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Note

Regioselective formation of 6-*O*-acylsucroses and 6,3′-di-*O*-acylsucroses via the stannylene acetal method

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Abstract—Regioselective formation of 6-*O*-acylsucroses and 6,3′-di-*O*-acylsucroses in one pot with good yields was achieved for the first time by a typical acylation method of sucrose via its dibutylstannylene acetal. Pure monoesters at OH-6 and diesters at OH-6,3′ obtained by these procedures were readily isolated by simple column chromatography, thus overcoming the main difficulties associated with regioselectivity, efficiency, and isolation techniques for the practical preparation. Explanations for the regioselectivities observed during this stannylene acetal-mediated reaction were also proposed based on the structures of the stannylene acetal in solution and the intramolecular migration of stannylenes.

Keywords: Sucrose; Esterification; Regioselective; Stannylene acetal

Sucrose esters synthesized from renewable resources continue to receive widespread attention owing to their superior performance and compatibility in the health and environmental arenas.[1] Most of the products are used as mixtures of regioisomers as well as mono-, di-, and triesters, with physicochemical properties depending on the average degree of substitution and on the length of the fatty chains. On the other hand, in order to get some precise structure–activity relationships in this series of compounds,[2,3] it is necessary to prepare pure sucrose fatty esters of defined structure. Many researchers have focused their attention on the search for regioselective reactions, since the regioselectivity is also one source of controlling the degree of substitution.[4,5] The standard procedure for the preparation of specific sucrose esters requires suitable, partially protected sucrose derivatives, thereby necessitating a number of tedious protection and deprotection steps. Selective acylation of unprotected sucrose has been accomplished by enzymatic approaches,[6–10] as well as by a method introduced by Plusquellec and co-workers.[11–14] These methods depend on the availability of enzymes and the activation of the acyl component, and can result in the monoesters at one of the primary OH-6, 6′, and 1′ or the secondary OH-2.[6–16] Acylation of unprotected sucrose under Mitsunobu conditions[5] results in the formation of 6,6′-diesters with good selectivity along with small amounts of the 6-ester and 6′-ester are obtained simultaneously. However, in spite of these efforts, to get another method giving selectively other compounds remains difficult at present because of the similar reactivity of the eight hydroxyl groups and the existence of intramolecular migration processes. As almost all of the selective acylations are at the primary hydroxyls (6, 6′ or 1′) or the secondary OH-2, highly regioselective synthesis of mono- or diesters at other secondary hydroxyls is more challenging. Herein, we wish to report a highly regioselective method for the one-pot syntheses of 6-*O*-acylsucroses and simultaneous 6,3′-di-*O*-acylsucroses via dibutylstannylene acetal intermediates.

The stannylene acetal method has been widely used to modify the reactivity of hydroxyl groups of both polyol systems (e.g., carbohydrates) and simple glycols and to effect their derivatization, via acylation, tosylation, and alkylation, with high specificity under mild conditions.[17–21] It accomplishes primary hydroxyl activation

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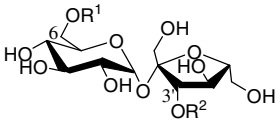
and temporary secondary hydroxyl protection in a single operation and has been proven to be especially useful in the selective acylation of sucrose. Linhardt and coworkers demonstrated that sucrose can be acylated in excellent yield at the 6-OH position via a dibutylstannylene intermediate.[22,23] In this paper, we describe the results of our investigations on the regioselective acylation of sucrose via a typical stannylene acetal method. Owing to this work 6,3′-di-*O*-acylsucroses could be obtained in a highly purified state with good yields for the first time.



1: $R^1 = R^2 = H$
3: $R^2 = H$, $R^1 = CO\text{-}R$
4: $R^1 = R^2 = CO\text{-}R$

2

a: $R = (CH_2)_6\text{-}CH_3$
b: $R = (CH_2)_8\text{-}CH_3$
c: $R = (CH_2)_{10}\text{-}CH_3$
d: $R = (CH_2)_{12}\text{-}CH_3$
e: $R = (CH_2)_{14}\text{-}CH_3$
f: $R = (CH_2)_{16}\text{-}CH_3$

The dibutylstannylene acetal intermediate could be prepared from sucrose (10 mmol) and dibutyltin oxide (1.0 equiv) in methanol as solvent. The reaction was driven to completion by removal of methanol and water to afford the required stannylene acetal. The resulting acetal was allowed to react first with lauroyl chloride **2c** (1.0 equiv) in the presence of pyridine (1.0 equiv) in anhyd DMF, resulting in a mixture containing 6-*O*-acylsucrose **3c** and 6,3′-di-*O*-acylsucrose **4c** (Fig. 1). Remarkably, of the possible diacylated products, **4c** was the sole product formed with a HPLC yield of 31% based on sucrose. Simultaneously, **3c** was obtained as the sole monoacylated product in 32% yield. The mixture was then subjected to further isolation by column

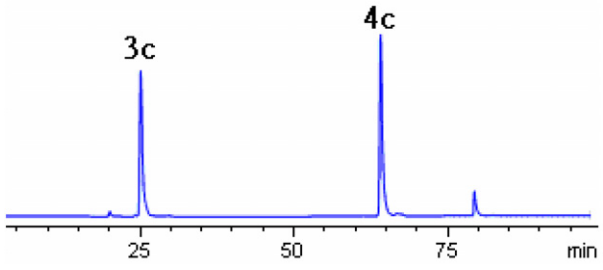


Figure 1. A typical HPLC chromatograph of the crude products (Table 1, entry 3) using an evaporative light-scattering detector (ELSD).

