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Sucrose esterification under Mitsunobu conditions: evidence for the formation of 6-*O*-acyl-3′,6′-anhydrosucrose besides mono and diesters of fatty acids

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Abstract—A series of sucrose monoesters and homogeneous or mixed diesters, which have various chain lengths and saturation levels, were prepared under Mitsunobu conditions with good regioselectivity. Among the anhydro derivatives arising from competitive intramolecular etherification, 3′,6′-anhydrosucrose 6-*O*-monoesters, which have never been reported, were identified.

1. Introduction

Sucrose esters are a good example of amphiphilic derivatives in which both the hydrophilic and the hydrophobic moieties come from vegetal resources, and have been acknowledged for their innocuousness. Due to their physicochemical properties, they are interesting derivatives, most notably as emulsifiers used in foods and cosmetics.[1–10] They have also recently been shown to inhibit some transferases.[11] We are currently involved in programs aimed at studying the selectivity of sucrose chemical transformations[12–14] and in this context, we herein report our new results on the preparation of esters of defined structure in terms of the degree of substitution (mono and diesters), regioselectivity and nature of the hydrophobic part. These compounds have been committed to further physicochemical studies in connection with our earlier observations on thermotropic liquid crystal behaviour of amphiphilic sucrose mono-*O*-hydroxyalkyl ethers, in which we have shown how much the position of the chain on the carbohydrate backbone could determine the geometry of the liquid crystalline phases.[15] Such studies require materials of high purity and stability. However, unlike ethers, sucrose esters can undergo acyl group migrations and in this respect, esters at primary positions are much more stable.[16,17] We therefore focussed on selective preparative accesses towards sucrose esters at primary positions.

Various methods can be used for making esters of sucrose, with different stereochemical outcomes. Direct base catalysed transesterification by methyl esters provides mixtures of isomers essentially composed of esters at primary positions OH-6, 1′ or 6′; however they are often difficult to purify. Furthermore, complex mixtures of more substituted esters can also form. Methods for the selective synthesis of primary esters of sucrose include protease catalysed esterification, which produces monoesters at the primary OH-1′,[18–22] esterification at OH-2 by activated esters followed by migration towards OH-6,[17,23] and Mitsunobu-type esterifications.[24–27] We herein report our own observations on this latter method, which we have used for preparing a series of new monoesters at OH-6 and OH-6′, homogeneous 6,6′-diesters and mixed 6,6′-diesters from monoacylated substrates, all of which have different chain lengths and saturation levels. We principally discuss the competition between dehydration and esterification and the identification of new 6-*O*-acyl-3′,6′-anhydrosucrose derivatives, which, because of chromatographic behaviour similar to that of diesters, imply careful purification when derivatives of physical chemistry grade are needed.

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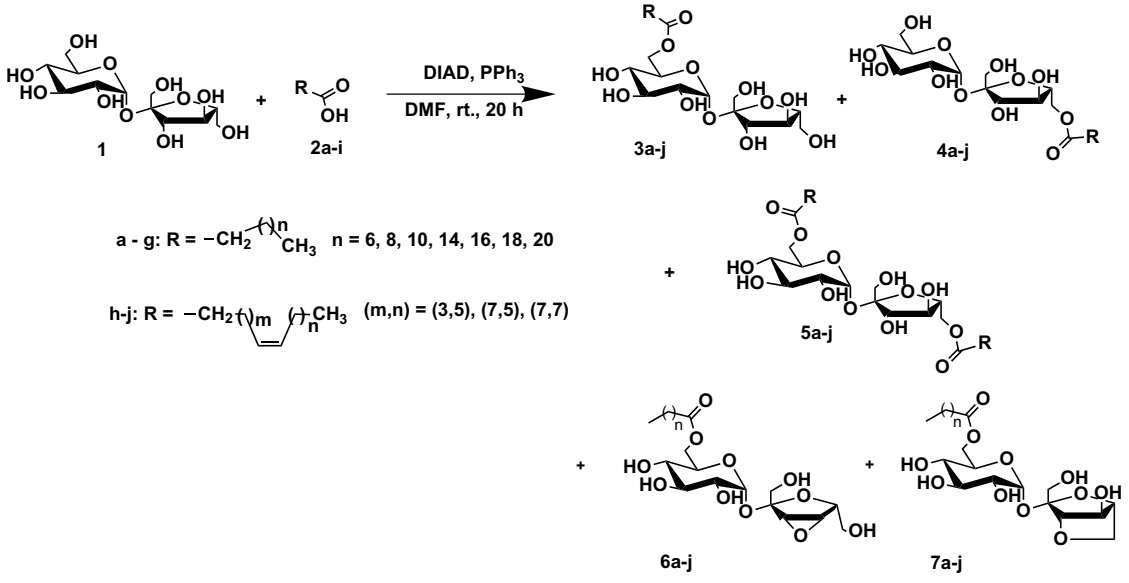
2. Results and discussion

2.1. Reaction of unprotected sucrose

The reaction was first applied to unprotected sucrose **1** using fatty acids **2** of various chain lengths (C8–C22) as well as unsaturated acids (C12:1, C16:1, C18:1). Using moderate excesses of reagents (DIAD: 2.7 equiv, PPh_3: 2.7 equiv, RCO_2H: 2.5 equiv), 6,6′-diesters **5** were formed with good selectivity; the third primary hydroxyl group (OH-1′), close to a quaternary carbon, was unreactive in this reaction (Scheme 1, Table 1). The reaction also provided monosubstituted esters at OH-6 **3** and OH-6′ **4** in a 85:15 ratio, constant for all cases. This is the result of the known faster reaction of unprotected sucrose at OH-6 and of a faster second esterification of the 6′-*O*-acyl sucrose derivatives, which still have its more reactive OH-6 available. Regioisomerically pure monoesters at OH-6 or OH-6′ obtained by this method are easier to purify (preparative HPLC) than mixtures obtained by other routes in which esters at other positions are present, and notably at OH-1′, which interfere in the chromatographic behaviour.

The competition between intermolecular esterifications and intramolecular etherifications results in the side formation of anhydro derivatives. Until now, only the 6-*O*-acyl-3′-4′ anhydrofructose **6** has been reported in the presence of a perfluoroalkyl carboxylic acid,[26] consistent with the results described by Guthrie et al. on the formation of α-D-glucopyranosyl-3,4-β-D-tagatofuranoside in the absence of any other nucleophile.[28] Although some 3′,6′-anhydrosucrose structures have already been observed,[29–31] they have never been mentioned in the case of esterifications.

Having an intermediate retention factor between monoesters and diesters, the 6-*O*-acyl-3′,4′-anhydro derivatives **6** can be at least partly purified by silica gel chromatography. NMR spectroscopic analysis of the faster moving chromatography fraction, which contains the diesters, revealed that another by-product was present in a significant proportion. Preparative HPLC allowed full purification of the diester and of the other product for which mass spectroscopy was consistent with a monoacylated anhydrosucrose derivative ((M+Na) = 529 (2M+Na) = 1035 for a lauric chain). For this latter product, 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 O-6. The other patterns of the glucosyl moiety remained unaffected when compared to a 6-*O*-acyl sucrose. Conversely, noticeable modifications of other patterns were observed showing that dehydration occurred on the fructosyl moiety. A characteristic feature was the very small coupling constants of H-5′ with all of its three neighbours. Also, a widening of the AB systems for protons H-1′a,b and H-6′a,b was observed, revealing a more restricted conformation. However, among these two CH_2 systems, only C-6′ exhibited a strongly increased ^{13}C chemical shift as well as a long-range coupling with H-3′ (HMBC). The symmetrical effect was seen between C-3′ and H-6′b, whereas no long-range coupling was observed between C-1′ and H-4′, or between C-4′ and H-1′a,b. These couplings, which can only exist through a newly formed ring, together with the other data, are consistent with structure **7** in which the anhydro bridge takes place between the 3′- and 6′-positions. The dioxanorbonane representation shown in Scheme 2 matches with the small coupling constants of H-5′. The 3′,4′-anhydro exhibits distinctive ^{13}C NMR chemical shifts for the C-3′ and C-4′ epoxide ring. Both anhydro derivatives arose from an attack of OH-3 on either one or the other oxyphosphonium salts A or B, both in equilibrium with a pentavalent phosphorane intermediate,[32,33] leading, respectively, to the 3′,4′ or to the 3′,6′ (Scheme 2). The yields of monosubstituted,

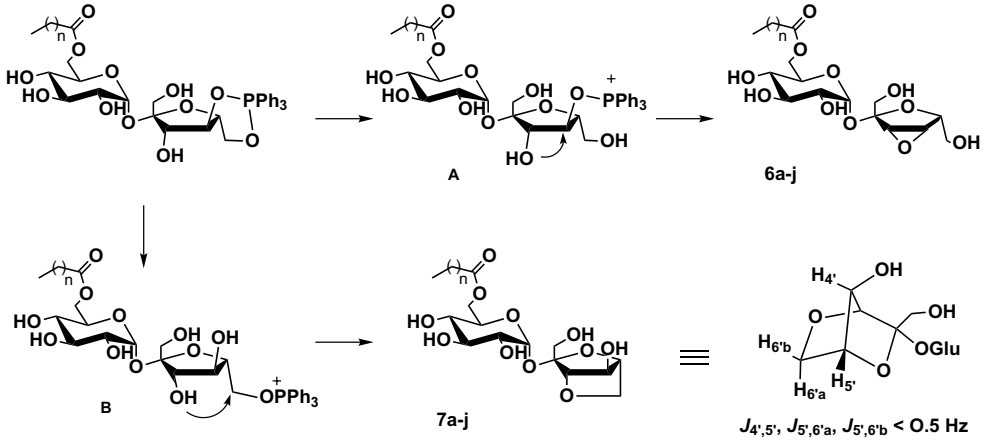


Scheme 1.

