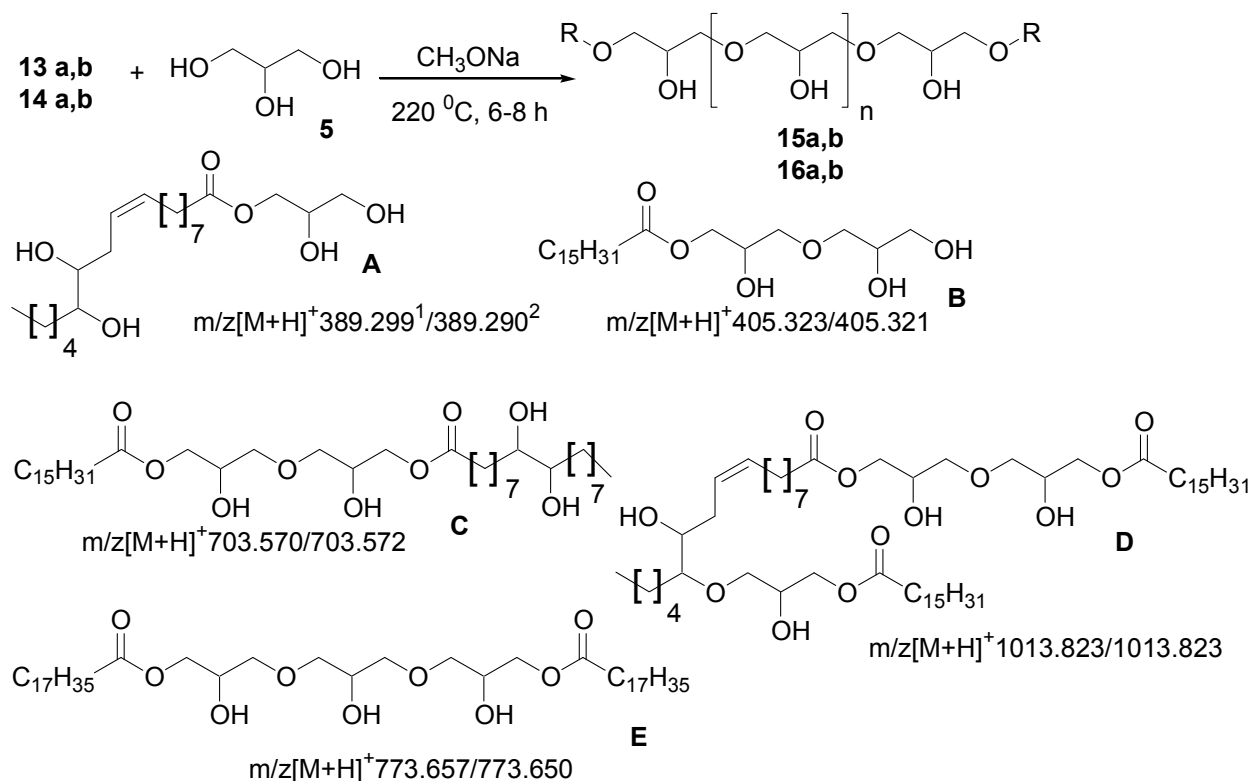167   suggest the following synthetic routes:
168   i) opening of oxirane rings resulting from the reaction of epoxy derivatives with glycerol or
169   hydroxyl-containing triglycerides and FAME;

170   ii) transesterification of triglycerides or FAME with glycerol or hydroxyl-containing
171   triglycerides and FAME;
172   iii) polycondensation of glycerol and similar reactions of polyglycerols in the directions (i) or
173   (ii).
174   Gas chromatography analysis followed by electron impact mass-spectrometric detection was
175   not possible due to the complex composition of the mixture and the presence of oligomeric
176   compounds. The use of high-performance liquid chromatography was also inexpedient for the same
177   reason. Therefore, to evaluate the qualitative composition of the products and confirm the proposed
178   directions of epoxy derivatives interaction with glycerol, we used electrospray ionization high
179   resolution mass spectrometry (ESI-HRMS) with direct input of samples, despite certain difficulties in
180   the analysis of spectra. It should be noted that the fragmentation of molecular ions was very
181   insignificant under these ionization conditions in comparison with electron impact.
182   In the mixture of products **15-16** dihydroxyoleic acid monoglyceride **A** was identified as a result
183   of transesterification. The presence of polyglycerol esters **B-E** confirmed both the polymerization of
184   glycerol and the subsequent transesterification. The formation of ester **D** also occurred as a result of
185   the oxirane ring disclosure in epoxyderived linolenic acid (Scheme 7).

186
187

188   **Scheme 7**. Epoxidation of FAME (**12**) and the structure of some products
189   ([1] calculated for molecular formula+H^{+} / [2]Founded by MS-ESI).

190

191   Similar processes occurred during the interaction of epoxidized derivatives **13-14** and
192   polyglycerol. The reaction products of epoxidized soybean oil FAME with polyglycerol **18b-e** were
193   obtained at different molar ratios of the reagents in order to better assess their surfactant properties.
194   The products composition in the reactions of the epoxy derivatives **13-14** with polyglycerol was also
195   analyzed by ESI-HRMS (Scheme 8).
196

13a,b + HO—[...]—OH $\xrightarrow[220\ ^0C,\ 6\text{-}8\ h]{CH_3ONa}$ R—O—[...]—O—R
14a,b

8, n=0-6   **17a,b**
                                                                            18a-e