Table 1. Syntheses of 6-*O*-acylsucrose and 6,3′-di-*O*-acylsucrose

Entry	Acylation conditions[a]		Isolated yields[b] (%)	
	Reagent	Time (h)	6-*O*-Acylsucrose	6,3′-Di-*O*-acylsucrose
1	**2a**	1.5	**3a**: 50	**4a**: 20
2	**2b**	2	**3b**: 45	**4b**: 21
3	**2c**	2	**3c**: 31	**4c**: 29
4	**2d**	5	**3d**: 29	**4d**: 26
5	**2e**	8	**3e**: 37	**4e**: 20
6	**2f**	8	**3f**: 37	**4f**: 15

[a] Sucrose and reagent were used in the molar ratio of 1:1; molecular equivalent of pyridine was 1.0 to acylating reagent.
[b] Based on sucrose.

chromatography, and pure compounds **3c** and **4c** were obtained in isolated yields of 31% and 29% (Table 1, entry 3), respectively.

Following the successful and unusual regioselectivity of the reaction, we sought to determine the generality of the system. We treated the acetal with different fatty acid chlorides **2a**–**f**, and the results are listed in Table 1. In all cases, good yields and high regioselectivities were obtained. The reaction times and conditions for all these reactions were comparable, though acyl chlorides with longer fatty chains required significantly longer reaction times (<8 h). Since the stannylene acetal method has been used in the regioselective acylation of sucrose,[22,23] it is somewhat surprising that the highly regioselective formation of 6,3′-di-*O*-acylsucroses in these procedures has not previously been reported. Furthermore, in comparison with those previously reported, our reactions are faster and more efficient.

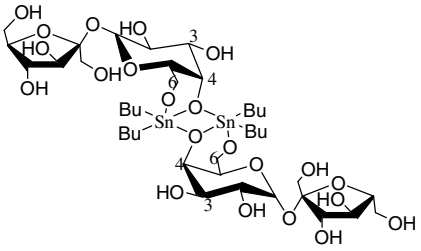
6-*O*-Acylsucroses **3a**–**f** and 6,3′-di-*O*-acylsucroses **4a**–**f** were fully characterized using ESI mass spectrometry and ^1H and ^{13}C NMR spectroscopy. Spectral assignments of ^1H and ^{13}C NMR spectra were performed using ^1H–^1H COSY, ^1H–^{13}C COSY, and HMBC techniques. For 6-*O*-acylsucroses, correlation in the HMBC NMR spectrum between the carbonyl group and protons H-6a,b, as well as the deshielding of protons H-6a and H-6b and of carbon C-6, ascertained the acylation position at OH-6. And for 6,3′-di-*O*-acylsucroses, correlation in the HMBC NMR spectrum between the carbonyl group and proton H-3′ as well as protons H-6a,b ascertained that the acylation positions are at OH-6 and OH-3′.

Encouraged by these initial results, we subjected this reaction to a further investigation to explore the scope and mechanistic aspects of it. The results are listed in Table 2. When the stannylene acetal of sucrose was treated with 0.5 equiv of lauroyl chloride, 6-*O*-acylsucrose **3c** was obtained in a higher yield (34%), and correspondingly a decreased yield of 6% was observed for 6,3′-di-*O*-acylsucrose **4c** (entry 1). However, treatment with 2.0 equiv of lauroyl chloride resulted in a complex

Table 2. Acylation of sucrose under various conditions: isolated yields in the crude products

Entry	Reagent **2c** (mol equiv)[a]	Pyridine (mol equiv)[b]	Isolated yields[c] (%)	
			6-*O*-Acylsucrose	6,3′-Di-*O*-acylsucrose
1	0.5	1	**3c**: 34	**4c**: 6
2	1	1	**3c**: 31	**4c**: 29
3	2	1	15[d]	45[d]
4	1	0.2	**3c**: 31	**4c**: 29
5	1	0	—	—

[a] Molecular equiv based on sucrose.
[b] Molecular equiv based on reagent **2c**.
[c] Based on sucrose.
[d] Mixture of several regioisomers.



Scheme 1. An idealized picture of the dimeric dibutylstannylene acetal of sucrose.

mixture of products containing mono-, di-, tri-, and higher acylsucroses; furthermore, several different positional isomers coexisted in each of the fractions (entry 3). These results indicate that the molar ratio of acyl chloride to sucrose is an essential factor to control the yields and regioselectivities in the acylating reaction.