Table 1. Yields of sucrose and anhydrosucrose esters obtained from unprotected sucrose[a]

Acid	Monoesters (%)[b]	Diester (%)[c]	3′,4′-Anhydro (%)[d]	3′,6′-Anhydro (%)[c]
Octanoic **2a**	**3a**, **4a** (16)	**5a** (20)	**6a** (11)	**7a** (4)
Decanoic **2b**	**3b**, **4b** (33)	**5b** (26)	ND	**7b** (8)
Lauric **2c**	**3c**, **4c** (35)	**5c** (15)	**6c** (11)	**7c** (4)
Palmitic **2d**	**3d**, **4d** (22)	**5d** (39)	**6d** (9)	**7d** (5)
Stearic **2e**	**3e**, **4e** (26)	**5e** (31)	**6e** (6)	**7e** (8)
Eicosanoic **2f**	**3f**, **4f** (27)	**5f** ([e])	([e])	([e])
Docosanoic **2g**	**3g**, **4g** (27)	**5f**([e])	([e])	([e])
Dodec-5*c*-enoic **2h**	**3h**, **4h** (39)	**5h** (15)	**6h** (7)	**7h** (4)
Hexadec-5*c*-enoic **2i**	**3i**, **4i** (34)	**5i** (9)	**6i** (6)	**7i** (4)
Octadec-5*c*-enoic **2j**	**3j**, **4j** (26)	**5j** (7)	**6j** (14)	**7j** (2)

[a] Conditions: DIAD: 2.7 equiv, PPh_3: 2.7 equiv, RCO_2H: 2.5 equiv, DMF, rt, 30 h.
[b] Isolated yields.
[c] Isolated yields confirmed by HPLC.
[d] Estimation from intermediate chromatographic fractions masses and NMR analysis.
[e] Not determined because of multiple purifications due to the low solubility of these derivatives.



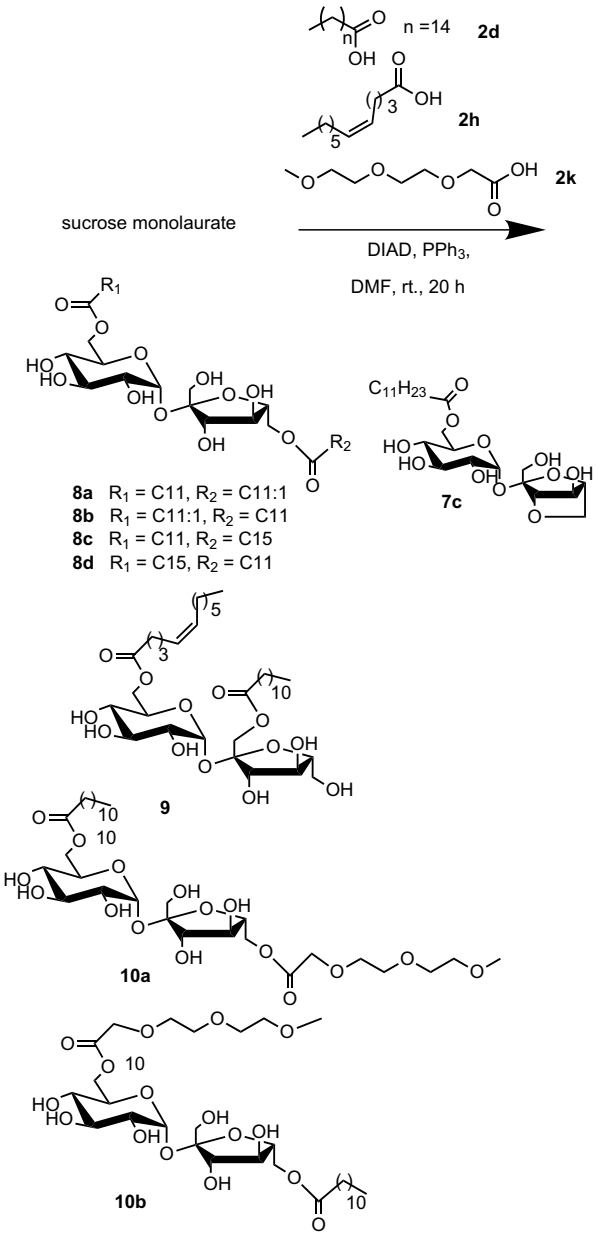
Scheme 2.

disubstituted and anhydro derivatives are given in Table 1 for aliphatic carboxylic acids (octanoic to stearic), as well as unsaturated ones. Longer acids were also used, producing slightly more 3′,6′-anhydro monoesters than the shorter chains. However, the low solubility of the starting materials and products in these cases did not allow accurate control of the actual stoichiometry of the reaction.

2.2. Reaction of sucrose monolaurate

In order to synthesise mixed diesters, with one chain saturated and the other containing one double bond, the reaction was applied to sucrose monolaurate samples in the presence of dodec-5*c*-enoic acid **2h** (Scheme 3, Table 2). From mixtures of sucrose monolaurates, diesters **8a** and **8b** were formed together with the 6-*O*-lauroyl-3′,6′-anhydrosucrose **7c** derivative. Pure 6-*O*-lauroylsucrose led to 6-*O*-lauroyl-6′-*O*-dodec-5*c*-enoyl sucrose **8a** and 6-*O*-lauroyl-3′,6′-anhydrosucrose **7c** whereas 6′-*O*-lauroylsucrose only led to the corresponding diester **8b** without formation of any other anhydrofructose derivatives. However, diesters **8a** and **8b** have identical chromatographic and spectroscopic properties, preventing us from proving that no transesterifications occurred. If 1′-*O*-lauroyl sucrose was present in the starting mixture, 1′-*O*-lauroyl-6-*O*-dodec-5*c*-enoyl sucrose **9** (7%) also formed. In all cases, the remaining unreacted monolaurate fraction was simplified, mainly being composed of the 6-*O*-isomer. This explains the higher reactivity of the hydroxyl group OH-6 position in this type of reaction, as confirmed by kinetic measurements for reactions conducted in parallel starting from samples containing increasing proportions of the 6-*O*-ester, exhibiting a consistent decrease in the rate of product formation.

Lauroyl–palmitoyl diesters were also prepared, but the relative position of the lauric and palmitic chains could not be ascertained when mixtures of regioisomers of sucrose laurates were used. Proof that no transesterification of the starting sucrose ester occurred in the process was provided by the example of 2-[2-(2-methoxyethoxy)ethoxy]acetic acid **2k**, for which 6-*O*-lauroyl-6′-*O*-2-[2-(2-methoxyethoxy)ethoxy]acetoxysucrose **10a** and 6-*O*-2-[2-(2-methoxyethoxy)ethoxy]-acetoxy-6′-*O*-lauroylsucrose **10b** could be separated by semi-preparative HPLC and identified by 2D NMR using multiple bond correlation (HMBC). The carbonyl



Scheme 3.

groups could be identified by their long-range coupling with protons H-6ab or H-6′ab and the position of the oxyethylenic chain, determined by the long-range coupling of the C=O with the CH_2 protons at the α-position of the oxyethylenic chain. The relative proportion of **10a**:**10b** was 27/73 (HPLC) when starting from a sucrose monolaurate sample containing 6-*O*-, 1′-*O*- and 6′-*O*-lauroyl sucrose in the ratio 40/10/33. The higher reactivity of the OH-6 position is highlighted here again.

3. Conclusion

The competition between intramolecular esterification and intramolecular etherification can proceed via two different reaction pathways in the Mitsunobu esterification of sucrose. One forms the already observed α-D-glucopyranosyl-3,4-β-D-tagatofuranoside, whereas the second yields 6-*O*-acyl-3′,6′-anhydrosucroses, which have so far never been described. Being close to the diesters in terms of polarity, their isolation requires careful HPLC purification. Based on these observations, monoesters and diesters, which have identical or different fatty chains with variable lengths and level of saturations, and the new monoacyl-3′,6′-anhydrosucroses can be prepared in high purity, a requirement for structural property relationship studies on sucrose esters. This has already allowed the observation of a new transition phase within the smectic A* phase in the case of 6,6′-sucrose distearate.[34] Detailed exploration of the physicochemical properties of these compounds, as pure materials or in solution, will be reported in due course.

4. Experimental

4.1. General methods

Sucrose was obtained from Béghin-Say. Chromatography solvents were purchased from SDS and Carlo Erba. HPLC solvents were purchased from SDS. Reactions were monitored by TLC using glass silica gel plates (Merck 60 F_{254}). The plates were developed using UV light and vaporisation with a solution of 10% H_2SO_4 in EtOH (v/v). Flash chromatography separations were performed using Merck Gerudan silica gel Si 60 (40–63 μm). NMR spectra were recorded on Bruker AC spectrometers at 75.47 MHz (or 125.77 MHz) for ^{13}C NMR and 300.13 MHz (or 500.13 MHz) for ^{1}H NMR. LSI-mass spectra were recorded by the Centre de Spectrométrie de Masse of the Université Claude Bernard (Villeurbanne). Microanalyses were performed by the Service Central d'Analyse of the CNRS (Vernaison). Optical rotations were measured with a Perkin Elmer 241 polarimeter. Analytical HPLC analyses were performed at 30 °C using a NH_2 spherisorb column

Table 2. Yields of sucrose and anhydrosucrose esters obtained from sucrose laurate[a]

Substrate	Acid	Diester (%)[b]	3′,6′-Anhydro (%)[b]
3c	Dodec-5*c*-enoic **2h**	**8a** (14)	**7c** (3)
4c	Dodec-5*c*-enoic **2h**	**8b** (30)	Not formed
3c+**4c** (1:1)	Dodec-5*c*-enoic **2h**	**8a**+**8b** (37)	**7c** (5)
Mixed monolaurates	Dodec-5*c*-enoic **2h**	**8a**+**8b** (31)+**9** (7)	**7c** (3)
Id	Palmitic **2d**	**8c**+**8d** (21)	**7c** (3)
Id	**2k**	**10a**+**10b** (32)	ND

[a] Conditions: DIAD: 2.5 equiv, PPh_3: 2.5 equiv, RCO_2H: 2 equiv, DMF, rt, 17 h.

[b] Calculated based on the mass of the chromatographic fraction of the mixture and the measurement of the molar proportions by ^{1}H NMR spectroscopy analysis. Further semi-preparative HPLC led to pure derivatives.

4.6×250 mm (Touzart&Matignon) with a refractometric detection. The eluting system was a CH_3CN/H_2O mixture 90/10 to 86/14 v/v (0.8 mL/min) for monoesters and 95/5 v/v for short chain diesters. For long chain diesters (for solubility reasons) the eluting system was a CH_3CN/THF/H_2O mixture 64/30/6 to 40/54/6 v/v. For analytical HPLC, the injected samples had a concentration of 1–5 mg/mL. Semi-preparative HPLC separations were performed on an NH_2 spherisorb column 20×250 mm with a refractometric detection. The system was equipped with a 2 mL-injection loop (maximum concentration of the injected sample: 100 mg/mL). The eluting system was identical to the one used for analytical HPLC (flow: 20 mL/min).

