PROCEEDINGS OF THE YEREVAN STATE UNIVERSITY

Chemistry and Biology 2016, № 2, p. 13–16

Chemistry

OBTAINING ESTERS OF MANNITOL AND SORBITOL USING STEARIC, PALMITIC AND OLEIC ACIDS

G. S. GRIGORYAN*, Z. G. GRIGORYAN, A. Ts. MALKHASYAN**

Chair of Organic Chemistry YSU, Armenia

The reaction of sorbitol and mannitol esterification with higher fatty acids has been investigated and the corresponding esters were obtained without using catalysts and solvents. The physical and chemical constants of esters were established. An optimal procedure of the reaction was developed.

***Keywords*:** sorbitol and mannitol esterification, oleic, stearic, palmitic acids, thin layer chromatography.

Introduction. Complex esters of glycols and polyols are important products of chemical synthesis and are produced in large amounts by chemical industry. They are widely used as lubricants, plasticizer, oil additives and etc. [1]. Esters of sucrose and certain polyols structurally related to the monosaccharides (mannitol, sorbitol, etc.) with high fatty acids (stearic, palmitic, and others.) are of a particular interest. Esters of mannitol, sorbitol, and high fatty acids with 1÷1–2 degree of substitution (DS) are used as emulsifiers in food industry [2]. The purpose of this research is to study the esterification of sorbitol and mannitol with stearic, palmitic and oleic acids with 1÷3–6 molar ratio to obtain oil-like compounds that may be used as dietary oil and fat substitutes [2, 3].

Experimental Part. The ^{1}H NMR spectra have been recorded on the device Varian Mercury 300 with 300 *MHz* operating frequency in the DMSO-d_6–CCl_4 (1: 3) with an internal standard TMS. Identification of control substances was carried out through a thin layer chromatography (TLC) in the system of butanol–toluene (4 : 1) on the filter paper, iodine vapor was used as a developer [4]. Standard reagents marked "clean", without additional purification have been used for mannitol, sorbitol, stearic, palmitic, oleic acids and the solvents used for chromatography.

***The General Procedure of the Esterification*.** The reaction was carried out in the combined reaction-distillation installation comprising a thermostated reactor with a magnetic stirrer and a distillation column with a Dean-Stark trap to condense the water vapor. The reactor was charged with 1.8 *g* (10 *mmol*) of mannitol, and 2.84 *g* (10 *mmol*) of stearic acid. The air was pumped out and heated up during the stirring (4 *mm* Hg). Helium was passed into the reactor once the temperature in the reactor reaches the set one (10–15 *mL*/*min*, 20–30 *mm* Hg).

* E-mail: grigor-1955@mail.ru ** E-mail: amalkhasyan@ysu.am

The reaction was monitored based on the release of water in the Dean-Stark trap flask, moreover, to control the course of the reaction, every 3 *h* a sample was taken and chromatographically the contents of the starting materials and products have been determined. Then reaction mixture was cooled and was dissolved in 25 *mL* of isopropyl ester the acid residue was separated and was washed with 4×20 *mL* of water to remove the reagent residues and dried to the constant weight. The yield was 97%. Reaction product, monostearate of mannitol is solid, paraffin like material with color varying from yellow to light brown. The described experiment is shown in the Table. In the experiments with oleic acid to the reaction mixture 0.03 *g* of 2,6-ditertbutil-4-methylphenol (P-23) was added to inhibit the polymerization.

Results of esterification of mannitol and sorbitol with fatty acids

№	Polyol	Acid	Ratio of polyol to acid	Temperature, °*C*	Duration of reaction, *h*	Yield, % *mol*	Freez. point, °*C*, physical property
1	Mannitol	stearic	1 : 1	190	6	97	64, hard
2			1 : 2	190	6	96	58–60, soft
3			1 : 4	190	6	93	60–62, hard
4			1 : 6	190	6 (20)	55 (92)	60–62, hard
5			1 : 4	170	6	68	60–62, hard
6			1 : 4	140	6	32	57–61, hard
7			1 : 4	220	6	82	60–62, hard burnt
8			1 : 4	190	12	96	60–62, hard
9			1 : 4	190	20	97	60–62, hard
10		palmitic	1 : 2	190	6	96	50–52, hard
11			1 : 4	190	6	96	47–48, hard
12*		oleic	1 : 4	190	6	97	0–2, liquid
13*		stearic+ oleic	1 : 2 : 2	190	6	96	8–12, viscous
14*			1 : 3 : 3	190	6 (16)	80 (96)	35–38, oleaginous
15	Sorbitol	stearic	1 : 4	190	6	95	53–55, hard
16			1 : 6	190	6 (16)	74 (93)	54–55, hard
17		palmitic	1 : 4	190	6	95	72, hard
18			1 : 2	190	6	95	52, caramelized
19*		oleic	1 : 4	190	6	95	–10–12, liquid
20*			1 : 6	190	6 (16)	72 (95)	–2, gelled
21*		stearic+ oleic	1 : 2 : 2	200	6	95	36–40, oleaginous
22*			1 : 3 : 3	190	6 (16)	84 (95)	34–37, oleaginous

* For inhibition of polymerization P-23 is added.