It was next important to consider the role of the amine base pyridine in the acylating reaction. We varied the amount of pyridine from 1.0 to 0.2 equiv (based on lauroyl chloride), and almost no difference in yields and regioselectivities of both **3c** and **4c** was obtained (entries 2 and 4). However, when the acylating reaction was conducted in the absence of pyridine, only small amounts of monoesters formed (entry 5). This suggests that in the stannylene acetal procedure, the base is a requisite but the amount of it is not crucial to the yield and regioselectivity, whereas a full 1 equiv base is required to remove HCl from the direct acylation of unprotected sucrose with acyl chloride. And this is consistent with the results of other typical acylations of stannylene acetals.[16] Therefore, it may be inferred that the acylations at both OH-6 and OH-3′ undergo the typical reaction of the stannylene acetal method.

The generally accepted explanation for the regioselectivities observed during stannylene acetal-mediated reactions invokes dimers, trimers, and higher oligomers of the five-coordinated tin as the reactive species.[24] However, the stannylene acetals of many carbohydrates do not undergo regioselective reactions, and neither the types of structures of substrates for which selective reactions can be anticipated, nor the cause of the selectivity have been fully defined. The stannylene acetal of sucrose has never been considered to exist as a dimer (Scheme 1) in both the solid states and in solutions.[22] In each of the monomeric subunit in the dimer, there is one apical dicoordinate oxygen (O-6) and one equatorial tricoordinate oxygen (O-4). The apical oxygen is reportedly much more reactive than the tricoordinate equatorial oxygen. However, our result indicated that stannylene acetal of sucrose might exist as a more complex mixture in part of which only OH-6 was activated and in some others both OH-6 and OH-3′ were activated. There is no doubt that stannylene acetals react much faster with electrophiles than do free hydroxyl groups because of the good yields and high regioselectivities we obtained.

Another explanation could be that intramolecular migration of stannylenes leads to the activation of OH-3′. This trend may be explained as follows: initially the acyl chloride attacks the O-6 and the chloride released from the acyl chloride leads to the intramolecular migration of stannylene to the site (OH-3′) where substitution is most rapid by displacement of equilibrium. It has been demonstrated that these universal migrations contribute efficiently to the regiospecificity of the stannylene reaction.[25]

In conclusion, we have introduced a convenient protocol for the regioselective synthesis of 6-*O*-acylsucrose and simultaneously 6,3′-di-*O*-acylsucrose via the dibutylstannylene acetal method in a one-pot reaction. The reactions are rapid and highly selective. It is noteworthy that a highly regioselective synthesis of 6,3′-di-*O*-acylsucrose with excellent yields is reported herein for the first time to the best of our knowledge. This strategy also provides a fast and efficient approach to diversify the pure sucrose esters of defined structures for precise structure–activity relationship studies. Further theoretical and applied works aimed at the expansion of the method should be pursued.

1. Experimental

1.1. General methods

HPLC analyses were carried using an HP 1050 HPLC system equipped with an Alltech 2000 evaporative light-scattering detector (ELSD). A reversed-phase C_{18}-ODSA column (150 × 4.6 mm, 5 μm particle size) purchased from Elite Analytical Instruments Co., Ltd (Dalian, China) was used for the HPLC analysis. Thin-layer chromatography (TLC) was performed on E. Merck $60F_{254}$ Silica Gel plates. An *n*-butanol–H_3PO_4–H_2O solution followed by heating at 90–100 °C was used to visualize the zones on the plates.

The relative ratios in mixed chromatography solvents refer to the volume/volume ratio. For column chromatography, E. Merck 60G Silica Gel was used. IR spectra were measured with a Thermo Nicolet NEXUS spectrometer and KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature using a Varian INOVA spectrometer in DMSO-d_6. ^{1}H and ^{13}C NMR chemical shifts were assigned on the basis of ^{1}H–^{1}H COSY, ^{1}H–^{13}C COSY, and HMBC experiments. Chemical shift values are reported in δ (ppm) relative to Me_4Si (using the DMSO residual peaks as reference). Coupling constants (J) are in Hz. ESI mass spectra (ESIMS) were measured using an HP 1100 MSD instrument. Elemental analyses were determined using a Vario EL III instrument. All reagents were of commercial quality and were purified according to general procedures.