4.2. Acylation of unprotected sucrose

Sucrose (3.42 g, 9.98 mmol) was dissolved in anhydrous DMF (80 mL) by stirring under N_2 at 70 °C. The mixture was cooled to room temperature before addition of triphenylphosphine (7.06 g, 2.7 equiv), carboxylic acid (e.g., lauric acid, 5.00 g, 2.5 equiv) and DMF (20 mL). After complete dissolution, the medium was cooled to 0 °C and DIAD (5.3 mL, 2.7 equiv) introduced. TLC showed near total consumption of sucrose after 30 h at room temperature. After removal of DMF under reduced pressure at $T = 36$–38 °C, the crude residue was purified by silica gel chromatography [elution gradient: dichloromethane/acetone/methanol/water 78/10/10/1.5 (A) to 67/15/15/3 v/v (B)]. Successively were collected a fraction containing the diester and the 3′,6′-anhydro derivative ($R_f = 0.63$ in mixture B), 1.30 g, then the 6-*O*-monoacylated 3′,4′-anhydrosucrose derivative ($R_f \sim 0.46$ in mixture B), and then the monoester fraction ($R_f = 0.35$ in mixture B, 1.86 g). The monoester fraction was further subjected to semi-preparative HPLC to isolate the 6-*O*-acylsucrose and the 6′-*O*-acylsucrose. The diester fraction was also repurified by semi-preparative HPLC to isolate 6-*O*-acyl-3′,6′-anhydrosucrose derivative and 6,6′-di-*O*-acylsucrose in pure forms. Compounds **3a**, **3c**, **3d**, **3e**, **4a**, **5c** and **5d** exhibited spectroscopic data identical to those already reported.[16,22,24,27,35–37]

4.3. 6-*O*-Decanoylsucrose 3b

$[\alpha]_D^{25} = +44$ (*c* 1, MeOH); Found: C, 50.65; H, 8.1. $C_{22}H_{40}O_{12}\cdot 1.4H_2O$ requires C, 50.6; H, 8.3%; δ_H (300 MHz, MeOD): 0.82–1.03 (3H, m, CH_3), 1.18–1.48 (12H, m $(CH_2)_6$), 1.51–1.75 (2H, m, $CH_{2\beta}$), 2.38 (2H, t, $J_{CH2-CH2} = 7.5$ Hz, $CH_{2\alpha}$), 3.31 (1H, t, $J_{4-3} = J_{4-5} = 9.4$ Hz, H_4), 3.44 (1H, dd, $J_{2-3} = 9.4$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.60 (1H, d, $J_{1'b-1'a} = 12.2$ Hz, H_1), 3.65 (1H, d, $J_{1'a-1'b} = 12.2$ Hz, H_1), 3.74 (1H, t, $J_{4-3} = J_{3-2} = 9.4$ Hz, H_3), 3.77–3.91 (3H, m, $H_{5'}$, $H_{6/b}$), 3.92–4.08 (2H, m, $H_{4'}$, H_5), 4.11 (1H, d, $J_{3'-4'} = 8.3$ Hz, $H_{3'}$), 4.18 (1H, dd, $J_{6b-6a} = 11.9$ Hz, $J_{6b-5} = 5.2$ Hz, H_{6b}), 4.42 (1H, dd, $J_{6a-6b} = 11.9$ Hz, $J_{6a-5} \sim 0$, H_{6a}), 5.39 (1H, d, $J_{1-2} = 3.8$ Hz, H_1); δ_C (75 MHz, MeOD): 14.7 ($1CH_3$), 26.3 ($1CH_{2\beta}$), 24.0–30.5–30.7–30.9–33.3 ($6CH_2$), 35.2 ($1CH_{2\alpha}$), 64.2 ($C_{6'}$), 64.4 ($C_{1'}$), 65.0 (C_6), 71.9 (C_4), 72.2 (C_5), 73.4 (C_2), 74.7 (C_3), 76.2 ($C_{4'}$), 79.5 ($C_{3'}$), 84.1 ($C_{5'}$), 93.7 (C_1), 105.5 ($C_{2'}$), 175.8 (1C=O on 6); *m*/*z* (LSIMS): 519.2416 (*m*/*z*+Na $C_{22}H_{40}O_{12}Na$ requires 519.2417).

4.4. 6-*O*-Eicosanoylsucrose 3f

$[\alpha]_D^{25} = +33$ (*c* 0.5, THF).^{1}H NMR (300 MHz, $CDCl_3$/MeOD): δ 0.80–0.96 (3H, m, CH_3), 1.15–1.43 (32H, m $(CH_2)_{16}$),1.52–1.71 (2H, m, $CH_{2\beta}$), 2.36 (2H, t, $J_{CH2-CH2} = 7.5$ Hz, $CH_{2\alpha}$), 3.32 (1H, t+MeOD, $J_{4-3} = J_{4-5} = 9.3$ Hz, H_4), 3.46 (1H, dd, $J_{2-3} = 9.7$ Hz, $J_{2-1} = 3.5$ Hz, H_2), 3.58 (1H, d, $J_{1'b-1'a} = 12.5$ Hz, H_1), 3.66 (1H, d, $J_{1'a-1'b} = 12.5$ Hz, H_1), 3.69–3.85 (4H, m, $H_{5'}$, $H_{6/b}$, H_3), 3.94–4.05 (2H, m, $H_{4'}$, H_5), 4.08 (1H, d, $J_{3'-4'} = 8.1$ Hz, $H_{3'}$), 4.23 (1H, dd, $J_{6b-6a} = 12.2$ Hz, $J_{6b-5} = 4.6$ Hz, H_{6b}), 4.38 (1H, dd, $J_{6a-6b} = 12.2$ Hz, $J_{6a-5} = 1.7$ Hz, H_{6a}), 5.39 (1H, d, $J_{1-2} = 3.5$ Hz, H_1). ^{13}C NMR (75 MHz, MeOD): δ 14.7 ($1CH_3$), 25.9 ($1CH_{2\beta}$), 23.6–30.2–30.4–30.5–30.7–32.9 ($16CH_2$), 35.0 ($1CH_{2\alpha}$), $C_{1'}$ and $C_{6'}$ not visible, 64.4 (C_6), 71.2 (C_4), 71.9 (C_5), 72.9 (C_2), 74.3 (C_3), 75.5 ($C_{4'}$), 79.7 ($C_{3'}$), 83.6 ($C_{5'}$), 93.3 (C_1), 105.0 ($C_{2'}$), 175.6 (1C=O on 6). HRMS *m*/*z* calcd for $C_{32}H_{60}O_{12}Na$ (*m*/*z*+Na): 659.3982; Found: 659.3985. Anal. Calcd for $C_{32}H_{60}O_{12}\cdot 0.8H_2O$: C, 59.02; H, 9.53; O, 31.45; Found: C, 58.93; H, 9.48; O, 31.24.

4.5. 6-*O*-Docosanoylsucrose 3g

$[\alpha]_D^{25} = +31$ (*c* 1, THF). HRMS *m*/*z* calcd for $C_{34}H_{64}O_{12}Na$ (*m*/*z*+Na): 687.4295; Found: 687.4292. Anal. Calcd for $C_{34}H_{64}O_{12}\cdot 0.9H_2O$: C, 59.96; H, 9.74; O, 30.30; Found: C, 60.00; H, 9.87; O, 30.54.

4.6. 6′-*O*-Palmitoylsucrose 4d

$[\alpha]_D^{25} = +42$ (*c* 1, MeOH); δ_H (300 MHz, MeOD): 0.91 (3H, t, $J_{CH3-CH2} \sim 7$ Hz, CH_3), 1.19–1.44 (24H, m $(CH_2)_{12}$), 1.53–1.71 (2H, m, $CH_{2\beta}$), 2.36 (2H, t, $J_{CH2-CH2} = 7.4$ Hz, $CH_{2\alpha}$), 3.35 (1H, t+MeOD, $J_{4-5} \sim J_{4-3} = 9.2$ Hz, H_4), 3.43 (1H, dd, $J_{2-3} = 9.8$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.60 (1H, d, $J_{1'b-1'a} = 12.4$ Hz, H_1), 3.67 (1H, d, $J_{1'a-1'b} = 12.4$ Hz, H_1), 3.69–3.79 (2H, m, H_{6b}, H_3), 3.79–3.89 (2H, m, H_{6a}, H_5), 3.93 (1H, td, $J_{5'-4'} = J_{5'-6'a} = 7.7$ Hz, $J_{5'-6'b} = 3.4$ Hz, $H_{5'}$), 4.03 (1H, t, $J_{4'-5'} = J_{4'-3'} = 8.0$ Hz, $H_{4'}$), 4.11 (1H, d, $J_{3'-4'} = 8.0$ Hz, $H_{3'}$), 4.32 (1H, dd, $J_{6'b-6'a} = 11.7$ Hz, $J_{6'b-5'} = 3.4$ Hz, H_6), 4.41 (1H, dd, $J_{6'a-6'b} = 11.7$ Hz, $J_{6'a-5'} = 7.7$ Hz, H_6), 5.36 (1H, d, $J_{1-2} = 3.8$ Hz, H_1); δ_C (75 MHz, MeOD): 14.8 ($1CH_3$), 26.2 ($1CH_{2\beta}$), 24.0–30.5–30.8–30.9–31.1–33.4 ($12CH_2$), 35.2 ($1CH_{2\alpha}$), 62.8 (C_6), 64.1 ($C_{1'}$), 67.2 ($C_{6'}$), 71.8 (C_4), 73.5 (C_2), 74.5 (C_5), 75.0 (C_3), 77.2 ($C_{4'}$), 79.3 ($C_{3'}$), 80.9 ($C_{5'}$), 93.7 (C_1), 105.8 ($C_{2'}$), 175.7 (1C=O on 6′); *m*/*z* (LSIMS): 603.3361 (*m*/*z*+Na $C_{28}H_{52}O_{12}Na$ requires 603.3356).