Results and Discussion. For the purpose of synthesis the reaction of esterification of sorbitol and mannitol with fatty acids without using catalysts and solvents (which are considered as the sources of food contamination) has been performed. The reaction can be presented by the following equation:

$$CH_2(OH)(CHOH)_4CH_2OH + n\text{RCOOH} \rightarrow$$
$$\rightarrow CH_2(OCOR)(CHOCOR)_n(CHOH)_{4-n}CH_2OCOR + (n+2)H_2O, \quad n \geq 4.$$

The reaction is carried out in the combined reaction-distillation installation comprising thermostated reactor with a magnetic stirrer and a distillation column.

The removal of water from the reaction zone accelerates the reaction rate. The water removal is facilitated using vacuum or passing the inert gas-helium into the reactor (see the Table).

Up to 2–4 DS the reaction easily passes within 6 *h*, but later it is significantly slowed down, because of the steric hindrances in the hydrocarbon skeleton of the partially substituted polyols. The duration of heating is to be increased to 12–20 *h* for obtaining hexa-substituted products. Prolonged heating of the reaction mixture at the temperature of 190°*C* leads to the darkening of the derived oils. Darkening is partially prevented but not completely avoided, if air is pumped up to 20–30 *mm*Hg, or through passing inert gases (nitrogen, helium) at a reduced pressure.

The structure of the obtained polyol esters was confirmed by the IR and ^{1}H NMR spectra.

Mannitol Monostearate. Freez. point 64º*C*. FTIR, cm^{-1}, 3150–3500 (OH), 2964, 2672 (CH_2), 1703 (C=O), 1490, 1420 (CH_2), 1280, 1080 (C–O). ^{1}H NMR, δ, ppm: 0.97 t (3H, CH_3); 1.3 m (28H, CH_2); 1.75 m (2H, CH_2); 2.3 t (2H, CH_2); 3.71 m (4H, CH); 3.85 dd (4H, CH_2); 4.8 s (5H, OH).

Mannitol Distearate. Freez. point 58–60º*C*. FTIR, cm^{-1}, 3150–3500 (OH), 2964, 2672 (CH_2), 1703 (C=O), 1490, 1420 (CH_2), 1280, 1080 (C–O). ^{1}H NMR, δ, ppm: 0.97 t (6H, CH_3); 1.3 m (56H, CH_2); 1.75 m (4H, CH_2); 2.3 t (4H, CH_2); 3.71 m (4H, CH); 3.85 dd (4H, CH_2); 4.8 s (4H, OH).

Mannitol Tristearate. Freez. point 60–62º*C*. FTIR, cm^{-1}, 3150–3500 (OH), 2964, 2672 (CH_2), 1703 (C=O), 1490, 1420 (CH_2), 1280, 1080 (C–O). ^{1}H NMR, δ, ppm: 0.97 t (9H, CH_3); 1.3 m (84H, CH_2); 1.75 m (6H, CH_2); 2.3 t (6H, CH_2); 3.71 m (4H, CH); 3.85 dd (4H, CH_2); 4.8 s (3H, OH).

Mannitol Tetrastearate. Freez. point 60–62º*C*. FTIR, cm^{-1}, 3150–3500 (OH), 2964, 2672 (CH_2), 1703 (C=O), 1490, 1420 (CH_2), 1280, 1080 (C–O). ^{1}H NMR, δ, ppm: 0.97 t (12H, CH_3); 1.3 m (112H, CH_2); 1.75 m (8H, CH_2); 2.3 t (8H, CH_2); 3.71 m (4H, CH); 3.85 dd (4H, CH_2); 4.8 s (2H, OH).

Mannitol Hexastearate. Freez. point 60–62º*C*. FTIR, cm^{-1}, 2964, 2672 (CH_2), 1703 (C=O), 1490, 1420 (CH_2), 1280, 1080 (C–O). ^{1}H NMR, δ, ppm: 0.97 t (18H, CH_3); 1.3 m (168H, CH_2); 1.75 m (12H, CH_2); 2.3 t (12H, CH_2); 3.71 m (4H, CH); 3.85 dd (4H, CH_2).

Mannitol Dipalmitinate. Freez. point 50–52º*C*. FTIR, cm^{-1}, 3150–3500 (OH), 2964, 2672 (CH_2), 1706 (C=O), 1490, 1420 (CH_2), 1280, 1080 (C–O). ^{1}H NMR, δ, ppm: 0.97 t (6H, CH_3); 1.3 m (48H, CH_2); 1.75 m (4H, CH_2); 2.3 t (4H, CH_2); 3.71 m (4H, CH); 3.85 dd (4H, CH_2); 4.8 s (4H, OH).

Mannitol Tetrapalmitinate. Freez. point 47–48º*C*. FTIR, cm^{-1}, 3150–3500 (OH), 2964, 2672 (CH_2), 1703 (C=O), 1490, 1420 (CH_2), 1280, 1080 (C–O). ^{1}H NMR, δ, ppm: 0.97 t (12H, CH_3); 1.3 m (96 H, CH_2); 1.75 m (8H, CH_2); 2.3 t (8H, CH_2); 3.71 m (4H, CH); 3.85 dd (4H, CH_2); 4.8 s (2H, OH).

Mannitol Tetraoleinate. Freez. point 0–2º*C*. FTIR, cm^{-1}, 3150–3500 (OH), 2964, 2672 (CH_2), 1703 (C=O), 1680 (CH=), 1490, 1420 (CH_2), 1280, 1080 (C–O). ^{1}H NMR, δ, ppm: 0.97 t (12H, CH_3); 1.3 m (92H, CH_2); 1.75 m (8H, CH_2); 2.34 dd (8H, CH=); 3.71 m (16H, CH); 3.85 dd (4H, CH_2); 4.8 s (2H, OH).

Sorbitol Tetrastearate. Freez. point 53–55°*C*. FTIR, cm^{-1}, 3150–3500 (OH), 2964, 2672 (CH_2), 1703 (C=O), 1490, 1440 (CH_2), 1300, 1100 (C–O). ^{1}H NMR, δ, ppm: 0.97 t (12H, CH_3); 1.3 m (112H, CH_2); 1.75 m (8H, CH_2); 2.3 t (8H, CH_2); 3.67–3.81 m (4H, CH); 3.63–3.84 dd (4H, CH_2); 4.84 s (2H, OH).

Sorbitol Hexastearate. Freez. point 54–55°*C*. FTIR, cm^{-1}, 3150–3500 (OH), 2964, 2672 (CH_2), 1703 (C=O), 1490, 1440, (CH_2), 1300, 1100 (C–O). ^{1}H NMR, δ, ppm: 0.97 t (18H, CH_3); 1.3 m (168H, CH_2); 1.75 m (12H, CH_2); 2.3 t (12H, CH_2); 3.67–3.81 m (4H, CH); 3.63–3.84 dd (4H, CH_2).

Sorbitol Dipalmitinate. Freez. point 52°*C*. FTIR, cm^{-1}, 3150–3500 (OH), 2964, 2672 (CH_2), 1706 (C=O), 1490, 1420 (CH_2), 1280, 1080 (C–O). ^{1}H NMR, δ, ppm: 0.97 t (6H, CH_3); 1.3 m (48H, CH_2); 1.75 m (4H, CH_2); 2.3 t (4H, CH_2); 3.71 m (4H, CH); 3.85 dd (4H, CH_2); 4.8 s (4H, OH).

Sorbitol Tetrapalmitinate. Freez. point 72°*C*. FTIR, cm^{-1}, 3150–3500 (OH), 2964, 2672 (CH_2), 1703 (C=O), 1490, 1420 (CH_2), 1280, 1080 (C–O). ^{1}H NMR, δ, ppm: 0.97 t (12H, CH_3); 1.3 m (96 H, CH_2); 1.75 m (8H, CH_2); 2.3 t (8H, CH_2); 3.71 m (4H, CH); 3.85 dd (4H, CH_2); 4.8 s (2H, OH).

Sorbitol Tetraoleinate. Freez. point 10–12°*C*. FTIR, cm^{-1}, 3150–3500 (OH), 2964, 2672 (CH_2), 1703 (C=O), 1680 (CH=), 1490, 1420 (CH_2), 1280, 1080 (C–O). ^{1}H NMR, δ, ppm: 0.97 t (12H, CH_3); 1.3 m (92H, CH_2); 1.75 m (8H, CH_2); 2.34 dd (8H, CH=); 3.71 m (16H, CH); 3.85 dd (4H, CH_2); 4.8 s (2H, OH).

Sorbitol Hexaoleinate. Freez. point –2°*C*. FTIR, cm^{-1}, 3150–3500 (OH), 2964, 2672 (CH_2), 1703 (C=O), 1680 (CH=), 1490, 1420 (CH_2), 1280, 1080 (C–O). ^{1}H NMR, δ, ppm: 0.97 t (18H, CH_3); 1.3 m (156H, CH_2); 1.75 m (12H, CH_2); 2.34 dd (12H, CH=); 3.71 m (4H, CH); 3.85 dd (4H, CH_2).

Received 13.04.2016

REFERENCES

1. **Tonkonogov B.P., Popova K.A., Hurumova A.F.** Perspective of Using Esters as a National Production as Basis of Oils for the Aircraft Equipment. // Proceedings of Gubkin Russian State University of Oil and Gas, 2015, v. 278, № 1, p. 109–120 (in Russian).
2. **Ha-Yull Chung, Jiyong Park, Jung-Han Kim, Un-Yong Kong.** Preparation of Sorbitol Fatty Acid Polyesters. Potential Fat Substitutes: Optimization of Reaction Conditions by Response Surface Methodology. // J. Am. Oil Chem. Soc., 1996, v.73, p. 637–643.
3. **Namal Senenayake S.P.J., Shahidi F.** Dietary Fat Substitutes. Chp. 15, v. 3, p. 502–534. In Book: Bailey's Industrial Oil and Fat Products (6th ed.), 2005, 3616 p.
4. Thin-Layer Chromatography (ed. E. Stahl). M.: Mir, 1965, 508 p. (in Russian).