O
m/z[M+H]$^+$973.795/973.792

D
m/z[M+H]$^+$1013.823/1013.823

P
m/z[M+H]$^+$1105.831/1105.834

Q
m/z[M+H]$^+$1149.898/1149.897

E-N

E $R_1 = R_2 = C_{17}H_{35}CO$, H, n = 1   m/z[M+H]$^+$773.657/773.650
F $R_1 = C_{15}H_{31}CO$, R_2 = H, n = 1   m/z[M+H]$^+$479.351/479.358
G $R_1 = CH_3(CH_2)_4(CHOH)_2CH_2(CHOH)_2(CH_2)_7CO$, R_2 = H, n = 2   m/z[M+H]$^+$645.409/645.406
H $R_1 = CH_3(CH_2)_7(CHOH)_2(CH2)_7CO$, R_2 = H, n = 3   m/z[M+H]$^+$687.455/687.453
I $R_1 = C_{15}H_{31}CO$, R_2 = H, n = 5   m/z[M+H]$^+$775,508/775.505
J $R_1 = CH_3(CH_2)_4(CHOH)_2CH_2(CHOH)_2(CH_2)_7CO$, R_2 = H, n = 7   m/z[M+H]$^+$1015.599/1015.590
K $R_1 = CH_3(CH_2)_4(CHOH)_2CH_2CH=CH(CH_2)_7CO$,
   $R_2 = CH_3(CH_2)_7(CHOH)_2(CH_2)_7CO$, n = 3   m/z[M+H]$^+$687.549/687.541
L $R_1 = C_{15}H_{31}CO$, $R_2 = CH_3(CH_2)_7(CHOH)_2(CH_2)_7CO$, n = 2   m/z[M+H]$^+$851.648/851.646
M $R_1 = C_{15}H_{31}CO$, $R_2 = CH_3(CH_2)_7(CHOH)_2(CH_2)_7CO$, n = 3   m/z[M+H]$^+$923.667/923.667
N $R_1 = C_{15}H_{31}CO$, $R_2 = C_{17}H_{35}CO$, n = 5   m/z[M+H]$^+$1074.085/1074.087

17: epoxidized sunflower oil (**a**), soybean oil (**b**)
18: epoxidized sunflower oil FAME (**a**), soybean oil FAME (**b-e**)
R - residues of fatty acids and its derivatives

197
198   **Scheme 8**. Interaction of epoxy derivatives **13-14** with polyglycerol.
199

200   Thus, as a result of the transesterification reaction, monoesters of fatty acids and polyglycerol
201   (**F,G,H,I,J**) with different degrees of polymerization were obtained. The presence of derivatives of
202   hepta- (**I**) and nonaglycerol (**J**) indicated an increase in the degree of polymerization under the
203   reaction conditions. Diesters of diglycerol (**K**), triglycerol (**E**), tetraglycerol (**L**) and pentaglycerol
204   (**M**), as well as branched chain oligomers (**D,N,O,P**) also were found in the mixture.
205   Of course, based on the ESI-HRMS data, other ethers were also the products of the interaction of
206   epoxidized derivatives **13-14** with glycerol or polyglycerol. Nevertheless, the selected identified
207   compounds unambiguously characterized the directions of the proceeding reactions.
208   The qualitative structural and functional composition of products **15-18** was characterized by
209   the position of absorption bands in IR spectra and signals in ^{1}H NMR spectra. In the IR spectra of the

210 obtained substances, there were intense characteristic absorption bands of the ester fragment at
211 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
212 was an intense wide band associated with the stretching vibrations of the hydroxyl groups.
213 Moreover, for the derivatives **17-18**, obtained from polyglycerol, this band was more intense than for
214 analogous derivatives **15-16**, obtained from glycerol (Figure 2, example of soybean oil derivatives).
215 The absence of absorption bands corresponding to oxirane cycles indicated their disclosure under
216 the reaction conditions, as well as the value of the oxirane number not exceeding 0.1% for all
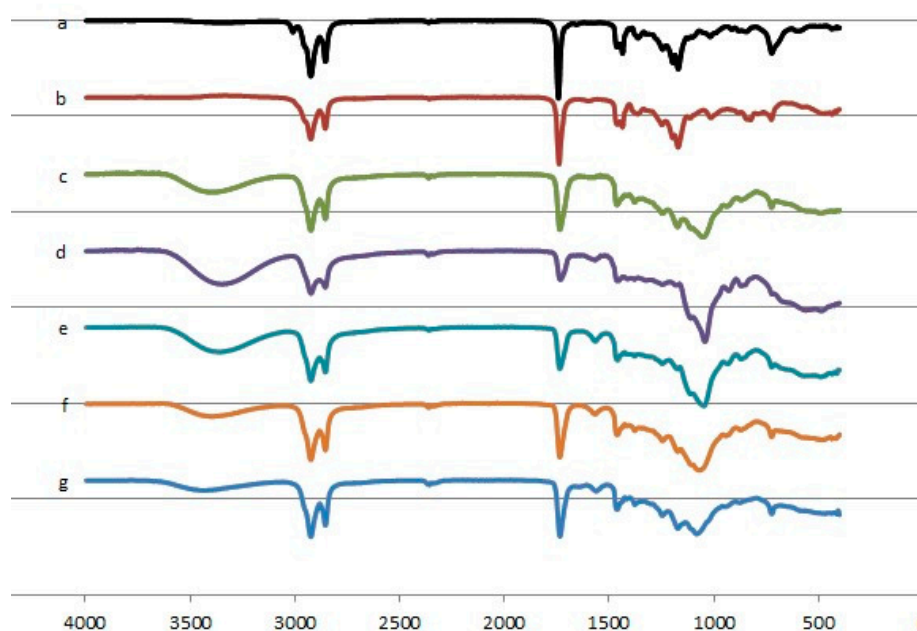217 products **15-18**.

218
219

Figure 2. IR spectra: (**a**) soybean oil FAME **12b**; (**b**) epoxidized soybean oil   FAME **14b**; (**c**) esters from
epoxidized soybean oiFAME 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).

223   In ^{1}H NMR spectra of esters **15-18**, proton signals of α- and β-methylene groups (2.22-2.32 ppm
224 and 1.51-1.53 ppm), the other methylene units (1.19-1.30 ppm), the set of triplets terminal methyl
225 groups (0.82-0.86 ppm) were remained. The complex multiplet of polyglycerol protons were
226 observed in the region 3.4-5.1 ppm. The presence of intense signals in the range 4.6-4.9 ppm,
227 characteristic for PGPR oligomers [32], in the spectra of compounds **15-16** indicated to the
228 polymerization of glycerol under esterification reaction conditions. In the product spectra, unlike the
229 spectra of epoxidized derivatives, there were no signals of protons of oxirane rings in the region of
230 2.8-3.2 ppm, which also confirmed their disclosure.
231   Some characteristics for a complex evaluation of the emulsifying ability were determined for
232 products **15-18**, obtained at 1 : 1 reagents molar ratio (Table 5). The known PGPR emulsifier
233 Palsgaard 4125 was chosen as the reference sample.

234

235

236   **Table 5.** Characteristics of products **15-18**, obtained at 1 : 1 reagents molar ratio.

