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NOVEL FUNCTIONAL DERIVATIVES OF METHYL-*CIS*9,10-EPOXY-OCTADECANOATE

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Abstract. The synthesis of functional derivatives of epoxystearic acid methyl ester by oxirane ring opening and transesterification of ester group has been described. Some novel surface-active and peroxide-containing compounds have been obtained. Major features of the process have been investigated and main characteristics have been determined.

Keywords: oleic acid, transesterification, epoxidation, epoxide ring opening, surface-active substances, peroxide, IR spectra.

1. Introduction

Today one of the main challenges for chemistry and technology of organic substances is the development of eco-friendly materials on the basis of renewable resources [1]. Over the past century rapid growth of greenhouse gases' concentration in the atmosphere, the contamination of ecosystems with products, which do not degrade biologically, the rise of gas and oil prices and efforts to diversify feedstock sources have led to rapid development in the leading countries around the world of chemistry and technologies relying on the alternative sources of feedstock for chemical and fuel industries. "Green chemistry", which is based on chemical and biochemical modification of natural compounds, is considered as the most promising concept. The derivatives of the fatty acid triglycerides, which are the main components of all plant oils and fats, are considered as a feedstock source with a lot of potential for many fields of chemical industry [2].

The main product today is biodiesel, which consists of fatty acid methyl (ethyl) esters and is produced on a big scale in the world leading countries by base-catalyzed transesterification [3]. Also there are experiments with acid catalysts, fermentative processes, homogenous and

inhomogeneous systems, and microwave and ultrasonic-assisted transesterification. In fact, most of the fatty acids present in plant oils have a lot of double C=C bonds that could be chemically modified [4]. Epoxidation of double C=C bond is the most promising modification method and a lot of investigations are focused on making epoxidation process eco-friendly. Such epoxidized derivatives are valuable products because they possess enhanced reactivity and are ecologically friendly. The derivatives on the basis of epoxidized fatty acid esters can be obtained by the epoxide ring opening as well as transesterification. One of the promising ways of investigation is the creation of reactive surfactants, monomers and initiators for modification of interfacial layer of different colloidal system types [5]. It is a well known fact that the incorporation of the fragments of naturally compounds such as carbohydrates, amino acids, and lipids into molecules often improves biological tolerance of materials derived on this basis. Improved performance of such compounds can contribute to effective transportation of medical substances as well as to the development of different biomedical materials.

A series of publications on modification of plant oils and their esters by epoxidation and following epoxide ring opening with different reagents have been published during the last ten years. Using peroxyformic, peroxyacetic acids [6] as well as hydrogen peroxide in the presence of enzymes [7] or heterogenic catalysts [8] several research groups have obtained polyols, epoxides and surface active compounds [9] on their basis. Also maleic and acrylic monomers have been obtained [10]. However, the information about surface-active peroxide containing derivatives with predicted activity has not been found.

Methods of obtaining novel types of surface-active initiators on the basis of methyl ester of 9,10-epoxystearic acid are described in this paper.

2. Experimental

2.1. Materials

Oleic acid of reagent grade was purified by recrystallization of 10 % solution in methanol under 253 K. Methanol, *n*-butanol, ethyl cellosolve reagent grade were absolutized and distilled. Sulfuric acid, sodium hydroxide, perchloric acid, acetic acid, hydrogen peroxide, boron trifluoride etherate, benzyl triethyl ammonium chloride, diazobicyclooctane, lithium, magnesium sulfate, sodium sulfate of reagent grade were used without purification. Solvents (chloroform, 2-propanol, dichloromethane (DCM), hexane) were purified according to the technique [11]. *Benzoyl chloride* of reagent grade has been distilled prior to usage. *Tert*-butyl hydroperoxide (TBHP) (84 % solution) was distilled under reduced pressure. The characteristics of initial reagents correspond to reference data [12].

2.2. Analytical Methods

Acid value was determined using 0.5 N NaOH ethanol solution, iodine value – using Vijs-Hanus method, active oxygen value was determined iodometrically, epoxy value – by titration with 0.1 N HClO₄ in glacial acetic acid in the presence of tetraethyl ammonium bromide [13].

IR spectra were recorded on spectrophotometer “Specord M80” in thin layer.

The reaction course and purity of products were controlled with thin-layer chromatography on Silica gel 60 F₂₅₄ (Merck) plates, eluent – hexane : ethyl acetate (10 : 4) and gas-liquid chromatography on “Buck Scientific”, capillary column MXT-5 (methylphenylsiloxane, 5 % phenyl groups) with 30 m long capillary column and flame-ionizing detector.

2.3. Synthesis Methods

Peroxybenzoic acid (5 % PBA/DCM solution).