1.2. General procedure for acylation of sucrose

A mixture of sucrose (3.42 g, 10 mmol) and dibutyltin oxide (2.49 g, 10 mmol) was refluxed in MeOH until the solution became clear, after which time the solvent was evaporated to leave the stannylene acetal as a white crystalline solid. A solution of acetal in 30 mL of anhyd DMF in the presence of pyridine was treated with the appropriate acyl chloride under the conditions reported in Tables 1 and 2 and stirred at room temperature. The reaction's progress was monitored by TLC using 9:1 EtOAC–MeOH. After extracting three times with 100 mL of petroleum ether in order to remove dibutyltin by-products, the solution was concentrated in vacuo to dryness. Acetone (100 mL) was then added to the solid residue, and the mixture was stored at 6 °C for 12 h. The unreacted sucrose precipitated out and was filtered off. The clear acetone solution was concentrated in vacuo to dryness, and then the crude product was subjected to HPLC analysis[26,27] (0:100 to 100:0 for 100 min, flow rate of 1.0 mL/min) and isolated by column chromatography (95:5 to 90:10, EtOAC–MeOH). The resulting products were isolated with yields as reported in Tables 1 and 2.

1.2.1. 6-*O*-Octanoylsucrose (3a). Colorless solid; R_f 0.24 (9:1 EtOAc–MeOH); IR (KBr) 3392 (OH) and 1740 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.86 (m, 3H, CH_3), 1.26 (m, 8H, $(CH_2)_4$), 1.53 (m, 2H, $CH_{2\beta}$), 2.32 (t, 2H, $J_{CH2\alpha,CH2\beta}$ 7.4 Hz, $CH_{2\alpha}$), 5.18 (d, 1H, $J_{1,2}$ 1.8 Hz, H-1), 3.47 (m, 1H, H-2), 3.65 (t, 1H, $J_{2,3}$ 8.4, $J_{4,3}$ 8.4 Hz, H-3), 3.17 (m, 1H, H-4), 3.16 (m, 1H, H-5), 3.96 (d, 1H, $J_{6a,6b}$ 12.0 Hz, H-6_a), 4.16 (d, 1H, $J_{6b,6a}$ 12.0 Hz, H-6_b), 3.47–3.56 (m, 2H, H-1′), 3.83 (m, 1H, H-3′), 3.80 (m, 1H, H-4′), 3.53 (m, 1H, H-5′), 3.50–3.54 (m, 2H, H-6′); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.91 (CH_3), 22.02, 24.44, 28.34, 31.08, 33.50 (CH_2), 92.06 (C-1), 72.75 (C-2), 72.89 (C-3), 71.35 (C-4), 69.78 (C-5), 62.21 (C-6), 60.44 (C-1′), 102.16 (C-2′), 76.53 (C-3′), 73.28 (C-4′), 82.76 (C-5′), 61.94 (C-6′), 172.34 (C=O); ESIMS m/z 491.2 $[M+Na]^+$, 549.0 $[M+2Na+Cl]^+$. The NMR data matched those previously reported.[14,28]

1.2.2. 6,3′-Di-*O*-octanoylsucrose (4a). Amorphous compound; R_f 0.69 (9:1 EtOAc–MeOH); IR (KBr) 3392 (OH) and 1740 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.86 (m, 6H, CH_3), 1.26 (m, 16H, $2(CH_2)_4$), 1.55 (m, 4H, $2CH_{2\beta}$), 2.33 (dd, 4H, $J_{a,b}$ 12.4, $J_{CH2\alpha,CH2\beta}$ 6.8 Hz, $CH_{2\alpha}$), 5.17 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 3.33 (t, 1H, $J_{1,2}$ 3.6, $J_{2,3}$ 9.2 Hz, H-2), 3.56 (m, 1H, H-3), 3.18 (t, 1H, $J_{4,5}$ 9.2 Hz, H-4), 3.15 (t, 1H, $J_{5,4}$ 9.2 Hz, H-5), 3.87 (d, 1H, $J_{6a,6b}$ 12.0 Hz, H-6_a), 4.03 (d, 1H, $J_{6b,6a}$ 12.0 Hz, H-6_b), 3.51–3.54 (m, 2H, H-1′), 5.15 (d, 1H, $J_{3',4'}$ 3.6 Hz, H-3′), 4.08 (t, 1H, $J_{3',4'}$ 3.6, $J_{4',5'}$ 8.6 Hz, H-4′), 3.71 (m, 1H, H-5′), 3.54–3.67 (m, 2H, H-6′); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.97 (CH_3), 22.07, 24.36, 24.48, 28.42, 31.15, 33.30, 33.52 (CH_2), 91.76 (C-1), 72.94 (C-2), 73.09 (C-3), 71.10 (C-4), 69.59 (C-5), 63.92 (C-6), 60.49 (C-1′), 100.92 (C-2′), 76.83 (C-3′), 71.10 (C-4′), 82.84 (C-5′), 61.61 (C-6′), 172.27, 172.49 (C=O); ESIMS: m/z 617.3 $[M+Na]^+$, 675.3 $[M+2Na+Cl]^+$. Anal. Calcd for $C_{28}H_{50}O_{13}\cdot 2H_2O$: C, 53.32; H, 8.63. Found: C, 53.39; H, 8.45.

