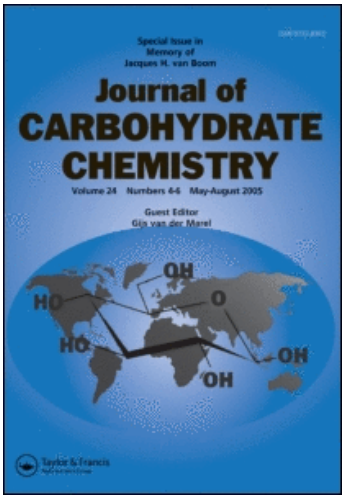

Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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Online publication date: 12 November 2003

To cite this Article Molinier, Valérie , Wisniewski, Krzysztof , Bouchu, Alain , Fitremann, Juliette and Queneau, Yves(2003) 'Transesterification of Sucrose in Organic Medium: Study of Acyl Group Migrations ', Journal of Carbohydrate Chemistry, 22: 7, 657 — 669
To link to this Article: DOI: 10.1081/CAR-120026466
URL: http://dx.doi.org/10.1081/CAR-120026466

JOURNAL OF CARBOHYDRATE CHEMISTRY
Vol. 22, Nos. 7 & 8, pp. 657–669, 2003

Transesterification of Sucrose in Organic Medium: Study of Acyl Group Migrations[†]

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ABSTRACT

The tendency of the acyl groups located on the glucose part of sucrose fatty acid esters to undergo intramolecular migrations in organic medium and the regioselectivity of some transesterifications of sucrose were investigated by HPLC, in situ NMR spectroscopy and preparative methods. Extensive acylation on secondary positions of the glucose moiety followed by migrations is general for base catalysed transesterification. The stability of 3- and 6-*O*-acyl derivatives, two isomers being thermodynamically favored compared to others, was studied in a series of conditions. It is shown that the presence of water catalyzes the migration of the ester at OH-3 towards OH-6 in organic basic medium, whereas the ester at OH-6 appears more stable under either acidic or basic conditions.

Key Words: Sucrose; Regioselective esterification; Acyl group migration; In situ NMR.

[†]This paper is dedicated to Professor Gérard Descotes on the occasion of his 70th birthday, in acknowledgement of his accomplishments in the field of carbohydrate chemistry, and of his continuing efforts for developing the use of renewable sugars for chemistry.

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DOI: 10.1081/CAR-120026466 0732-8303 (Print); 1532-2327 (Online)

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INTRODUCTION

Finding renewable raw materials for chemistry, alternative to fossil resources, is of considerable interest. In this context, the use of carbohydrates, and notably of sucrose as starting material, has been extensively studied.[a][5] Among derivatives having industrial applications, the amphiphilic sucrose fatty acid esters, also known as sucroesters, have interesting physicochemical properties in particular as emulsifiers, and are used in the food and cosmetic fields.[6–10] An important issue in their synthesis is the control of the degree of substitution, which is connected with their emulsifying properties.[11–17] This search for selective processes has been part of our work in the field of the use of sucrose as a chemical,[18–21] with emphasis on the search for regioselective reactions, as the regioselectivity is the source of control of the degree of substitution. Indeed, when one of the 8 hydroxyl groups exhibits a preeminent reactivity towards an electrophilic species, the second substitution occurs in a slower manner, thus allowing trapping of a low substituted derivative. This regioselectivity has, in fact, to be considered as a chemoselectivity of one alcohol function compared to another.

Even though the kinetic relative reactivity of sucrose hydroxyl groups is now rather well understood, in the case of esters, the potency of acyl groups to migrate perturbs the easy correlation between the regiochemical distribution of the substituents and the relative reactivity of the sucrose 8 hydroxyl groups. Although most base catalyzed transesterifications lead finally to primary esters, the preeminent reactivity of OH-2 has been established,[22–26] with examples consistent with spectroscopic and theoretical studies. Even in aqueous medium, we showed that the perturbation of the hydrogen bond network by solvation did not prevent secondary OH-groups, and notably OH-2, from being esterified first, before migrations to OH-3 and OH-6 could occur,[27,28] as in organic medium.

In a program aimed at the understanding of the influence of the position of the chain on the physicochemical properties of sucrose amphiphilic derivatives, we showed recently that the thermotropic behavior of sucrose amphiphilic ethers was very dependant on the geometry of the connection between the polar and the hydrophobic parts of the molecule.[29] In order to obtain similar information in the case of sucrose esters, we needed to ascertain the stability of some isomers, and in particular that of derivatives esterified at OH-3 and OH-6. We report here our study of the migration pathways in the case of the preparation of sucrose fatty acid esters in organic medium, as well as some aspects helping the preparation of 6-*O*-acyl sucrose derivatives using the sequential migration method.[30]

RESULTS AND DISCUSSION

To study the stability of the acyl group located on the glucose moiety of sucrose, we synthesized samples of 2-*O*, 3-*O*-, and 6-*O*-alkanoyl sucroses (Scheme 1), using the transesterification of *N*-acylthiazolidinethiones, as described by Plusquellec,[22,30–32] followed by preparative HPLC for full identification of pure isomers. A catalytic

[a]For reviews in the field of the use of carbohydrates as chemicals, see Refs. [1–4].