4.7. 6′-*O*-Stearoylsucrose 4e

$[\alpha]_D^{25} = +42$ (*c* 0.3, MeOH). ^{1}H NMR (300 MHz, MeOD): δ_H 0.85–0.99 (3H, m, CH_3), 1.20–1.43 (28H, m,

$(CH_2)_{14}$), 1.55–1.70 (2H, m, $CH_{2\beta}$), 2.36 (2H, t, $J_{CH2-CH2} = 7.4$ Hz, $CH_{2\alpha}$), 3.35 (1H, t+MeOD, $J_{4-3} = J_{4-5} = 9.4$ Hz, H_4), 3.42 (1H, dd, $J_{2-3} = 9.8$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.60 (1H, d, $J_{1'b-1'a} = 12.4$ Hz, H_1), 3.65 (1H, d, $J_{1'a-1'b} = 12.4$ Hz, H_1), 3.68–3.77 (2H, m, H_{6b}, H_3), 3.79–3.88 (2H, m, H_{6a}, H_5), 3.93 (1H, td, $J_{5'-4'} = J_{5'-6'a} = 7.7$ Hz, $J_{5'-6'b} = 3.4$ Hz, $H_{5'}$), 4.02 (1H, t, $J_{4'-5'} = J_{4'-3'} = 8.0$ Hz, $H_{4'}$), 4.11 (1H, d, $J_{3'-4'} = 8.0$ Hz, $H_{3'}$), 4.32 (1H, dd, $J_{6'b-6'a} = 11.7$ Hz, $J_{6'b-5'} = 3.4$ Hz, H_6), 4.41 (1H, dd, $J_{6'a-6'b} = 11.7$ Hz, $J_{6'a-5'} = 7.5$ Hz, H_6), 5.36 (1H, d, $J_{1-2} = 3.8$ Hz, H_1). ^{13}C NMR (75 MHz, MeOD): δ_C 14.7 ($1CH_3$), 26.3 ($1CH_{2\beta}$), 24.0–30.5–30.8–30.9–31.1–33.4 ($14CH_2$), 35.2 ($1CH_{2\alpha}$), 62.8 (C_6), 64.1 ($C_{1'}$), 67.2 ($C_{6'}$), 71.8 (C_4), 73.6 (C_2), 74.5 (C_5), 75.0 (C_3), 77.2 ($C_{4'}$), 79.3 ($C_{3'}$), 81.0 ($C_{5'}$), 93.8 (C_1), 105.8 ($C_{2'}$), 175.8 (1C=O on 6′). m/z (LSIMS) (m/z+Na): 631.3672 ($C_{30}H_{56}O_{12}Na$ requires 631.3669).

4.8. 6-*O*-Dodec-5*c*-enoylsucrose 3h

$[\alpha]_D^{25} = +43$ (c 2, MeOH). ^{1}H NMR (300 MHz, MeOD): δ 0.85–0.99 (3H, m, CH_3), 1.18–1.45 (8H, m, $(CH_2)_4$), 1.68 (2H, q, $J_{CH2-CH2} = 7.3$ Hz, $CH_{2\beta}$), 1.95–2.19 (4H, m, $CH_2CH{=}CHCH_2$), 2.40 (2H, t, $J_{CH2-CH2} = 7.3$ Hz, $CH_{2\alpha}$), 3.31 (1H, t+MeOD, $J_{4-3} = 9.2$ Hz, $J_{4-5} = 9.8$ Hz, H_4), 3.44 (1H, dd, $J_{2-3} = 9.8$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.59 (1H, d, $J_{1'a-1'b} = 12.4$ Hz, H_1), 3.65 (1H, d, $J_{1'a-1'b} = 12.4$ Hz, H_1), 3.69–3.89 (4H, m, H_3, $H_{5'}$, $H_{6/b}$), 3.94–4.08 (2H, m, $H_{4'}$, H_5), 4.11 (1H, d, $J_{3'-4'} = 8.3$ Hz, $H_{3'}$), 4.19 (1H, dd, $J_{6b-6a} = 11.9$ Hz, $J_{6b-5} = 5.3$ Hz, H_{6b}), 4.42 (1H, dd, $J_{6a-6b} = 11.9$ Hz, $J_{6a-5} = 1.9$ Hz, H_{6a}), 5.29–5.49 (3H, m, H_1, CH=CH). ^{13}C NMR (75 MHz, MeOD): δ 14.7 ($1CH_3$), 26.3 ($1CH_{2\beta}$), 27.8-28.4 ($2CH_{2\alpha}CH{=}CH$), 24.0–30.3–31.0–33.2 ($4CH_2$), 34.6 ($1CH_{2\alpha}$), 64.2 ($C_{6'}$), 64.3 ($C_{1'}$), 65.0 (C_6), 71.9 (C_4), 72.2 (C_5), 73.4 (C_2), 74.7 (C_3), 76.1 ($C_{4'}$), 79.5 ($C_{3'}$), 84.1 ($C_{5'}$), 93.6 (C_1), 105.5 ($C_{2'}$), 132.2–129.9 (CH=CH), 175.6 (1C=O on 6). HRMS: m/z calcd for $C_{24}H_{42}O_{12}Na$ (m/z+Na): 523.2754; Found: 523.2749. Anal. Calcd for $C_{24}H_{42}O_{12}\cdot 1.1H_2O$: C, 53.15; H, 8.21; O, 38.64; Found: C, 53.07; H, 8.21; O, 38.10.

4.9. 6-*O*-Hexadec-9*c*-enoylsucrose 3i

$[\alpha]_D^{25} = +32$ (c 0.2, MeOH). ^{1}H NMR (300 MHz, MeOD): δ 0.80–1.00 (3H, m, CH_3), 1.17–1.50 (16H, m, $(CH_2)_8$), 1.53–1.73 (2H, m, $CH_{2\beta}$), 1.90–2.15 (4H, m, $CH_2CH{=}CHCH_2$), 2.39 (2H, t, $J_{CH2-CH2} = 7.4$ Hz, $CH_{2\alpha}$), 3.31 (1H, dd+MeOD, $J_{4-3} = 9.0$ Hz, $J_{4-5} = 10.0$ Hz, H_4), 3.43 (1H, dd, $J_{2-3} = 9.8$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.59 (1H, d, $J_{1'b-1'a} = 12.4$ Hz, H_1), 3.64 (1H, d, $J_{1'a-1'b} = 12.4$ Hz, H_1), 3.68–3.87 (4H, m, H_3, H_5', $H_{6/b}$), 3.94–4.07 (2H, m, $H_{4'}$, H_5), 4.10 (1H, d, $J_{3'-4'} = 8.5$ Hz, $H_{3'}$), 4.18 (1H, dd, $J_{6b-6a} = 11.9$ Hz, $J_{6b-5} = 5.4$ Hz, H_{6b}), 4.41 (1H, dd, $J_{6a-6b} = 11.9$ Hz, $J_{6a-5} = 2.0$ Hz, H_{6a}), 5.26–5.45 (3H, m, H_1, CH=CH).). ^{13}C NMR (75 MHz, MeOD): δ 14.7 ($1CH_3$), 26.3 ($1CH_{2\beta}$), 28.4 ($2CH_{2\alpha}$ CH=CH), 24.0–30.3–30.5–30.6–31.1–33.2 ($8CH_2$), 35.2 ($1CH_{2\alpha}$), 64.2 ($C_{6'}$), 64.4 ($C_{1'}$), 65.0 (C_6), 71.9 (C_4), 72.3 (C_5), 73.5 (C_2), 74.8 (C_3), 76.2 ($C_{4'}$), 79.5 ($C_{3'}$), 84.2 ($C_{5'}$), 93.7 (C_1), 105.5 ($C_{2'}$), 131.1-131.2 (CH=CH), 175.8 (1C=O on 6). HRMS: m/z calcd for $C_{28}H_{50}O_{12}Na$ (m/z+Na): 601.3200; Found: 601.3195.

4.10. 6-*O*-Octadec-9*c*-enoylsucrose 3j

$[\alpha]_D^{25} = +39$ (c 0.8, MeOH).^{1}H NMR (300 MHz, MeOD): δ 0.84–0.99 (3H, m, CH_3), 1.17–1.50 (20H, m, $(CH_2)_{10}$), 1.53–1.73 (2H, m, $CH_{2\beta}$), 1.95–2.13 (4H, m, $CH_2CH{=}CHCH_2$), 2.39 (2H, t, $J_{CH2-CH2} = 7.4$ Hz, $CH_{2\alpha}$),3.31 (1H, dd+MeOD, $J_{4-3} = 9.2$ Hz, $J_{4-5} = 10.0$ Hz, H_4), 3.43 (1H, dd, $J_{2-3} = 9.8$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.58 (1H, d, $J_{1'b-1'a} = 12.3$ Hz, H_1), 3.64 (1H, d, $J_{1'a-1'b} = 12.3$ Hz, H_1), 3.68–3.87 (4H, m, $H_{5'}$, $H_{6/b}$, H_3), 4.07–3.94 (2H, m, $H_{4'}$, H_5), 4.10 (1H, d, $J_{3'-4'} = 8.3$ Hz, $H_{3'}$), 4.18 (1H, dd, $J_{6a-6b} = 11.9$ Hz, $J_{6b-5} = 5.4$ Hz, H_{6b}), 4.41 (1H, dd, $J_{6a-6b} = 11.9$ Hz, $J_{6a-5} = 1.9$ Hz, H_{6a}), 5.28–5.44 (3H, m, H_1, CH=CH). ^{13}C NMR (75 MHz, MeOD): δ 14.8 ($1CH_3$), 26.3 ($1CH_{2\beta}$), 28.4 ($2CH_{2\alpha}CH{=}CH$), 24.0–30.5–30.6–30.8–30.9–31.1–33.4 ($10CH_2$), 35.2 ($1CH_{2\alpha}$), 64.2 ($C_{6'}$), 64.3 ($C_{1'}$), 64.9 (C_6), 71.8 (C_4), 72.2 (C_5), 73.3 (C_2), 74.7 (C_3), 76.1 ($C_{4'}$), 79.4 ($C_{3'}$), 84.1 ($C_{5'}$), 93.6 (C_1), 93.6 (C_1), 105.4 ($C_{2'}$), 131.1–131.1 (CH=CH), 175.7 (1C=O on 6). HRMS: m/z calcd for $C_{30}H_{54}O_{12}Na$ (m/z+Na): 629.3513; Found: 629.3516. Anal. Calcd for $C_{30}H_{54}O_{12}\cdot 1.2H_2O$: C, 57.34; H, 9.05; Found: C, 57.27; H, 8.62.