1.2.3. 6-*O*-Decanoylsucrose (3b). Colorless solid; R_f 0.25 (9:1 EtOAc–MeOH); IR (KBr) 3393 (OH) and 1742 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.86 (m, 3H, CH_3), 1.25 (m, 12H, $(CH_2)_6$), 1.52 (m, 2H, $CH_{2\beta}$), 2.31 (t, 2H, $J_{CH2\alpha,CH2\beta}$ 7.4 Hz, $CH_{2\alpha}$), 5.18 (d, 1H, $J_{1,2}$ 3.2 Hz, H-1), 3.45 (m, 1H, H-2), 3.65 (m, 1H, H-3), 3.18 (m, 1H, H-4), 3.14 (m, 1H, H-5), 3.96 (d, 1H, $J_{6a,6b}$ 12.2 Hz, H-6_a), 4.16 (d, 1H, $J_{6b,6a}$ 12.2 Hz, H-6_b), 3.45–3.52 (m, 2H, H-1′), 3.84 (m, 1H, H-3′), 3.81 (m, 1H, H-4′), 3.52 (m, 1H, H-5′), 3.50–3.54 (m, 2H, H-6′); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.94 (CH_3), 22.07, 24.45, 28.43, 28.65, 28.72, 28.84, 31.26, 33.51 (CH_2), 92.07 (C-1), 72.76 (C-2), 72.90 (C-3), 71.36 (C-4), 69.79 (C-5), 62.22 (C-6), 60.45 (C-1′), 102.16 (C-2′), 76.54 (C-3′), 73.27 (C-4′), 82.76 (C-5′), 61.93 (C-6′), 172.35 (C=O); ESIMS: m/z 519.2 $[M+Na]^+$, 577.3 $[M+2Na+Cl]^+$. The NMR data matched those previously reported.[5,16]

1.2.4. 6,3′-Di-*O*-decanoylsucrose (4b). Amorphous compound; R_f 0.75 (9:1 EtOAc–MeOH); IR (KBr) 3393 (OH) and 1742 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.86 (m, 6H, CH_3), 1.24 (m, 24H, $2(CH_2)_6$), 1.53 (m, 4H, $2CH_{2\beta}$), 2.32 (dd, 4H, $J_{a,b}$ 13.4, $J_{CH2\alpha,CH2\beta}$ 6.6 Hz, $CH_{2\alpha}$), 5.17 (d, 1H, $J_{1,2}$ 2.8 Hz, H-1), 3.33 (t, 1H, $J_{2,1}$ 2.8, $J_{2,3}$ 9.0 Hz, H-2), 3.58 (m, 1H, H-3), 3.17 (m, 1H, H-4), 3.15 (m, 1H, H-5), 3.87 (d, 1H, $J_{6a,6b}$ 11.6 Hz, H-6_a), 4.02 (d, 1H, $J_{6b,6a}$ 11.6 Hz, H-6_b), 3.55–3.59 (m, 2H, H-1′), 5.15 (d, 1H,

$J_{3',4'}$ 3.2 Hz, H-3′), 4.08 (t, 1H, $J_{3',4'}$ 3.2, $J_{4',5'}$ 8.4 Hz, H-4′), 3.71 (m, 1H, H-5′), 3.59–3.62 (m, 2H, H-6′); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.87 (CH_3), 22.01, 24.29, 24.39, 28.39, 28.59, 28.66, 28.80, 31.22, 33.25, 33.46 (CH_2), 91.70 (C-1), 72.95 (C-2), 73.11 (C-3), 71.06 (C-4), 69.61 (C-5), 63.91 (C-6), 60.49 (C-1′), 100.89 (C-2′), 76.87 (C-3′), 71.06 (C-4′), 82.76 (C-5′), 61.52 (C-6′), 172.24, 172.37 (C=O); ESIMS: *m*/*z* 673.3 $[M+Na]^+$, 731.3 $[M+2Na+Cl]^+$. Anal. Calcd for $C_{32}H_{58}O_{13}\cdot 2H_2O$: C, 55.96; H, 9.10. Found: C, 56.04; H, 8.99.