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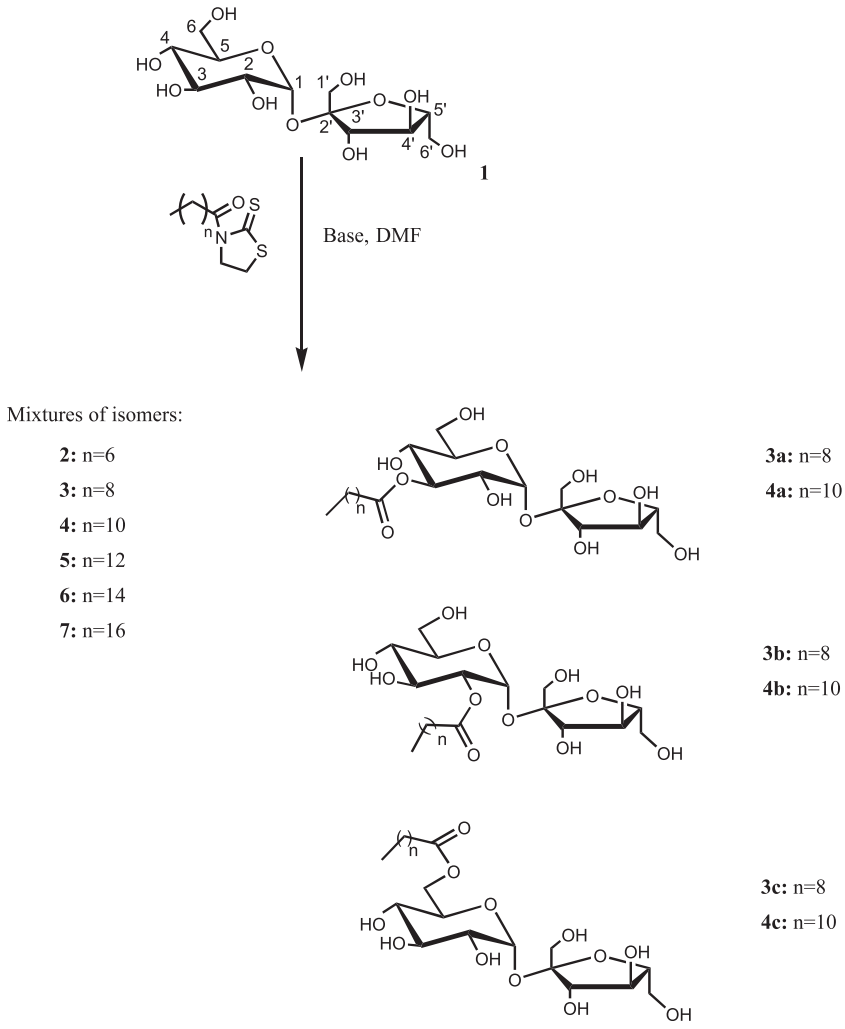

Scheme 1.

amount of a base such as sodium hydride was reported to provide good yields of sucrose esters, with a predominance of the isomer at OH-2. To obtain supplementary information on the regioisomeric distribution evolution, we studied the effect of other bases, and notably of solid salts such as carbonates and phosphates (Table 1). Starting from *N*-decanoylthiazolidinethione, moderate to good yields of monodecanoyl sucrose were obtained. The best yield was observed for the reaction achieved in the presence of two equivalents of dipotassium hydrogenophosphate. In this case, the monoesters were essentially the isomers at position 2 and 3. The structure (in particular the position of the esterified OH) of these regioisomers was ascertained by ^{1}H and ^{13}C NMR spectroscopy. It is interesting to note that only moderate amounts (less than 10%) of esters at position 1′ and 6′ were present in the mixture, indicating again the superior

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Table 1. Transesterification of sucrose (2 equiv) with *N*-decanoylthiazolidinethione (1.2 equiv) in DMF.