Solution of 40 ml of 2-propanol, 0.1 g MgSO₄, 13 g (0.125 mol) 30 % H₂O₂ was loaded into reactor and stirred. The temperature of the reaction should not exceed 283–288 K. The following reagents were loaded sequentially dropwise into reactor and stirred for 15 minutes: 12.7 ml (0.14 mol) 30 % NaOH/water solution, 36.7 ml (0.057 mol) 22 % benzoyl chloride/DCM solution. Next 35 % H₂SO₄ was added dropwise to pH = 5 and stirred for 15 min and then the mixture was separated. Water-alcohol layer was extracted 3 times by 15 ml of DCM. Combined organic layers were washed with water and dried over MgSO₄. 5.4 % DCM solution with 8 g of PBA was used directly for epoxidation. The yield was 95 %.

Methyl-cis-9,10-epoxy-octadecanoate (MES) (3).

7.4 g (0.025 mol) of methyl oleate was added dropwise to 62.12 g of 5.6 % (0.025 mol) PBA/DCM

solution at 283–288 K and stirred for 5 h. Then the mixture was washed with 5 % cold sodium bicarbonate solution and water and then dried over Na₂SO₄. The product was purified by short-path distillation (fraction 433–443 K at 13.3–26.7 Pa). The yield was 97 %.

Methyl-trans-9(10)-hydroxy-10(9)-butoxy-octadecanoate (MESB) (4).

0.005 g of triethyl benzyl ammonium chloride and 0.08 g (0.002 mol) NaOH were added to solution of 3.12 g (0.01 mol) of MES, 3.7 g (0.05 mol) of 1-butanol and the reaction mixture was stirred for 4 h at 333 K. Then the mixture was washed to neutral pH, dried over Na₂SO₄ and kept for 2 h at 333 K under reduced pressure 13.3–26.7 Pa. The yield was 94 %.

Methyl-trans-9(10)-hydroxy-10(9)-tert-butylhydroperoxy-octadecanoate (MESTBHP) (5).

Boron trifluoride etherate was added to solution of 0.34 ml (0.003 mol) TBHP in 10 ml DCM and kept for 10 min at 303–313 K. Then the solution of 0.55 ml (0.0015 mol) of MES in 10 ml of DCM was added and stirred for 3 h at 333 K. Then the mixture was diluted with hexane and washed sequentially with cold NaCl solution and with cold water until neutral and dried over MgSO₄. The solvent was evaporated under reduced pressure of 13.3–26.7 Pa and kept for 6 h at 303 K. The yield was 92 %.

2-Etoxyethyl-cis-9,10-epoxy-octadecanoate (EES) (6).

0.00075 g (0.0001 mol) of lithium was added to 1.16 g (0.006 mol) of ethyl cellosolve. When the solution became homogenous 1.54 g (0.0048 mol) of MES was added and kept for 4 h at 373 K. Then the mixture was diluted with hexane, washed with water to neutral pH and dried over Na₂SO₄. The solvent was evaporated under reduced pressure of 13.3–26.7 Pa and kept for 6 h at 353 K. The yield was 82 %.

Monomethyl-PEG-550 ester of cis-9,10-epoxystearic acid (M-550-PEGES) (7).

0.00075 g (0.0001 mol) of lithium was added to 5.6 g (0.01 mol) of monomethyl PEG-550. When the mixture became homogenous 3.12 g (0.01 mol) of MES was added dropwise and stirred for 4 h at 373 K. Then the mixture was diluted with hexane, washed with cold water to neutral pH, dried over Na₂SO₄, and kept under reduced pressure of 133.3 Pa at 353 K. The yield was 78 %.

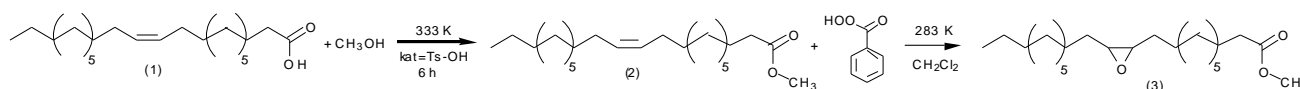
Monomethyl-PEG-200 ester of cis-9,10-epoxystearic acid (M-200-PEGES) (8) was obtained by the same method as (7). The yield was 80 %.

2-Etoxyethyl-trans-9(10)-hydroxy-10(9)-tert-butylhydroperoxy octadecanoate (EESTBHP) (8).

Boron trifluoride etherate was added to 0.308 ml (0.008 mol) of TBHP in 5 ml of DCM and kept for 10 min at 303–313 K. Then the solution of 0.12 g (0.0004 mol) of EES in 2 ml of DCM was added and kept for 6 h at 333 K. Next the mixture was diluted with hexane, washed with brine and washed with cold water to neutral pH, dried over MgSO₄ and kept under reduced pressure of 133.3 Pa at 303 K for 6 h. The yield was 76 %.