Comp	Iodine value, g I$_2$/100g	Acid value, mg KOH/g	Saponif value, mg KOH/g	Viscosity, mPa.s (25 °C)		Emulsifying effect (emulsion life half-period, min) [1]		HLB
				Oil:H$_2$O 4:1	Oil:H$_2$O 1:1	Oil:H$_2$O 4:1	Oil:H$_2$O 1:1	
15a	5.3	0.7	173.2	61.1	5.8	10	9	3.9
15b	9.3	1.5	168.2	62.6	10.0	23	28	4.7
16a	6.7	0.5	161.6	56.2	8.6	10	22	5.0
16b	4.7	0.9	147.2	58.3	10.2	4	4	6.5
17a	9.0	1.4	129.8	54.0	5.9	46	16	7.9
17b	3.1	1.1	120.6	62.5	8.2	35	14	9.0
18a	4.6	0.6	83.6	62.1	5.3	58	17	12.2
18b	1.6	0.5	70.6	71.9	6.5	60	27	13.7
PGPR	100.3	2.0	156.2	81.5	48.4	120 [2]	120 [2]	9.5

237   [1] For 1.0 % solution. [2] For 0.5% solution.

238   Compared with the starting epoxy derivatives **13-14**, no significant changes in the iodine, acid
239   and saponification values were observed except for decrease in the saponification value for
240   polyglycerol based products **17,18,** due to their less esterification. The emulsifying activity of the
241   latter was higher than that of the analogous glycerol derivatives **15, 16**. The most interesting was the
242   esters **18b** obtained by reaction of epoxidized FAME soybean oil **14b** with polyglycerol **8**. Therefore,
243   we obtained products **18c-e** with a molar ratio of **8** : **14b** reagents equal to 1 : 2 (**18c**), 1 : 3.5 (**18d**) and
244   1 : 7 (**18e**). The use of a sevenfold excess of FAME **14b** resulted in the formation of highly
245   polymerized product **18e**, insoluble in water and most organic solvents, which did not allow it to be
246   characterized (Table 6).
247

248   **Table 6.** Characteristics of polyglycerol esteres **18c,d**.

Comp (8 : 14b)	Iodine value, g I$_2$/100g	Acid value, mg KOH/g	Saponif value, mg KOH/g	Viscosity, mPa.s (25 °C)		Emulsifying effect (emulsion life half-period, min) [1]		HLB
				Oil:H$_2$O 4:1	Oil:H$_2$O 1:1	Oil:H$_2$O 4:1	Oil:H$_2$O 1:1	
18c (1:2)	3.5	0.5	101.4	75.2	5.2	36	20	10.7
18d (1:3.5)	5.1	0.5	141.4	71.4	5.8	40	19	7.1

249   [1] For 1.0 % solution.
250

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

255   *2.3. Emulsifying ability of esters based on epoxidized vegetable oils derivatives.*

256
257   HLB values were calculated for all synthesized compounds **15-18** [40]. The emulsifying ability
258   and viscosity were determined for emulsions containing (v/v) 80% oil and 20% water (4: 1), as well
259   as 50% oil and 50% (1 : 1) at test concentration 1% (Tables 5,6).

260   It was noted above that the emulsifying ability of products obtained from polyglycerol was
261   higher than for glycerol analogues, and for epoxidized FAME polyglycerol esters, the emulsifying
262   action is higher than for derivatives derived from epoxidized triglycerides. In the transition from an
263   emulsion containing 20% water to an emulsion with higher water content (50%), the emulsifying
264   action of the polyglycerol-based derivatives was reduced by about half, while for the glycerol
265   derivatives this value were not decreased, but for compounds **15b** and **16a** was increased. Thus, the
266   obtained esters, as well as PGPR, stabilized the emulsion with a high water content.
267   Despite the fact that esters **15-18** worse were stabilized emulsions than commercial PGPR
268   Palsgaard 4125, nevertheless, the prospects of their research in this direction is not in doubt.
269   It is known [40] that from the HLB values of the surfactant molecules, their properties can be
270   predicted. The values of HLB of the esters **15-18** shown in Table 5 were in a wide range. Thus, it
271   could be assumed that all glycerol-based esters and epoxidized derivatives of vegetable oils would
272   form a water-in-oil emulsion (w/o), while polyglycerol-based emulsions - an oil-in-water emulsion
273   (o/w). However, with an increase in the degree of esterification, the type of emulsion formed might
274   change. With a visual study of emulsions (an increase of x100), it was found that, for system
275   containing 80% oil and 20% water (4 : 1), regardless of the ester type and difference in HLB, the
276   emulsion w/o predominantly were formed. The images of emulsions of compounds **15b** (HLB = 4.7)
277   (a), **18d** (HLB = 7.1) (b), **17b** (HLB = 10.7) (c) and **18b** (HLB = 13.7) (d) have been showed that the type
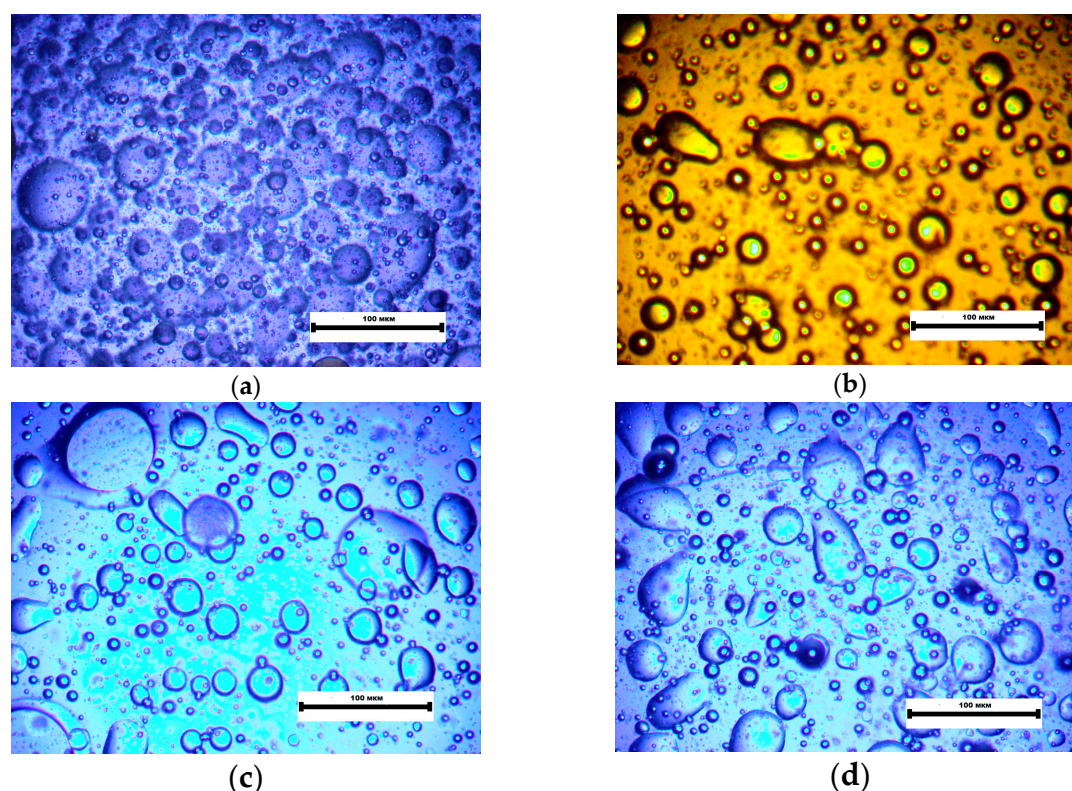278   the emulsion was the same (Figure 3).
279