Conditions base (equiv), T, t	Monoester **3** yield %	Regioisomeric distribution %						
		3-*O*-	3′-*O*- 4-*O*-	2-*O*-	4′-*O*-	6-*O*-	1′-*O*-	6′-*O*-
K_2HPO_4 (2), rt, 21 h	71	16	15	54	1	4	1	8
K_2CO_3 (0.5), rt, 40 min	47	36	14	27	1	9	10	1
K_2CO_3 (0.5), rt, 6 h	65	27	12	12	2	27	15	3
Li_2CO_3 (0.5), rt, 24 h	53	13	20	57	0	3	5	1
Cs_2CO_3 (1), rt, 20 min	46	34	14	14	2	19	15	2
Cs_2CO_3 (1), − 10°C, 18 h	54	16	9	5	2	48	16	4

reactivity of the glucosyl moiety. In the presence of lithium carbonate, little amounts of 1′ or 6′ esters were also observed. Potassium and cesium carbonates led to more complex mixtures, resulting from extensive acyl transfer to OH-3 and OH-6, and a significantly larger amount of esterification at position 1′ (ca. 15% of the mixture). These ratios are very similar to those described for the reaction involving catalytic sodium hydride. The use of catalytic butyllithium gave sucrose laurates in similar yields and regioselectivity. In this case, the *N*-acylthiazolidinethione was compared with cyanoethyl-, methylthioethyl- and methylesters as acyl donnors (Table 2), confirming the unique ability of the *N*-acylthiazolidinethiones to afford 2-*O*-acylated sucrose esters as the major product, in connection with the role of the thiazolidinetione anion as the active base in the medium.[22] With the other acylating agents, the major ester is formed at OH-6. This, as well as the small proportion of esters at 1′ and 6′, indicates that the reaction is again rather selective on the glucose moiety. This can either be the result of a selective esterification at OH-2 followed by migrations to OH-3 and OH-6, or a direct selective esterification at OH-6, without concomitant esterification at the other primary positions 6′ and 1′. This latter mechanism is less likely to

Table 2. Transesterification of sucrose with different acyl donors in DMF, in the presence of catalytic butyl lithium (sucrose/$C_{11}H_{23}COX$/BuLi = 1/1/0.05, 3 h, rt).

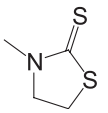
X	Monoester **4** yield %	Diester yield %	Monoester regioisomeric distribution %						
			3-*O*-	3′-*O*- 4-*O*-	2-*O*-	4′-*O*-	6-*O*-	1′-*O*-	6′-*O*-
	48	11	12	14	66	1	1	6	–
$CNCH_2O-$	37	14	12	5	6	4	57	10	6
$MeSCH_2$-CH_2O-	11	8	16	6	9	4	52	7	6
MeO–	11	–	15	7	6	6	53	6	7

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Table 3. Lithium carbonate catalyzed transesterification of sucrose with various *N*-acylthiazolidinethiones (sucrose/*N*-acylthiazolidinethione/Li_2CO_3 = 1/1/0.05, 3 h, rt).

R	Monoester (yield) %	Monoester regioisomeric distribution %						
		3-*O*-	3′-*O*- 4-*O*-	2-*O*-	4′-*O*-	6-*O*-	1′-*O*-	6′-*O*-
C_7H_{15}	**2** (86)	2	11	72	1	3	10	1
C_9H_{19}	**3** (65)	10	17	59	1	3	9	1
$C_{11}H_{23}$	**4** (81)	9	14	63	1	3	8	1
$C_{13}H_{27}$	**5** (76)	14	16	58	<1	4	7	<1
$C_{15}H_{31}$	**6** (49)	11	15	61	<1	4	8	<1
$C_{17}H_{35}$	**7** (91)	10	16	65	1	3	5	–

occur as we observed that in some cases, even though the reaction was less selective at OH-6, the other isomers present were essentially those at OH-2 and OH-3.

The lithium carbonate catalyzed reaction was used to prepare a series of sucrose esters (C_8, C_{10}, C_{12}, C_{14}, C_{16}, C_{18}) starting from the corresponding *N*-acylthiazolidinethiones, in moderate to good yields, and with consistently the same distribution of regioisomers (Table 3).

We then studied in detail the outcome of the reaction of sucrose with *N*-lauroylthiazolidine thione using Et_3N/DBU, as reported for the final obtention of 6-*O*-esters.[30] Our data confirm that indeed migration to OH-6 occurs only when DBU is added, but also that esters at OH-3 are present in the final mixture, and this in a larger amount after work-up than expected from HPLC-monitoring during the course of the reaction (Table 4). The inconsistency between HPLC and NMR data revealed the important role of the aqueous work-up. This led us to look more closely at the behavior of esters at OH-3 and OH-6 at the early stage of the reaction under these conditions. The 3-*O*-monolaurate was treated under conditions allowing the isomerization to the OH-6 position (Table 5). The samples which were analyzed by HPLC without any work-up revealed the presence of the 6-*O*-ester. It was hypothesized that, when base is still present, water in the HPLC eluent promotes the very fast acyl migration, together with extensive hydrolysis. On the contrary, after acidification, aqueous work-up and

Table 4. Transesterification of sucrose with *N*-lauroylthiazolidinethione in DMF, in the presence of Et_3N/DBU. (sucrose/*N*-lauroylthiazolidinethione/Et_3N = 1/0.2/1.5, 30 h then + DBU (1.5 equiv), 15 h, rt). Yield **4**: 45%.

