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Improved synthesis of sucrose fatty acid monoesters under ultrasonic irradiation

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ABSTRACT

Sucrose fatty acid esters were synthesized by the transesterification of sucrose with aliphatic esters under ultrasound irradiation in good yield (⩾73%). The optimum reaction conditions for the transesterification reaction include a molar ratio of sucrose to fatty acid ethyl ester of 2:1 and the use of a 13% mol anhydrous K_2CO_3 catalyst. The optimum reaction temperature was set at 70 °C, the optimum reaction time was 2 h, and the optimum reaction pressure was 11 kPa. The reaction had excellent monoester selectivity. The proportion of monoester (6-monoester + 6′-monoester) in the purified products was up to 92–95% via flash column chromatography over silica gel, the ratios of 6-monoester/6′-monoester are 2.1–2.7, and the sucrose monoesters were identified by HPLC–MS, NMR and IR.

1. Introduction

Sucrose esters are nonionic surfactants that may be produced from renewable, economical and readily available resources [1]. The free alcoholic hydroxyl groups of sucrose react with aliphatic or aromatic acids to produce sucrose esters. They are widely used in foods, cosmetics, detergents, agriculture, bioengineered enzymes and pharmaceuticals [2,3]. Apart from their emulsifying properties, they are completely biodegradable, harmless to the environment, nontoxic, skin-compatible, odorless, tasteless, a good insecticide, and are digested as a blend of sucrose and fatty acids in the stomach [4].

Although the reactivities of the different primary and secondary hydroxyl groups vary slightly in sucrose, attempts to acylate sucrose often involve non-specific reactions leading to mixtures of compounds differing in their degree of esterification and the position of acylation [5]. Even if for many applications these mixtures of mono-, di-, and triesters are convenient, selective reactions would be valuable because the hydroxyl groups of sucrose could be effectively distinguished and sucrose monoesters in a single procedure could be preferentially produced. Selective acylation of unprotected sucrose has been accomplished by enzymatic approaches [6–8]. However, the selective monoacylation of sucrose is difficult to achieve by chemical approaches due to the similar reactivity of the eight hydroxyl groups and the existence of intramolecular migration processes [9]. Linhardt reported the direct, one-pot, regioselective synthesis of 6-acyl esters of sucrose (yield: 47–70%) by means of transforming sucrose into the dibutyltin acetal, enhancing the nucleophilicity at the C-6 oxygen and restricting the subsequent acylation reaction, but such methods need a long reaction time (48–96 h) [10]. Plou reported the synthesis of four sucrose fatty acid esters (caprylate, laurate, myristate, and palmitate) in dimethylsulfoxide by transesterification of sucrose with the corresponding vinyl esters using disodium hydrogen phosphate as catalyst. Since vinyl alcohol formed during the process tautomerizes to the low-boiling-point acetaldehyde, the equilibrium is shifted toward the ester formation, resulting in high yields (85%), with 2-*O*-acylsucrose as the major product (60–70%), but a molar ratio sucrose/vinyl ester (4:1) was high [11]. By employing alkyl fatty acid esters the transesterification reactions became reversible, resulting in low yields. Furthermore, none of the current processes is particularly selective. They all afford mixtures of compounds differing in their degree of esterification [5].

Ultrasonic irradiation is a useful tool for emulsification of immiscible liquids. The collapse of the cavitation bubbles disrupts the phase boundary and causes emulsification, by ultrasonic jets that impinge from one liquid to another [12]. Stavarache and coworkers reported the transesterification of vegetable oil with short-chain alcohols for biodiesel fabrication by low frequency ultrasound [13–15].

Recently, in our study, we found that transesterification of sucrose with fatty acid esters can be accelerated by ultrasonic irradiation. Here, we reported the preparation of a homologous series of sucrose monoesters with *n*-acyl chains of 8, 12, 14, and 16 carbon atoms under ultrasonic irradiation. Good yield (⩾73%) and high percentage of monoesters (⩾92%) were obtained.

