

OBTAINING NONGLYCERIDE OILS BY ESTERIFICATION OF ERYTHRITOL, 1,2,3-BUTANETRIOL AND 1,2,4-BUTANETRIOL BY CARBOXYLIC ACIDS OF SUNFLOWER, OLIVE AND CORN OILS

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The esterification reaction of erythritol, 1,2,3-butanetriol and 1,2,4-butanetriol with carboxylic acids of sunflower, olive and corn oils has been used to synthesize non-glyceride analogues of the corresponding edible oils. Effective methods for the preparation of tetraacyl erythritol, triacyl erythritol and triacyl butanetrioles have been developed. The physicochemical properties of the obtained compounds are defined.

Keywords: saponification, sunflower, olive and corn oils, esterification, erythritol, 1,2,3-butanetriol, 1,2,4-butanetriol, tetraacyl erythritol, triacyl erythritol, triacyl butanetriol, nonglyceride oils.

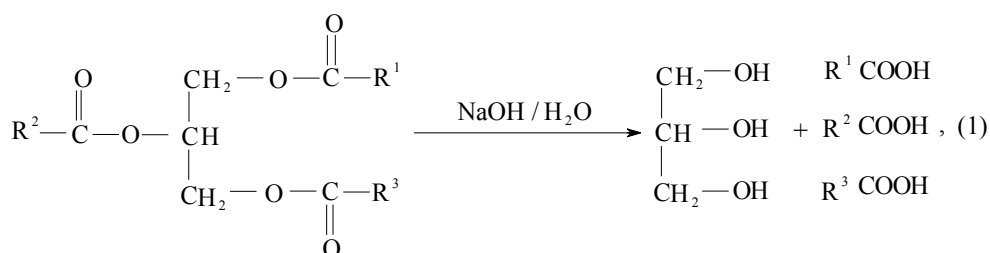
Introduction. Screening of dietary substitutes for edible oils and fats is of interest for modern food industry, cooking and medicine [1, 2]. The esters of polyatomic alcohols (erythritol, xylitol, sorbitol, etc.) with higher fatty acids (stearic, palmitic, etc.) were obtained as dietary substitutes for oils and fats [3–5]. The previously synthesized nonglyceride esters of carboxylic acids differ from natural oils and fats in that only one sample of fatty acid was present in each sample of oil. However, the composition of natural oils, as a rule, contains a complex of various carboxylic acids, which determines a greater variety of their nutritional and culinary characteristics. Therefore, the goal of this research was to obtain a new variety of nonglyceride oils, where the polyols are esterified with a natural complex of fatty acids obtained from the hydrolysis of vegetable oils. With their composition, these nonglyceride oils are very close to the similar natural products.

The studies were performed according to the following scheme: a) hydrolysis of edible oils with an alkali solution; b) neutralization of alkaline salts with acid, isolation and drying of mixtures of fatty acids; c) synthesis of nonglyceride oils by esterification of erythritol, 1,2,3-butanetriol and 1,2,4-butanetriol with fatty acid complexes derived from sunflower, olive and corn oils; d) cleaning and drying of the reaction products; e) determination of the main physicochemical properties of the compositions obtained. Newly obtained compounds (tetraacyl erythritol, triacyl erythritol and triacylbutanetriol) are of interest as dietary substitutes for oils and fats.

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Results and Discussion.

Obtaining Fatty Acids of Sunflower, Olive and Corn Oils. The reaction of hydrolysis of oils was carried out by the method of water-alkaline saponification with 20% sodium hydroxide solution, taken in twofold excess at a temperature of 90°C (1). The chromatogram of the separation of the mixture of methyl esters of standard samples of the Gas Liquid Chromatography (GLC) is shown in Fig. 1. Identification and mass fractions of fatty acids in the studied samples are given in the Tab. 1.



where R^n ($n=1,2,3$) are various alkenyl and alkyl groups may be different or identical.