Conditions	Monoester regioisomeric distribution %						
	3-*O*-	3′-*O*- 4-*O*-	2-*O*-	4′-*O*-	6-*O*-	1′-*O*-	6′-*O*-
aliquot of the medium at the end of the reaction	7	5	0	5	64	10	8
after acidification and extractions	14	5	6	4	58	8	5
after column-chromatography and freeze-drying	13	5	5	4	59	8	5

Table 5. Behavior of 3-*O*-sucrose monolaurate (**4a**) placed in the reaction isomerization conditions (0.1 M in DMF, in the presence of DBU).

	Monoester regioisomeric distribution % (100 μL of the medium + 1 mL CH_3CN/H_2O 90/10)						
Conditions	3-*O*-	3′-*O*- 4-*O*-	2-*O*-	4′-*O*-	6-*O*-	1′-*O*-	6′-*O*-
Starting sample	95	5	0	0	0	0	0
+ DBU (1 equiv)	13	5	2	–	73	7	–
id. after 15 min	9	5	2	–	76	9	–
id. after 35 min	9	6	3	–	71	11	1
after 40 min, + AcOH and evaporation of DMF	**72**	**3**	**13**	**0**	**11**	**0**	**0**
Starting sample	73	20	0	4	3	0	0
+ DBU (1.3 equiv)	11	5	2	4	67	9	2
evaporation of DMF without neutralisation	**3**	**4**	**2**	**3**	**38**	**11**	**39**

Table 6. Behavior of 6-*O*-sucrose monolaurate (trial 1) and 6-*O*-sucrose monodecanoate (**3c**) (trial 2) placed in the same isomerization conditions.

	Monoester regioisomeric distribution % (50 μL of the medium + 0.5 mL (trial 1) and 1 mL (trial 2) CH_3CN/H_2O 90/10)						
Conditions	3-*O*-	3′-*O*- 4-*O*-	2-*O*-	4′-*O*-	6-*O*-	1′-*O*-	6′-*O*-
Starting sample	0	1	1	0	84	0	14
+ AcOH (50 μL), t = 0	0	0	0	0	86	0	14
after 1 h, + AcOH (50 μL)	0	0	0	0	86	0	14
After 2 h, evaporation of DMF	**0**	**1**	**1**	**0**	**85**	**0**	**13**
Starting sample	0	0	0	0	100	0	0
+ DBU (0.8 equiv), t = 0	10	5	2	0	83	0	0
after 15 min, + AcOH (60 μL)	0	5	0	0	93	0	2
id. after 5h15	0	0	0	0	100	0	0
id. after 1 night	0	0	0	0	100	0	0
after 1 night, + DBU (1.2 equiv), t′ = 0	0	5	2	0	92	0	0
after 10 min, + AcOH (100 μL)	0	4	0	0	96	0	0
after 2 h30, + AcOH (50 μL)	0	5	0	0	95	0	0
after 24 h, evaporation of DMF	**0**	**4**	**0**	**0**	**95**	**0**	**1**

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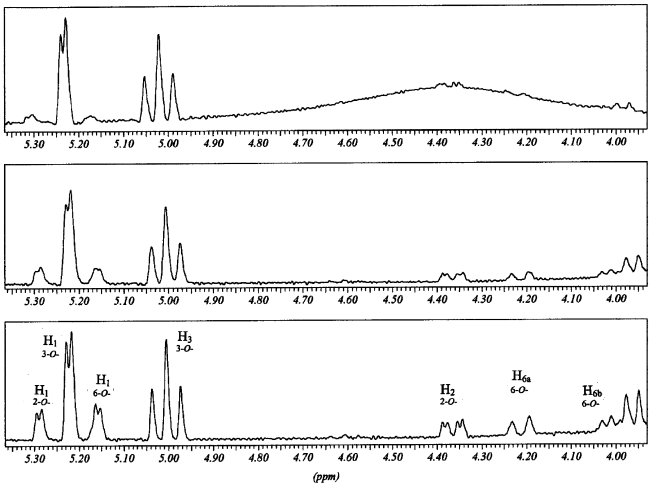
Conditions: 3-*O*-sucrose monolaurate (**4a**) (54.3 mg, 0.1 mmol) + DBU (21.3 mg, 1.3 equiv) in 750 µL DMSO-d_6.



Comparison of Spectrum 3 with ^{1}H NMR spectra of 6-*O*-, 2-*O*- and 3-*O*-sucrose monolaurate (**4c**), (**4b**) and (**4a**) in DMSO-d_6 + D_2O:

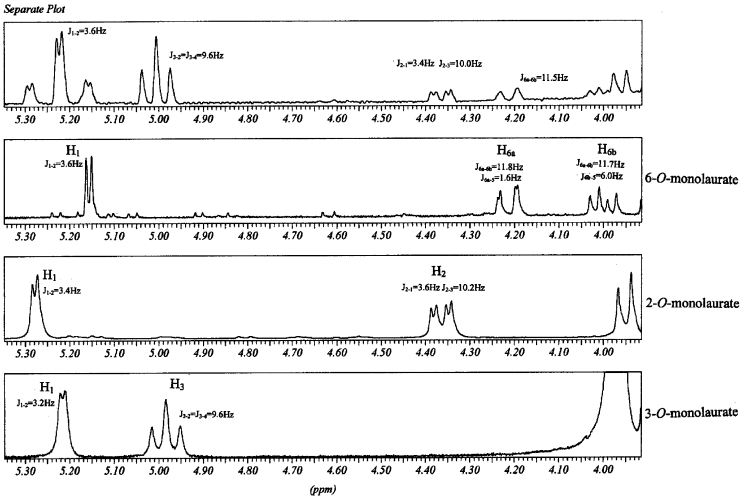


Figure 1. ^{1}H NMR monitoring of the migration from the 3 position.

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purification, mostly unchanged 3-*O*-ester, as indicated by the deshielding of the characteristic triplet at 5.23 ppm ($J_{3-4} = J_{3-2} = 9.7$ Hz), together with a significant proportion (13%) of 2-*O*-ester, were detected in the final mixture. Sucrose ester self transesterifications to diesters and sucrose, both observed as traces, could not account for the important changes in the regioisomeric distribution. However, when no acidic treatment is performed before evaporation of the solvent, extensive late transesterification is observed, leading to a lower yield of a mixture of esters, essentially at OH-6, 1′ and 6′.

As shown in Table 6, it was ascertained that treatment of the 6-*O*-ester in all possible conditions (with or without DBU and with or without reacidification) did not lead to any reverse migration of the acyl moiety towards the secondary hydroxyl groups. It can thus be concluded that the rate of the migration from OH-3 to OH-6 is dramatically accelerated in the presence of water and occurs during the aqueous work-up. The same process occurred during HPLC samples preparations (MeCN-water as a solvent). The absolute HPLC integrations confirm that migration and hydrolysis take place on the HPLC column during analysis, since the total integration of the monoesters decreased strongly after addition of DBU, before increasing to the starting value after acidification of the medium.

Those results were confirmed by studying the outcome of the reaction by in situ NMR in deuterated DMSO, allowing us to follow directly in the medium the presence of the various isomers. It was possible to observe that indeed no significant acyl migration from OH-3 to OH-6 or OH-2 occurred in the presence of DBU and absence of water. When a small amount of water is added to a mixture of 3-*O*-monolaurate and DBU in DMSO-d_6, the characteristic signals of H_2 and H_{6a} become distinctively visible and increase upon prolongation of the reaction (Figure 1), indicating that the addition of water triggers off the migration process under these conditions. These observations, together with those reported until now,[30,32] reflect an easy migration from OH-2 to OH-3 (reversible but in favor of 3-*O*-esters), and a slow migration from OH-3 to OH-6. The 6-*O*-acylated derivative appears nearly as stable as its regioisomers acylated at positions 1′ and 6′, respectively, which were prepared by other methods.[33,34] These observations could also be the effect of changes in the conformation of sucrose due to the presence of water[35] which would modify the relative distances between OH-groups and therefore the rates of migrations in an aqueous medium compared to an organic one.

CONCLUSION

In conclusion, the stability of acyl groups at OH-3 and OH-6 of sucrose has been studied by in situ NMR spectroscopy in DMSO-d_6, together with HPLC analysis and preparative experiments. Notably, it was shown that, unlike the rapid OH-2 to OH-3 acyl migration, the acyl transfer from OH-3 to OH-6 is less favored. However, the latter is accelerated by the presence of water. Attention must therefore be paid to possibly misleading HPLC data, owing to the aqueous conditions in use. In the absence of any acidic work-up, only the 6-*O*-ester is obtained. However, depending on the reaction time, various proportions of the 2-*O*, 3-*O* and 6-*O* esters are obtained after acidic aqueous work-up. The ester at OH-6 is shown to be much more stable. We have also described the use of lithium carbonate as the base for the transesterification of the *N*-acylthiazolidinethione leading also to esters at OH-2 as the major product. These results provide useful complement to this method for which we have confirmed the

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synthetic usefulness for the preparation of defined sucrose derivatives with ester functions on the glucose moiety.

EXPERIMENTAL

General methods. Sucrose was obtained from Béghin-Say. Chromatography and HPLC solvents were purchased from SDS. Reactions were monitored by TLC using aluminium or 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 for ^{13}C NMR and 300.13 MHz for ^{1}H NMR. Mass spectra were recorded by the Centre de Spectrométrie de Masse of the Université Claude Bernard (Villeurbanne). Micro-analyses were performed by the Service Central d′Analyse of the CNRS (Solaize). Optical rotations were measured with a Perkin Elmer 241 polarimeter. Analytical HPLC analyses were performed at 30°C, using an NH_2 spherisorb column 4.6 × 250 mm (Touzart & Matignon), eluted with a CH_3CN/H_2O mixture 90/10 to 86/14 v/v (0.8 mL/min) and with refractometric detection.

