

SYNTHESIS OF SUCROSE ESTERS WITH STEARIC, PALMITIC AND OLEIC ACIDS

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The esterification of sucrose with stearic, palmitic and oleic acids yields the corresponding esters. Effective methods have been developed for carrying out the esterification reaction at temperatures of 150–170°C in high-boiling aprotic dipolar solvents.

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Introduction. Esters of sugars and polyhydric alcohols with aliphatic carboxylic acids C₆–C₂₂ are widely used as plasticizers and lubricating oils in the food industry, cosmetics, medicine and chemical production [1, 2]. Sucrose esters with higher fatty acids with a degree of substitution of 1 : 1 ÷ 2 are used in the food industry as emulsifiers and antibacterial agents [3]. Sucrose esters with higher fatty acids (stearic, palmitic, oleic and others) are of particular interest as they can be used as dietary substitutes for oils and fats [4].

In our early studies, it was shown that polyatomic alcohols can be directly esterified with higher fatty acids to form esters [5, 6]. Depending on the synthesis conditions, the degree of substitution of esters varied from 1 : 2 to 1 : 6. It was interesting to synthesize sucrose esters because it has 8 hydroxyl groups and, therefore, an appropriate degree of substitution can be achieved. Sucrose does not contain a free aldehyde group and by chemical properties it is similar to polyols.

The aim of this investigation is to study the possibility of obtaining sucrose esters with stearic, palmitic and oleic acids in molar ratios of 1 : 4 ÷ 8. The resulting compounds can be considered for dietary substitution of oils and fats [1].

It is known that for the synthesis of esters, the direct esterification with or without acidic or basic catalysts is often used [7]. However, unlike the ordinary polyols, at the melting point of sucrose (above 186°C), its' decomposition begins. Alternative reaction routes have been developed to avoid overheating. Numerous studies have shown the preference for the synthesis of esters through anhydrides or carboxylic acid chlorides [7]. Many patent publications emphasize the benefits of

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using the transesterification reaction of polyatomic alcohols and sugars with carboxylic acid esters [8, 9].

In this work of obtaining esters, we used the direct reaction of sucrose esterification with higher carboxylic acids without catalysts at temperatures not above 170°C. We have particularly focused on esters with a degree of substitution greater than 3, since mono- and di-substituted sucrose esters are well-known emulsifiers. To homogenize the reaction mixtures of sucrose with aliphatic acids, high-boiling aprotic dipolar solvents N-methylpyrrolidone and DMSO were used, in which both reagents are soluble upon heating [3].

Experimental Part. The ^1H NMR spectra were taken on a Varian Mercury 300VX instrument with an operating frequency of 300.08 MHz in DMSO + d_6 / CCl_4 (1 : 3) with an internal TMS standard. The individuality control of substances was performed on an Agilent Infinity II HPLC 1260 System instrument. Column: Zorbax Eclipse XDB – (C_{18}), column dimensions: 250×4.4 mm, 5 μm ; stationary phase octadecyl silica gel, eluent acetonitrile + methanol 50 : 50. HPLC solvents and water were HPLC-Grade. The reaction was monitored by thin layer chromatography in a toluene + butanol system (4 : 1) on filter paper with the developer of iodine vapor [10]. We used standard reagents of sucrose (GOST 5833-75 Reagent), stearic, palmitic, oleic acid and solvents marked “clean” without additional purification.

General Method of Esterification. The reaction was carried out on a combined reactive distillation unit, including a thermostatic reactor with a magnetic stirrer and a distillation column with a Dean-Stark nozzle for condensation of water vapor. 3.42 g (10 mmol) of sucrose, 8.52 g (30 mmol) of stearic acid and 20 mL of N-methylpyrrolidone were placed in the reactor. The air was pumped out with stirring (4 mm Hg) and heating the reaction mixture. Upon reaching the set temperature, nitrogen was passed into the reactor (15–20 mL/min, 20 ± 5 mm Hg). By removing water from the reaction zone, we achieved an acceleration of its flow, whereas the measurement of the volume of condensate in the Dean-Stark nozzle was used to monitor the progress of the reaction. In addition, a sample was taken every 3 h and the approximate content of reactants and products was determined by paper chromatography (rapid analysis). Then the reaction mixture was cooled down, dissolved in 40 mL of diisopropyl ether. The remaining unreacted reagents were separated, washed with water (4 × 30 mL) to remove residual sucrose and dried to constant weight. The yield was 86%. The reaction product was a mixture of polysubstituted sucrose stearates – a solid paraffin-like mass of dark yellow color. The described experiment is shown in Table, # 2. In experiments with oleic acid, 0.03 g of 2,6-di-*tert*-butyl-4-methylphenol (P-23) was added to the reaction mixture to inhibit the polymerization.