1.2.5. 6-*O*-Lauroylsucrose (3c). Colorless solid; R_f 0.25 (9:1 EtOAc–MeOH); IR (KBr) 3392 (OH) and 1740 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.79 (m, 3H, CH_3), 1.18 (m, 16H, $(CH_2)_8$), 1.46 (m, 2H, $CH_{2\beta}$), 2.25 (t, 2H, $J_{CH2\alpha,CH2\beta}$ 7.2 Hz, $CH_{2\alpha}$), 5.11 (d, 1H, $J_{1,2}$ 3.2 Hz, H-1), 3.41 (m, 1H, H-2), 3.59 (t, 1H, $J_{2,3}$ 9.6, $J_{4,3}$ 9.6 Hz, H-3), 3.11 (m, 1H, H-4), 3.09 (m, 1H, H-5), 3.89 (d, 1H, $J_{6a,6b}$ 12.0 Hz, H-6_a), 4.10 (d, 1H, $J_{6b,6a}$ 12.0 Hz, H-6_b), 3.42–3.52 (m, 2H, H-1′), 3.78 (m, 1H, H-3′), 3.76 (m, 1H, H-4′), 3.51 (m, 1H, H-5′), 3.50–3.54 (m, 2H, H-6′); ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.02 (CH_3), 22.17, 24.52, 28.27, 28.52, 28.78, 28.81, 28.98, 29.08, 29.10, 31.37, 33.56 (CH_2), 92.13 (C-1), 72.80 (C-2), 72.97 (C-3), 71.40 (C-4), 69.80 (C-5), 62.24 (C-6), 60.47 (C-1′), 103.17 (C-2′), 76.55 (C-3′), 73.28 (C-4′), 82.80 (C-5′), 61.97 (C-6′), 172.45 (C=O); ESIMS: *m*/*z* 547.2 $[M+Na]^+$, 605.3 $[M+2Na+Cl]^+$. The NMR data matched those previously reported.[14,16]

1.2.6. 6,3′-Di-*O*-lauroylsucrose (4c). Amorphous compound; R_f 0.78 (9:1 EtOAc–MeOH); IR (KBr) 3392 (OH) and 1740 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.86 (m, 6H, CH_3), 1.24 (m, 32H, $2(CH_2)_8$), 1.54 (m, 4H, $2CH_{2\beta}$), 2.32 (dd, 4H, $J_{a,b}$ 13.0, $J_{CH2\alpha,CH2\beta}$ 7.2 Hz, $CH_{2\alpha}$), 5.17 (d, 1H, $J_{1,2}$ 2.8 Hz, H-1), 3.32 (m, 1H, H-2), 3.58 (m, 1H, H-3), 3.17 (m, 1H, H-4), 3.14 (m, 1H, H-5), 3.87 (d, 1H, $J_{6a,6b}$ 12.0 Hz, H-6_a), 4.02 (d, 1H, $J_{6b,6a}$ 12.0 Hz, H-6_b), 3.55–3.59 (m, 2H, H-1′), 5.15 (d, 1H, $J_{3',4'}$ 2.0 Hz, H-3′), 4.08 (dd, 1H, $J_{3',4'}$ 2.0, $J_{4',5'}$ 8.4 Hz, H-4′), 3.71 (m, 1H, H-5′), 3.59–3.62 (m, 2H, H-6′); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.97 (CH_3), 22.15, 24.37, 24.51, 28.50, 28.79, 29.00, 29.10, 31.37, 33.30, 33.54 (CH_2), 91.79 (C-1), 72.95 (C-2), 73.11 (C-3), 71.13 (C-4), 69.62 (C-5), 63.97 (C-6), 60.51 (C-1′), 100.94 (C-2′), 76.84 (C-3′), 71.04 (C-4′), 82.81 (C-5′), 61.59 (C-6′), 172.24, 172.45 (C=O); ESIMS: *m*/*z* 729.5 $[M+Na]^+$. Anal. Calcd for $C_{36}H_{66}O_{13}\cdot 1.8H_2O$: C, 58.48; H, 9.49. Found: C, 58.54; H, 9.35.

1.2.7. 6-*O*-Myristoylsucrose (3d). Colorless solid; R_f 0.26 (9:1 EtOAc–MeOH); IR (KBr) 3393 (OH) and 1741 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.85 (m, 3H, CH_3), 1.23 (m, 20H, $(CH_2)_{10}$), 1.51 (m, 2H, $CH_{2\beta}$), 2.30 (t, 2H, $J_{CH2\alpha,CH2\beta}$ 7.4 Hz, $CH_{2\alpha}$), 5.17 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 3.45 (m, 1H, H-2), 3.65 (t, 1H, $J_{2,3}$ 9.6, $J_{4,3}$ 9.6 Hz, H-3), 3.16 (m, 1H, H-4), 3.14 (m, 1H, H-5), 3.96 (d, 1H, $J_{6a,6b}$ 12.0 Hz, H-6_a), 4.15 (d, 1H, $J_{6b,6a}$ 12.0 Hz, H-6_b), 3.46–3.56 (m, 2H, H-1′), 3.82 (m, 1H, H-3′), 3.80 (m, 1H, H-4′), 3.56 (m, 1H, H-5′), 3.51–3.54 (m, 2H, H-6′); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.95 (CH_3), 22.11, 24.47, 28.47, 28.73, 28.92, 29.04, 31.31, 33.52 (CH_2), 92.10 (C-1), 72.77 (C-2), 72.92 (C-3), 71.38 (C-4), 69.80 (C-5), 62.24 (C-6), 60.46 (C-1′), 102.19 (C-2′), 76.56 (C-3′), 73.29 (C-4′), 82.76 (C-5′), 61.94 (C-6′), 172.37 (C=O); ESIMS: *m*/*z* 575.2 $[M+Na]^+$. The NMR data matched those previously reported.[22]