Preparation of sucrose decanoates (3) in the presence of solid salts. The mixture of sucrose (2 equiv), *N*-decanoylthiazolidinethione (1.2 equiv) and solid base was stirred in anhyd DMF at rt for 24 h. The mixture was then filtered and analyzed by HPLC. The monoesters were obtained after evaporation of the solvent and purification on a silica gel column using a 56/20/20/4 (v/v) mixture of $CH_2Cl_2/Me_2CO/MeOH/H_2O$.

Preparation of sucrose laurates (4) in the presence of catalytic BuLi. Sucrose (1 equiv) was dissolved in anhyd DMF, before the appropriate acyl donor (1 equiv) and BuLi (0.05 equiv) were added at rt. The mixture was stirred at the same temperature for 3 h. The base was then neutralised with acetic acid, and the solvent removed under reduced pressure. The residue was partitioned between a phosphate buffer (pH 7) and a mixture of ethyl acetate/1-butanol 1/1 (v/v). After evaporation of the solvents, sucrose esters were purified by silica gel column chromatography using a 56/20/20/4 (v/v) mixture of $CH_2Cl_2/Me_2CO/MeOH/H_2O$.

Preparation of sucrose esters of fatty acids (2–7). Sucrose (6.4 g, 20 mmol) was dissolved in anhyd DMF (60 mL). The appropriate *N*-acylthiazolidinethione (10 mmol) was added, followed by lithium carbonate (740 mg, 10 mmol) at room temperature. The mixture was stirred for 24 h at rt. The base was then filtered and the solvent removed under reduced pressure. The residue was chromatographed on a silica gel column using a 56/20/20/4 (v/v) mixture of $CH_2Cl_2/Me_2CO/MeOH/H_2O$.

Purification of isomers 3a, 3b, 3c and 4a, 4b, 4c. Monoesters **3** and **4** were further purified by semi-preparative chromatography to obtain pure isomers **3a**, **3b**, **3c** and **4a**, **4b**, **4c**. Separations were performed on an NH_2 spherisorb column 20 × 250 mm with refractometric detection. The system was equipped with a 2 mL-injection loop (concentration of the injected sample: 100 mg/mL). The eluting system was a CH_3CN/H_2O mixture 90/10 to 86/14 (v/v) (flow: 20 mL/min).

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Data for the mono-*O*-decanoylsucroses and mono-*O*-lauroylsucroses. Anal. Calcd were performed on the 6-*O*-isomer. Optical rotations, HRMS (FAB +) and NMR data are given for each isomer, in order of elution from the semi-preparative HPLC (3-*O*-, 2-*O*-, 6-*O*-).

3-*O*-Decanoylsucrose (3a). $[\alpha]_D$ + 61 (*c* 1, MeOH). ^{1}H NMR (300 MHz, MeOD): δ 0.91 (3H, m, CH_3), 1.31 (12H, m, $(CH_2)_6$), 1.66 (2H, m, $CH_{2\beta}$), 2.41 (2H, m, $CH_{2\alpha}$), 3.53 (1H, t, $J_{4-3} = J_{4-5} = 9.6$ Hz, H-4), 3.60 (1H, dd, $J_{2-1} = 3.8$ Hz, $J_{2-3} = 10.0$ Hz, H-2), 3.62 (1H, d, $J_{1'a-1'b} = 12.1$ Hz, H-1′b), 3.68 (1H, d, $J_{1'a-1'b} = 12.2$ Hz, H-1′a), 3.78–3.93 (6H, m, H-5′, H-6′a, H-6′b, H-5, H-6a, H-6b), 4.05 (1H, t, $J_{4'-3'} = J_{4'-5'} = 7.9$ Hz, H-4′), 4.13 (1H, d, $J_{3'-4'} = 8.3$ Hz, H-3′), 5.23 (1H, t, $J_{3-4} = J_{3-2} = 9.6$ Hz, H-3), 5.45 (1H, d, $J_{1-2} = 3.8$ Hz, H-1). ^{13}C NMR (75 MHz, MeOD): δ 14.7 ($1CH_3$), 26.3 ($1CH_{2\beta}$), 24.0, 30.4, 30.7, 30.7, 30.8, 33.3 ($6CH_2$), 35.6 ($1CH_{2\alpha}$), 62.1, 63.7 (C-6, C-6′), 64.3 (C-1′), 69.6 (C-4), 71.7 (C-5), 74.5 (C-2), 76.0 (C-3), 76.9 (C-4′), 79.5 (C-3′), 84.1 (C-5′), 93.8 (C-1), 105.8 (C-2′), 175.9 (1C = O). HRMS: *m/z* calcd for $C_{22}H_{40}O_{12}Na$: 519.2417. Found: 519.2417.