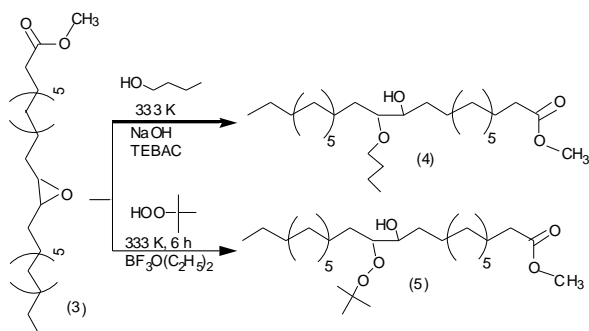
3. Results and Discussion

cis-9-Octadecenic acid (1) has been esterified with methanol in the presence of *p*-toluenesulfonic acid [14]. MES has been obtained by epoxidation of methyl *cis*-9,10-octadecenoate (2) with solution of peroxybenzoic acid [15].



The product (4) has been obtained by epoxide ring opening with *n*-butanol catalyzed with sodium hydroxide and interface-interaction catalyst – triethylammonium chloride.

The product (5), which contains *di-tert* peroxide group, esteric and *sec*-hydroxy groups has been obtained by epoxide ring opening with *tert*-butyl hydroperoxide catalyzed by boron trifluoride etherate.



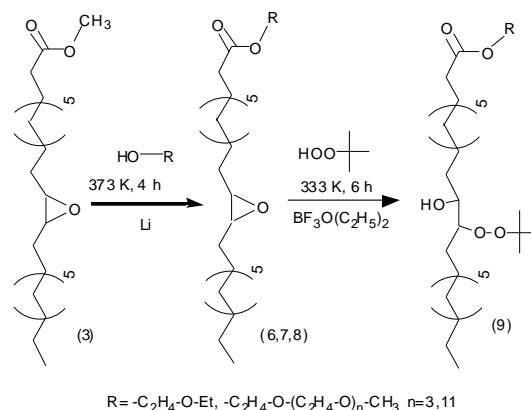
Base- and acid-catalyzed transesterification of MES by polyglycols with saving epoxy group has been investigated. Such compounds could be potential non-ionic surface-active intermediates with reactive epoxide group.

The interaction of MES with ethyl cellosolve in the presence of diazobicyclooctane, which was synthesized according to [16] (base-catalysed) has not been observed. Transesterification of MES with ethyl cellosolve in the presence of lithium yielded product (6), which has hydrophilic part of cellosolve and hydrophobic part of fatty acid carbon chain with epoxide ring. The epoxide ring presence was confirmed by epoxy value (11.0 det./11.6 calc.). By the variation of hydrophilic chain nature one can obtain non-ionic surface-active intermediates with a different interface activity.

The row of non-ionic surface-active epoxy monomers (7, 8) has been obtained via the interaction of MES with monomethyl esters of polyethyleneglycols (PEG-550, PEG-200) catalyzed with weak base. Epoxy values were determined for M-550-PEGES (4.9 det./5.11 calc.) and for M-200-PEGES (8.6 det./8.8 calc.).

Acid-catalyzed epoxy ring opening of compound (6) with *tert*-butyl hydroperoxide has been investigated as well. Non-ionic surface-active initiator (9) has been obtained with the high yield.

MES is a bifunctional compound and it is possible to obtain its derivatives such as surface-active monomers and initiators by epoxy group opening as well as by transesterification of ester group. The determined epoxy value of MES was 13.7 (calc. 13.76).



In IR spectra of MES intensive peaks of $\nu(\text{C}=\text{O})$ at 1744 cm^{-1} $\delta(\text{C}=\text{O})$ and at 1168 cm^{-1} $\delta(\text{C}-\text{O})$, as well as epoxide ring peaks at $840\text{--}780\text{ cm}^{-1}$ are present [16]. The peak at 1240 cm^{-1} indicates *cis*-epoxy ring and no peaks are present for *sec*-OH. This means that the epoxidation with PBA yields only epoxide. Peaks for $\text{C}=\text{C}$ bond are not observed.

IR spectra of MESB differ from MES: new intensive peaks at 3472 , 3450 , 3400 , 3300 , and 3200 cm^{-1} indicate epoxide ring opening and *sec*-OH group. Also the stretching of 1255 cm^{-1} (δOH) and new peak at 1100 cm^{-1} prove the *sec*-OH group presence. New intensive peak at 1070 cm^{-1} $\nu(\text{C}-\text{O}-\text{C}-)$ indicates $\text{C}-\text{O}-\text{C}-$ bond. The peak at 1740 cm^{-1} shows that ester group did not change in the reaction. The peaks at $870\text{--}750\text{ cm}^{-1}$ are not available indicating opening of all epoxide groups.