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2. Experiment

2.1. Apparatus and analysis

A Ultrasonic Cleaner (KQ-100E) operating at a frequency of 40 kHz came from Ultrasonic Cleaner Co. Ltd. of Kun-Shang China; ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer as solutions in CD_3OD. All chemical shifts are reported in ppm relative to tetramethylsilane. Infrared spectra were recorded on a Nicolet FT-IR 500 spectrometer using KBr pellets and absorption is reported in wave-numbers (cm^{-1}). Mass spectrometer analyses were performed at a Waters Synapt MS.

Flash column chromatography was carried out on Merck silica gel (230–400 mesh). Thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} plates (Merck) with chloroform/methanol 4:1 (vol/vol) as eluent; spots were detected by dipping the plates into the solution (1 g carbamide + 4.8 mL 85% phosphoric acid + 48 mL water saturated 1-butanol solution), drying, and heating at 80 °C for 30 min. The separation and analysis of the ratio of sucrose monoesters (regioisomers) were achieved using an Agilent. The HPLC was equipped with a Diamonsil column (4.6 mm × 250 mm) packed with 5 μm C18 and a ELSD detector and with a methanol/water as the mobile phase. The gradient program was 85% of solvent A from 0 to 10 min at a flow rate of 1 mL/min, and 90% solvent A from 10 to 25 min at a flow rate of 1.0 mL/min.

2.2. Reagents and materials

Sucrose, dimethylsulfoxide (DMSO), anhydrous K_2CO_3, anhydrous disodium hydrogen phosphateethyl, PEG-400, ethyl caprylate, ethyl laurate, ethyl myristate, ethyl palmitate and 1-butanol were purchased from Sinopharm Chemical Reagent Co. Ltd. and were used as received.

2.3. Synthesis of sucrose esters

In a dry Erlenmeyer type flask equipped with stopper, milled sucrose 34 g (100 mmol) and anhydrous K_2CO_3 0.9 g (6.5 mmol) were added to 30 mL DMSO. After the sucrose was completely dissolved in the DMSO, ethyl octanoate 1 mL was added to the mixture and sonicated for a preset time at 60–80 °C under reduced pressure. The desired reaction temperature was controlled by setting the ultrasound apparatus and then maintaining temperature (±3 °C) by use of a circulating water bath. After the complete conversion of the fatty acid ester, as determined by TLC analysis, the reaction was stopped and DMSO was evaporated off by vacuum distillation. The residue was dissolved in 25% aqueous sodium chloride/1-butanol 1:1 (vol/vol) under stirring, and the mixture was allowed to separate into two phases. In order to eliminate the non-reacted sucrose, the organic phases were washed with fresh aqueous sodium chloride solution. The above process should be repeated twice. After phases separation, the organic phase was dried with anhydrous Na_2SO_4. The solvent was then evaporated off, and the residue was further purified by the addition of ethyl acetate (preheated to 40 °C) with vigorous stirring until dissolution was completed. The solution was allowed to stand while cooling. The precipitated sucrose esters were then filtered off and dried under vacuum at 45 °C to a constant weight. The sucrose ester (a white amorphous solid) was obtained at a yield of 17.5 g (74.8%, based on ethyl fatty acid ester as the limiting reagent and assuming that product is entirely monoester). The sucrose monoester was isolated by thin-layer chromatography (TLC) with chloroform/methanol 4:1 (vol/vol) as eluent and characterized by IR and MS. The isomers of the monoester were separated by HPLC and identified by ^{1}H NMR and ^{13}C NMR. Reactions with longer carboxylic ester (lauroyl, myristoyl and palmitoyl) were performed following the same procedure as ethyl octanoate, and the variously substituted sucrose esters were isolated using the same eluents. Spectral data for monoesters are given as follows.