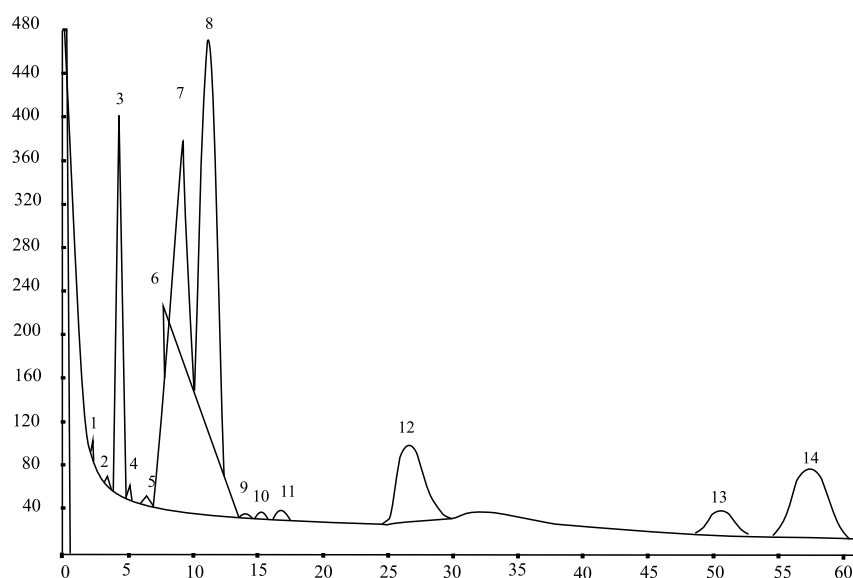


Fig. 1. Chromatogram of a mixture of methyl esters. The sequence of the peaks of methyl esters of acids: 1 – myristic; 2 – pentadecanoic; 3 – palmitic; 4 – palmitoleic; 5 – margaric; 6 – stearic; 7 – oleic; 8 – linoleic; 9 – linolenic; 10 – eicosenoic; 11 – eicosadienoic; 12 – behenic; 13 – arachidic; 14 – lignoceric (literary data) [6].

The composition of fatty acids obtained from sunflower, olive and corn oils corresponds to the literature data and the relevant regulatory documents [7–9].

In terms of their physicochemical properties, olive and corn oils are slightly different from the sunflower oil. The difference is hardly detectable with the IR spectra, as well (Fig. 2). However, by saponification of olive or corn oils, a mixture of carboxylic acids with similar composition was obtained, that mainly consisted of oleic, linoleic, stearic and palmitic acids, with close ratios [7, 10].

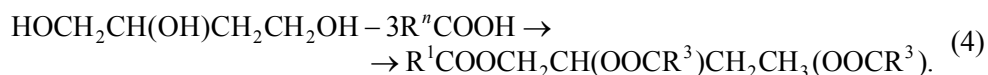
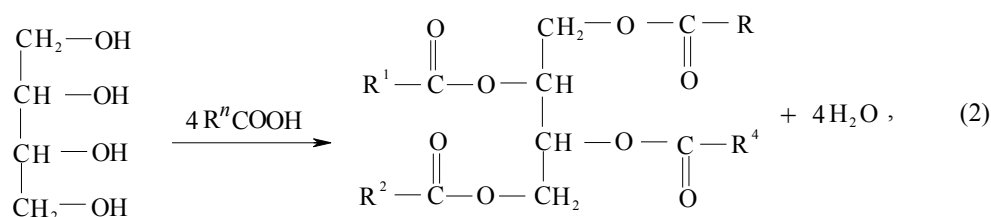
Table 1

Composition of fatty acid methyl esters of refined vegetable oils used to obtain tetraacyl erythritol and tetraacyl butanetriol

Nos.	Fatty acids	Sunflower oil	Corn oil	Olive oil
saturated fatty acids, %				
1	myristic	0.07	–	–
2	palmitic	8.42	13.77	11.0
3	stearic	6.83	3.42	4.0
4	margaric	0.07	0.10	–
5	arachidic	0.45	0.73	0.3
6	behenic	1.26	0.26	–
monounsaturated fatty acids, %				
1	palmitoleic	0.14	0.17	–
2	oleic	25.09	31.78	75.0
3	gondoic	0.28	0.50	–
polyunsaturated fatty acids, %				
1	linoleic	54.51	45.05	7.0
2	linolenic	0.1	–	0.2

Preparation of Tetraacyl and Triacyl Erythritol and Triacylbutanetriol.

The esterification reaction of polyols with carboxylic acids is carried out according to a known method [1, 3].



Reactions are carried out in a molar ratio of polyol : acid = 1 : (3÷4), which most closely corresponds to the purpose of obtaining analogues of natural oils. The reactions temperature ranges between 140–190°C, without the use of catalysts. To ensure the homogeneity of the reaction environment and to optimize the reaction conditions, a solvent N-methylpyrrolidone (N-MP) is used [1]. The results of the experiments are shown in Tabs. 2 and 3.