In IR spectra of MESTBHP there are peaks $\nu(\text{C}=\text{O})$ at 1744 cm^{-1} and $\nu(\text{C}-\text{O}-)$ at 1180 cm^{-1} indicating ester group. *Sec*-OH is indicated with peaks at 3520 , 3472 , 3300 cm^{-1} . $\nu(\text{C}-\text{O}-)$ and $\delta(\text{OH})$ correspond to peaks at 1104 cm^{-1} and at 1305 cm^{-1} . Peaks of epoxide ring are not present. New peaks corresponding to $\text{C}(\text{CH}_3)_3$ -peaks at 1380 , 1360 cm^{-1} ; *tert*-butoxy – at 880 cm^{-1} , skeleton vibrations at $\text{C}(\text{CH}_3)_3$ – 1220 and 1200 cm^{-1} indicate the presence of *di-tert*-peroxide group [16].

The IR spectra of EES as well as M-550-PEGES and M-200-PEGES present $\nu(\text{C}=\text{O})$ at 1744 cm^{-1} and $\nu(\text{C}-\text{O}-)$ at 1180 cm^{-1} peaks indicating ester group. There are also epoxide ring peaks at $840\text{--}780\text{ cm}^{-1}$. The peak at 1240 cm^{-1} indicates *cis*-epoxy ring and no peaks are present corresponding to *sec*-OH.

Table 1

Characteristics of products

Product	Molecular formula	M	n_D^{20}	MR _d calc./det.	Melting point, K	Elemental composition calc./det., % mass		Yield, %
						C	H	
1	C ₁₈ H ₃₄ O ₂	282.5	1.4585	87.06	286.4	76.5/ 76.4	12.1/ 12.0	-
2	C ₁₉ H ₃₆ O ₂	296.5	1.4520	92.49	283.2	76.9/ 77.1	12.2/ 12.3	95
3	C ₁₉ H ₃₆ O ₃	312.5	1.4510	90.76	289.2	73.0/73.2	11.6/ 11.3	97
4	C ₂₃ H ₄₆ O ₄	386.6	1.4572	112.80	286.5	71.4/ 71.5	11.9/ 12.0	94
5	C ₂₃ H ₄₆ O ₅	402.6	1.4582	115.32	287.2	68.6/ 68.5	11.5/ 11.6	92
6	C ₂₂ H ₄₂ O ₄	370.6	1.4562	106.48	286.4	71.3/ 71.4	11.4/ 11.3	82
7	C ₄₃ H ₈₄ O ₁₅	841.1	1.4642	151.55	293.6	61.4/ 61.3	10.0/ 10.1	78
8	C ₂₇ H ₅₂ O ₇	488.7	1.4610	134.46	290.1	66.4/ 66.3	10.7/ 10.8	80
9	C ₃₁ H ₆₂ O ₇	546.8	1.4576	150.99	291	68.1/ 68.0	11.4/ 11.5	76

In IR spectra of EESTBHP there are peaks at 2860, 2928 and 2856 cm⁻¹ – $\nu(-CH_3$ and $-CH_2-)$; 1456, 1420, 1380, 1364 cm⁻¹ – $\delta(-CH_3$ and $-CH_2-)$, and peak at 1420 cm⁻¹, which indicates that $-CH_2-$ is linked to $-C(O)O-$. Ester group peaks are present at 1744 cm⁻¹ $\nu(C=O)$ and at 1168 cm⁻¹ $\nu(C-O)$. This proves the process of transesterification of MES with ethyl cellosolve. *Sec-OH* is proved with peaks at 3520–3310 cm⁻¹. The peaks at 1260 cm⁻¹ $\delta(-OH)$ and at 1035 cm⁻¹ $\nu(-OH)$ also prove the availability of *sec-OH* group [16].

4. Conclusions

The synthesis of derivatives of methyl-*cis*-9,10-epoxystearate have been carried out by epoxy group and ester group. Some novel non-ionic surface-active monomers and initiators have been obtained. The IR spectra of the obtained compounds have been analyzed and their main characteristics have been described.

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ОДЕРЖАННЯ ФУНКЦІОНАЛЬНИХ ПОХІДНИХ МЕТИЛ-ЦИС-9,10-ЕПОКСИ-ОКТАДЕКАНОАТУ

Анотація. Описано одержання функціональних похідних метилового естеру епоксистеаринової кислоти за оксирановим кільцем та естерною групами. Отримано ряд поверхнево активних та пероксидовмісних сполук. Встановлено основні закономірності перебігу реакцій та основні характеристики продуктів.

Ключові слова: олеїнова кислота, транс-естерифікація, епоксидування, епоксидне кільце, поверхнево-активні речовини, пероксид, ІЧ спектр.