(a)   (b)

(c)   (d)

280

281   **Figure 3.** Images of emulsions at oil : water ratio 4 : 1 for compounds: (**a**) **15b**; (**b**) **18d**; (**c**) **17b**; (**d**) **18b**

282   For 1 : 1 emulsions and esters, the HLB values of which were higher than 10, the characteristic
283   type was o/w, at lower HLB values - w/o, while with HLB 8-9 both types emulsions were formed
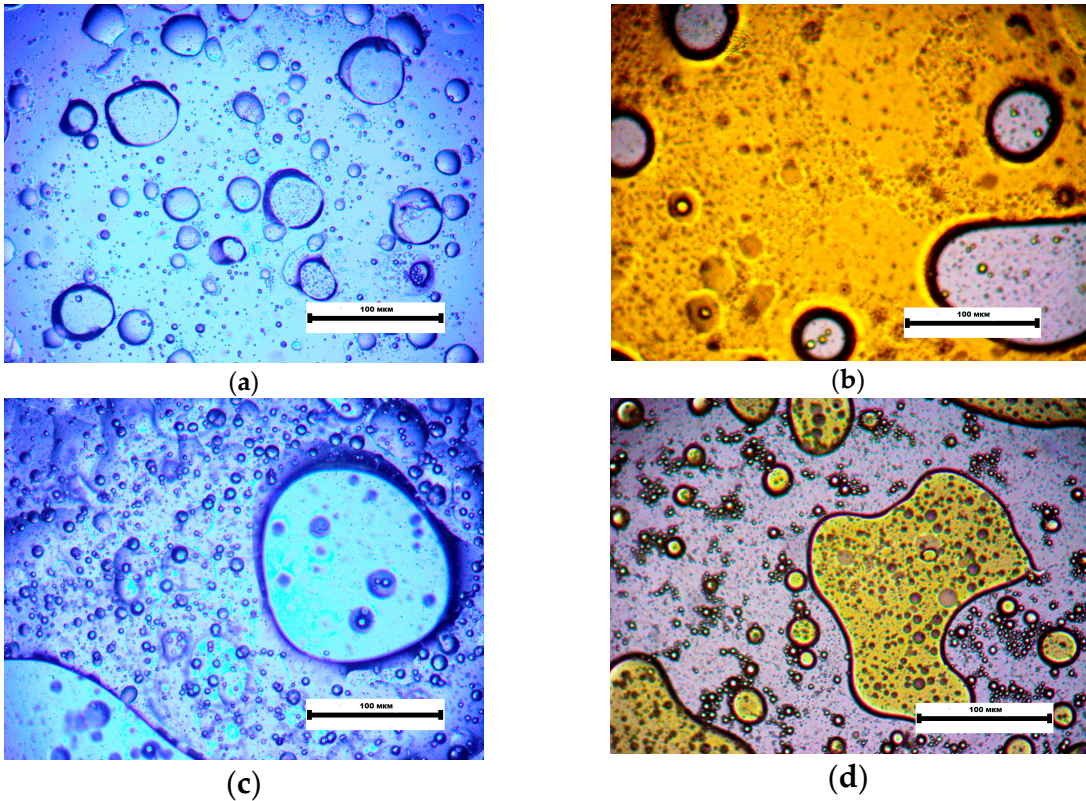284   (Figure 4, the same compounds).
285
286

287

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).
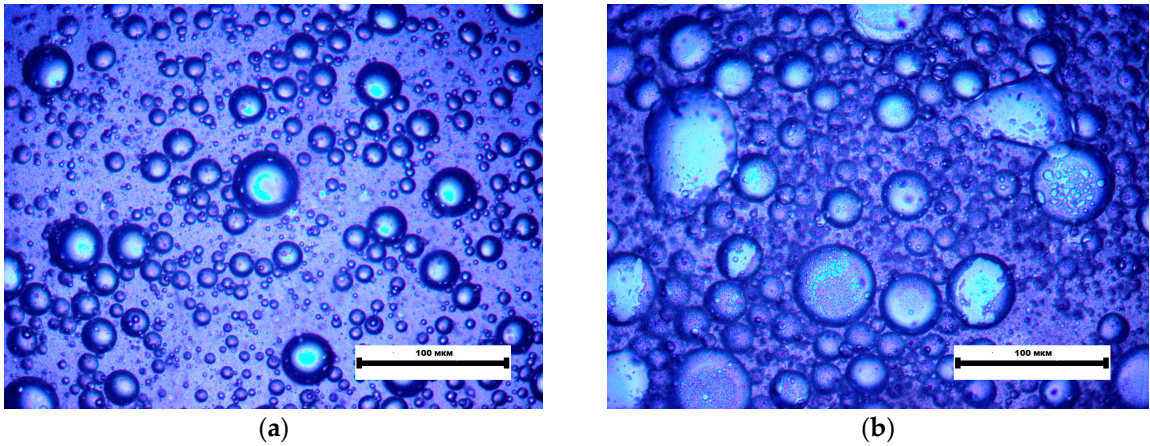

Figure 5. Images of PGPR Palsgaard 4125 emulsion at oil : water ratio: (**a**) 4 : 1; (**b**) 1 : 1.