1.2.8. 6,3′-Di-*O*-myristoylsucrose (4d). Colorless solid; R_f 0.82 (9:1 EtOAc–MeOH); IR (KBr) 3393 (OH) and 1741 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.85 (m, 6H, CH_3), 1.24 (m, 40H, $2(CH_2)_{10}$), 1.54 (m, 4H, $2CH_{2\beta}$), 2.32 (dd, 4H, $J_{a,b}$ 14.0, $J_{CH2\alpha,CH2\beta}$ 6.8 Hz, $CH_{2\alpha}$), 5.17 (d, 1H, $J_{1,2}$ 2.8 Hz, H-1), 3.32 (m, 1H, H-2), 3.58 (m, 1H, H-3), 3.17 (m, 1H, H-4), 3.15 (m, 1H, H-5), 3.88 (d, 1H, $J_{6a,6b}$ 12.0 Hz, H-6_a), 4.02 (d, 1H, $J_{6b,6a}$ 12.0 Hz, H-6_b), 3.52–3.58 (m, 2H, H-1′), 5.15 (d, 1H, $J_{3',4'}$ 3.2 Hz, H-3′), 4.09 (dd, 1H, $J_{3',4'}$ 3.2, $J_{4',5'}$ 8.4 Hz, H-4′), 3.71 (m, 1H, H-5′), 3.56–3.62 (m, 2H, H-6′); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.89 (CH_3), 22.07, 24.32, 24.45, 28.44, 28.71, 28.75, 28.93, 29.03, 29.07, 31.29, 33.25, 33.50 (CH_2), 91.75 (C-1), 72.93 (C-2), 73.05 (C-3), 71.09 (C-4), 69.62 (C-5), 63.96 (C-6), 60.50 (C-1′), 100.91 (C-2′), 76.84 (C-3′), 71.04 (C-4′), 82.76 (C-5′), 61.55 (C-6′), 172.17, 172.37 (C=O); ESIMS: *m*/*z* 785.5 $[M+Na]^+$, 843.3 $[M+2Na+Cl]^+$. Anal. Calcd for $C_{40}H_{74}O_{13}\cdot 1.6H_2O$: C, 60.67; H, 9.83. Found: C, 60.64; H, 9.75.

1.2.9. 6-*O*-Palmitoylsucrose (3e). Colorless solid; R_f 0.26 (9:1 EtOAc–MeOH); IR (KBr) 3402 (OH) and 1744 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.85 (m, 3H, CH_3), 1.23 (m, 24H, $(CH_2)_{12}$), 1.52 (m, 2H, $CH_{2\beta}$), 2.30 (t, 2H, $J_{CH2\alpha,CH2\beta}$ 7.2 Hz, $CH_{2\alpha}$), 5.17 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 3.41 (m, 1H, H-2), 3.65 (m, 1H, H-3), 3.18 (m, 1H, H-4), 3.15 (m, 1H, H-5), 3.96 (d, 1H, $J_{6a,6b}$ 12.0 Hz, H-6_a), 4.16 (d, 1H, $J_{6b,6a}$ 12.0 Hz, H-6_b), 3.41–3.52 (m, 2H, H-1′), 3.81 (m, 1H, H-3′), 3.79 (m, 1H, H-4′), 3.53 (m, 1H, H-5′), 3.50–3.54 (m, 2H, H-6′); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.93 (CH_3), 22.08, 24.45, 28.46, 28.70, 28.74, 28.91, 29.04, 31.28, 33.51 (CH_2), 92.07 (C-1), 72.76 (C-2), 72.91 (C-3), 71.36 (C-4), 69.79 (C-5), 62.22 (C-6), 60.45 (C-1′), 102.16 (C-2′), 76.54 (C-3′), 73.26 (C-4′), 82.74 (C-5′), 61.92 (C-6′), 172.33 (C=O); ESIMS: *m*/*z* 603.3 $[M+Na]^+$. The NMR data matched those previously reported.[14,22]

1.2.10. 6,3′-Di-*O*-palmitoylsucrose (4e). Amorphous compound; R_f 0.85 (9:1 EtOAc–MeOH); IR (KBr) 3402 (OH) and 1744 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.85 (m, 6H, CH_3), 1.24 (m, 48H, 2$(CH_2)_{12}$), 1.54 (m, 4H, 2$CH_{2\beta}$), 2.32 (m, 4H, $CH_{2\alpha}$), 5.17 (d, 1H, $J_{1,2}$ 2.8 Hz, H-1), 3.32 (m, 1H, H-2), 3.58 (m, 1H, H-3), 3.17 (m, 1H, H-4), 3.15 (m, 1H, H-5), 3.88 (d, 1H, $J_{6a,6b}$ 12.0 Hz, H-6$_a$), 4.01 (d, 1H, $J_{6b,6a}$ 12.0 Hz, H-6$_b$), 3.52–3.58 (m, 2H, H-1′), 5.15 (d, 1H, $J_{3',4'}$ 3.2 Hz, H-3′), 4.09 (m, 1H, H-4′), 3.71 (m, 1H, H-5′), 3.56–3.62 (m, 2H, H-6′); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.88 (CH_3), 22.06, 24.30, 24.45, 25.51, 28.40, 28.69, 29.05, 31.27, 33.23, 33.49 (CH_2), 91.73 (C-1), 72.92 (C-2), 73.04 (C-3), 71.09 (C-4), 69.60 (C-5), 63.96 (C-6), 60.48 (C-1′), 100.90 (C-2′), 76.82 (C-3′), 71.04 (C-4′), 82.75 (C-5′), 61.55 (C-6′), 172.17, 172.36 (C=O); ESIMS: m/z 853.6 [M+Cl]$^-$. Anal. Calcd for $C_{44}H_{82}O_{13}\cdot 1.9H_2O$: C, 61.93; H, 10.13. Found: C, 61.95; H, 9.91.

