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OBTAINING ESTERS OF CITRIC ACID WITH HIGH ALIPHATIC ALCOHOLS

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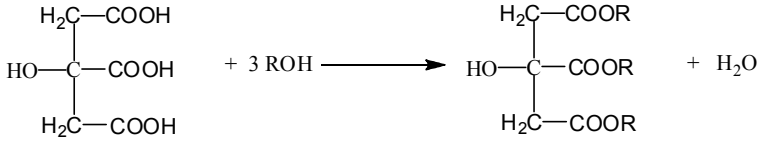
By esterification reaction of citric acid with pentadecylic, dodecylic, decyilic, and other alcohols the corresponding esters have been obtained. The effective novel methodologies of esterification reaction of citric acid at temperatures of 120–180°*C* with or without solvents are developed. The physical and chemical constants of the obtained compounds have been defined.

***Keywords*:** citric acid esterification, pentadecylic, dodecylic alcohols.

Introduction. Citric acid, its salts and esters are important products of chemical synthesis, food, pharmaceutical and cosmetic industries [1]. Citric acid alone (E330) and its monosubstituted esters (stearylcitrate, E484) are used in food industry as acidity regulators, emulsifiers, stabilizers and antioxidants [2–4]. It is known that some esters of polyhydric alcohols of non-glyceride structure can be used as dietary substitutes of edible oils [5]. Their low calorific value is explained by the difficult enzymatic cleavage of non-glyceride esters. Consequently, zero-calories can be expected by using esters of polyhydric acids with high aliphatic alcohols as substitutes for edible oils and fats [5]. The monosubstituted esters of citric acid and palmitic alcohol were synthesized by esterification in the presence of *p*-toluenesulfonic acid or sulfonic acid type ion exchange resins [6]. The esterification (catalized by acids) of mannitol and sorbitol with high carboxylic acids was studied in [7].

The aim of this study was to investigate the possibility of obtaining citric acid esters of pentadecylic, dodecylic, decylic and other alcohols in a molar ratio of 1:3 without using of acid catalysts. It was supposed to determine the optimal conditions for esterification reaction to produce the most "pure" oil substitutes, that is uncontaminated by side substances and catalyst. By maximizing the purity of the products, obtained compounds may be of interest, as a dietary substitutes for oils and fats:



where R–$C_{15}H_{31}$; –$C_{12}H_{25}$; –$C_{10}H_{21}$; –C_9H_{19};–C_8H_{17};–cyclo–C_6H_{11} or –$HO(CH_2)_2$–OC_4H_9.

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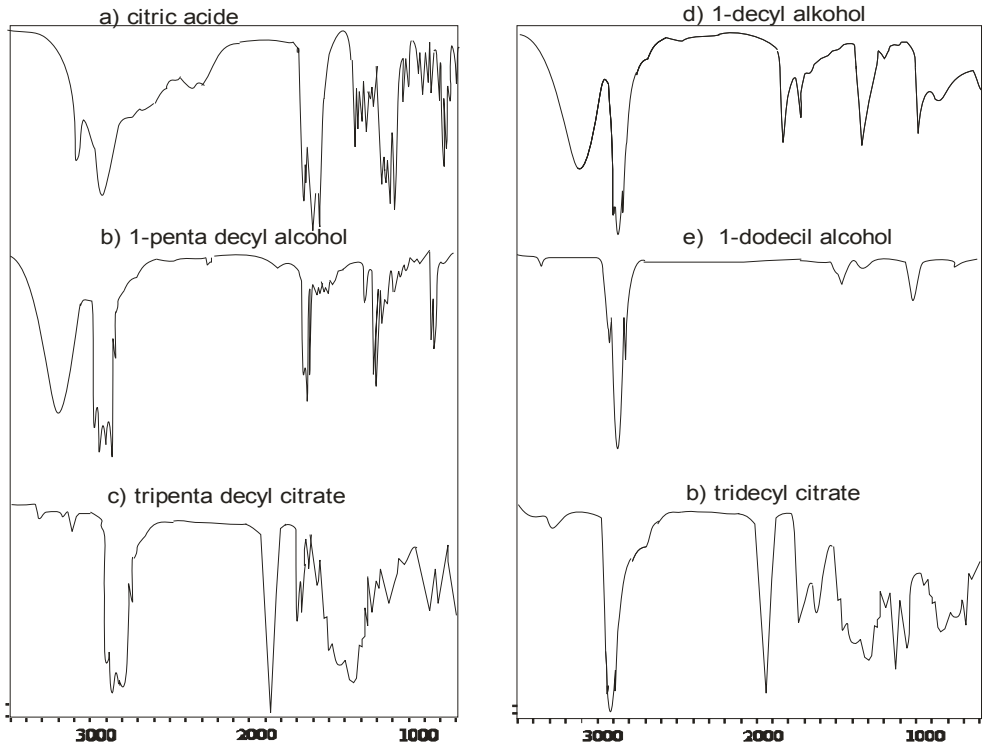
Results and Discussion.