4.11. 6,6′-Di-*O*-octanoylsucrose 5a

$[\alpha]_D^{25} = +52$ (c 1, THF). ^{1}H NMR (300 MHz, MeOD): δ 0.83–1.00 ($2CH_3$),1.15–1.45 (16H, m, $2(CH_2)_4$), 1.50–1.73 (4H, m, $2CH_{2\beta}$), 2.25–2.50 (4H, m, $2CH_{2\alpha}$), 3.25 (1H, t, $J_{4-3} = 9.0$ Hz, $J_{4-5} = 9.6$ Hz, H_4), 3.43 (1H, dd, $J_{2-3} = 9.7$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.60 (1H, d, $J_{1'a-1'b} = 12.3$ Hz, H_1), 3.65 (1H, d, $J_{1'a-1'b} = 12.3$ Hz, H_1), 3.72 (1H, t, $J_{3-4} = 9.0$ Hz, $J_{3-2} = 9.7$ Hz, H_3), 3.88–3.98 (1H, m, $H_{5'}$), 4.02 (1H, t, $J_{4'-3'} = J_{4'-5'} = 8.0$ Hz, $H_{4'}$), 4.03–4.18 (2H, m, H_{6b}, $H_{3'}$, H_5), 4.31–4.41 (2H, m, $H_{6/b}$), 4.45 (1H, dd, $J_{6a-6b} = 11.3$ Hz, $J_{6a-5} = 1.3$ Hz, H_{6a}), 5.35 (1H, d, $J_{1-2} = 3.8$ Hz, H_1).^{13}C NMR (75 MHz, MeOD): δ 14.7 ($2CH_3$), 26.3 ($2CH_{2\beta}$), 24.0–30.4–33.2 ($8CH_2$), 35.2 ($2CH_{2\alpha}$), 64.2 ($C_{1'}$), 65.5 (C_6), 67.2 ($C_{6'}$), 72.2 (C_5, C_4), 73.5 (C_2), 74.9 (C_3), 77.1 ($C_{4'}$), 79.2 ($C_{3'}$), 81.0 ($C_{5'}$), 93.5 (C_1), 105.6 ($C_{2'}$), 175.5 (1C=O on 6′), 175.8 (1C=O on 6). HRMS: m/z calcd for $C_{28}H_{50}O_{13}Na$ (m/z+Na): 617.3148; Found: 617.3148. Anal. Calcd for $C_{28}H_{50}O_{13}\cdot 0.8H_2O$: C, 55.21; H, 8.54; Found: C, 55.28; H, 8.71.

4.12. 6,6′-Di-*O*-decanoylsucrose 5b

$[\alpha]_D^{25} = +49$ (c 1, THF). HRMS: m/z calcd for $C_{32}H_{58}O_{13}Na$ (m/z+Na): 673.3775; Found: 673.3779. Anal. Calcd for $C_{32}H_{58}O_{13}\cdot 0.5H_2O$: C, 58.25; H, 9.01; Found: C, 58.26; H, 8.89.

4.13. 6,6′-Di-*O*-stearoylsucrose 5e

$[\alpha]_D^{25} = +39$ (c 0.4, THF). ^{1}H NMR (300 MHz, $CDCl_3$/MeOD 2/1): δ 0.89 (6H, m, $2CH_3$), 1.28 (56H, m,

2(CH_2)$_{14}$), 1.62 (4H, m, 2$CH_{2\beta}$), 2.35 (4H, m, 2$CH_{2\alpha}$), 3.27 (1H, t+MeOD, $J_{4-3} = J_{4-5} = 9.4$ Hz, H_4), 3.46 (1H, dd, $J_{2-1} = 3.7$ Hz, $J_{2-3} = 10.0$ Hz, H_2), 3.59 (1H, d, $J_{1'b-1'a} = 12.2$ Hz, H_1), 3.66 (1H, d, $J_{1'a-1'b} = 12.6$ Hz, H_1), 3.72 (1H, t, $J_{3-4} = J_{3-2} = 9.3$ Hz, H_3), 3.88–4.10 (4H, m, $H_{5\prime}$, t, $J_{4'-3'} = J_{4'-5'} = 7.6$ Hz, $H_{4\prime}$, H_5, $H_{3\prime}$), 4.15 (1H, dd, $J_{6b-6a} = 11.8$ Hz, $J_{6b-5} = 6.1$ Hz, H_{6b}), 4.36 (2H, m, $H_{6/b}$), 4.44 (1H, dd, $J_{6a-6b} = 11.3$ Hz, J_{6a-5} low, H_{6a}), 5.36 (1H, d, $J_{1-2} = 3.8$ Hz, H_1). ^{13}C NMR (75 MHz, MeOD/$CDCl_3$ (4/1 v/v) at 50 °C): δ 14.4 (2CH_3), 25.4 (2$CH_{2\beta}$), 23.2–29.7–29.8–30.0–30.2–32.4 (28CH_2), 34.6–34.7 (2$CH_{2\alpha}$), 64.4 ($C_{1\prime}$), 64.5 (C_6), 66.2 ($C_{6\prime}$), 71.1 (C_4), 71.4 (C_5), 72.4 (C_2), 74.2 (C_3), 76.8 ($C_{4\prime}$), 80.1 ($C_{3\prime}$), 80.3 ($C_{5\prime}$), 92.5 (C_1), 104.7 ($C_{2\prime}$), 174.7 (1C=O on 6′), 175.1 (1C=O on 6). HRMS: m/z calcd for $C_{48}H_{90}O_{13}Na$ (m/z+Na): 897.6279; Found: 897.6271. Anal. Calcd for $C_{48}H_{90}O_{13}$: C, 65.87; H, 10.36; O, 23.76; Found: C, 65.51; H, 10.51; O, 23.26.

4.14. 6,6′-Di-*O*-eicosanoylsucrose 5f

$[\alpha]_D^{25} = +37$ (c 0.2, THF). ^{13}C NMR (75 MHz, MeOD/$CDCl_3$ (4/1 v/v) at 50 °C): δ 14.4 (2CH_3), 25.4 (2$CH_{2\beta}$), 23.1–29.7–29.8–30.0–30.2–32.4 (32CH_2), 34.5–34.6 (2$CH_{2\alpha}$), 64.4 ($C_{1\prime}$), 64.5 (C_6), 66.2 ($C_{6\prime}$), 71.0 (C_4), 71.3 (C_5), 72.4 (C_2), 74.1 (C_3), 76.8 ($C_{4\prime}$), 80.1 ($C_{3\prime}$), 80.3 ($C_{5\prime}$), 92.5 (C_1), 104.6 ($C_{2\prime}$), 174.6 (1C=O on 6′), 175.1 (1C=O on 6). HRMS: m/z calcd for $C_{52}H_{98}O_{13}Na$ (m/z+Na): 841.5653; Found: 841.5649. Anal. Calcd for $C_{52}H_{98}O_{13}$: C, 67.06; H, 10.61; Found: C, 67.26; H, 10.52.

4.15. 6,6′-Di-*O*-dodec-5*c*-enoylsucrose 5h

$[\alpha]_D^{25} = +42$ (c 2, THF). ^{1}H NMR (300 MHz, MeOD): δ 0.92 (6H, t, $J_{CH3-CH2} \sim 7$ Hz, 2CH_3), 1.22–1.45 (16H, m, 2(CH_2)$_4$), 1.61–1.76 (4H, m, 2$CH_{2\beta}$), 1.98–2.17 (8H, m, 2CH_2CH=CHCH_2), 2.31–2.49 (4H, m, 2$CH_{2\alpha}$), 3.26 (1H, t, $J_{4-3} = 9.0$ Hz, $J_{4-5} = 9.8$ Hz, H_4), 3.43 (1H, dd, $J_{2-3} = 9.8$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.59 (1H, d, $J_{1'b-1'a} = 12.3$ Hz, H_1), 3.65 (1H, d, $J_{1'a-1'b} = 12.3$ Hz, H_1), 3.72 (1H, t, $J_{3-4} = 9.0$ Hz, $J_{3-2} = 9.8$ Hz, H_3), 3.89–3.98 (1H, m, $H_{5\prime}$), 4.02 (1H, t, $J_{4'-3'} = J_{4'-5'} = 8.2$ Hz, $H_{4\prime}$), 4.10 (1H, d, $J_{3'-4'} = 8.2$ Hz, $H_{3\prime}$), 4.06–4.17 (2H, m, H_{6b}, H_5), 4.34–4.43 (2H, m, $H_{6/b}$), 4.46 (1H, dd, $J_{6a-6b} = 11.3$ Hz, $J_{6a-5} = 1.3$ Hz, H_{6a}), 5.28–5.50 (5H, m, H_1, 2CH=CH). ^{13}C NMR (75 MHz, MeOD): δ 14.8 (2CH_3), 26.2–26.3 (2$CH_{2\beta}$), 27.8–28.5 (4$CH_{2\alpha}$CH=CH), 24.0–30.3–31.1–33.2 (8CH_2), 34.6 (2$CH_{2\alpha}$), 64.3 ($C_{1\prime}$), 65.5 (C_6), 67.2 ($C_{6\prime}$), 72.1 (C_5, C_4), 73.4 (C_2), 74.8 (C_3), 77.1 ($C_{4\prime}$), 79.2 ($C_{3\prime}$), 80.9 ($C_{5\prime}$), 93.4 (C_1), 105.5 ($C_{2\prime}$), 132.0–132.0–130.1–130.2 (2CH=CH), 175.2 (1C=O on 6′), 175.6 (C=O on 6). HRMS: m/z calcd for $C_{36}H_{62}O_{13}Na$ (m/z+Na): 725.4088; Found: 725.4091. Anal. Calcd for $C_{36}H_{62}O_{13}$. 1.1H_2O: C, 59.83; H, 8.95; Found: C, 59.78; H, 8.84.