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).
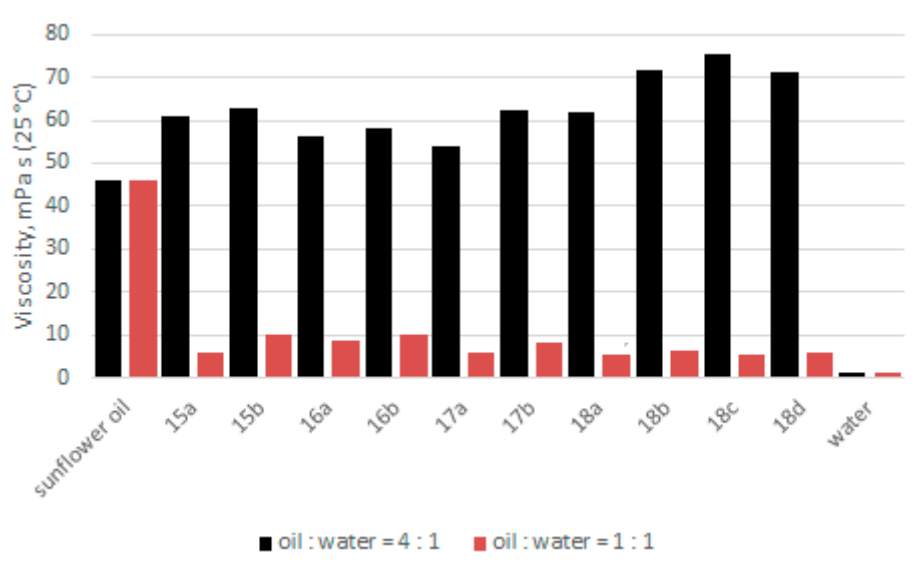
303

Figure 6. Viscosity values for various emulsions and esters.

305   Thus, the new polyglycerol esters obtained by condensing epoxidized derivatives of
306   unsaturated fatty acids of sunflower and soybean oil with glycerol and its oligomers showed
307   emulsifying activity against oil-water emulsions. Further optimization of the structural-functional
308   composition of these esters will make it possible to improve their surface-active properties for
309   practical use.

310   **3. Materials and Methods**

311   *3.1. General.*

312   Sunflower and soybean oils were provided by EFKO GC (Alekseevka, Belgorod region, Russia).
313   Other reagents were purchased from commercial suppliers and used as received.
314   All synthetic procedures were carried out in a batch reactor UNIC -150-2 (Lenz Laborglas
315   GmbH & Co. KG, Wertheim, Germany) with reaction vessel (volume 2 l, with thermostatic jacket
316   and bottom discharge valve) which could be equipped with reflux condenser, dropping funnel, etc.
317   Heating of the reaction mass was carried out with a circulation thermostat Huber CC – 202 with
318   controller Pilot ONE, providing the temperature constancy 0.02 °C (Peter Huber Kältemaschinenbau
319   AG, Offenburg, Germany). The reaction mixture was stirred using an overhead stirrer IKA – Werke
320   Eurostar 40 digital with electronic speed control (Vacuuming was carried out usingchemistry
321   pumping unit PC 3004 VARIO, capable fully solvent recovery, efficient recycling and active
322   environmental protection (Vacuubrandt GmbH + Co. KG, Wertheim, Germany).NMR ^{1}H spectra
323   were registered on Bruker DRX 500 (500.13 MHz) spectrometer in DMSO-d_6, internal standard was
324   TMS. IR spectra were acquired using a Vertex 70 FTIR spectrometer with Platinum ATR (Bruker
325   Ltd., Moscow, Russia). Refractive index measurements were carried out on an IRF-454 BM
326   refractometer (KOMZ JSC, Kazan, Russia). The emulsion type was determined by a Biomed 6
327   microscope (Biomed Ltd., St. Petersburg, Russia) with a ToupCam digital camera (Hangzhou
328   ToupTek Photonics Co. Ltd, Hangzhou, China). Viscosity was measured using sine-wave vibro
329   viscometer SV-10A (A&D Company Ltd., Tokyo, Japan).
330   The acid, saponification, and hydroxyl values of products were calculated by the known
331   techniques, the oxiran oxygen content (value) was determined according to the AOCS official
332   method Cd 9-57 [37]. The molar mass of triglycerides was calculated from saponification value: M =
333   56000 x 3/SV, where M is the triglyceride molar mass g/mol, 56000 is the molar mass of KOH
334   (mg/mol), 3 is the stoichiometric coefficient, SV is the saponification value of triglycerides (mg
335   KOH/g).

336   Gas-chromato-mass spectrometric analysis (GC–MS) was carried out by an Agilent
337 Technologies 7890B GC system with an Agilent Technologies mass selective detector 5977A MSD
338 (Agilent Technologies, Santa Clara, CA, USA). Sample inlet temperature was 280 °C, analytic
339 interface - 150/230 °C. Electron impact ionization energy was 70 eV. Separation was done on a
340 HP-5ms UI capillary column (30 m x 0.250 mm x 0.25 μm, stationary phase - 5%
341 phenylmethylpolysiloxane). The gas flow rate was 1.0 ml/min, with continuous flow. The sample
342 volume was 1 μl; split injection - 20 : 1. Temperature regimes were as follows: isotherm 120 °C (2
343 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/
344 min to 300 °C (3 min). Signal registration was performed using total ion current (TIC) in a scanning
345 region of 35 – 650 m/z. Polyglycerol was pre-silylated with BSFTA (Merck KGaA, Darmstadt,
346 Germany) for 40 min at 70 °C.
347   High performance liquid chromatography with high resolution mass-spectrometric detection
348 under electrospray ionization (HPLC-HRMS-ESI) in combination with UV detection was used to
349 determine the molecular weight of the condensation products of epoxidized derivatives with
350 glycerol and polyglycerol. The device consisted of liquid chromatograph — Agilent 1269 Infinity
351 and time-of-flight high resolution mass detector — Agilent 6230 TOF LC/MS (Agilent
352 Technologies, Santa Clara, CA, USA). Block ionization was double electrospray, detection mass
353 range was from 50 to 2 000   Dalton (positive ions mode). Capillary voltage was 4,0 kV, fragmentor +
354 191 V, skimmer + 66 V, OctRF 750 V. Column Poroshell 120 EC-C18 (4,6 x 50 mm; 2,7 mkm)
355 was used. Gradient eluation: acetonitrile /water (0.1 % formic acid); flow rate: 0,4 mL/min.
356 Software for collection and elaboration of research results was MassHunter Workstation/Data
357 Acquisition V.06.00.