The conversion was calculated by chromatogram, by the residue of aliphatic acid. The total yields of sucrose esters were determined by the weight of the separated washed and dried in vacuum product (see Table).

Results and Discussion. The reaction of sucrose with aliphatic acids is represented in Fig. 1.

The Table shows the experimental conditions and data on the yields of the reaction products.

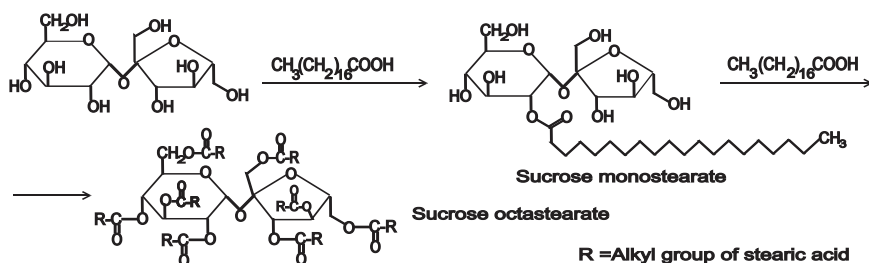


Fig. 1. Sucrose fatty acid esters production by esterification of sucrose with stearic acid.

The esterification of sucrose by higher carboxylic acids in N-methylpyrrolidone

#	Acid	Ratio of sucrose to acid	Temperature, °C	Duration of reaction, h	Yield, mol. %	Freez. point, °C, physical property
1	stearic	1 : 4	170	12	96	90–94, hard
2	stearic	1 : 6	170	12	87	108–110, hard
3	stearic	1 : 8	170	12	86	146–154, hard
4	stearic	1 : 6	150	12	60	96–101, hard
5	stearic	1 : 6	130	12	34	80–83, hard
6	stearic	1 : 6	100	12	18	97–90, hard
7	stearic	1 : 6	200	12	83	140–146, hard, burnt
8	stearic	1 : 6	170	6	69	80–83, hard
9	stearic	1 : 6	170	18	94	130–137, hard, dark
10	palmitic	1 : 4	170	12	98	87–90, soft
11	palmitic	1 : 6	170	12	97	106–110, hard
12	palmitic	1 : 8	170	12	91	120–128, hard
13	palmitic	1 : 6	150	12	90	100–103, hard
14	palmitic	1 : 8	170	6	91	96–101, hard
15	palmitic	1 : 8	190	12	88	117–122, hard, caramelized
16 ¹⁾	oleic	1 : 4	170	6	95	22–25, liquid
17 ¹⁾	oleic	1 : 6	170	6	93	30–33, soft, honey-like
18 ¹⁾	oleic	1 : 8	170	6	92	44–48, soft, gelled
19 ¹⁾	stearic + oleic	1 : 2 : 2	170	6	95	55–61, soft, oleaginous
20 ¹⁾	stearic + oleic	1 : 3 : 3	170	6	91	50–56, soft, gelled
21 ¹⁾	stearic + oleic	1 : 4 : 4	170	6	87	88–92, caramelized
22 ¹⁾	palmitic + oleic	1 : 2 : 2	170	6	93	49–54, soft
23 ¹⁾	palmitic + oleic	1 : 3 : 3	170	6	93	55–60, gelled
24 ¹⁾	palmitic + oleic	1 : 4 : 4	170	6	89	58–62, caramelized
25 ²⁾	stearic	1 : 6	170	12	90	108–110, hard, dark
26 ²⁾	palmitic	1 : 8	190	12	96	114–120, hard, burnt
27 ^{1, 2)}	oleic	1 : 4	170	6	92	12–15, liquid

¹⁾ P-23 is added to inhibit polymerization;

²⁾ the reaction is carried out in DMSO.