IR spectrum and mass spectrometric data for the monoesters – mixture of isomers (6 and 6′): mono-*O*-octanoylsucroses: IR(KBr) (cm^{-1}): 3362 (a strong peak, O–H stretch of free hydroxyl in sucrose); 2857, 2928, 2945 (C–H stretch of methyl and methylene), 1728 (C=O stretch of ester), 1056, 1107 (C–O stretch of C–O–C), 955 (glycosidic bond stretch of sucrose). HRMS (ES^+) *m*:*z* requires 491.2105 $[M+Na]^+$, found 491.2214. Mono-*O*-lauroylsucroses: IR(KBr) (cm^{-1}): 3383 (a strong peak, O–H stretch of free hydroxyl in sucrose); 2853, 2924 (C–H stretch of methyl and methylene), 1737 (C=O stretch of ester), 1019, 1109 (C–O stretch of C–O–C), 953 (glycosidic bond stretch of sucrose). HRMS (ES^+) *m*:*z* requires 547.2731 $[M+Na]^+$, found 547.2952. Mono-*O*-myristoylsucroses: IR(KBr) (cm^{-1}): 3331 (a strong peak, O–H stretch of free hydroxyl in sucrose); 2852, 2923 (C–H stretch of methyl and methylene), 1737 (C=O stretch of ester), 1016, 1108 (C–O stretch of C–O–C), 952 (glycosidic bond stretch of sucrose). HRMS (ES^+) *m*:*z* requires 575.3044 $[M+Na]^+$, found 575.3224. Mono-*O*-palmitoylsucroses: IR(KBr) (cm^{-1}): 3433 (a strong peak, O–H stretch of free hydroxyl in sucrose); 2850, 2918 (C–H stretch of methyl and methylene), 1740 (C=O stretch of ester), 1061, 1107 (C–O stretch of C–O–C), 995 (glycosidic bond stretch of sucrose). HRMS (ES^+) *m*:*z* requires 603.3357 $[M+Na]^+$, found 603.3500.

6-O-Octanoylsucrose: ^{1}H NMR (400 MHz, CD_3OD) δ(ppm): 0.91 (t, J = 4.8 Hz, 3H), 1.32 (s, 8H), 1.61–1.64 (m, 2H), 2.29 (t, J = 7.2 Hz, 2H), 3.32 (dd, J = 8.0 Hz and J = 8.4 Hz, H-4) 3.41 (dd, J = 4.0 Hz and J = 3.2 Hz, H-2), 3.57–3.64 (m, H-1′), 3.72 (dd, J = 8.8 Hz, H-3), 3.78–3.84 (m, H-6′), 3.91–3.96 (m, H-5′), 3.99 (t, J = 8.4 Hz, H-4′), 4.03–4.10 (m, H-5), 4.16 (d, J = 6.0 Hz, H-3′), 4.40 (dd, J = 12, H-6_a), 4.60 (dd, J = 12, H-6_b), 5.37 (d, J = 2.8, H-1); ^{13}C NMR (100 MHz, CD_3OD) δ(ppm): 14.5, 23.4, 25.7, 30.0, 32.4, 34.1 (alkyl), 63.4 (C-1′), 63.9 (C-6′), 64.6 (C-6), 71.2 (C-4), 71.7 (C-2), 72.8 (C-5), 74.3 (C-3), 75.2 (C-4′), 78.7 (C-3′), 83.4 (C-5′), 92.3 (C-1), 104.8 (C-2′), 175.1 (C=O).

6′-O-Octanoylsucrose. ^{1}H NMR (400 MHz, CD_3OD) δ(ppm): 0.91 (t, J = 4.8 Hz, 3H), 1.32 (s, 8H), 1.61–1.64 (m, 2H), 2.29 (t, J = 7.2 Hz, 2H), 3.32 (dd, J = 8.0 Hz and J = 8.4 Hz, H-4), 3.41 (dd, J = 4.0 Hz and J = 3.2 Hz, H-2), 3.64 (s, H-1′), 3.69–3.76 (m, H-3, H-5, H-6), 3.79–3.84 (m, H-5′), 3.96–4.08 (m, H-4′), 4.14–4.19 (m, H-6′), 4.40 (d, J = 12, H-3′), 5.37 (d, J = 2.8, H-1); ^{13}C NMR (100 MHz, CD_3OD) δ(ppm): 14.5, 23.4, 25.7, 30.0, 32.4, 34.1 (alkyl), 62.2 (C-6), 63.1 (C-1′), 66.6 (C-6′), 71.0 (C-4), 72.9 (C-2), 74.1 (C-3), 74.5 (C-5), 76.5 (C-4′), 78.7 (C-3′), 80.6 (C-5′), 93.3 (C-1), 105.1 (C-2′), 175.4 (C=O).

