

PRODUCING OF ERYTHRITOL ESTERS WITH STEARIC,
PALMITIC AND OLEIC ACIDS

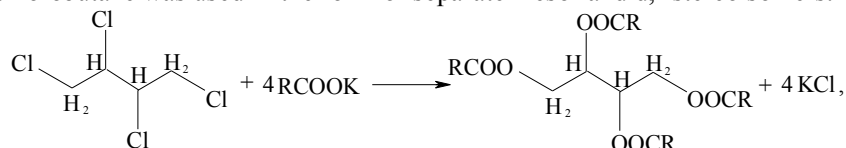
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By esterification reaction of 1,2,3,4-tetrachlorobutane with salts of stearic, palmitic and oleic acids corresponding erythritol esters are obtained. The effective methodology for esterification reaction at temperatures 100–190°C with or without solvents is worked out. The physical and chemical constants of the obtained compounds are defined.

Keywords: 1,2,3,4-tetrachlorobutane esterification, stearic, palmitic and oleic acid salts, erythritol esters.

Introduction. Complex esters of polyhydric alcohols are important products of chemical synthesis. They are widely used as lubricants, plasticizers, additives for oils and etc. [1]. Of particular interest are esters of sucrose and certain mono-saccharides (erythritol, mannitol, sorbitol, etc.) with high fatty acids (stearic, palmitic and others) that are used as dietary substitutes for oils and fats. Erythritol complex esters of high fatty acids with 1–1.2 degree of substitution are used in the food industry as emulsifiers [2, 3]. Individually erythritol (E968) is used in food as a sweetener, stabilizer and a wetting agent [4]. The purpose of this research is to study the possibility of obtaining erythritol esters of stearic, palmitic and oleic acids in molar ratios of 1–3:4. The resulting compounds may be of interest as dietary oils and fat substitutes [5]. In research [6] to obtain esters of mannitol and sorbitol was used polyols esterification reaction by high carboxylic acids at 140–190°C with and without acid catalysts. At the same time it is known, that the preparation of complex esters proceed under milder conditions when using additional reaction of an alkyl halide salts to carboxylic acids [7]. Therefore, for obtaining erythritols with high carboxylic acid esters, in this work the possibility of using the reaction of 1,2,3,4-tetrachlorobutane with appropriate acid salts were studied. Tetrachlorobutane was used in the form of separate meso- and d,l-stereoisomers:



where R are: $-\text{C}_{17}\text{H}_{35}$, $-\text{C}_{15}\text{H}_{31}$ or $-\text{C}_{17}\text{H}_{33}$.

Results and Discussion.

Characteristics of the Synthesized Compounds. Individuality of the synthesized esters is confirmed by IR and ^1H NMR spectra (Fig. 1, 2). Erythritol oscillation strips,

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the bands of the chlorine atoms oscillation and CH_2Cl groups were observed in the range of 3000–3500, 850–550 and 1300–1150 cm^{-1} respectively. After obtaining an esterification product erythritol tetrapalmitate these bands disappear. This result indicates that the reaction between the fatty acid salt and tetrachlorobutane was complete, and all chlorine atoms of tetrachlorobutane were converted into ester bonds. The carbonyl group peaks of formed tetraesters also confirmed the esterification reaction. In the case of disubstituted and trisubstituted erythritol esters, in the reaction mixture disubstituted, trisubstituted and tetrasubstituted products are present.

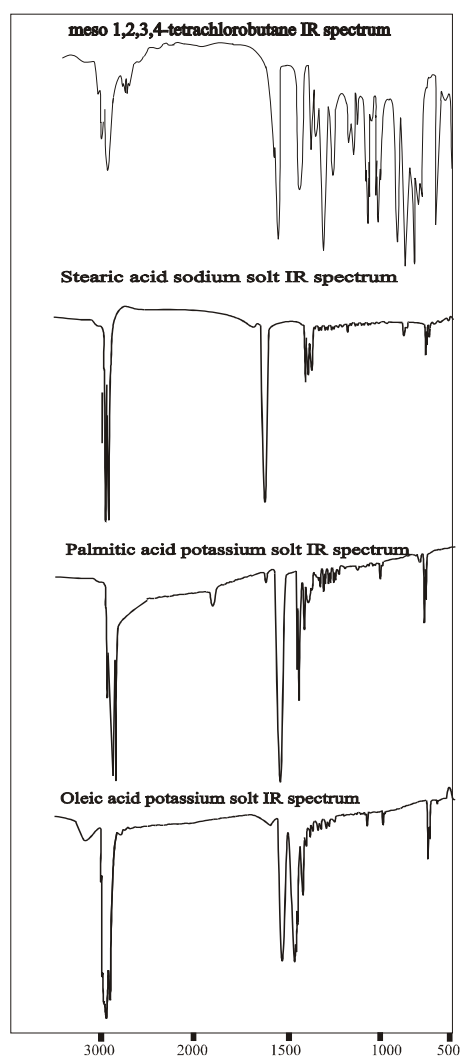


Fig. 1. The IR spectra of salts of stearic, palmitic and oleic acids.