358 *3.2. Synthesis*

359 3.2.1. Polyglycerol **8**.

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

365 3.2.2. Fatty acids methyl esters (FAME) **12a,b.**

366   FAME **12a,b** were prepared according to a known procedure [21,41], modified for the batch
367 reactor UNIC -150-2.
368   Methanol (3.75 mol, 210 g, 256 mL), sodium methoxide (0.035 mol, 1.89 g) and the
369 corresponding vegetable oil **11a,b** (1 mol) were placed in the reactor. The reaction mixture was
370 refluxed for 2 h. After cooling, the mixture was left for ~ 2 h until completely separated into two
371 layers. The lower, glycerol layer was removed through the bottom discharge valve. Crude FAME
372 twice was washed with water (2 x 200 mL). After separating of water, the solvent residues are
373 removed under reduced pressure and product was poured through the bottom discharge valve.
374 Esters were used in epoxidation reactions without further purification.
375   *Sunflower oil* (**11a**). IR (neat), ν (cm^{-1}): 2922, 2852 (CH), 1744 (C=O), 1196, 1161, 1095 (C–O), 723
376 (CH=); ^{1}H-NMR (DMSO-d$_6$), δ (ppm): 0.82-0.89 (CH$_3$), 1.15-1.30 (CH$_{2acid}$), 1.43-1.52 (βCH$_{2acid}$),
377 1.90-2.05 (C$\underline{H}_2$CH=CH$_{acid}$), 2.10-2.30 (αCH$_{2acid}$), 2.61-2.75 (CH=CHC$\underline{H}_2$CH=CH$_{acid}$), 3.92-4.25
378 (CH$_{2glycerol}$), 5.15-5.35 (CH=CH+CH$_{glycerol}$).
379   *Soybean oil* (**11b**). IR (neat), ν (cm^{-1}): 2922, 2852 (CH), 1744 (C=O), 1197, 1161, 1095 (C–O), 721
380 (CH=); ^{1}H-NMR (DMSO-d$_6$), δ (ppm): 0.83-0.87 (CH^3), 1.15-1.30 (CH$_{2acid}$), 1.47-1.53 (CH$_{2acid}$), 1.99-2.02
381 (C$\underline{H}_2$CH=CH$_{acid}$), 2.23-2.29 (αCH$_{2acid}$), 2.63-2.74 (CH=CHC$\underline{H}_2$CH=CHacid), 3.94-4.28 (CH$_{2glycerol}$),
382 5.18-5.37 (CH=CH+CH$_{glycerol}$).
383   *Sunflower oil FAME* (**12a**). Esters were synthesized from 889 g sunflower oil **11a**. Colorless
384 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=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.84-0.87 (CH$_3$), 1.23-1.33 (CH$_{2acid}$),
386   1.49-1.52   (βCH$_{2acid}$),   1.96-2.03   (<u>CH$_2$</u>CH=CH$_{acid}$),   2.26-2.29   (αCH$_{2acid}$),   2.72-2.75
387   (CH=CH<u>CH$_2$</u>CH=CH$_{acid}$), 3.58 (CH$_3$O), 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), 1176,
390   1170, 1105 (C–O), 725 (CH=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.84-0.87 (CH$_3$), 1.23-1.33 (CH$_{2acid}$),
391   1.49-1.52   (βCH$_{2acid}$),   1.96-2.04   (<u>CH$_2$</u>CH=CH$_{acid}$),   2.26-2.29   (αCH$_{2acid}$),   2.72-2.75
392   (CH=CH<u>CH$_2$</u>CH=CH$_{acid}$), 3.58 (CH$_3$O), 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 NaHCO$_3$ (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=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.82-0.89 (CH$_3$), 1.17-1.30 (CH$_{2acid}$), 1.32-1.47 (<u>CH$_2$</u>CHOCH$_{acid}$),
410   1.48-1.52   (βCH$_{2acid}$),   1.89-2.03   (<u>CH$_2$</u>CH=CH$_{acid}$),   2.17-2.29   (αCH$_{2acid}$),   2.61-2.75
411   (CHOCH<u>CH$_2$</u>CHOCH$_{acid}$),   2.82-3.02   (CHO$_{acid}$),   4.04-4.28   (CH$_{2glycerol}$+OH$_{acid}$),   5.15-5.51
412   (CH=CH+CH$_{glycerol}$).

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=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.85-0.88 (CH$_3$), 1.23-1.32 (CH$_{2acid}$), 1.36-1.44 (<u>CH$_2$</u>CHOCH$_{acid}$),
416   1.48-1.52   (βCH$_{2acid}$),   1.93-2.03   (<u>CH$_2$</u>CH=CH$_{acid}$),   2.26-2.29   (αCH$_{2acid}$),   2.71-2.75
417   (CHOCH<u>CH$_2$</u>CHOCH$_{acid}$),   2.88-3.03   (CHO$_{acid}$),   4.08-4.29   (CH$_{2glycerol}$+OH$_{acid}$)),   5.15-5.22
418   (CH=CH+CH$_{glycerol}$).

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=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.84-0.87 (CH$_3$), 1.19-1.29 (CH$_{2acid}$), 1.32-1.41
422   (<u>CH$_2$</u>CHOCH$_{acid}$), 1.48-1.52 (βCH$_{2acid}$), 1.98-2.03 (<u>CH$_2$</u>CH=CH$_{acid}$), 2.26-2.29 (αCH$_{2acid}$), 2.61-2.65
423   (CHOCH<u>CH$_2$</u>CHOCH$_{acid}$), 3.07-3.17 (CHO$_{acid}$), 3.58 (OCH$_3$), 4.09 (OH$_{acid}$), 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=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.84-0.88 (CH$_3$), 1.21-1.32 (CH$_{2acid}$), 1.39-1.44
427   (<u>CH$_2$</u>CHOCH$_{acid}$), 1.48-1.52 (βCH$_{2acid}$), 1.95-2.03 (<u>CH$_2$</u>CH=CH$_{acid}$), 2.26-2.30 (αCH$_{2acid}$), 2.61-2.64
428   (CHOCH<u>CH$_2$</u>CHOCH$_{acid}$), 2.80-3.05 (CHO$_{acid}$), 3.58 (OCH$_3$), 4.12 (OH$_{acid}$), 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

434 transesterification was distilled off. The product was cooled to a temperature of 60 ° C under an inert
435 atmosphere, and then was poured through the bottom discharge valve into a storage container.