1.2.11. 6-*O*-Stearoylsucrose (3f). Colorless solid; R_f 0.28 (9:1 EtOAc–MeOH); IR (KBr) 3400 (OH) and 1740 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.87 (m, 3H, CH_3), 1.24 (m, 28H, $(CH_2)_{14}$), 1.53 (m, 2H, $CH_{2\beta}$), 2.31 (t, 2H, $J_{CH2\alpha,CH2\beta}$ 6.6 Hz, $CH_{2\alpha}$), 5.18 (d, 1H, $J_{1,2}$ 3.6 Hz, H-1), 3.41 (m, 1H, H-2), 3.65 (m, 1H, H-3), 3.18 (m, 1H, H-4), 3.15 (m, 1H, H-5), 3.96 (d, 1H, $J_{6a,6b}$ 12.0 Hz, H-6$_a$), 4.16 (d, 1H, $J_{6b,6a}$ 12.0 Hz, H-6$_b$), 3.41–3.52 (m, 2H, H-1′), 3.81 (m, 1H, H-3′), 3.79 (m, 1H, H-4′), 3.53 (m, 1H, H-5′), 3.50–3.54 (m, 2H, H-6′); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.91 (CH_3), 22.10, 24.46, 28.48, 28.73, 28.77, 28.94, 29.07, 31.31, 33.51 (CH_2), 92.10 (C-1), 72.77 (C-2), 72.93 (C-3), 71.38 (C-4), 69.81 (C-5), 62.23 (C-6), 60.48 (C-1′), 102.17 (C-2′), 76.57 (C-3′), 73.25 (C-4′), 82.74 (C-5′), 61.89 (C-6′), 172.32 (C=O); ESIMS: m/z 643.5 [M+Cl]$^-$. The NMR data matched those previously reported.[14,22]

1.2.12. 6,3′-Di-*O*-stearoylsucrose (4f). Colorless solid; R_f 0.88 (9:1 EtOAc–MeOH); IR (KBr) 3400 (OH) and 1740 (C=O); ^{1}H NMR (400 MHz, DMSO-d_6): δ 0.85 (m, 6H, CH_3), 1.23 (m, 56H, 2$(CH_2)_{14}$), 1.54 (m, 4H, 2$CH_{2\beta}$), 2.32 (m, 4H, $CH_{2\alpha}$), 5.17 (d, 1H, $J_{1,2}$ 2.4 Hz, H-1), 3.32 (m, 1H, H-2), 3.58 (m, 1H, H-3), 3.18 (m, 1H, H-4), 3.16 (m, 1H, H-5), 3.89 (d, 1H, $J_{6a,6b}$ 11.8 Hz, H-6$_a$), 4.01 (d, 1H, $J_{6b,6a}$ 11.8 Hz, H-6$_b$), 3.52–3.58 (m, 2H, H-1′), 5.15 (d, 1H, $J_{3',4'}$ 1.6 Hz, H-3′), 4.09 (dd, 1H, $J_{3',4'}$ 1.6, $J_{4',5'}$ 6.4 Hz, H-4′), 3.71 (m, 1H, H-5′), 3.56–3.62 (m, 2H, H-6′); ^{13}C NMR (100 MHz, DMSO-d_6): δ 13.88 (CH_3), 22.07, 24.30, 24.46, 28.44, 28.71, 28.78, 29.07, 31.29, 33.22, 33.50 (CH_2), 91.75 (C-1), 72.92 (C-2), 73.05 (C-3), 71.10 (C-4), 69.61 (C-5), 63.98 (C-6), 60.50 (C-1′), 100.92 (C-2′), 76.83 (C-3′), 71.03 (C-4′), 82.74 (C-5′), 61.56 (C-6′), 172.16, 172.35 (C=O); ESIMS: m/z 909.5 [M+Cl]$^-$. Anal. Calcd for $C_{48}H_{90}O_{13}\cdot 1.8H_2O$: C, 63.52; H, 10.39. Found: C, 63.51; H, 10.24.

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