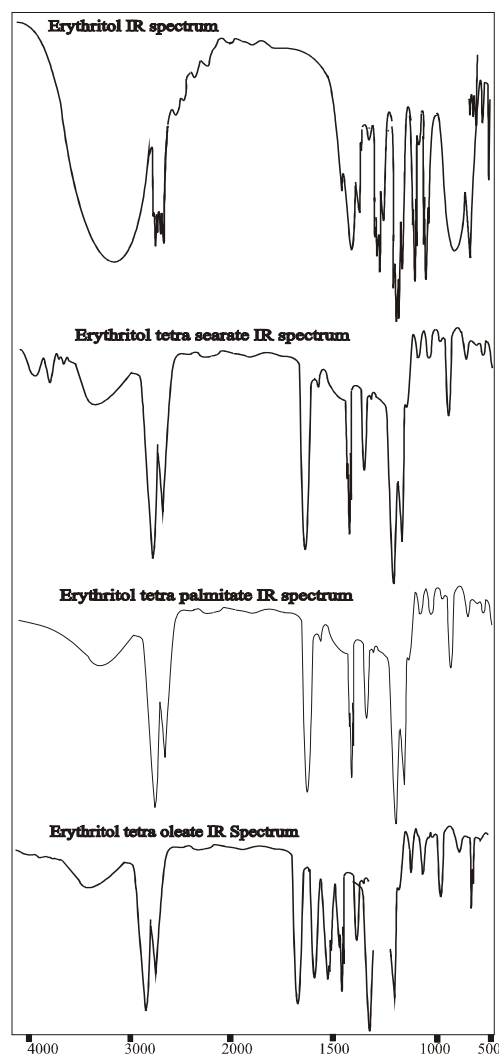


Fig. 2. IR spectra of erythritol and its tetraesterate, tetrapalmitate and tetraoleate.

As seen from the Table, the esterification reaction of tetrachlorobutane with high fatty acids alkali salts successfully proceeds at temperatures of 130–150°C for 16–20 h. To a degree 2–3 of substitution reaction proceeds for 8–12 h, but then significantly slowed down due to the occurrence of steric hindrances in the hydrocarbon skeleton partially substituted product. For tetra substituted esters is apparently required to

increase the heating duration to 16–20 h. Heating the reaction mixture at temperatures of 150–190°C for more than 20 h leads to darkening derived oils. Darkening is partially prevented by pumping air up to 20–40 mm Hg or by passing inert gases (nitrogen, helium) at a reduced pressure, but it is not possible to avoid completely. Erythritol tetra palmitinate and tetra stearate are similar to paraffin solid products with softening point 97–103°C. Disubstituted and trisubstituted products expectedly have less high softening temperature. Obtained erythritol oleates are liquids with the vegetable oil consistency. Mixed esters of palmitic and oleic, or stearic and oleic acids of the consistency and softening temperature approached to animal oils and margarines.

Using the meso- and d,l-isomers of tetrachlorobutane did not reveal significant differences in their reactivity or physical and chemical properties of the product. Apparently, both isomers, or a mixture of them may be used in the reaction.

Experimental Part. ¹H NMR spectra have been recorded on device Varian Mercury 300 with 300 MHz operating frequency in DMSO-*d*₆-CCl₄ (1:3) with an internal standard TMS. Identification of substances was carried out through a thin layer chromatography (TLC) in the system of butanol + toluene (4:1) on the filter paper, iodine vapor used as a developer [9]. Meso- and d,l-tetrachlorobutane has been prepared by chlorination of technical 3,4-dichloro-1-butene (product “Nairit” plant, purity 99.6%), d,l-tetrachlorobutane was distilled at 110–111°C, meso-tetrachlorobutane was distilled at 130–132°C (40 mm Hg) and recrystallized from ethanol, the purity of 99.3% [8]. Standart reagents marked “clean”, without additional purification have been used for potassium palmitate, sodium oleate and calcium stearate. In other cases, the carboxylic acid salts have been prepared from the corresponding carboxylic acid and an alkali, *in situ*. Stearic, palmitic, oleic acids and the solvents for chromatography were used standard reagents mark “clean”. Experimental data are summarized in the Table.