6-O-Lauroylsucrose. ^{1}H NMR (CD_3OD, 400 MHz) δ(ppm): 0.89 (*t*, J = 5.0 Hz, 3H), 1.28 (s, 16H), 1.60–1.64 (m, 2H), 2.39 (t, J = 6.8 Hz, 2H), 3.31 (dd, J = 8.4 Hz and J = 8.8 Hz, H-4) 3.38 (dd, J = 5.2 Hz and J = 4.0 Hz, H-2), 3.55–3.66 (m, H-1′), 3.72 (dd, J = 7.6 Hz, 3-H), 3.79–3.85 (m, H-6′), 3.91–3.96 (m, H-5′), 3.99 (t, J = 8.4 Hz, 4′-H), 4.01–4.09 (m, H-5), 4.16 (d, J = 6.4 Hz, H-3′), 4.42 (dd, J = 12, H-6_a), 4.61 (dd, J = 12, H-6_b), 5.38 (d, J = 3.6, H-1); ^{13}C NMR (100 MHz, CD_3OD) δ(ppm): 14.5, 23.6, 25.9, 30.1, 30.4, 30.6, 30.7, 33.1, 34.8 (alkyl), 63.5 (C-1′), 63.9 (C-6′), 64.6 (C-6), 71.4 (C-4), 71.7 (C-2), 73.0 (C-5), 74.3 (C-3), 75.5 (C-4′), 78.9 (C-3′), 83.6 (C-5′), 92.4 (C-1), 104.9 (C-2′), 175.1 (C=O).

6′-O-Lauroylsucrose. ^{1}H NMR (400 MHz, CD_3OD) δ(ppm): 0.89 (*t*, J = 5.0 Hz, 3H), 1.28 (s, 16H), 1.60–1.64 (m, 2H), 2.39 (t, J = 6.8 Hz, 2H), 3.30 (dd, J = 8.0 Hz and J = 8.4 Hz, H-4), 3.41 (dd, J = 5.2 Hz and J = 4.0 Hz, H-2), 3.64 (s, H-1′), 3.69–3.76 (m, H-3, H-5, H-6), 3.79–3.84 (m, H-5′), 3.96–4.08 (m, H-4′), 4.14–4.19 (m, H-6′), 4.40 (d, J = 12, H-3′), 5.37 (d, J = 2.8, H-1); ^{13}C NMR (100 MHz, CD_3OD) δ(ppm): 14.5, 23.6, 25.9, 30.1, 30.4, 30.6, 30.7, 33.1, 34.8 (alkyl),

62.5 (C-6), 64.0 (C-1′), 66.6 (C-6′), 71.2 (C-4), 73.0 (C-2), 74.1 (C-3), 74.5 (C-5), 76.5 (C-4′), 78.9 (C-3′), 80.6 (C-5′), 93.2 (C-1), 105.2 (C-2′), 175.2 (C=O).

6-O-Myristoylsucrose. ^{1}H NMR (400 MHz, CD_3OD) δ(ppm): 0.90 (t, J = 4.8 Hz, 3H), 1.29 (s, 20H), 1.61–1.64 (m, 2H), 2.29 (t, J = 7.2 Hz, 2H), 3.32 (dd, J = 8.0 Hz and J = 8.4 Hz, H-4) 3.41 (dd, J = 4.0 Hz and J = 3.2 Hz, H-2), 3.57–3.64 (m, H-1′), 3.72 (dd, J = 8.8 Hz, H-3), 3.78–3.84 (m, H-6′), 3.91–3.96 (m, H-5′), 3.99 (t, J = 8.4 Hz, H-4′), 4.03–4.10 (m, H-5), 4.16 (d, J = 6.0 Hz, H-3′), 4.40 (dd, J = 12, H-6_a), 4.60 (dd, J = 12, H-6_b), 5.37 (d, J = 2.8, H-1); ^{13}C NMR (100 MHz, CD_3OD) δ(ppm): 14.5, 23.5, 26.0, 30.1, 30.5, 30.6, 30.8, 33.1, 34.8 (alkyl), 63.6 (C-1′), 64.0 (C-6′), 64.6 (C-6), 71.5 (C-4), 71.8 (C-2), 73.0 (C-5), 74.4 (C-3), 75.7 (C-4′), 79.1 (C-3′), 83.7 (C-5′), 92.4 (C-1), 105.0 (C-2′), 175.1 (C=O).