As can be seen from Tab. 2, the main patterns of esterification of erythritol with carboxylic acids of sunflower oil are the following. The reaction successfully proceeds at 140–190°C for 16–20 h (experiments 1, 2, 7, 8, 12). During the process visible condensation of water vapor occurs in the first 6–8 h. As the degree of substitution increases and the reaction slows down, a prolonged heating is required for another 8–10 h. In the IR spectrum of the product, there are no bands characterizing hydroxyl groups, but the bands at 1740, 1230 and 1290 cm^{-1} , that

characterize carbonyl group are retained. This result indicates that the reaction between erythritol and the fatty acids complex is finished, and all hydroxyl and carboxyl groups are converted to ester bonds. The reaction product is thick, oily yellow liquid with solidification temperature of -15 to 21°C . The color of the oil turns much lighter when oxidation and polymerization inhibitors are added to the reaction mixture, in particular 2,6-di-tert-butyl-4-methylphenol (P-23). Lowering the temperature of reaction down to 140°C leads to a slowdown and a decrease in the yield which is below the reasonable level (experiments Nos. 5, 6). The temperature increase up to 190°C , in contrast, significantly speeds up the process, however, leading to the darkening of the product which also impairs its properties (experiments Nos. 9, 10). A partial destruction of the oil at 190°C is observed even in the presence of an inhibitor of free-radical reactions, P-23.

Another factor that ensures a smooth flow of the reaction is the use of a solvent. Erythritol melts at a temperature of 118°C , though higher carboxylic acids cannot dissolve it, even if the temperature is increased up to 150 – 160°C . The dissolution of the reagents is achieved by adding N-MP. Under the reaction conditions the solvent does not volatilize or decompose, and can be easily removed from the reaction products by washing with water. In the absence of a solvent the oil yield decreases significantly (experiment No. 4).

Table 2

Esterification of erythritol, 1,2,3-butanetriol and 1,2,4-butanetriol with carboxylic acids of sunflower ($R^1\text{COOH}$) oil

Exp. No.	Polyols, 20 mmol	Carboxylic acids, mmol	N-MP weight parts to RCOOH	Reaction temperature, $^{\circ}\text{C}$	Reaction time, h	Yield, % mol	Freezing temperature, $^{\circ}\text{C}$
1	Erythritol	$R^1\text{COOH}$, 80	1 : 2	150	16	93	-15 – 21
2	Erythritol	$R^1\text{COOH}$, 60	1 : 2	150	16	95	-18 – 22
3	Erythritol	$R^1\text{COOH}$, 60	1 : 1	150	16	90	-16 – 22
4	Erythritol	$R^1\text{COOH}$, 80	absence	150	16	67	-18 – 24
5	Erythritol	$R^1\text{COOH}$, 80	1 : 2	140	16	88	-18 – 22
6	Erythritol	$R^1\text{COOH}$, 60	1 : 2	140	16	91	-14 – 19
7*	Erythritol	$R^1\text{COOH}$, 80	1 : 2	160	16	96	-16 – 21
8*	Erythritol	$R^1\text{COOH}$, 60	1 : 2	160	16	95	-12 – 17
9**	Erythritol	$R^1\text{COOH}$, 80	1 : 2	190	16	84	-19 – 24
10**	Erythritol	$R^1\text{COOH}$, 60	1 : 2	190	16	87	-19 – 24
11	Erythritol	$R^1\text{COOH}$, 80	1 : 2	150	8	77	-14 – 20
12	Erythritol	$R^1\text{COOH}$, 80	1 : 2	150	20	96	-16 – 21
13	1,2,3- butanetriol	$R^1\text{COOH}$, 60	1 : 2	150	16	96	-12 – 18
14	1,2,3- butanetriol	$R^1\text{COOH}$, 60	1 : 1	150	16	94	-13 – 18
15	1,2,3- butanetriol	$R^1\text{COOH}$, 60	1 : 2	140	16	93	-11 – 16
16	1,2,3- butanetriol	$R^1\text{COOH}$, 60	1 : 2	190	16	89	-12 – 16
17	1,2,3- butanetriol	$R^1\text{COOH}$, 60	1 : 2	190	8	90	-14 – 19
18	1,2,4- butanetriol	$R^1\text{COOH}$, 60	1 : 2	150	16	95	-13 – 16
19	1,2,4- butanetriol	$R^1\text{COOH}$, 60	1 : 1	150	16	93	-12 – 16
20	1,2,4- butanetriol	$R^1\text{COOH}$, 60	1 : 2	140	16	92	-11 – 15
21	1,2,4- butanetriol	$R^1\text{COOH}$, 60	1 : 2	160	16	96	-13 – 16
22	1,2,4- butanetriol	$R^1\text{COOH}$, 60	1 : 2	190	16	88	-14 – 19
23	1,2,4- butanetriol	$R^1\text{COOH}$, 60	1 : 2	190	8	90	-12 – 17