The esterification of tetrachlorobutane with fatty acid salts

Fatty acid salt (molar ratio to tetrachlorobutane)	Solvent, wt. parts	T, °C	Reaction duration, h	Yield, % mol	Freez. point, °C,
Potassium palmitate (1 : 2)	–	150	16	97	57–59
Potassium palmitate (1 : 3)	–	150	16	96	58–62
¹⁾ Potassium palmitate (1 : 4)	–	150	16	93	97–102
¹⁾ Potassium palmitate (1 : 4)	–	150	8 (24)	80 (94)	97–102
Potassium palmitate (1 : 3)	N-MP (1:3)	150	6 (20)	75 (92)	60–62
Potassium palmitate (1 : 4)	–	100	16	90	72–99
Potassium palmitate (1 : 4)	–	130	16	98	87–99
Potassium palmitate (1 : 4)	–	190	16	80	101–103
Sodium palmitate (1 : 4)	–	150	16	95	97–102
Oleate stearate (1 : 4)	–	150	16	97	100–103
Calcium stearate (1 : 4)	–	150	16	96	100–103
Sodium palmitate (1 : 4)	DMFA (1:3)	150	16	87	57–59
Sodium palmitate (1 : 4)	DMFA (1:3)	100	16	63	57–59
²⁾ Potassium oleate (1 : 4)	N-MP (1:3)	130	16	95	–28–25
²⁾ Potassium oleate (1 : 3)	N-MP (1:3)	130	16	97	–32–28
²⁾ Potassium palmitate + potassium oleate (1:2:2)	–	150	16	96	42–45
²⁾ Potassium stearate + potassium oleate (1:2:2)	–	150	16	96	45–51
²⁾ Potassium palmitate + potassium oleate (1:1:3)	–	150	16	96	40–43
²⁾ Sodium stearate + potassium oleate (1:1:3)	–	150	16	96	38–43

¹⁾ Experiments were carried out in parallel with meso- and d,l-isomers of tetrachlorobutane.

²⁾ For inhibition of polymerization P-23 is added.

General Procedure for the Esterification. The reaction was carried out in the combined reaction-distillation installation comprising a thermostated reactor with a magnetic stirrer and reflux condenser column for condensing the water vapor released by the formation of carboxylic acid salts. The reactor was charged 1.96 g (10 mmol) tetrachlorobutane and 6.04 g (22 mmol) of potassium palmitate. The air was pumped out and heated up during the stirring (20–40 mm Hg). To control the course of the reaction, every 4 h, a sample was taken and chromatographically content of starting materials and products have been determined. Then reaction mixture was cooled and recrystallized from 25 mL of 80° ethanol, the product was washed with water (4×20 mL) to remove residual reactants and the solvent, and dried to constant weight. Yield 97%. The reaction product erythritol dipalmitate is soft paraffin-like material of yellow or beige. In the first row of the Table the described experiment is presented, the results of other experiments also are summarized in the Table. In experiments containing oleic acid into the reaction mixture to inhibit polymerization are added 0.03 g of 2,6-di-tert-butyl-4-methylphenol (P-23). Similarly, the reaction is carried out with solvents: dimethylformamide (DMFA) and N-methylpyrrolidone (N-MP). The structure of the obtained erythritol esters was confirmed by the IR and ¹H NMR spectra.

Erythritol tetrastearate. Freez. point 97–102°C. FTIR cm^{-1} , 2919, 2850 (CH₂); 1737 (C=O); 1463, 1420 (CH₂); 1176, 1132 (C–O). ¹H NMR, δ , ppm: 0.95 t (12H, CH₃); 1.3 m (104H, CH₂); 1.4 m (8H, CH₂CH₃); 1.65 m (8H, CH₂); 2.3 m (8H, CH₂COO); 4.08 m (4H, CH₂COO); 7.25 s (2H, CH).

Erythritol tetrapalmitate. Freez. point 100–103°C. FTIR cm^{-1} , 2920, 2850 (CH₂); 1738 (C=O); 1463, 1420 (CH₂); 1176, 1132 (C–O). ¹H NMR, δ , ppm: 0.95 t (12H, CH₃); 1.3 m (88H, CH₂); 1.4 m (8H, CH₂CH₃); 1.65 m (8H, CH₂); 2.3 m (8H, CH₂COO); 4.08 m (4H, CH₂COO); 7.25 s (2H, CH).

Erythritol tetraoleinate. Freez. point –25–28°C. FTIR cm^{-1} , 3006, 2950, 2920, (CH₂); 1671 (C=O); 1645 (CH=); 1463, 1447 (CH₂); 1196, 1099 (C–O).

¹H NMR, δ , ppm: 0.97 t (12H, CH₃); 1.32 m (8H, COCH₂); 1.45 m (80H, CH₂); 1.60 m (8H, CH₂); 2.22 dd (16H, CH₂CH=); 2.35 m (8H, CH=); 4.08 m (4H, CH₂COO); 7.25 s (2H, CH).

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