6′-O-Myristoylsucrose. ^{1}H NMR (400 MHz, CD_3OD) δ(ppm): 0.90 (t, J = 4.8 Hz, 3H), 1.29 (s, 20H), 1.61–1.64 (m, 2H), 2.29 (t, J = 7.2 Hz, 2H), 3.32 (dd, J = 8.0 Hz and J = 8.4 Hz, H-4), 3.41 (dd, J = 4.0 Hz and J = 3.2 Hz, H-2), 3.64 (s, H-1′), 3.69–3.76 (m, H-3, H-5, H-6), 3.79–3.84 (m, H-5′), 3.96–4.08 (m, H-4′), 4.14–4.19 (m, H-6′), 4.40 (d, J = 12, H-3′), 5.37 (d, J = 2.8, H-1); ^{13}C NMR (100 MHz, CD_3OD) δ(ppm): 14.5, 23.5, 26.0, 30.1, 30.5, 30.6, 30.8, 33.1, 34.8 (alkyl), 62.2 (C-6), 63.3 (C-1′), 66.6 (C-6′), 71.0 (C-4), 72.9 (C-2), 74.1 (C-3), 74.6 (C-5), 76.5 (C-4′), 78.7 (C-3′), 80.6 (C-5′), 93.3 (C-1), 105.1 (C-2′), 175.4 (C=O).

6-O-Palmitoylsucrose. ^{1}H NMR (400 MHz, CD_3OD) δ(ppm): 0.91 (t, J = 4.8 Hz, 3H), 1.32 (s, 24H), 1.61–1.64 (m, 2H), 2.29 (t, J = 7.2 Hz, 2H), 3.33 (dd, J = 8.4 Hz and J = 8.8 Hz, H-4) 3.40 (dd, J = 4.4 Hz and J = 3.6 Hz, H-2), 3.58–3.65 (m, H-1′), 3.72 (dd, J = 8.4 Hz, H-3), 3.78–3.84 (m, H-6′), 3.91–3.95 (m, H-5′), 3.98 (t, J = 8.4 Hz, H-4′), 4.03–4.11 (m, H-5), 4.16 (d, J = 6.0 Hz, H-3′), 4.40 (dd, J = 12, H-6_a), 4.60 (dd, J = 12, H-6_b), 5.37 (d, J = 3.2, H-1); ^{13}C NMR (100 MHz, CD_3OD) δ(ppm): 14.5, 23.5, 26.0, 30.1, 30.5, 30.6, 30.8, 33.1, 34.8 (alkyl), 63.6 (C-1′), 64.0 (C-6′), 64.6 (C-6), 71.5 (C-4), 71.8 (C-2), 73.0 (C-5), 74.4 (C-3), 75.7 (C-4′), 79.1 (C-3′), 83.7 (C-5′), 92.4 (C-1), 105.0 (C-2′), 175.1 (C=O).

6′-O-Palmitoylsucrose. ^{1}H NMR (400 MHz, CD_3OD) δ(ppm): 0.91 (t, J = 4.8 Hz, 3H), 1.32 (s, 24H), 1.61–1.64 (m, 2H), 2.29 (t, J = 7.2 Hz, 2H), 3.32 (dd, J = 8.0 Hz and J = 8.4 Hz, H-4), 3.41 (dd, J = 4.4 Hz and J = 3.6 Hz, H-2), 3.64 (s, H-1′), 3.68–3.76 (m, H-3, H-5, H-6), 3.79–3.85 (m, H-5′), 3.96–4.09 (m, H-4′), 4.14–4.18 (m, H-6′), 4.40 (d, J = 12, H-3′), 5.37 (d, J = 3.2, H-1); ^{13}C NMR (100 MHz, CD_3OD) δ(ppm): 14.5, 23.5, 26.0, 30.1, 30.5, 30.6, 30.8, 33.1, 34.8 (alkyl), 62.3 (C-6), 63.3 (C-1′), 66.6 (C-6′), 71.0 (C-4), 72.9 (C-2), 74.1 (C-3), 74.6 (C-5), 76.5 (C-4′), 78.7 (C-3′), 80.6 (C-5′), 93.3 (C-1), 105.1 (C-2′), 175.4 (C=O).