* Product color is brown; ** product color is black.

When the ratio of erythritol to the complex of carboxylic acids is equal to 1:3, the reaction finishes within 8–10 h and lighter oils are obtained (experiments Nos. 3, 6, 8). The reactions of carboxylic acids with 1,2,3-butanetriol and 1,2,4-butanetriol proceed similarly.

Expected nonglyceride oils were obtained, by esterification of erythritol, 1,2,3-butanetriol and 1,2,4-butanetriol with carboxylic acid complexes obtained by saponification of olive ($R^2\text{COOH}$) and corn ($R^3\text{COOH}$) oils (Tab. 3). Tab. 3 presents the data summarizing the influence of reaction conditions (ratios of reactants, temperature, reaction time, solvent and inhibitor of radical reactions) on the products' yields and the characteristics of the obtained polyesters.

The process of esterification of 1,2,3-butanetriol and 1,2,4-butanetriol proceeds similar to the patterns as of erythritol. Under optimal conditions (temperature 150–160°C), in an N-MP solvent, with the addition of a P-23 inhibitor, the reactions are completed in 16 h.

Table 3

Esterification of erythritol, 1,2,3-butanetriol and 1,2,4-butanetriol with carboxylic acids of olive ($R^2\text{COOH}$) and corn ($R^3\text{COOH}$) oils

Exp. No.	Polyols, 20 mmol	Carboxylic acids, mmol	N-MP weight parts to RCOOH	Reaction temperature, °C	Reaction time, h	Yield, % mol	Freezing temperature, °C
1	Erythritol	$R^2\text{COOH}$, 80	1 : 2	150	16	93	– 5–8
2	Erythritol	$R^2\text{COOH}$, 60	1 : 2	150	16	95	– 8–10
3	Erythritol	$R^2\text{COOH}$, 60	1 : 1	150	16	90	– 9–11
4	Erythritol	$R^2\text{COOH}$, 80	1 : 2	140	16	88	– 10–14
5	Erythritol	$R^3\text{COOH}$, 60	1 : 2	160	16	93	– 15–20
6*	Erythritol	$R^1\text{COOH}$, 80	1 : 2	160	16	96	– 17–21
7	1,2,3- butanetriol	$R^1\text{COOH}$, 60	1 : 2	150	16	95	– 13–18
8*	1,2,3- butanetriol	$R^2\text{COOH}$, 60	1 : 2	160	16	95	– 9–12
9**	1,2,3- butanetriol	$R^3\text{COOH}$, 60	1 : 2	190	16	84	– 15–19
10	1,2,4- butanetriol	$R^1\text{COOH}$, 60	1 : 2	150	16	96	– 18–24
11	1,2,4- butanetriol	$R^2\text{COOH}$, 60	1 : 2	150	8	82	– 11–14
12	1,2,4- butanetriol	$R^3\text{COOH}$, 60	1 : 2	150	20	96	– 13–18

* Product color is brown; ** product color is black.

Characteristics of the Synthesized Compounds. The identity of the synthesized esters is confirmed by the IR spectra (Figs. 2 and 3). The vibration bands of erythritol, 1,2,3-butanetriol and 1,2,4-butanetriol are observed in the range of 3000–3500 cm^{-1} . Absorption in the region of 1230 and 1290 cm^{-1} also refers either to deformation vibrations of the OH group, or to the stretching vibrations of C–O in the carboxylic acid groups. In the IR spectra of carboxylic acids, an intense band at 940 cm^{-1} indicates out-of-plane bending vibrations of OH in carboxyl groups. In addition, the presence of carboxyl groups of fatty acids is confirmed by wide absorption bands in 1740, 2500–2700 cm^{-1} and 3000–3300 cm^{-1} region. After obtaining the products of erythritol–nonglyceride oils' esterification, the bands of hydroxyl groups disappear, but the bands at 1740, 1230 and 1290 cm^{-1} remain.

This result indicates that the reaction between erythritol and the carboxylic acid is complete, and all the hydroxyl groups of erythritol and carboxylic acids are converted into ester bonds. In case of obtaining trisubstituted erythritol esters, there are disubstituted, trisubstituted and tetrasubstituted products simultaneously present in the reaction mixture.

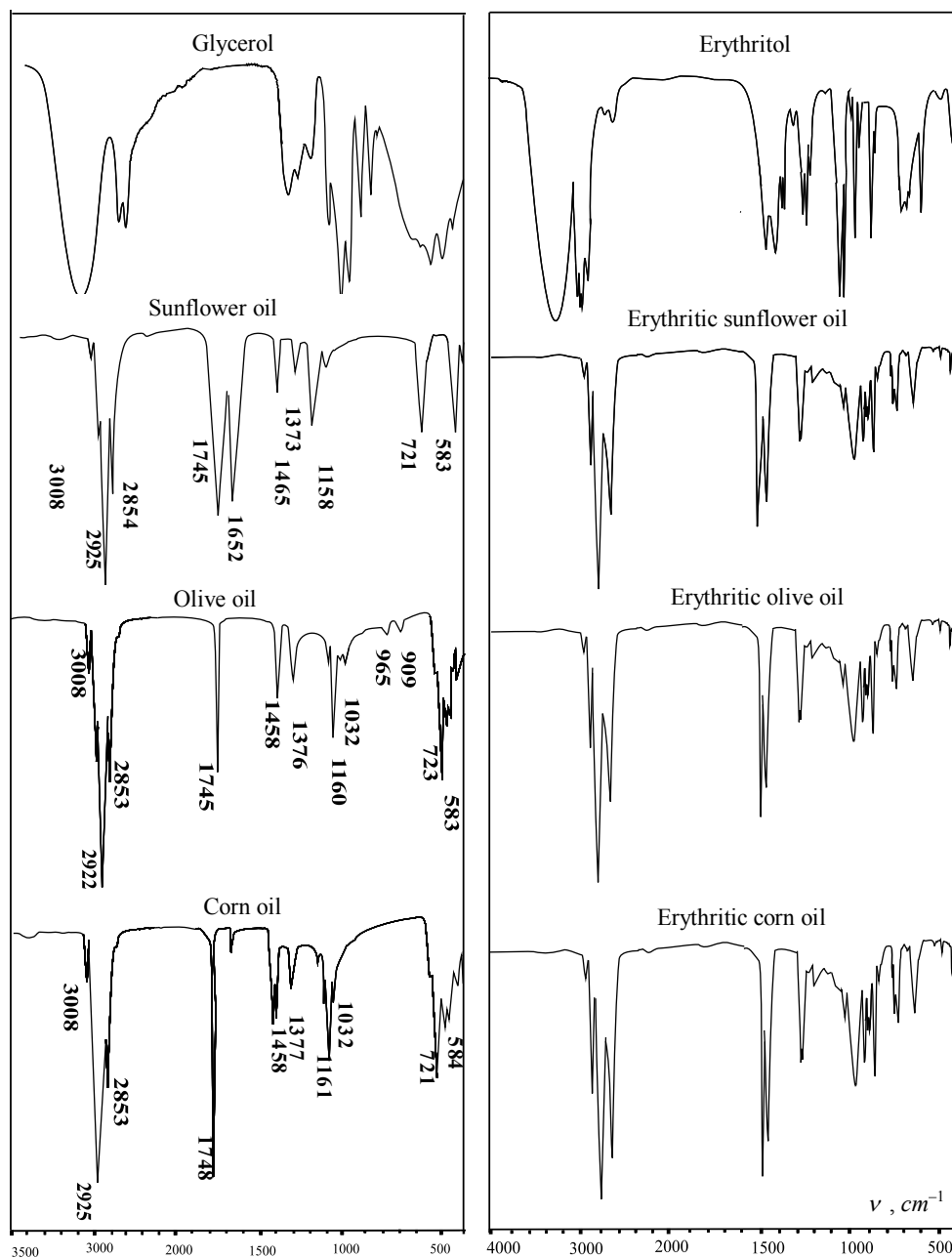


Fig. 2. IR spectra of glycerol, sunflower, olive and corn oils.

Fig. 3. IR spectra of erythritol and erythritol esters with fatty acids sunflower, olive and corn oils.

Experimental Part. The ^1H NMR spectra were taken on a Varian Mercury 300 instrument with an operating frequency of 300 MHz in $\text{DMSO-}d_6\text{-CCl}_4$ (1 : 3) with the internal TMS standard. IR spectra are obtained on an instrument IRS 29. Spectra of solid samples are taken in vaseline oil on KBr plates in the 4000–400 cm^{-1} region. Analysis of fatty acid methyl esters by gas-liquid chromatography (GLC) are performed on a Tsvet-600 (Russia) with a flame ionization detector, steel columns 3×3000 mm, stationary phase 5% E-30 and 5% polyethylene glycol adipate on Inerton-5 Super. The control of identification process of obtained polyesters was carried out by thin layer chromatography in the toluene + butanol system (4 : 1) on filter paper, with the developer – iodine vapor [11]. Erythritol, 2,6-ditretbutyl-4-methylphenol, solvents and other reagents were used standard reagents marked “clean”, without additional purification. “Golden sunflower” seed oil (GOST 1129-2013), “Filippo Berio” olive oil (Italy) and “Sloboda” corn oil (GOST 8808-2000) were used as samples from the commercial network without further purification.

Synthesis of the Original Polyols. For the synthesis of 1,2,3-butanethriol, 1-chloro-2-butene was used, and 4-chloro-1-butene was used for the synthesis of 1,2,4-butanethriol, which are by-products of the production of chloroprene from butadiene at the chemical plant CJSC “Nairit”, Yerevan, Armenia [3].

The General Method of Obtaining Carboxylic Acids from Oils. The reaction was carried out in a thermostated flask with a mechanical stirrer and reflux condenser. 89 g of sunflower oil (about 100 mmol, in terms of oleic acid) and 40 g of 20% sodium hydroxide solution (200 mmol) are placed in the reactor. With the mixer turned on, the air was pumped out (40–60 mm Hg) and heated to a temperature of 90°C. It took 4 h for full consumption of the oil. During cooling the resulting mixture of alkaline salts was treated with 430 mL (220 mmol) of diluted (5%) sulfuric acid, the separated oily layer (mixture of sunflower oil acids, R^1COOH , 81g (95.4%)) was extracted with diethyl ether (2×100 mL), washed with water (to remove residues of acid and glycerol) and dried over calcium chloride. The ether was evaporated, the residue was analyzed by GLC of methyl esters, according to GOST RF 31663 and 31665 [8, 9]. The hydrolysis of olive and corn oils was conducted similarly. Chromatographically identified basic acids were: oleic, linoleic, linolenic, stearic, palmitic and others in the composition of vegetable oils (Fig. 1, Tab. 1). The total acid yield was 93–96%.

The General Method of Polyols Esterification. The reaction is carried out on a combined reactive distillation unit, including a thermostatically controlled reactor with a magnetic stirrer and a column with a reflux condenser and a water vapor condenser. A flask is charged with 45 g of N-MP, 2.44 g (20 mmol) of erythritol, 22.56 g (80 mmol) of a mixture of acids of sunflower oil, and 0.3 g of an inhibitor of the free radical reaction P-23. With the mixer turned on, the air was pumped out (10–20 mm Hg) and heated to the set temperature. To control the course of the reaction, a sample of reaction mixture was taken every 2 h and the content of reactants and products was determined by chromatography. Then the reaction mixture was cooled, the product was washed with water (4×80 mL) to remove the residual reagents and N-MP. The resulting oil was reprecipitated from 40 mL of 80% ethanol and dried to constant weight. The yield of erythritol

tetraester was 23.08 g (92%). The reaction product tetraacyl erythritol was an oily liquid with a color from light beige to yellow. The described experiment is shown in Tab. 2 for No. 1. The results of other experiments on the production of other tetraacyl erythritol, triacyl erythritol and triacyl butanetriol derivatives of sunflower oil are summarized in Tab. 2. The results of the experiments on the production of tetraacyl erythritol, triacyl erythritol and triacyl butanetriol derivatives of olive and corn oils are presented in Tab. 3. The new types of nonglyceride oils (triacyl- and tetraacyl butane polyols) most closely resemble the natural vegetable oils (triacylglycerides) in terms of their structures and physicochemical properties. This fact will have a significant value for the screening of dietary substitutes of oils and fats.

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