Characteristics of Synthesized Compounds. Individuality of the synthesized esters is confirmed by IR and ^1H NMR spectra (see Figure). The oscillation strips of citric acid's carboxyl groups are observed in the ranges of 2500–2700 and 3000–3300 cm^{-1}, as well as at 940, 1230 and 1290 cm^{-1}. After obtaining the esterification product tripentadecylcitrate, the oscillation strips of carboxyl groups disappear; however the peak of alcohol carboxyl group remains at 3600 cm^{-1}. This result indicates that the reaction between citric acid and pentadecyl alcohol was complete, and all carboxyl groups of acid were converted into ester bonds. The carbonyl group peaks of formed trisubstituted esters also confirm the esterification reaction. In the case of mono- or disubstituted citric acid esters, as usual, in the reaction mixture disubstituted and trisubstituted products are present.



IR spectra of starting materials, tripentadecylcitrate and tridecylcitrate.

As it can be seen in the table, the esterification reaction of citric acid with high aliphatic alcohols successfully proceeds at temperatures of 120–180º*C* for 12–20 *h*. To the degree of 1–2 substitutions, the reaction proceeds for 8 *h*, but then significantly slows down due to the occurrence of steric hindrances in the hydrocarbon skeleton of the partially substituted product. For obtaining trisubstituted esters, apparently, an increase in the heating duration up to 20 *h* is required. Heating the reaction mixture at temperatures of 150–180º*C* for more than 20 *h* leads to the darkening of the derived oils. The darkening is partially prevented by pumping out the air up to 20–40 *mm* Hg or by passing inert gases (nitrogen, helium) at a reduced pressure, however it is not possible to avoid darkening

completely. Tripentadecylcitrate and tridodecylcitrate are solid waxy products with softening point 53–56ºC and 40–43ºC respectively. Disubstituted and monosubstituted products as it was expected have lower softening temperatures. Depending on the conditions of preparation color of products varies from milky white to brown.

Esterification of citric acid with aliphatic alcohols

№	Alcohol, *mol* ratio to acid	Solvent	*T*, ºC	Duration of reaction, *h*	Reaction product		
					Yield, *mol* %	Freez. point, ºC	Color
1	pentadecylic, 1: 3.3	abs	150	20	97	53–56	light yellow
2	pentadecylic, 1: 2.2	abs	150	20	100	48–52	white
3	pentadecylic, 1: 1.1	abs	150	20	100	43–46	white
4	pentadecylic, 1: 3.3	abs	120	20	95	53–56	white
5	pentadecylic, 1: 3.3	abs	180	20	96	54–56	brown
6	pentadecylic, 1: 3.3	abs	150	12	95	52–53	white
7	pentadecylic, 1:3.3	abs	150	24	97	54–56	brown
8	dodecylic, 1: 3.3	abs	150	20	98	40–43	brown
9	decylic 1: 3.3	abs	150	20	98	36–38	light yellow
10	nonylic, 1: 3.3	abs	150	20	99	– 14–16	light yellow
11	octylic, 1: 3.3	abs	150	20	96	– 16–18	light yellow
12	cyclohexylic, 1: 3.3	abs	150	20	98	31–33	light yellow
13	2-butoxiethanol 1: 3.3	abs	150	20	97	30–33	beige
14	dodecylic, 1: 3.3	N-MP	150	20	98	39–40	white
15	dodecylic, 1: 3.3	DMF	150	20	98	39–40	white
16	dodecylic, 1: 3.3	DMSO	150	20	98	39–40	brown
17	pentadecylic + dodecylic (1:1), 1: 3.3	abs	150	20	98	24–26	white
18	pentadecylic + dodecylic (2:1), 1: 3.3	abs	150	20	97	4–7	light yellow
19	pentadecylic + octylic (1:1), 1: 3.3	abs	150	20	99	– 12 – 13	light yellow

Experimental part. ^{1}H NMR spectra have been recorded on Varian Mercury 300 with 300 *MHz* operating frequency in DMSO-d_6–CCl_4 (1: 3) with an internal standard TMS. Identification of substances was carried out through a thin layer chromatography (TLC) in the system butanol–toluene (4 : 1) on the filter paper, with iodine vapor used as a developer [7]. Citric acid marked "clean", pentadecylic, dodecylic, decylic, nonylic, octylic, cyclohexylic alcohols and ethyleneglycolmonobutyl ether (2-butoxiethanol), dimethylformamide (DMF), N-methylpyrrolidone (N-MP) and dimethylsulfoxyde (DMSO), standard reagents marked "clean" were used without additional purification.