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

438   *Esters* (**15a**) were obtained from glycerol and 851 g epoxidized sunflower oil (**13a**). Viscous
439 yellow liquid. Yield 916 g. IR (neat), ν (cm^{-1}): 3452 (OH), 2922, 2852 (CH), 1731 (C=O), 1248, 1174, 1058
440 (C–O), 725 (CH=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.82-0.88 (CH$_3$), 1.17-1.32 (CH$_{2acid}$), 1.34-1.42
441 (<u>CH$_2$</u>CHO$_{acid}$), 1.47-1.55 (βCH$_{2acid}$), 1.92-2.05 (<u>CH$_2$</u>CH=CH$_{acid}$), 2.17-2.32 (αCH$_{2acid}$), 2.78-2.88
442 (OCH<u>CH$_2$</u>CHO$_{acid}$), 3.44-5.50 (CH$_{2glycerol}$+OH+CH=CH+CH$_{glycerol}$).

443   *Esters* (**15b**) were obtained from glycerol and 857 g epoxidized soybean oil (**13b**). Viscous yellow
444 liquid. Yield 923 g. IR (neat), ν (cm^{-1}): 3395 (OH), 2922, 2852 (CH), 1732 (C=O), 1247, 1174, 1056 (C–O),
445 723 (CH=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.79-0.88 (CH$_3$), 1.16-1.29 (CH$_{2acid}$), 1.34-1.40 (<u>CH$_2$</u>CHO$_{acid}$),
446 1.45-1.55 (βCH$_{2acid}$), 1.92-2.05 (<u>CH$_2$</u>CH=CH$_{acid}$), 2.21-2.32 (αCH$_{2acid}$), 2.78-2.88 (OCH<u>CH$_2$</u>CHO$_{acid}$),
447 3.44-5.55 (CH$_{2glycerol}$+OH+CH=CH+CH$_{glycerol}$).

448   *Esters* (**16a**) were obtained from glycerol and 281 g epoxidized sunflower oil FAME (**14a**).
449 Viscous yellow liquid. Yield 308 g. IR (neat), ν (cm^{-1}): 3383 (OH), 2922, 2852 (CH), 1732 (C=O), 1247,
450 1120, 1047 (C–O), 723 (CH=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.80-0.89 (CH$_3$), 1.16-1.31 (CH$_{2acid}$),
451 1.34-1.40 (<u>CH$_2$</u>CHO$_{acid}$), 1.45-1.55 (βCH$_{2acid}$), 1.92-2.05 (<u>CH$_2$</u>CH=CH$_{acid}$), 2.21-2.32 (αCH$_{2acid}$), 2.70-2.78
452 (OCH<u>CH$_2$</u>CHO$_{acid}$), 3.44-5.55 (CH$_{2glycerol}$ + OH + CH=CH + CH$_{glycerol}$).

453   *Esters* (**16b**) were obtained from glycerol and 290 g epoxidized soybean oil FAME (**14b**). Viscous
454 yellow liquid. Yield 317 g. IR (neat), ν (cm^{-1}): 3382 (OH), 2922, 2852 (CH), 1731 (C=O), 1246, 1176, 1047
455 (C–O), 725 (CH=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.80-0.90 (CH$_3$), 1.16-1.31 (CH$_{2acid}$), 1.35-1.42
456 (<u>CH$_2$</u>CHO$_{acid}$), 1.47-1.57 (βCH$_{2acid}$), 1.95-2.03 (<u>CH$_2$</u>CH=CH$_{acid}$), 2.20-2.32 (αCH$_{2acid}$), 2.76-2.84
457 (OCH<u>CH$_2$</u>CHO$_{acid}$), 3.44-5.45 (CH$_{2glycerol}$ + OH + CH=CH + CH$_{glycerol}$).

458   *Esters* (**17a**) were obtained from polyglycerol and 851 g epoxidized sunflower oil (**13a**). Viscous
459 dark yellow liquid. Yield 1075 g. IR (neat), ν (cm^{-1}): 3346 (OH), 2922, 2852 (CH), 1733 (C=O), 1247,
460 1095, 1045 (C–O), 675 (CH=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.82-0.88 (CH$_3$), 1.17-1.32 (CH$_{2acid}$),
461 1.36-1.42 (<u>CH$_2$</u>CHO$_{acid}$), 1.47-1.55 (βCH$_{2acid}$), 1.92-2.05 (<u>CH$_2$</u>CH=CH$_{acid}$), 2.21-2.31 (αCH$_{2acid}$), 2.78-2.88
462 (OCH<u>CH$_2$</u>CHO$_{acid}$), 3.44-5.54 (CH$_{2glycerol}$ + OH + CH=CH + CH$_{glycerol}$).

463   *Esters* (**17b**) were obtained from polyglycerol and 857 g epoxidized soybean oil (**13b**). Viscous
464 dark yellow liquid. Yield 1093 g. IR (neat), ν (cm^{-1}): 3394 (OH), 2922, 2852 (CH), 1732 (C=O), 1247,
465 1145, 1047 (C–O), 725 (CH=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.82-0.90 (CH$_3$), 1.16-1.33 (CH$_{2acid}$),
466 1.35-1.42 (<u>CH$_2$</u>CHO$_{acid}$), 1.45-1.56 (βCH$_{2acid}$), 1.95-2.05 (<u>CH$_2$</u>CH=CH$_{acid}$), 2.21-2.34 (αCH$_{2acid}$), 2.72-2.76
467 (OCH<u>CH$_2$</u>CHO$_{acid}$), 3.34-5.45 (CH$_{2glycerol}$ + OH + CH=CH + CH$_{glycerol}$).

468   *Esters* (**18a**) were obtained from polyglycerol and 281 g epoxidized sunflower oil FAME (**14a**).
469 Viscous dark yellow liquid. Yield 489 g. IR (neat), ν (cm^{-1}): 3334 (OH), 2922, 2852 (CH), 1732 (C=O),
470 1247, 1085, 1041 (C–O), 703 (CH=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.82-0.90 (CH$_3$), 1.16-1.33 (CH$_{2acid}$),
471 1.35-1.42 (<u>CH$_2$</u>CHO$_{acid}$), 1.45-1.56 (βCH$_{2acid}$), 1.95-2.05 (<u>CH$_2$</u>CH=CH$_{acid}$), 2.21-2.34 (αCH$_{2acid}$), 2.72-2.76
472 (OCH<u>CH$_2$</u>CHO$_{acid}$), 3.34-5.45 (CH$_{2glycerol}$+OH+CH=CH+CH$_{glycerol}$).

473   *Esters* (**18b**) were obtained from polyglycerol and 290 g epoxidized soybean oil FAME (**14b**).
474 Viscous dark yellow liquid. Yield 496 g. IR (neat), ν (cm^{-1}): 3357 (OH), 2922, 2852 (CH), 1731 (C=O),
475 1247, 1091, 1043 (C–O), 723 (CH=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.82-0.91 (CH$_3$), 1.16-1.31 (CH$_{2acid}$),
476 1.35-1.42 (<u>CH$_2$</u>CHO$_{acid}$), 1.47-1.56 (βCH$_{2acid}$), 1.95-2.05 (<u>CH$_2$</u>CH=CH$_{acid}$), 2.21-2.32 (αCH$_{2acid}$), 2.72-2.76
477 (OCH<u>CH$_2$</u>CHO$_{acid}$), 3.34-5.50 (CH$_{2glycerol}$ + OH + CH=CH + CH$_{glycerol}$).

478   *Esters* (**18c**) were obtained from polyglycerol 275 g (1 mol) and 580 g (2 mol) of epoxidized
479 soybean oil FAME (**14b**). Viscous dark yellow liquid. Yield 715 g. IR (neat), ν (cm^{-1}): 3340 (OH), 2925,
480 2856 (CH), 1732 (C=O), 1242, 1089, 1053 (C–O), 723 (CH=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.80-0.90
481 (CH$_3$), 1.17-1.30 (CH$_{2acid}$), 1.33-1.44 (<u>CH$_2$</u>CHO$_{acid}$), 1.45-1.53 (βCH$_{2acid}$), 1.95-2.05 (<u>CH$_2$</u>CH=CH$_{acid}$),
482 2.21-2.32 (αCH$_{2acid}$), 2.70-2.75 (OCH<u>CH$_2$</u>CHO$_{acid}$), 3.34-5.50 (CH$_{2glycerol}$+OH+CH=CH+CH$_{glycerol}$).

483   *Esters* (**18d**) were obtained from polyglycerol 147.5 g (0.5 mol) and 507.5 g (1.75 mol) epoxidized
484 soybean oil FAME (**14b**). Viscous dark yellow liquid. Yield 526 g. IR (neat), ν (cm^{-1}): 3357 (OH),
485 2922, 2852 (CH), 1731 (C=O), 1247, 1091, 1043 (C–O), 723 (CH=); ^{1}H-NMR (DMSO-d_6), δ (ppm):

486 0.81-0.92 (CH$_3$), 1.16-1.30 (CH$_2$acid), 1.35-1.42 (C$\underline{H_2}$CHO$_{acid}$), 1.45-1.55 (βCH$_2$acid), 1.95-2.05
487 (C$\underline{H_2}$CH=CH$_{acid}$), 2.21-2.32 (αCH$_2$acid), 2.70-2.76 (OCHC$\underline{H_2}$CHO$_{acid}$), 3.34-5.45 (CH$_2$glycerol + OH +
488 CH=CH + CH$_{glycerol}$).

489   *Esters* (**18e**) were obtained from polyglycerol 147.5 g (0.5 mol) and 1015 g (3.5 mol) epoxidized
490 soybean oil FAME (**14b**). Viscous dark yellow liquid. Yield 963 g. IR (neat), ν (cm^{-1}): 3357 (OH), 2922,
491 2852 (CH), 1731 (C=O), 1247, 1091, 1043 (C–O), 723 (CH=); ^{1}H-NMR (DMSO-d_6), δ (ppm): 0.82-0.92
492 (CH$_3$), 1.17-1.32 (CH$_2$acid), 1.36-1.44 (C$\underline{H_2}$CHO$_{acid}$), 1.48-1.53 (βCH$_2$acid), 1.93-2.03 (C$\underline{H_2}$CH=CH$_{acid}$),
493 2.21-2.32 (αCH$_2$acid), 2.79-2.80 (OCHC$\underline{H_2}$CHO$_{acid}$), 3.63-5.50 (CH$_2$glycerol + OH + CH=CH + CH$_{glycerol}$).

494 *3.3. Emulsifying properties determination of esters (**15-18**)*

495   The emulsification ability was evaluated visually in time of spontaneous stratification
496 (destruction) of the emulsion column in a high vessel after emulsification [15,36,42].   The volume of
497 the separated disperse phase was fixed at regular time intervals. For the stability measure of the
498 emulsion, a "half-life" was accepted – this is the time during which 50% of the dispersed phase is
499 separated.
500   In the described procedure, sunflower refined deodorized oil was a fat phase, the aqueous
501 phase was distilled water. A sample of the emulsifier (1.2 g) was dissolved in 96 ml of oil at 60 ° C
502 and agitation at 700 rpm, then water (24 ml) was added and the mixture was held for 15 minutes.
503 For 1: 1 emulsions the volumes of oil and water were 60 ml.
504   A small amount of a neutral fat-soluble dye (1- (phenylazo) -naphtole-2) was added to 1 ml of
505 the resulting emulsion and the type of emulsion was determined with a microscope at x100
506 magnification.

507 **4. Conclusions**

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

524 **Author Contributions:** Denis Lyapun performed synthesis of compounds, Khidmet Shikhaliev and Mikhail
525 Krysin conceived and designed the experiments, analyzed the data and wrote the paper, Nadezhda
526 Stolpovskaya analyzed the data and wrote the paper, Anna Zorina performed the synthesis and analyzed
527 compounds, Fedor Zubkov performed spectral analysis of compounds and analyzed the data.

528 **Conflicts of Interest:** The authors declare no conflict of interest.
529

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