2-*O*-Decanoylsucrose (3b). (contains 9% of 3a). $[\alpha]_D$ + 66 (*c* 1, MeOH). ^{1}H NMR (300 MHz, MeOD): δ 0.91 (3H, m, CH_3), 1.31 (12H, m, $(CH_2)_6$), 1.65 (2H, m, $CH_{2\beta}$), 2.41 (2H, m, $CH_{2\alpha}$), 3.41 (1H, d, H-1′b), 3.45 (1H, t, $J_{4-3} = J_{4-5} = 9.8$ Hz, H-4), 3.53 (1H, d, $J_{1'a-1'b} = 12.1$ Hz, H-1′a), 3.65–3.93 (7H, m, H-3, H-5, H-5′, H-6′a, H-6′b, H-6a, H-6b), 4.03 (1H, t, $J_{4'-3'} = J_{4'-5'} = 8.1$ Hz, H-4′), 4.20 (1H, d, $J_{3'-4'} = 8.7$ Hz, H-3′), 4.63 (1H, dd, $J_{2-1} = 3.7$ Hz, $J_{2-3} = 10.3$ Hz, H-2), 5.55 (1H, d, $J_{1-2} = 3.6$ Hz, H-1). ^{13}C NMR (75 MHz, MeOD): δ 14.7 ($1CH_3$), 26.0 ($1CH_{2\beta}$), 23.9, 30.5, 30.6, 30.7, 30.8, 33.2 ($6CH_2$), 35.3 ($1CH_{2\alpha}$), 62.3, 63.6 (C-6, C-6′), 63.4 (C-1′), 71.7 (C-4), 72.1 (C-5), 74.3 (C-2), 74.5 (C-3), 75.4 (C-4′), 77.6 (C-3′), 83.8 (C-5′), 91.0 (C-1), 105.5 (C-2′), 175.5 (1C = O). HRMS: *m/z* calcd for $C_{22}H_{40}O_{12}Na$: 519.2417. Found: 519.2418.

6-*O*-Decanoylsucrose (3c). $[\alpha]_D$ + 44 (*c* 1, MeOH). ^{1}H NMR (300 MHz, MeOD): δ 0.91 (3H, m, CH_3), 1.32 (12H, m, $(CH_2)_6$), 1.63 (2H, m, $CH_{2\beta}$), 2.38 (2H, m, $CH_{2\alpha}$), 3.31 (1H, t, $J_{4-3} = J_{4-5} = 9.4$ Hz, H-4), 3.44 (1H, dd, $J_{2-1} = 3.8$ Hz, $J_{2-3} = 9.6$ Hz, H-2), 3.60 (1H, d, $J_{1'a-1'b} = 12.2$ Hz, H-1′b), 3.65 (1H, d, $J_{1'a-1'b} = 12.1$ Hz, H-1′a), 3.74 (1H, t, $J_{3-4} = J_{3-2} = 9.3$ Hz, H-3), 3.77–3.91 (3H, m, H-5′, H-6′a, 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, $J_{6a-6b} = 12.0$ Hz, $J_{6b-5} = 5.2$ Hz, H-6b), 4.42 (1H, dd, $J_{6a-6b} = 10.9$ Hz, H-6a), 5.39 (1H, d, $J_{1-2} = 3.77$ Hz, H-1); ^{13}C NMR (75 MHz, MeOD): δ 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). HRMS: *m/z* calcd for $C_{22}H_{40}O_{12}Na$: 519.2417. Found: 519.2416.

Anal. Calcd for $C_{22}H_{40}O_{12}.1.4H_2O$: C, 50.64; H, 8.27. Found: C, 50.65; H, 8.08.

3-*O*-Lauroylsucrose (4a). $[\alpha]_D$ + 54 (*c* 1, MeOH). Lit.[22] ^{1}H NMR (300 MHz, MeOD): δ 0.91 (3H, m, CH_3), 1.31 (16H, m, $(CH_2)_8$), 1.66 (2H, m, $CH_{2\beta}$), 2.41 (2H, m, $CH_{2\alpha}$), 3.53 (1H, t, $J_{4-3} = J_{4-5} = 9.7$ Hz, H-4), 3.59 (1H, dd, $J_{2-1} = 3.8$ Hz, $J_{2-3} = 10.0$ Hz, H-2), 3.62 (1H, d, $J_{1'a-1'b} = 12.2$ Hz, H-1′b), 3.68 (1H, d, $J_{1'a-1'b} = 12.2$ Hz, H-1′a), 3.71–3.87, 3.88–3.98 (6H, 2 m, H-6′a, H-6′b, H-5, H-6a, H-6b, H-5′), 3.99–4.09 (1H,

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m, H-4′), 4.10 (1H, d, $J_{3'-4'}$ = 8.3 Hz, H-3′), 5.23 (1H, t, $J_{3-4} = J_{3-2}$ = 9.7 Hz, H-3), 5.45 (1H, d, J_{1-2} = 3.8 Hz, H-1). ^{13}C NMR (75 MHz, MeOD): δ 14.7 ($1CH_3$), 26.3 ($1CH_{2\beta}$), 24.0, 30.5, 30.8, 30.9, 31.0, 33.4 ($8CH_2$), 35.6 ($1CH_{2\alpha}$), 62.1, 63.7 (C-6, C-6′), 64.3 (C-1′), 69.7 (C-4), 71.7 (C-5), 74.5 (C-2), 76.0 (C-3), 77.0 (C-4′), 79.5 (C-3′), 84.2 (C-5′), 93.9 (C-1), 105.8 (C-2′), 175.9 (1C = O). HRMS: *m/z* calcd for $C_{24}H_{44}O_{12}Na$: 547.2730. Found: 547.2731.

2-*O*-Lauroylsucrose (4b). $[\alpha]_D$ + 63 (*c* 1, MeOH). Lit.[22] ^{1}H NMR (300 MHz, MeOD): δ 0.91 (3H, m, CH_3), 1.31 (16H, m, $(CH_2)_8$), 1.66 (2H, m, $CH_{2\beta}$), 2.43 (2H, m, $CH_{2\alpha}$), 3.39 (1H, d, $J_{1'a-1'b}$ = 11.7 Hz, H-1′b), 3.44 (1H, t, $J_{4-3} = J_{4-5}$ = 9.3 Hz, H-4), 3.53 (1H, d, $J_{1'a-1'b}$ = 11.9 Hz, H-1′a), 3.65–3.97 (7H, m, H-3, H-5, H-5′, H-6′a, H-6′b, H-6a, H-6b), 4.03 (1H, t, $J_{4'-3'} = J_{4'-5'}$ = 8.2 Hz, H-4′), 4.19 (1H, d, $J_{3'-4'}$ = 8.7 Hz, H-3′), 4.61 (1H, dd, J_{2-1} = 3.6 Hz, J_{2-3} = 10.2 Hz, H-2), 5.55 (1H, d, J_{1-2} = 3.8 Hz, H-1). ^{13}C NMR (75 MHz, MeOD): δ 14.7 ($1CH_3$), 26.0 ($1CH_{2\beta}$), 24.0, 30.5, 30.8, 30.9, 31.0, 33.3 ($8CH_2$), 35.3 ($1CH_{2\alpha}$), 62.4, 63.7 (C-6, C-6′), 63.5 (C-1′), 71.8 (C-4), 72.2 (C-5), 74.4 (C-2), 74.6 (C-3), 75.5 (C-4′), 77.7 (C-3′), 84.0 (C-5′), 91.1 (C-1), 105.9 (C-2′), 175.6 (1C = O). HRMS: *m/z* calcd for $C_{24}H_{44}O_{12}Na$: 547.2730. Found: 547.2728.

6-*O*-Lauroylsucrose (4c). $[\alpha]_D$ + 45 (*c* 1, MeOH). Lit.[30]^{1}H NMR (300 MHz, MeOD): δ 0.91 (3H, m, CH_3), 1.31 (16H, m, $(CH_2)_8$), 1.63 (2H, m, $CH_{2\beta}$), 2.38 (2H, m, $CH_{2\alpha}$), 3.31 (1H, t, $J_{4-3} = J_{4-5}$ = 9.0 Hz, H-4), 3.44 (1H, dd, J_{2-1} = 3.8 Hz, J_{2-3} = 9.8 Hz, H-2), 3.60 (1H, d, $J_{1'a-1'b}$ = 12.2 Hz, H-1′b), 3.65 (1H, d, $J_{1'a-1'b}$ = 12.2 Hz, H-1′a), 3.74 (1H, t, $J_{3-4} = J_{3-2}$ = 9.3 Hz, H-3), 3.77–3.89 (3H, m, H-5′, H-6′a, 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_{6a-6b} = 12.0 Hz, J_{6b-5} = 5.4 Hz, H-6b), 4.41 (1H, dd, J_{6a-6b} = 12.0 Hz, J_{6a-5} = 1.8 Hz, H-6a), 5.4 (1H, d, J_{1-2} = 3.8 Hz, H-1). ^{13}C NMR (75 MHz, MeOD): δ 14.7 ($1CH_3$), 26.3 ($1CH_{2\beta}$), 24.0, 30.5, 30.7, 30.9, 33.3 ($8CH_2$), 35.2 ($1CH_{2\alpha}$), 64.2 (C-6′), 63.4 (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). HRMS: *m/z* calcd for $C_{24}H_{44}O_{12}Na$: 547.2730. Found: 547.2736.

Anal. Calcd for $C_{24}H_{44}O_{12}.0.8H_2O$: C, 53.48; H, 8.53. Found: C, 53.31; H, 8.48.

ACKNOWLEDGMENTS

Financial support from the CNRS and Béghin-Say is greatly acknowledged. We thank Béghin-Say and l'Agence Nationale de la Recherche et de la Technologie for a grant to VM (contrat CIFRE).

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Received March 5, 2003
Accepted July 30, 2003

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