General Procedure for 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 formation of esters. The reactor was charged with 1.96 *g* (10 *mmol*) citric acid and 7.54 *g* (33 *mmol*) pentadecanol. The air was pumped out and heated up to the set temperature during the stirring (20–40 *mm* Hg). To control the course of the reaction, every 4 *h*, a sample was taken and chromatographically the content of starting materials and products has been determined. Then, at the end of the reaction, the reaction mixture was cooled down and recrystallized from 25 *mL* of

80ºC ethanol, the product was washed with water (4×20 *mL*) to remove the residuals of reactants and the solvent, and dried up to a constant weight. The yield was 97%. The reaction product tripentadecylester of citric acid is soft paraffin-like material of light yellow color (№ 1 in the Table). The results of other experiments are summarized in the Table. Similarly, the reactions are carried out with solvents DMF, N-MP and DMSO. The structure of the trisubstituted esters of citric acid are confirmed by the IR and ^{1}H NMR spectra.

Tripentadecyl Citrate. FTIR, cm^{-1}: 2920, 2850 (CH_2); 1773 (C=O); 1480, 1435 (CH_2); 1185, 1130 (C–O). ^{1}H NMR spectrum, δ, *ppm*: 0.95 m (9H, CH_3); 1.18–1.86 m (78H, CH_2); 2.82–2.86 dd (4H, CH_2COO); 4.09–4.21 m (6H, CH_2O); 4.14 s (1H, OH).

Tridodecyl Citrate. FTIR cm^{-1}: 2920, 2850 (CH_2); 1773 (C=O); 1480, 1435 (CH_2); 1185, 1130 (C–O). ^{1}H NMR spectrum, δ, *ppm*: 0.95 m (9H, CH_3); 1.18–1.86 m (60H, CH_2); 2.82–2.86 dd (4H, CH_2COO); 4.09–4.21 m (6H, CH_2O); 4.14 s (1H, OH).

Tridecyl Citrate. FTIR cm^{-1}: 2920, 2850 (CH_2); 1773 (C=O); 1480, 1435 (CH_2); 1185, 1130 (C–O). ^{1}H NMR spectrum, δ, *ppm*: 0.95 m (9H, CH_3); 1.18–1.86 m (48H, CH_2); 2.82–2.86 dd (4H, CH_2COO); 4.09–4.21 m (6H, CH_2O); 4.14 s (1H, OH).

Trinonyl Citrate. FTIR cm^{-1}: 2920, 2850 (CH_2); 1773 (C=O); 1480, 1435 (CH_2); 1165, 1135 (C–O). ^{1}H NMR spectrum, δ, *ppm*: 0.95 m (9H, CH_3); 1.18–1.86 m (42H, CH_2); 2.82–2.86 dd (4H, CH_2COO); 4.09–4.21 m (6H, CH_2O); 4.14 s (1H, OH).

Trioctyl Citrate. FTIR cm^{-1}: 2920, 2850 (CH_2); 1773 (C=O); 1480, 1435 (CH_2); 1185, 1130 (C–O). ^{1}H NMR spectrum, δ, *ppm*: 0.95 m (9H, CH_3); 1.18–1.86 m (36H, CH_2); 2.82–2.86 dd (4H, CH_2COO); 4.09–4.21 m (6H, CH_2O); 4.14 s (1H, OH).

Tricyclohexylcitrate. FTIR cm^{-1}: 3623 (CH); 2934, 2850 (CH_2); 1466, 1453 (CH_2); 1160, 1135 (C–O). ^{1}H NMR spectrum, δ, *ppm*: 1.04 m (30H, CH_2); 2.86 dd (4H, CH_2COO); 3.58 bs (3H, CH); 4.15 s (1H, OH).

Tributyleneglycolcitrate. FTIR cm^{-1}: 3632 (OH); 2979, 2935, 2880 (CH_2); 1720 (C–O); 1396, 1334 (CH_2); 1135 (C–O).

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