4.16. 6,6′-Di-*O*-hexadec-9*c*-enoylsucrose 5i

$[\alpha]_D^{25} = +38$ (c 1, THF).^{1}H NMR (300 MHz, MeOD): δ 0.80–1.00 (6H, m, 2CH_3), 1.15–1.47 (32H, m, 2(CH_2)$_8$), 1.50–1.73 (4H, m, 2$CH_{2\beta}$), 1.90–2.15 (8H, m, 2CH_2CH=CHCH_2), 2.27–2.47 (4H, m, 2$CH_{2\alpha}$), 3.26 (1H, t, $J_{4-3} = 9.0$ Hz, $J_{4-5} = 9.6$ Hz, H_4), 3.43 (1H, dd, $J_{2-3} = 9.7$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.59 (1H, d, $J_{1'b-1'a} = 12.5$ Hz, H_1), 3.64 (1H, d, $J_{1'a-1'b} = 12.5$ Hz, H_1), 3.73 (1H, t, $J_{3-4} = 9.0$ Hz, $J_{3-2} = 9.7$ Hz, H_3), 4.05–4.17 (5H, m, H_{6b}, $H_{3\prime}$, H_5, $H_{4\prime}$, $H_{5\prime}$), 4.32–4.41 (2H, m, $H_{6/b}$), 4.46 (1H, dd, $J_{6a-6b} = 11.1$ Hz, J_{6a-5} small, H_{6a}), 5.25–5.47 (5H, m, H_1, 2CH=CH). ^{13}C NMR (75 MHz, MeOD): δ 14.8 (2CH_3), 26.3 (2$CH_{2\beta}$), 28.5 (4$CH_{2\alpha}$CH=CH), 24.0–30.4–30.5–30.7–31.2–33.3 (16CH_2), 35.2 (2$CH_{2\alpha}$), 64.3 ($C_{1\prime}$), 65.5 (C_6), 67.2 ($C_{6\prime}$), 72.2 (C_5, C_4), 73.5 (C_2), 74.9 (C_3), 77.1 ($C_{4\prime}$), 79.2 ($C_{3\prime}$), 81.0 ($C_{5\prime}$), 93.4 (C_1), 105.6 ($C_{2\prime}$), 131.1–131.2 (4CH, 2CH=CH), 175.4 (1C=O on 6′), 175.8 (1C=O on 6). HRMS: m/z calcd for $C_{44}H_{78}O_{13}Na$ (m/z+Na): 837.5340; Found: 837.5338. Anal. Calcd for $C_{44}H_{78}O_{13}$·1.2H_2O: C, 63.16; H, 9.68; Found: C, 63.12; H, 9.54.

4.17. 6,6′-Di-*O*-octadec-9*c*-enoylsucrose 5j

$[\alpha]_D^{25} = +35$ (c 2, THF). ^{1}H NMR (300 MHz, MeOD): δ 0.83–1.00 (6H, m, 2CH_3), 1.17–1.47 (40H, m, 2(CH_2)$_{10}$), 1.53–1.73 (4H, m, 2$CH_{2\beta}$), 1.95–2.15 (8H, m, 2CH_2CH=CHCH_2), 2.37–2.47 (4H, m, 2$CH_{2\alpha}$), 3.26 (1H, t, $J_{4-3} = 9.0$ Hz, $J_{4-5} = 9.6$ Hz, H_4), 3.44 (1H, dd, $J_{2-3} = 9.7$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.58 (1H, d, $J_{1'b-1'a} = 12.4$ Hz, H_1), 3.65 (1H, d, $J_{1'a-1'b} = 12.4$ Hz, H_1), 3.73 (1H, t, $J_{3-4} = 9.0$ Hz, $J_{3-2} = 9.7$ Hz, H_3), 3.89–4.17 (5H, m, H_{6b}, $H_{3\prime}$, H_5, $H_{4\prime}$, $H_{5\prime}$), 4.32–4.42 (2H, m, $H_{6/b}$), 4.46 (1H, dd, $J_{6a-6b} = 11.3$ Hz, J_{6a-5} small, H_{6a}), 5.25–5.45 (5H, m, H_1, 2CH=CH). ^{13}C NMR (75 MHz, MeOD): δ 14.9 (2CH_3), 26.3 (2$CH_{2\beta}$), 28.5 (4$CH_{2\alpha}$CH=CH), 24.1–30.6–30.7–30.8–31.0–31.2–33.4 (20CH_2), 35.2 (2$CH_{2\alpha}$), 64.3 ($C_{1\prime}$), 65.5 (C_6), 67.2 ($C_{6\prime}$), 72.2 (C_5, C_4), 73.4 (C_2), 74.9 (C_3), 77.2 ($C_{4\prime}$), 79.3 ($C_{3\prime}$), 81.0 ($C_{5\prime}$), 93.4 (C_1), 105.6 ($C_{2\prime}$), 131.1–131.2 (4CH, 2CH=CH), 175.3 (1C=O on 6′), 175.7 (1C=O on 6). HRMS: m/z calcd for $C_{48}H_{86}O_{13}Na$ (m/z+Na): 893.5966; Found: 893.5969.

4.18. 6-*O*-Octanoyl-α-D-glucopyranosyl-3,4-anhydro-β-D-tagatofuranoside 6a

($R_f = 0.46$ in dichloromethane/acetone/methanol/water 67/15/15/3 v/v). ^{1}H NMR (300 MHz, MeOD): δ 0.90–1.00 (3H, m, CH_3), 1.17–1.45 (8H, m (CH_2)$_4$), 1.53–1.73 (2H, m, $CH_{2\beta}$), 2.34 (2H, t, $J_{CH2-CH2} = 7.4$ Hz, $CH_{2\alpha}$), 3.29 (1H, dd, $J_{4-3} = 10.0$ Hz, $J_{4-5} = 8.9$ Hz, H_4), 3.41 (1H, dd, $J_{2-3} = 9.7$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.60–3.77 (5H, m, $H_{6/b}$, H_1, H_3, H_1), 3.81–3.88 (2H, m, $H_{4\prime}$, $H_{3\prime}$), 3.98–4.14 (2H, m, $H_{5\prime}$, H_5), 4.23 (1H, dd, $J_{6a-6b} = 11.7$ Hz, $J_{6a-5} = 6.2$ Hz, H_{6b}), 4.37 (1H, dd, $J_{6a-6b} = 11.7$ Hz, $J_{6a-5} = 2.2$ Hz, H_{6a}), 5.40 (1H, d, $J_{1-2} = 3.8$ Hz, H_1). ^{13}C NMR (75 MHz, MeOD): δ 14.7 (CH_3), 26.2 ($CH_{2\beta}$), 23.9–30.3–30.4–33.1 (4CH_2), 35.2 ($CH_{2\alpha}$), 56.5 ($C_{3\prime}$), 58.2 ($C_{4\prime}$), 62.0 ($C_{6\prime}$), 65.2 (C_6), 65.7 ($C_{1\prime}$), 71.9 (C_5), 72.2 (C_4), 73.3 (C_2), 75.0 (C_3), 78.9 ($C_{5\prime}$), 94.1 (C_1), 105.5 ($C_{2\prime}$), 175.7 (1C=O on 6). HRMS: m/z calcd for $C_{20}H_{34}O_{11}Na$ (m/z+Na): 473.1999; Found: 473.1999.

4.19. 6-*O*-Octanoyl-α-D-glucopyranosyl-3,6-anhydro-β-D-fructofuranoside 7a

$[\alpha]_D^{25} = +76$ (*c* 1, THF). ^{1}H NMR (300 MHz, MeOD): δ 0.90–1.00 (3H, m, CH_3), 1.23–1.43 (8H, m, $(CH_2)_4$), 1.53–1.70 (2H, m, $CH_{2\beta}$), 2.34 (2H, t, $J_{CH2-CH2} = 7.4$ Hz, $CH_{2\alpha}$), 3.29 (1H, dd+MeOD, $J_{4-3} = 9.1$ Hz, $J_{4-5} = 9.8$ Hz, H_4), 3.50 (1H, dd, $J_{2-3} = 9.5$ Hz, $J_{2-1} = 3.7$ Hz, H_2), 3.61 (1H, d, $J_{1'b-1'a} = 12.8$ Hz, H_1), 3.72 (1H, t, $J_{3-4} = 9.1$ Hz, $J_{3-2} = 9.5$ Hz, H_3), 3.93 (1H, dd, $J_{6'b-6'a} = 8.2$ Hz, $J_{6'b-5'} = 1.4$ Hz, H_6), 4.00 (1H, d, $J_{1'a-1'b} = 12.8$ Hz, H_1), 4.08–4.24 (4H, m, H_{6b}, H_6, H_5, $H_{3'}$), 4.29 (1H, 's', $H_{5'}$), 4.36–4.48 (2H, m, H_{6a}, $H_{4'}$), 5.39 (1H, d, $J_{1-2} = 3.7$ Hz, H_1). ^{13}C NMR (75 MHz, MeOD): δ 14.7 (CH_3), 26.3 ($CH_{2\beta}$), 23.9–30.4–30.4–33.1 ($4CH_2$), 35.3 ($CH_{2\alpha}$), 63.0 ($C_{1'}$), 65.4 (C_6), 72.0 ($C_{6'}$), 72.1 (C_4), 72.4 (C_5), 73.7 (C_2), 75.1 (C_3), 78.2 ($C_{4'}$), 79.5 ($C_{3'}$), 83.0 ($C_{5'}$), 94.5 (C_1), 110.6 ($C_{2'}$), 175.7 (1C=O on 6). HRMS: *m*/*z* calcd for $C_{20}H_{34}O_{11}Na$ (*m*/*z*+Na): 473.1999; Found: 473.1998. Anal. Calcd for $C_{20}H_{34}O_{11}\cdot 0.8H_2O$: C, 51.67; H, 7.72; Found: C, 51.71; H, 7.53.

4.20. 6-*O*-Lauroyl-α-D-glucopyranosyl-3,6-anhydro-β-D-fructofuranoside 7c

$[\alpha]_D^{25} = +68$ (*c* 1, THF). ^{1}H NMR (300 MHz, MeOD): δ 0.92 (3H, t, $J_{CH2-CH3} \sim 7$ Hz, CH_3), 1.23–1.43 (16H, m $(CH_2)_8$), 1.55–1.70 (2H, m, $CH_{2\beta}$), 2.34 (2H, t, $J_{CH2-CH2} = 7.4$ Hz, $CH_{2\alpha}$), 3.29 (1H, dd+MeOD, $J_{4-3} = 9.2$ Hz, $J_{4-5} = 9.8$ Hz, H_4), 3.50 (1H, dd, $J_{2-3} = 9.6$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.61 (1H, d, $J_{1'b-1'a} = 12.8$ Hz, H_1), 3.72 (1H, dd, $J_{3-4} = 9.2$ Hz, $J_{3-2} = 9.6$ Hz, H_3), 3.93 (1H, dd, $J_{6'b-6'a} = 8.2$ Hz, $J_{6'b-5'} = 1.4$ Hz, H_6), 4.01 (1H, d, $J_{1'a-1'b} = 12.8$ Hz, H_1), 4.10–4.23 (4H, m, H_{6b}, H_6, H_5, $H_{3'}$), 4.29 (1H, 's', $H_{5'}$), 4.36–4.47 (2H, m, H_{6a}, $H_{4'}$), 5.39 (1H, d, $J_{1-2} = 3.8$ Hz, H_1). ^{13}C NMR (75 MHz, MeOD): δ 14.7 (CH_3), 26.3 ($CH_{2\beta}$), 33.4–31.0–30.9–30.8–30.7–30.5–24.0 ($8CH_2$), 35.3 ($CH_{2\alpha}$), 63.0 ($C_{1'}$), 65.5 (C_6), 72.0 ($C_{6'}$), 72.1 (C_4), 72.4 (C_5), 73.7 (C_2), 75.2 (C_3), 78.2 ($C_{4'}$), 79.5 ($C_{3'}$), 83.1 ($C_{5'}$), 94.5 (C_1), 110.6 ($C_{2'}$), 175.7 (1C=O on 6). HRMS: *m*/*z* calcd for $C_{24}H_{42}O_{11}Na$ (*m*/*z*+Na): 529.2625; Found: 529.2625. Anal. Calcd for $C_{24}H_{42}O_{11}\cdot 0.4H_2O$: C, 56.10; H, 8.40; Found: C, 56.07; H, 8.34.