3. Results and discussion

3.1. The choice of esterification conditions under ultrasonic irradiation

Experimental conditions that affect the yield including the type and concentration of the catalyst, reaction time and system pressure were investigated with ethyl caprylate as the acylating agent (Scheme 1).

Initially, esterification of sucrose was performed using 10 mmol sucrose and 5 mmol ethyl caprylate with anhydrous disodium hydrogen phosphate (Na_2HPO_4), potassium carbonate (K_2CO_3) and K_2CO_3 + PEG-400, respectively as catalyst at different reduced pressures. The results are summarized in Table 1. K_2CO_3 was found to be the best catalyst with regard to yield and catalytic activity for the transesterification of sucrose and ethyl caprylate, and the best yield was obtained when the quantity of catalyst was 13% (mol/mol) to ethyl caprylate (Table 1, entry 7).

Furthermore, the influence of the molar ratio of sucrose to ethyl caprylate, reaction time and temperatures were analyzed in the presence of the optimized anhydrous catalyst K_2CO_3 (13% mmol). The results are summarized in Table 2.

These results show that as molar ratio was increased from 1:1 to 2:1, the reaction yield increased accordingly, but when the molar ratio was increased to 2.5:1 the yield decreased gradually. It was also observed that the yield of reaction increased from 21.5% to 74.8% when temperature rose from 50 °C to 70 °C, but decreased

Table 1
The choice of catalysts.[a]

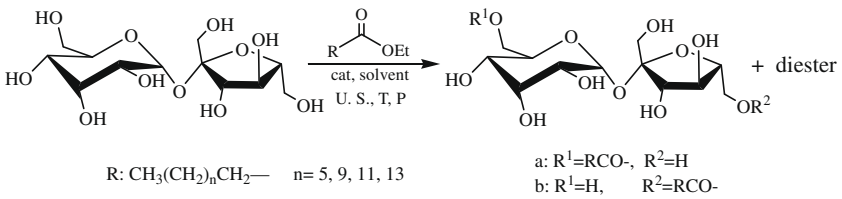
Entry	Catalyst	Mol (%)[b]	Pressure (kPa)	Time	Yield (%)
1	None	0	11	5	0
2	NaH_2PO_4	200	100	4	0
3	NaH_2PO_4	200	11	3	2
4	K_2CO_3	10	100	2	10.5
5	K_2CO_3	8	11	2	63.6
6	K_2CO_3	10	11	2	67.7
7	**K_2CO_3**	**13**	**11**	**2**	**74.8**
8	K_2CO_3	16	11	2	68.1
9	K_2CO_3	20	11	2	60.4
10	K_2CO_3 + PEG-400	10	100	3	0
11	K_2CO_3 + PEG-400	10	11	2.5	10.1

[a] Reactions were carried out with 10 mmol sucrose and 5 mmol ethyl caprylate in 6 mL DMSO at entries 1–9, solution-free at entries 10 and 11 at 70 °C.
[b] The quantity of catalyst was mole percentage to ethyl caprylate in reactions 2–9 and mixture of 10% mmol anhydrous K_2CO_3 and 3 mL PEG-400 in reactions 10 and 11.

Table 2
The effect of the molar ratio of reactant, temperature and time.*

Entry	Sucrose/ethyl caprylate (mol/mol)	T (°C)	Time (h)	Yield (%)
1	1:1	70	2	55.3
2	1.5:1	70	2	63.1
3	2:1	50	2	21.5
4	2:1	60	2	49.3
5	2:1	70	0.5	30.1
6	2:1	70	1	37.2
7	2:1	70	1.5	56.1
8	**2:1**	**70**	**2**	**74.8**
9	2:1	70	2.5	67.3
10	2:1	70	3	63.8
11	2:1	80	2	64.8
12	2.5:1	70	2	70.3

* Reaction was carried out using 13% mmol anhydrous K_2CO_3 to ethyl caprylate as catalyst, with dimethylsulfoxide (DMSO) as solvent, in system pressure of 11 kPa under ultrasonic irradiation.