As shown in the Table, the sucrose esters with stearic and palmitic acids of high degrees of substitution are solid paraffin-like products. Compared to the obtained substances, monosubstituted esters have melting points of about 60°C, and di-substituted esters about 80°C and 108°C, respectively. Sucrose esters with oleic acid are liquids (experiment 16) or soft and thick masses. The products of sucrose esterification with compositions of stearic and oleic acid or palmitic and oleic acid taken in different ratios give products with melting points within the range of 50–92°C. An increase in the degree of substitution in the series 1 : 4, 1 : 6 and 1 : 8 for all acids leads to an expected increase in melting points. In addition, a decrease in the yield of esters was revealed with an increase in the ratio of sucrose to acid (1 : 4, 1 : 6 and 1 : 8). In the case of a molar excess of sucrose, higher results in acid conversion and product yields were observed.

Chromatographic observation of the reaction revealed the following patterns. To a degree of substitution of 2–4, the reaction proceeds easily in 6 h, but then naturally slows down due to a decrease in the concentration of reagents and the occurrence of steric hindrances in the structure of partially substituted sucrose esters (Fig. 2 and 3). The Fig. 2 shows the temperature dependence of the yields of esterification reaction products. At a temperature of 170°C and an initial ratio of sucrose to stearic acid of 1 : 6, the reaction is practically completed in 18 h with an acid conversion of 98%. The total yield of sucrose esters reaches 94%.

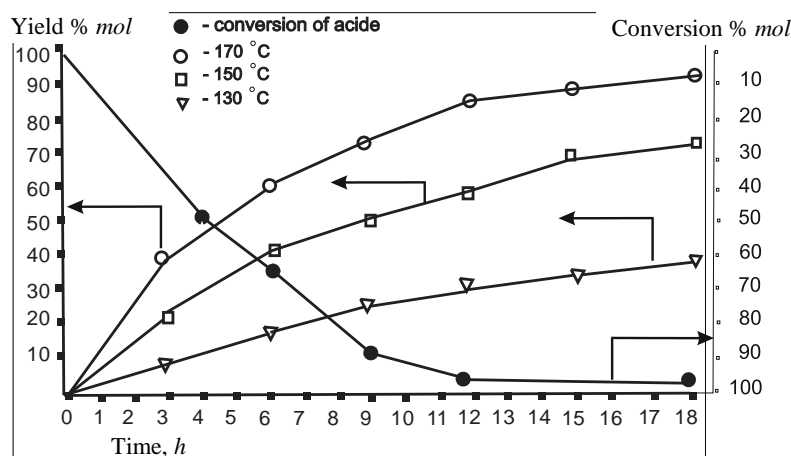


Fig. 2. Temperature dependence of the accumulation rate of reaction products and sucrose conversion. The ratio of sucrose: stearic acid 1 : 6. 1) 170°C; 2) 150°C; 3) 130°C; 4) conversion of stearic acid at 170°C.

Chromatographic monitoring of the accumulation of the products of the esterification reaction, the consumption of stearic acid and intermediate esters are shown in Fig. 3.

Here we see that at the initial stage, at a temperature of 170°C, monoesters and diesters quickly accumulate. In the second hour, the amount of diesters and triesters increases, and the amount of monoesters decreases. The concentration of triesters achieves the highest value within the range of 3 to 7 h. After 4 h, there is an increase in the concentration of only higher esters. After 12 h, only traces of mono and

diesters are detected in the reaction mixture. After 12 h, the amount of the mixture of higher polyesters reaches 85%. Apparently, to obtain polysubstituted products, an increase in the reaction time up to 20 h or more is required. However, prolonged heating of the reaction mixture in a solvent at temperatures of 170–190°C leads to darkening and decomposition of the resulting oils. In fact, this conclusion coincides with the observation that the melting and decomposition of sucrose mixed with emulsifiers can occur about 20°C below the melting point of pure sucrose [3]. The passage of inert gases under reduced pressure does not prevent darkening and partial decomposition of sucrose or other products.

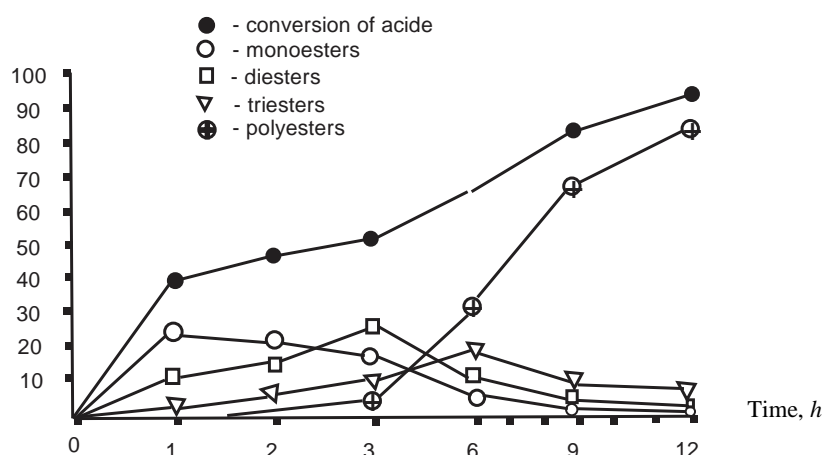


Fig. 3. The conversion of stearic acid and accumulation of sucrose with stearic acid esterification products at 170°C: 1) the conversion of stearic acid; 2) monoesters; 3) diesters; 4) triesters; 5) higher polyesters.