4.21. 6-*O*-Palmitoyl-α-D-glucopyranosyl-3,6-anhydro-β-D-fructofuranoside 7d

$[\alpha]_D^{25} = +67$ (*c* 1, THF). ^{1}H NMR (300 MHz, $CDCl_3$/MeOD 1/1): δ 0.87 (3H, t, $J_{CH2-CH3} \sim 7$ Hz, CH_3), 1.15–1.40 (24H, m $(CH_2)_{12}$), 1.53–1.67 (2H, m, $CH_{2\beta}$), 2.32 (2H, t, $J_{CH2-CH2} = 7.5$ Hz, $CH_{2\alpha}$), 3.29 (1H, dd+MeOD, $J_{4-3} = 9.2$ Hz, $J_{4-5} = 9.4$ Hz, H_4), 3.53 (1H, dd, $J_{2-3} = 9.6$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.62 (1H, d, $J_{1'b-1'a} = 12.8$ Hz, H_1), 3.75 (1H, dd, $J_{3-4} = 9.2$ Hz, $J_{3-2} = 9.6$ Hz, H_3), 3.92 (1H, dd, $J_{6'b-6'a} = 8.3$ Hz, $J_{6'b-5'} = 1.3$ Hz, H_6), 3.99 (1H, d, $J_{1'a-1'b} = 12.8$ Hz, H_1), 4.07–4.25 (4H, m, H_{6b}, H_6, H_5, $H_{3'}$), 4.30 (1H, 's', $H_{5'}$), 4.36–4.45 (2H, m, H_{6a}, $H_{4'}$), 5.39 (1H, d, $J_{1-2} = 3.8$ Hz, H_1). ^{13}C NMR (75 MHz, MeOD): δ 14.6 (CH_3), 25.7 ($CH_{2\beta}$), 23.5–30.0–30.2–30.4–30.5–32.8 ($12CH_2$), 35.0 ($CH_{2\alpha}$), 62.5 ($C_{1'}$), 65.1 (C_6), 71.5 ($C_{6'}$), 71.5 (C_4), 71.7 (C_5), 72.9 (C_2), 74.6 (C_3), 77.6 ($C_{4'}$), 78.9 ($C_{3'}$), 82.4 ($C_{5'}$), 93.9 (C_1), 110.1 ($C_{2'}$), 175.3 (1C=O on 6). HRMS: *m*/*z* calcd for $C_{28}H_{50}O_{11}Na$ (*m*/*z*+Na): 585.3251; Found: 585.3254. Anal. Calcd for $C_{28}H_{50}O_{11}\cdot 0.2H_2O$: C, 59.39; H, 8.97; Found: C, 59.33; H, 8.91.

4.22. 6-*O*-Stearoyl-α-D-glucopyranosyl-3,6-anhydro-β-D-fructofuranoside 7e

$[\alpha]_D^{25} = +62$ (*c* 0.4, THF). ^{1}H NMR (300 MHz, $CDCl_3$/MeOD 1/1): δ 0.92 (3H, t, $J_{CH2-CH3} \sim 7$ Hz, CH_3), 1.20–1.45 (28H, m $(CH_2)_{14}$), 1.55–1.70 (2H, m, $CH_{2\beta}$), 2.34 (2H, t, $J_{CH2-CH2} = 7.4$ Hz, $CH_{2\alpha}$), 3.29 (1H, t+MeOD, $J_{4-3} = 9.2$ Hz, $J_{4-5} = 9.6$ Hz, H_4), 3.50 (1H, dd, $J_{2-3} = 9.6$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.61 (1H, d, $J_{1'b-1'a} = 12.7$ Hz, H_1), 3.75 (1H, t, $J_{3-4} = 9.2$ Hz, $J_{3-2} = 9.6$ Hz, H_3), 3.93 (1H, dd, $J_{6'b-6'a} = 8.2$ Hz, $J_{6'b-5'} = 1.4$ Hz, $H_{6'b}$), 4.00 (1H, d, $J_{1'a-1'b} = 12.7$ Hz, $H_{1'a}$), 4.08–4.24 (4H, m, H_{6b}, H_6, H_5, $H_{3'}$), 4.29 (1H, 's', $H_{5'}$), 4.35–4.50 (2H, m, H_{6a}, $H_{4'}$), 5.39 (1H, d, $J_{1-2} = 3.8$ Hz, H_1). HRMS: *m*/*z* calcd for $C_{30}H_{54}O_{11}Na$ (*m*/*z*+Na): 613.3564; Found: 613.3569. Anal. Calcd for $C_{30}H_{54}O_{11}\cdot 1H_2O$: C, 59.19; H, 9.27; O, 31.54; Found: C, 58.99; H, 9.08;, O, 31.10.

4.23. Acylation of sucrose monolaurate

Sucrose monolaurate (mixture of isomers (6/1′/6′40/10/33), 1.00 g, 1.9 mmol) was dissolved in anhydrous DMF (20 mL) under N_2 at room temperature. Triphenylphosphine (1.26 g, 2.5 equiv) and the carboxylic acid (dodec-5*c*-enoic, 0.84 mL, 2 equiv) were then added. After complete dissolution, the mixture was cooled to 0 °C and DIAD (0.94 mL, 2.5 equiv) introduced under N_2. After 17 h at room temperature, TLC showed the formation of less polar products without total consumption of the sucrose monolaurate. DMF was removed under reduced pressure at $T = 36$–38 °C and the crude residue submitted to silica gel chromatography (elution gradient: dichloromethane/acetone/methanol/water 78/10/10/1.5 (A) to 67/15/15/3 (B) v/v). A first fraction was isolated ($R_f = 0.60$ in solvent B, 1′-*O*-dodec-5*c*-enoyl-6-*O*-lauroylsucrose, 94 mg, 7%) and the main products then isolated ($R_f = 0.49$ in solvent B, 6-*O*-dodec-5*c*-enoyl-6′-*O*-lauroylsucrose and 6-*O*-lauroyl-6′-*O*-dodec-5*c*-enoylsucrose, 453 mg, 34%). The diester was further purified by semi-preparative HPLC to remove the anhydro derivative contaminant.

4.24. 6-*O*-Palmitoyl-6′-*O*-lauroylsucrose 8c and 6-*O*-lauroyl-6′-*O*-palmitoylsucrose 8d

^{1}H NMR (300 MHz, MeOD/$CDCl_3$ 25/75): δ 0.77–0.95 (6H, m, $2CH_3$), 1.15–1.40 (40H, m $(CH_2)_{20}$), 1.50–1.67 (4H, m, $2CH_{2\beta}$), 2.25–2.43 (4H, m, $2CH_{2\alpha}$), 3.26 (1H, dd, $J_{4-3} = 9.0$ Hz, $J_{4-5} = 10.0$ Hz, H_4), 3.46 (1H, dd, $J_{2-3} = 9.6$ Hz. $J_{2-1} = 3, 7$ Hz, H_2), 3.57 (1H, d, $J_{1'b-1'a} = 12.4$ Hz, $H_{1'b}$), 3.66 (1H, d, $J_{1'a-1'b} = 12.4$ Hz, H_1), 3.76 (1H, dd, $J_{3-4} = 9.0$ Hz, $J_{3-2} = 9.6$ Hz, H_3), 3.88–4.08 (4H, m, H_5, $H_{3'}$, $H_{4'}$, $H_{5'}$), 4.17 (1H, dd, $J_{6b-6a} = 11.8$ Hz, $J_{6b-5} = 5.9$ Hz, H_{6b}), 4.23–4.45 (3H, m, H_{6a}, $H_{6/b}$), 5.36 (1H, d, $J_{1-2} = 3.7$ Hz, H_1). ^{13}C NMR (75 MHz, MeOD):

δ 14.6 ($2CH_3$), 25.6 ($2CH_{2\beta}$), 23.4–29.9–30.1–30.3–30.4–32.7 ($20CH_2$), 34.7–34.8 ($2CH_{2\alpha}$), 64.3 ($C_{1\prime}$), 64.7 (C_6), 66.6 ($C_{6\prime}$), 71.2 (C_4), 71.4 (C_5), 72.6 (C_2), 74.1 (C_3), 76.6 ($C_{4\prime}$), 79.7 ($C_{3\prime}$), 80.3 ($C_{5\prime}$), 92.6 (C_1), 104.6 ($C_{2\prime}$), 175.0 (1C=O on 6′), 175.4 (1C=O on 6). HRMS: m/z calcd for $C_{40}H_{74}O_{13}Na$ (m/z+Na): 785.5027; Found: 785.5023. Anal. Calcd for $C_{40}H_{74}O_{13}\cdot 0.7H_2O$: C, 61.94; H, 9.80; O, 28.26; Found: C, 61.88; H, 9.79; O, 28.06.

4.25. 6-*O*-Dodec-5*c*-enoyl-6′-*O*-lauroylsucrose 8a and 6-*O*-lauroyl-6′-*O*-dodec-5*c*-enoylsucrose 8b

^{1}H NMR (500 MHz, MeOD): δ 0.88–0.97 (6H, m, $2CH_3$), 1.25–1.42 (24H, m $(CH_2)_{12}$), 1.58–1.75 (4H, m, $2CH_{2\beta}$), 2.01–2.16 (4H, m, $CH_2CH{=}CHCH_2$), 2.32–2.49 (4H, m, $2CH_{2\alpha}$), 3.27 (1H, dd, $J_{4-3} = 9.1$ Hz, $J_{4-5} = 9.8$ Hz, H_4), 3.45 (1H, dd, $J_{2-3} = 9.5$ Hz, $J_{2-1} = 3.9$ Hz, H_2), 3.61 (1H, d, $J_{1'b-1'a} = 12.3$ Hz, H_1), 3.65 (1H, d, $J_{1'a-1'b} = 12.3$ Hz, H_1), 3.74 (1H, dd, $J_{3-4} = 9.1$ Hz, $J_{3-2} = 9.5$ Hz, H_3), 3.98–3.92 (1H, m, $H_{5\prime}$), 4.03 (1H, t, $J_{4'-3'} = J_{4'-5'} = 8.2$ Hz, $H_{4\prime}$), 4.16–4.05 (3H, m, H_{6b}, $H_{3\prime}$, H_5), 4.42–4.35 (2H, m, $H_{6/b}$), 4.47 (1H, dd, $J_{6a-6b} = 11.7$ Hz, $J_{6a-5} = 1.6$ Hz, H_{6a}), 5.39 (3H, m, H_1 and CH=CH). ^{13}C NMR (125 MHz, MeOD): δ 14.8 ($2CH_3$), 26.3 ($2CH_{2\beta}$), 28.5–27.8 ($2CH_{2\alpha}CH{=}CH$), 24.0–30.4–30.5–30.8–30.9–31.0–31.1–33.2–33.4 ($12CH_2$), 34.6–35.2 ($2CH_{2\alpha}$), 64.3 ($C_{1\prime}$), 65.5 (C_6), 67.2 ($C_{6\prime}$), 72.1 (C_5, C_4), 73.4 (C_2), 74.8 (C_3), 77.1 ($C_{4\prime}$), 79.2 ($C_{3\prime}$), 81.0 ($C_{5\prime}$), 93.4 (C_1), 105.6 ($C_{2\prime}$), 130.0–131.2 (CH=CH), 175.4 (1C=O on 6′), 175.6 (1C=O on 6). HRMS: m/z calcd for $C_{30}H_{54}O_{11}Na$ (m/z+Na): 727.4245; Found: 727.4248. Anal. Calcd for $C_{36}H_{64}O_{13}\cdot 0.9H_2O$: C, 59.96, H, 9.20; Found: C, 59.95, H, 9.13.

4.26. 6-*O*-Lauroyl-6′-*O*-2-[2-(2-methoxyethoxy)ethoxy]-acetoxysucrose 10a

$[\alpha]_D^{25} = +11$ (c 7, THF). ^{1}H NMR (500 MHz, MeOD): δ 0.92 (3H, t, $J_{CH2-CH3} \sim 7$ Hz, CH_3), 1.25–1.43 (16H, m $(CH_2)_8$), 1.57–1.70 (2H, m, $CH_{2\beta}$), 2.41 (2H, t, $J_{CH2-CH2} = 7.4$ Hz, $CH_{2\alpha}$), 3.27 (1H, t, $J_{4-3} = J_{4-5} = 9.3$ Hz, H_4), 3.35–3.41 (3H, m, CH_3O), 3.43 (1H, dd, $J_{2-3} = 9.7$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.52–3.60 (2H, m, CH_2O), 3.60–3.70 (6H, m, $H_{1/b}$, $2CH_2O$), 3.70–3.76 (3H, m, H_3, CH_2O), 3.92–3.99 (1H, m, $H_{5\prime}$), 4.00–4.09 (2H, m, H_5, $H_{4\prime}$), 4.09–4.15 (2H, m, H_{6b}, $H_{3\prime}$), 4.19–4.26 (2H, m, $CH_{2\alpha}O$), 4.40–4.51 (3H, m, H_{6a}, $H_{6/b}$), 5.34 (1H, d, $J_{1-2} = 3.8$ Hz, H_1). ^{13}C NMR (125 MHz, MeOD): δ 14.5 (CH_3), 26.0 ($CH_{2\beta}$), 23.8–25.3–30.5–30.7–30.8–33.1 ($8CH_2$), 34.9 ($CH_{2\alpha}$), 59.2 (OCH_3), 63.9 ($C_{1\prime}$), 65.2 (C_6), 67.0 ($C_{6\prime}$), 69.2 ($1CH_{2\alpha}O$),71.3–71.6 ($3CH_2O$), 71.9 (C_4), 71.9 (C_5), 73.0 ($1CH_2O$), 73.2 (C_2), 74.6 (C_3), 76.7 ($C_{4\prime}$), 78.8 ($C_{3\prime}$), 80.5 ($C_{5\prime}$), 93.3 (C_1), 105.4 ($C_{2\prime}$), 172.1 (1C=O oxyethylenic on 6′), 175.5 (1C=O laurate on 6). HRMS: m/z calcd for $C_{31}H_{56}O_{16}Na$ (m/z+Na): 707.3466; Found: 707.3465.

4.27. 6-*O*-2-[2-(2-Methoxyethoxy)ethoxy]acetoxy-6′-*O*-lauroylsucrose 10b

$[\alpha]_D^{25} = +9$ (c 9, THF). ^{1}H NMR (500 MHz, MeOD): δ 0.91 (3H, t, $J_{CH2-CH3} \sim 7$ Hz, CH_3), 1.25–1.40 (16H, m $(CH_2)_8$), 1.55–1.70 (2H, m, $2CH_{2\beta}$), 2.36 (2H, t, $J_{CH2-CH2} = 7.4$ Hz, $CH_{2\alpha}$), 3.24 (1H, dd, $J_{4-3} = 8.9$ Hz, $J_{4-5} = 9.9$ Hz, H_4), 3.36–3.42 (3H, m, CH_3O), 3.43 (1H, dd, $J_{2-3} = 9.8$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.53–3.78 (8H, m, $4CH_2O$, H_3, $H_{1/b}$), 3.89–3.98 (1H, m, $H_{5\prime}$), 4.02 (1H, dd, $J_{4'-3'} = 8.2$ Hz, $J_{4'-5'} = 8.5$ Hz, $H_{4\prime}$), 3.91–3.98 (1H, m, H_5), 4.10 (1H, d, $J_{3'-4'} = 8.1$ Hz, $H_{3\prime}$), 4.18 (1H, dd, $J_{6a-6b} = 11.7$ Hz, $J_{6b-5} = 6.6$ Hz, H_{6b}), 4.23–4.32 (2H, m, $CH_{2\alpha}O$), 4.33–4.41 (2H, m, $H_{6/b}$), 4.55 (1H, dd, $J_{6a-6b} = 11.7$ Hz, $J_{6a-5} = 1.8$ Hz, H_{6a}), 5.35 (1H, d, $J_{1-2} = 3.8$ Hz, H_1). ^{13}C NMR (125 MHz, MeOD): δ 14.5 (CH_3), 26.0 ($CH_{2\beta}$), 23.8–30.2–30.5–30.7–33.1 ($8CH_2$), 34.9 ($CH_{2\alpha}$), 59.1 (CH_3O), 64.0 ($C_{1\prime}$), 65.7 (C_6), 66.9 ($C_{6\prime}$), 69.2 ($CH_{2\alpha}O$), 71.3–71.8 ($3CH_2O$), 71.9 (C_5), 71.9 (C_4), 72.9 ($1CH_2O$), 73.2 (C_2), 74.6 (C_3), 76.7 ($C_{4\prime}$), 78.8 ($C_{3\prime}$), 80.7 ($C_{5\prime}$), 93.1 (C_1), 105.4 ($C_{2\prime}$), 172.32 (1C=O oxyethylenic on 6), 175.3 (1C=O laurate on 6′). HRMS: m/z calcd for $C_{31}H_{56}O_{16}Na$ (m/z+Na): 707.3466; Found: 707.3464. Anal. Calcd for $C_{31}H_{56}O_{16}$: C, 52.72; H, 8.54; O, 38.74; Found: C, 52.67; H, 8.30; O, 38.52.

4.28. 1′-*O*-Dodec-5*c*-enoyl-6-*O*-lauroylsucrose 9

$[\alpha]_D^{25} = +31$ (c 0.4, THF). ^{1}H NMR (500 MHz, MeOD): δ 0.80–1.00 (6H, m, $2CH_3$), 1.20–1.50 (24H, m, $(CH_2)_{12}$), 1.55–1.75 (4H, m, $2CH_{2\beta}$), 2.00–2.20 (4H, m, $CH_2CH{=}CHCH_2$), 2.30–2.50 (4H, m, $2CH_{2\alpha}$), 3.31 (1H, dd+MeOD, $J_{4-3} = 9.4$ Hz, J_{4-5} and, H_4), 3.42 (1H, dd, $J_{2-3} = 9.8$ Hz, $J_{2-1} = 3.8$ Hz, H_2), 3.68 (1H, dd, $J_{3-4} = 9.4$ Hz, $J_{3-2} = 9.8$ Hz, H_3), 3.73–3.85 (3H, m, $H_{6/b}$, $H_{5\prime}$), 4.00–4.08 (2H, m, H_5, $H_{4\prime}$), 4.09 (1H, d, $J_{3'-4'} = 8.5$ Hz, $H_{3\prime}$), 4.14 (1H, d, $J_{1'b-1'a} = 12.0$ Hz, H_1), 4.19 (1H, dd, $J_{6b-6a} = 11.8$ Hz, $J_{6b-5} = 5.5$ Hz, H_{6b}), 4.38 (1H, d, $J_{1'a-b} = 12.0$ Hz, H_1), 4.43 (1H, dd, $J_{6a-6b} = 11.8$ Hz, $J_{6a-5} = 1.9$ Hz, H_{6a}), 5.41 (3H, m, H_1, CH=CH). ^{13}C NMR (125 MHz, MeOD): δ 14.7 ($2CH_3$), 26.3 ($2CH_{2\beta}$), 27.8–28.5 ($2CH_{2\alpha}CH{=}CH$), 24.0–30.4–30.5–30.7–30.8–30.9–31.0–31.1–33.3–33.4 (12 CH_2), 34.6–35.3 ($2CH_{2\alpha}$), 64.0 ($C_{1\prime}$, $C_{6\prime}$), 65.0 (C_6), 72.0 (C_4), 72.3 (C_5), 73.3 (C_2), 74.7 (C_3), 75.6 ($C_{4\prime}$), 79.0 ($C_{3\prime}$), 84.3 ($C_{5\prime}$), 94.3 (C_1), 104.4 ($C_{2\prime}$), 129.9–132.3 (CH=CH), 175.0 (1C=O on 1′), 175.7 (1C=O on 6). HRMS: m/z calcd for $C_{30}H_{54}O_{11}Na$ (m/z+Na): 727.4245; Found: 727.4245.

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