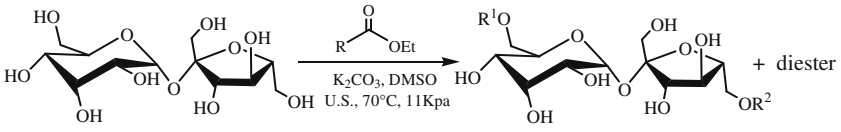


R: $CH_3(CH_2)_nCH_2$— n= 5, 9, 11, 13

a: R^1=RCO-, R^2=H
b: R^1=H, R^2=RCO-

Scheme 1. Reaction of sucrose with fatty acid esters.

Table 3
The synthesis of sucrose esters under ultrasonic irradiation.[a]



R: $CH_3(CH_2)_nCH_2$— n= 5, 9, 11, 13

a: R^1=RCO-, R^2=H
b: R^1=H, R^2=RCO-

Entry	Acyl donor	Yield[b] (%)	Monoester[c] (%) (6-*O*:6′-*O*)[d]
1	Ethyl caprylate	75	92 (2.5:1)
2	Ethyl laurate	78	95 (2.7:1)
3	Ethyl myristate	74	94 (2.1:1)
4	Ethyl palmitate	73	92 (2.2:1)

[a] Experiment conditions: 10 mmol sucrose, 5 mmol ethyl fatty acid ester, 11% anhydrous K_2CO_3, 70 °C, 11 kPa, 6 mL DMSO.
[b] Based on ethyl fatty acid ester as limiting reagent and assuming that product is entirely the monoester.
[c] Referred to the percentage of the monoester fraction, determined by flash column chromatography over silica gel.
[d] Referred to the ratio of 6-*O*-monoester and 6′-*O*-monoester, as identified by HPLC.

when temperature exceeded 70 °C. The reason is that while a higher temperature accelerated the reaction, too high of a temperature caused the caramelization and degradation of sucrose. The observation also showed that the yield of reaction increased with prolonging reaction time within 2 h, but decreased above 2 h. The best conditions of the reaction were as follows: the molar ratio sucrose/ethyl caprylate was 2:1, reaction temperature was 70 °C, reaction time was 2 h, the quantity of catalyst accounted for ethyl caprylate was 13% mol, the reaction pressure was 11 kPa under ultrasonic irradiation and the yield was 75% (Table 2, entry 8).

3.2. The synthesis of sucrose esters under ultrasonic irradiation

After establishing the best reaction conditions (on the basis of higher conversion to monoester in the shortest time), the transesterification was performed with ethyl caprylate (C8), laurate (C12), myristate (C14) and palmitate(C16), and sucrose mono- and diesters were isolated by flash column chromatography over silica gel. Monoesters were further purified by HPLC, and monoesters were analyzed by electrospray ionization-mass spectrometry (ESI-MS) and nuclear magnetic resonance. The percentage of each monoester was identified by HPLC. The results are summarized in Table 3.

It is easy to see that the reaction of sucrose with ethyl fatty acid esters was carried out in good yields under ultrasound irradiation. Although there is similar reactivity between the eight hydroxyl groups in sucrose and the existence of intramolecular migration processes can occur in reaction, the products were substantially monoesters, with a higher monoester/diester ratio and purity. Identification of each monoester was based on the chemical shifts of the hydrogen atom(s), which is in the α position next to the acylated hydroxyl group (ca. +0.5), and, in ^{13}C NMR, the carbon atom directly concerned (ca. +1–2 ppm) and those next to it (ca. −2 ppm)[16]. ^1H NMR and ^{13}C NMR analyses of the monoesters (see Section 2) showed that 6- and 6′-monoesters were the major compounds in the products, with their ratio given in Table 3. The above demonstrates that the acylation of the primary hydroxyl group (6-OH and 6′-OH) of sucrose was easiest under ultrasound irradiation. Presently the mechanism of the selective monoacylation of sucrose is still unclear, and further study is in progress.

4. Conclusion

In conclusion, we have found an efficient and convenient procedure for the preparation of sucrose monoesters via sucrose with fatty acid ethyl ester under ultrasound irradiation. The method not only shortened the reaction time, reduced the quantity of catalyst and improved quality of product, but also led to a higher selectivity in the reaction.

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