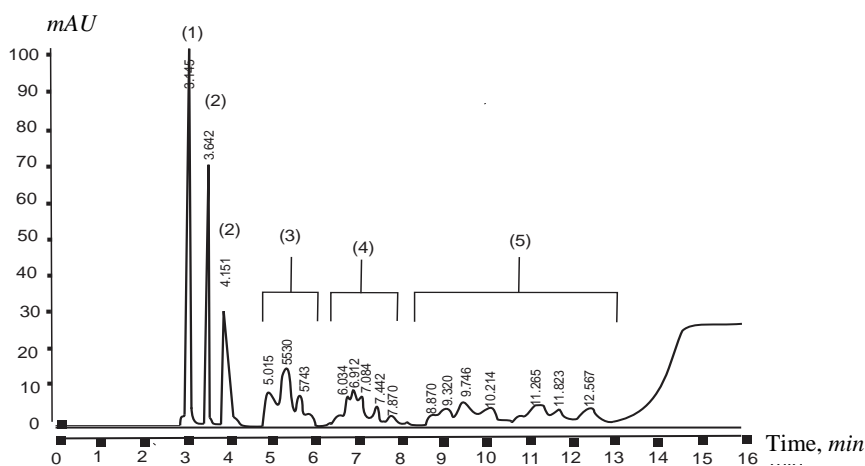


Fig. 4. Chromatogram of the sucrose esterification reaction mixture with stearic acid. Reaction conditions: 170°C, 6 h. (1) – sucrose monostearate; (2), (3) – sucrose distearate; (4) – sucrose tristearate; (5) – higher sucrose esters.

The Fig. 4 shows an HPLC chromatogram of sucrose esters with stearic acid. The reaction time is 6 h, at 170°C. Only monoesters, diesters and triesters are distinctly separated.

The identification of individual products, starting from the stage of tetraesters, becomes difficult, especially considering the impossibility of determining the individual isomers.

Conclusion. The study shows, that direct esterification of sucrose with carboxylic acids leads to the formation of a variety of esters. Obtaining products with a degree of substitution up to 4 is easy to carry out and can be identified. Prolonged heating of the reaction mixture in a solvent at temperatures above 170°C leads to the projected mixture of higher sucrose esters. The main disadvantage of the process is the decomposition of sucrose, which causes an undesirable color in the final product.

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**СИНТЕЗ СЛОЖНЫХ ЭФИРОВ САХАРОЗЫ СО СТЕАРИНОВОЙ,
ПАЛЬМИТИНОВОЙ И ОЛЕИНОВОЙ КИСЛОТАМИ**

Реакцией этерификации сахарозы стеариновой, пальмитиновой и олеиновой кислотами получены соответствующие сложные эфиры. Разработаны эффективные методики проведения реакции этерификации при температурах 150–170°C в высококипящих апротонных диполярных растворителях.

Գ. Ս. ԳՐԻԳՈՐՅԱՆ, Ա. Ց. ՄԱԼԽԱՍՅԱՆ

**ՍՏԵԱՐԻՆԱԹԹՎԻ, ՊԱԼՄԻՏԻՆԱԹԹՎԻ ԵՎ ՕԼԵԻՆԱԹԹՎԻ
ՍԱԽԱՐՈՉԱՅԻ ՀԵՏ ԷՍԹԵՐՆԵՐԻ ՍԻՆՏԵԶ**

Ստեարինաթթվի, պալմիտինաթթվի և օլեինաթթվի սախարոզայով էսթերիֆիկացման ռեակցիայով ստացված են համապատասխան էսթերներ: Մշակվել են բարձր եռացող սպրոտիկ երկրևեռ լուծիչներում 150–170°C ջերմաստիճաններում էսթերիֆիկացման ռեակցիա իրականացնելու արդյունավետ մեթոդներ: