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Syntheses of four fatty acid esters of sucrose found in type B trichomes of *Solanum berthaultii* Hawkes (wild potato), including the major component, 6-*O*-decanoyl-3,4-di-*O*-isobutyrylsucrose*†

Stefan Oscarson‡ and Helena Ritzén
Department of Organic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm (Sweden)

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ABSTRACT

6-*O*-Decanoyl-3,4-di-*O*-isobutyrylsucrose,6-*O*-decanoyl-3-*O*-isobutyryl-4-*O*-[(*S*)-2-methylbutyryl]sucrose,6-*O*-decanoyl-4-*O*-isobutyryl-3-*O*[(*S*)-2-methylbutyryl]sucrose, and 6-*O*-decanoyl-3,4-di-*O*-[(S)-2-methylbutyryl]sucrose have been synthesized from 3-*O*-allyl-3′,4′,6′-tri-*O*-benzyl-4,6-*O*-(4-methoxybenzylidene)-sucrose.

INTRODUCTION

Fatty acid esters of sucrose, found in Oriental tobacco[2,3] and species of wild potato[4–6], are present on the surface of the leaves, inhibit plant growth, and function as bactericides[7,8]. These properties are related to the contents of fatty acids. Extraction from the plant yields an array of sucrose esters, which differ in composition and pattern of substitution. Often, only the principal component can be isolated, and the minor components are obtained as mixtures. We have described the synthesis of the major component from Oriental tobacco, namely, 6-*O*-acetyl-2,3,4-tri-*O*-[(*S*)-3-methylpentanoyl]sucrose[1], and now report the synthesis of the major component extracted from a wild potato, *Solanum berthaultii* Hawkes, namely, 6-*O*-decanoyl-3,4-di-*O*-isobutyrylsucrose, together with three minor components.

RESULTS AND DISCUSSION

3-*O*-Allyl-3′,4′,6′-tri-*O*-benzyl-4,6-*O*-(4-methoxybenzylidene)sucrose[1] was benzylated using benzyl bromide and sodium hydride in *N,N*-dimethylformamide to give the 2,1′,3′,4′,6′-penta-*O*-benzyl derivative **1**, from which the 4,6-acetal was removed by mild acid hydrolysis to give the 4,6-diol **2**. Regioselective acylation of **2** with decanoyl chloride in pyridine yielded solely the 6-ester **3**. The allyl group was removed from **3** by

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‡ Author for correspondence.

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isomerization to the 1-propenyl group with tris(triphenylphosphine)rhodium(I) chloride, followed by mild acid treatment to give the 3,4-diol **4**. Acylation of **4** with isobutyryl chloride in pyridine gave **5**, which was hydrogenolyzed (Pd–C) to give the title compound **6** (49% from **1**). Tables I and II contain the n.m.r. data with assignments for the sugar moieties of **6** (synthetic and natural products). As found[1] for the tobacco compound, there are slight discrepancies in the n.m.r. spectra due to the amphoteric properties of the sucrose esters. Addition of methanol improved the solvation of the fructose moiety and made it easier to resolve all signals in the ^{1}H-n.m.r. spectra (Table II). The penta-acetate (**7**) of **6** has a melting point that is the same as that reported for the penta-acetate of the natural poduct[4].

TABLE I

^{13}C-N.m.r. chemical shift data and assignments

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-1'*	*C-2'*	*C-3'*	*C-4'*	*C-5'*	*C-6'*
6[a]	92.3	70.6	73.3	66.9	68.8	60.6	64.3	104.0	80.0	73.5	82.0	61.0
6[b]	92.5	70.5	73.1	67.1	68.7	61.1	63.6	104.2	79.1	73.8	82.0	61.1
6[c]	92.6	70.5	73.1	68.2	68.9	61.9	64.0	104.7	79.2	74.5	82.9	62.3
11[c]	92.7	70.6	73.1	68.4	69.0	62.1	63.9	104.8	79.1	74.7	83.0	62.5
18[c]	92.6	70.6	73.3	68.3	68.9	62.2	64.0	104.8	79.2	74.7	83.0	62.5
23[c]	92.7	70.7	73.2	68.5	68.9	62.3	64.0	104.9	79.1	74.8	83.1	62.6

[a] Ref. 4. [b] Synthetic product in $CDCl_3$. [c] Synthetic product in 1:1 $CDCl_3$–CD_3OD.

The first minor component was synthesized as follows. Acylation of **3** with isobutyryl chloride in pyridine gave **8**, from which the allyl group was removed as described above to yield the 3-hydroxy derivative **9**. Acetylation of **9** with (*S*)-2-methylbutyryl chloride in pyridine was not succesful, but when (*S*)-2-methylbutyric acid and dicyclohexylcarbodi-imide in carbon tetrachloride were used, **10** was obtained in a good yield. Hydrogenolysis of **10** then gave the second target compound **11** (37% from **1**).

The syntheses of the remaining two sucrose esters could not be performed in the above manner since both **3** and **4** resisted acylation with the C_5 fatty acid at HO-4. Therefore, **1** was treated with sodium cyanoboro-hydride and trifluoroacetic acid to give regioselectively[9] the 6-*O*-(4-methoxybenzyl) derivative **12**, which was acylated with (*S*)-2-methyl-butyric acid and dichyclohexylcarbodi-imide in carbon tetrachloride to give **13**. Deallylation of **13**, as described above, gave **14**, acylation of which with isobutyryl chloride yielded **15**, from which the 4-methoxybenzyl group was removed by mild oxidation with cerium(IV) ammonium nitrate. Acylation of the product (**16**) with decanoyl chloride in pyridine was then straightforward and gave **17**, which was hydrogenolyzed to give the third target compound **18** (19% from **1**).

Compound **12** was also deallylated to give the 3,4-diol **19**, which was acylated with (*S*)-2-methylbutyric acid, demethoxybenzylated, acylated at O-6 with decanoyl chloride, and hydrogenolyzed as described for **14**, to give the last target compound **23**

TABLE II

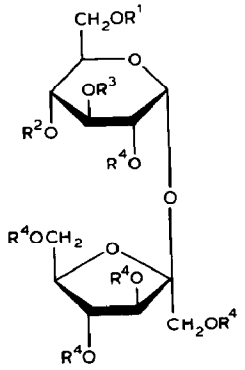
^{1}H-N.m.r. chemical shift data and assignments

Compound	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-6a*	*H-6b*	*H-1'a*	*H-1'b*	*H-3'*	*H-4'*	*H-5'*	*H-6'*
6[a]	5.52	3.80	5.31	5.11	4.33	4.15	4.15			4.22	4.39	3.88	
	(4.1)[d]	(9.8)	(9.7)	(9.7)									
6[b]	5.51	3.80	5.32	5.10	4.32								
	(3.7)		(9.8)	(9.8)									
6[c]	5.50		5.35	5.06	4.35	4.12	4.22	3.63	3.69	4.13	4.07	3.83	
	(3.9)		(9.8)	(10.2)		(12.7)	(12.7)	(12.4)	(12.4)				
				(9.4)		(2.2)	(3.6)						
11[c]	5.49		5.36	5.06	4.36	4.10	4.23	3.63	3.69			3.82	
	(3.8)		(10.3)	(10.3)		(12.6)	(12.6)	(12.4)	(12.4)				
			(9.4)	(9.4)		(2.1)	(3.3)						
18[c]	5.48	3.76	5.36	5.09	4.36	4.16	4.16	3.62	3.68			3.80	
	(4.0)	(9.8)	(9.8)	(10.1)	(10.0)	(3.1)	(3.1)	(12.2)	(12.2)				
		(4.3)		(9.4)	(5.6)								
					(2.7)								
23[c]	5.48	3.74	5.37	5.09	4.36	4.16	4.16	3.63	3.69	4.12	4.07	3.82	
	(4.0)	(10.1)	(9.7)	(9.8)	(10.2)	(2.7)	(2.7)	(12.3)	(12.3)	(8.1)	(15.4)		
		(3.8)			(5.5)						(7.3)		
					(2.7)								

[a] Ref. 5. [b] Synthetic product in $CDCl_3$. [c] Synthetic product in 1:1 $CDCl_3$–CD_3OD. [d] *J* in Hz in brackets.

(28% from **1**). The ^{1}H- and ^{13}C-n.m.r. data for the sucrose moieties of **11**, **18**, and **23** are shown in Tables I and II.

Since the position of the decanoyl moiety in **3** was difficult to determine unambiguously by n.m.r. spectroscopy, **6** was also prepared by an alternative route starting from **19**. The position of the 4-methoxybenzyl group in this compound (and in **12**) was determined easily by ^{13}C-n.mr. spectroscopy, since the absence of a resonance for an unsubstituted primary carbon at ~61 p.p.m. showed the benzyl group to be in that position. Treatment of **19** as described above, except that isobutyryl chloride was



1 R^1, R^2=*p*-$MeOC_6H_4CH$, R^3= allyl,R^4= Bn
2 R^1, R^2=H,R^3= allyl, R^4= Bn
3 R^1= $CH_3(CH_2)_8CO$, R^2= H, R^3 = allyl, R^4= Bn
4 R^1= $CH_3(CH_2)_8CO$, R^2, R^3 = H,R^4 = Bn
5 R^1= $CH_3(CH_2)_8CO$, R^2, R^3 = $(CH_3)_2CHCO$, R^4 = Bn
6 R^1 = $CH_3(CH_2)_8CO$, R^2, R^3 = $(CH_3)_2CHCO$, R^4 = H
7 R^1 = $CH_3(CH_2)_8CO$, R^2, R^3 = $(CH_3)_2CHCO$, R^4 = Ac
8 R^1 = $CH_3(CH_2)_8CO$, R^2 = $(CH_3)_2CHCO$, R^3 = allyl, R^4 = Bn
9 R^1 = $CH_3(CH_2)_8CO$, R^2 = $(CH_3)_2CHCO$, R^3 = H, R^4 = Bn
10 R^1 = $CH_3(CH_2)_8CO$, R^2 = $(CH_3)_2CHCO$, R^3 = $CH_3CH_2CH(CH_3)CO$, R^4 = Bn
11 R^1 = $CH_3(CH_2)_8CO$, R^2 = $(CH_3)_2CHCO$, R^3 = $CH_3CH_2CH(CH_3)CO$, R^4 = H
12 R^1 = *p*-$MeOC_6H_4CH_2$, R^2 = H, R^3 = allyl, R^4 = Bn
13 R^1 = *p*-$MeOC_6H_4CH_2$, R^2 = $CH_3CH_2CH(CH_3)CO$, R^3 = allyl, R^4 = Bn
14 R^1 = *p*-$MeOC_6H_4CH_2$, R^2 = $CH_3CH_2CH(CH_3)CO$, R^3 = H, R^4 = Bn
15 R^1 = *p*-$MeOC_6H_4CH_2$, R^2 = $CH_3CH_2CH(CH_3)CO$, R^3 = $(CH_3)_2CHCO$, R^4 = Bn
16 R^1 = H, R^2 = $CH_3CH_2CH(CH_3)CO$, R^3 = $(CH_3)_2CHCO$, R^4 = Bn
17 R^1 = $CH_3(CH_2)_8CO$, R^2 = $CH_3CH_2CH(CH_3)CO$, R^3 = $(CH_3)_2CHCO$, R^4 = Bn
18 R^1 = $CH_3(CH_2)_8CO$, R^2 = $CH_3CH_2CH(CH_3)CO$, R^3 = $(CH_3)_2CHCO$, R^4 = H
19 R^1 = *p*-$MeOC_6H_4CH_2$, R^2, R^3 = H, R^4 = Bn
20 R^1 = *p*-$MeOC_6H_4CH_2$, R^2, R^3 = $CH_3CH_2CH(CH_3)CO$, R^4 = Bn
21 R^1 = H, R^2, R^3 = $CH_3CH_2CH(CH_3)CO$, R^4 = Bn
22 R^1 = $CH_3(CH_2)_8CO$, R^2, R^3 = $CH_3CH_2CH(CH_3)CO$, R^4 = Bn
23 R^1 = $CH_3(CH_2)_8CO$, R^2, R^3 = $CH_3CH_2CH(CH_3)CO$, R^4 = H

used instead of (*S*)-2-methylbutyric acid in the first acylation step, gave a product which was identical with **6**, thereby proving the 6-*O*-decanoyl substitution expected and assumed in **3**. The yield in the last synthesis was lower than in the original one, but it can be a useful route if derivatives are required with isomeric decanoyl moieties, as found in the natural products.

EXPERIMENTAL

General methods. — These were as described[1]. The ^{1}H- and ^{13}C-n.m.r. assignments were made from H,H- and C,H-COSY spectra. Column chromatography was performed on silica gel (0.035–0.070, Amicon). The ^{1}H-and ^{13}C-n.m.r. data for the sucrose moieties of **6**, **11**, **18** and **23** are shown in Tables I and II.

3-O-Allyl-2,1',3'4',6'-penta-O-benzyl-4,6-O-(4-methoxybenzylidene)sucrose (**1**). — 3-*O*-Allyl-3',4',6'-tri-*O*-benzyl-4,6-*O*-(4-methoxybenzylidene)sucrose (200 mg) and sodium hydride (25 mg) were dissolved in *N*,*N*-dimethylformamide (3 mL). After 15 min, benzyl bromide (0.10 mL) was added, the mixture was stirred for 2 h, methanol was added dropwise, and the mixture was concentrated. Column chromatography [light petroleum (b.p.40–60°)–chloroform–ethyl acetate, 4:1:1] of the residue gave **1** (232 mg, 94%), $[\alpha]_D$ +39° (*c* 1.1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 55.3 (CH_3O), 62.8, 68.9, 70.9, 71.6, 72.5, 72.9, 73.0, 73.3, 73.4, 73.8, 78.2, 79.1, 79.5, 81.6, 82.1, 83.6 (C-1',3',4',5',6',2,3,4,5,6, Ph*C*H_2, CH_2=C*H*CH_2), 90.6 (C-1), 101.2 (Ph*C*H), 104.5 (C-2'), 113.5 ($CH_3OC_6H_4CH_2$), 116.3 (*C*H_2=CH), 127.5–130.3 (aromatic C), 135.4 (CH_2=*C*H), 138.0–138.4 (aromatic C-1), 159.9 (C-1 in *p*-methoxybenzyl).

Anal. Calc. for $C_{58}H_{62}O_{12}$: C, 73.2; H, 6.6. Found: C, 73.3; H, 6.5

3-O-Allyl-2,1',3',4',6'-penta-O-benzylsucrose (**2**). — 3-*O*-Allyl-3',4',6'-tri-*O*-benzyl-4,6-*O*-(4-methoxybenzylidene)sucrose[1] (200 mg) and sodium hydride (20 mg) were treated with benzylbromide, as described above, to give crude **1**, a solution of which in acetonitrile (0.5 mL) and aqueous acetic acid (90%, 1 mL) was kept for 3 h and then concentrated. Column chromatography (2:1 toluene–ethyl acetate) of the residue gave **2** (203 mg, 94%), $[\alpha]_D$ +43° (*c* 1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 62.5 (C-6), 70.0, 70.4, 71.3, 71.6, 72.6, 73.0, 73.2, 73.4, 74.0, 79.1, 79.4, 80.9, 81.0, 83.5, (C-1',3',4',5',6',2,3,4,5, Ph*C*H_2, CH_2=C*H*CH_2), 89.3 (C-1), 104.4 (C-2'), 116.8 (*C*H_2=CH), 127.5–128.3 (aromatic C), 135.2 (CH_2=*C*H), 138.0, 138.1, 138.2, (aromatic C-1).

Anal. Calc. for $C_{50}H_{56}O_{11}$: C, 72.1; H, 6.8. Found: C, 72.2; H, 6.7

3-O-Allyl-2,1',3',4',6'-penta-O-benzyl-6-O-decanoylsucrose (**3**). — A solution of decanoyl chloride (74 μL, 1.5 equiv.) in pyridine (0.5 mL) was added to an ice-cooled solution of **2** (200 mg) in pyridine (2 mL). After stirring for 6 h, methanol was added. Concentration and column chromatography (9:1 toluene–ethyl acetate) of the residue yielded **3** (215 mg, 91%), $[\alpha]_D$ +27° (*c* 0.9, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 14.1 (CH_3), 22.7, 24.7, 24.9, 29.2, 29.3, 29.5, 31.9, [$(CH_2)_7$], 34.2 (*C*H_2CO), 63.0 (C-6), 69.8, 69.9, 70.9, 71.4, 72.0, 72.6, 73.1, 73.2, 73.5, 74.2, 79.3, 79.5, 80.7, 82.0, 83.9, (C-1',3',4',5',6',2,3,4,5, Ph*C*H_2, CH_2=C*H*CH_2), 89.9 (C-1), 104.6 (C-2'), 116.9

(CH_2=CH), 127.6–128.3 (aromatic C), 135.3 (CH_2=*C*H), 138.2 (aromatic C-1), 174.4 (carbonyl C).

Anal. Calc. for $C_{60}H_{74}O_{12}$: C, 73.0; H, 7.6. Found: C, 73.6; H, 7.7.

*2,1',3',4',6'-Penta-*O*-benzyl-6-*O*-decanoylsucrose* (**4**). — A solution of **3** (150 mg) and tris(triphenylphosphine)rhodium(I) chloride (50 mg) in 6:3:1 ethanol–toluene–water (10 mL) was boiled under reflux for 3 h, then cooled to room temperature. Mercury(II) bromide (100 mg) was added, the mixture was stirred for 3 h, then filtered through silica gel, and concentrated. Column chromatography (3:1 toluene–ethyl acetate) of the residue gave **4** (116 mg, 81%), $[\alpha]_D$ +29° (*c* 0.9, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 14.1 (CH_3), 22.6, 24.9, 29.1, 29.2, 29.4, 31.8 [$(CH_2)_7$], 34.1 (*C*H_2CO), 62.9 (C-6), 69.7, 69.8, 70.3, 71.4, 72.4, 72.6, 73.1, 73.2, 73.5, 78.3, 79.2, 81.1, 83.7 (C-1',3',4',5',6',2,3,4,5, Ph*C*H_2), 89.0 (C-1), 104.4 (C-2'), 127.6–128.3 (aromatic C), 137.7, 137.8, 138.0 (aromatic C-1), 174.6 (carbonyl C).

Anal. Calc. for $C_{57}H_{70}O_{12}$: C, 72.3; H, 7.4. Found: C, 72.3; H, 7.5.

*2,1',3',4',6'-Penta-*O*-benzyl-6-*O*-decanoyl-3,4-di-*O*-isobutyrylsucrose* (**5**). — A solution of **4** (110 mg) in pyridine (2 mL) was stirred with isobutyryl chloride (75 μL) for 2 h at room temperature. Methanol (1 mL) was added and the mixture was concentrated. Column chromatography (4:1 iso-octane–ethyl acetate) of the residue gave **5** (120 mg, 95%), $[\alpha]_D$ +54° (*c* 0.9, chloroform). ^{13}C-N.m.r. data ($CDCl_3$) δ: 14.1 [*C*H_3(CH_2)$_8$], 18.7, 18.8, 18.9, 19.0 [4 (CH_3)$_2$CH], 22.6 24.7, 29.1, 29.2, 29.3, 29.4, 31.9 [CH_3(*C*H_2)$_7$*C*H_2], 33.9, 33.9, 34.0 [$(CH_3)_2$*C*H, $CH_3(CH_2)_7$*C*H_2], 61.5 (C-6), 67.7, 67.7, 70.4, 71.4, 71.5, 71.7, 72.6, 73.2, 73.4, 73.5, 76.5, 79.4, 81.0, 83.8 (C-1',3',4',5',6',2,3,4,5, Ph*C*H_2), 88.9 (C-1) 104.4 (C-2'), 127.4–128.4 (aromatic C), 137–138.1 (aromatic C-1), 173.4, 175.5, 176.0 (carbonyl C).

Anal. Calc. for $C_{65}H_{82}O_{14}$: C, 71.8; H, 7.6; Found: C, 71.4; H, 7.8.

*6-*O*-Decanoyl-3,4-di-*O*-isobutyrylsucrose* (**6**). — A solution of **5** (55 mg) in ethanol (3 mL) was hydrogenolyzed over Pd–C (10%, 25 mg) at 400 kPa for 16 h, then filtered, and concentrated. Column chromatography (9:1 chloroform–methanol) of the residue yielded **6** (28 mg, 72%), $[\alpha]_D$ +73° (*c* 0.4, chloroform). N.m.r. data ($CDCl_3$–CD_3OD, 1:1): ^{13}C, δ 14.2 [CH_3(CH_2)$_8$], 19.0, 19.1 [2 (*C*H_3)$_2$CH], 23.0, 25.1, 29.5, 29.6, 29.8, 32.2 [CH_3(*C*H_2)$_7$*C*H_2], 34.3, 34.4, 34.5 [$(CH_3)_2$*C*H, *C*H_2CO)], 174.5, 176.3, 177.7 (carbonyl C); ^{1}H δ 0.83–0.92 (3 H), 1.13 (d, 3 H, *J* 7.0 Hz), 1.13 (d, 3 H, *J* 7.0 Hz), 1.14 (d, 3 H, *J* 7.0 Hz), 1.56 (d, 3 H, *J* 7.0 Hz), 1.19–1.39 (12 H), 1.52–1.69 (2 H), 2.32–2.40 (2 H), 2.51 [sep, *J* 7.0 Hz, (CH_3)$_2$ C*H*,], 2.57 [sep, *J* 7.0 Hz, (CH_3)$_2$C*H*], 3.70–3.83 (m, 3 H, H-2, 6').

Anal. Calc. for $C_{30}H_{52}O_{14}\cdot H_2O$: C, 55.0; H, 8.3. Found: C, 55.5; H, 8.3.

*2,1',3',4',6'-Penta-*O*-acetyl-6-*O*-decanoyl-3,4-di-*O*-isobutyrylsucrose* (**7**). — Compound **6** was treated with acetic anhydride–pyridine conventionally to give **7**, $[\alpha]_D$ +47° (*c* 0.7, chloroform), m.p. 67–68° (lit.[4] m.p. 63–64°). ^{13}C-N.m.r. data ($CDCl_3$): δ 14.1 [CH_3(CH_2)$_8$], 18.7, 18.8, 18.8, 19.0 [4 (CH_3)$_2$CH], 20.5, 20.6, 20.6, 20.7 (*C*H_3CO), 22.7, 24.7, 29.1, 29.3, 29.5, 31.9 [CH_3(*C*H_2)$_7$*C*H_2], 33.9, 33.9 [$(CH_3)_2$*C*H, $CH_3(CH_2)_7$*C*H_2], 61.3, 62.8, 63.6, 67.4, 68.8, 69.1, 70.4, 75.1, 75.8, 79.3 (C-1',3',4',5',6', 2,3,4,5,6), 90.1 (C-1), 104.2 (C-2'), 169.7, 169.9, 170.1, 170.1, 170.5 (5 CH_3*C*O), 173.5, 175.3, 176.0 (carbonyl C).

Anal. Calc. for $C_{40}H_{62}O_{19}$: C, 56.7; H, 7.4. Found: C, 56.9; H, 7.5.

6-O-Decanoyl-4-O-isobutyryl-3-O-[(S)-2-methylbutyryl]sucrose (**11**). — Compound **3** (190 mg) was acetylated with isobutyryl chloride (40 μL), as described for **4**, to give, after column chromatography (4:1 iso-octane–ethyl acetate), 3-*O*-allyl-2,1',3',4',6'-penta-*O*-benzyl-6-*O*-decanoyl-4-*O*-isobutyrylsucrose (**8**; 145 mg, 71%), $[\alpha]_D$ +36° (*c* 0.7, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 14.1 [$CH_3(CH_2)_8$], 18.8, 19.0 [2 (CH_3)$_2$CH], 22.7, 24.7, 29.2, 29.3, 29.5, 31.9 [$CH_3(CH_2)_7CH_2$], 34.0, 34.0 [$(CH_3)_2CH$,$CH_3(CH_2)_7CH_2$], 61.8 (C-6), 68.1, 68.9, 70.7, 71.5, 72.2, 72.6, 73.1, 73.2, 73.5, 73.9, 78.9, 79.3, 79.4, 81.7, 83.9 (C-1',3',4',5',6',2,3,4,5,6, PhCH_2, CH_2=$CH$$CH_2$), 89.6 (C-1), 104.5 (C-2'), 116.3 (CH_2=CH), 127.6–128.5 (aromatic C), 135.0 (CH_2=CH), 137.9, 138.0, 138.1 (aromatic C-1), 173.5, 175.4 (carbonyl C).

Compound **8** (145 mg) was deallylated as described for **3**, to give, after column chromatography (19:1 toluene–ethyl acetate), 2,1',3',4',6'-penta-*O*-benzyl-6-*O*-decanoyl-4-*O*-isobutyrylsucrose (**9**; 102 mg, 73%), $[\alpha]_D$ +46° (*c* 1.4, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 14.1 [$CH_3(CH_2)_8$], 18.9 [$(CH_3)_2CH$], 22.7, 24.7, 29.1, 29.3, 29.4, 31.9 [$CH_3(CH_2)_7CH_2$], 34.0 [$(CH_3)_2CH$, $CH_3(CH_2)_7CH_2$], 61.8 (C-6), 67.7, 69.6, 70.2, 71.0, 71.2, 71.7, 72.7, 73.2, 73.3, 73.5, 78.8, 79.3, 81.0, 83.9 (C-1',3',4',5',6',2,3,4,5,6, PhCH_2), 88.7 (C-1), 104.4 (C-2'), 127.6–128.4 (aromatic C), 137.7–138.0 (aromatic C-1), 173.5, 176.2 (carbonyl C).

Dicyclohexylcarbodi-imide (12 mg) was added to a solution of **9** (27 mg), (*S*)-2-methylbutyric acid (6 μL), and 4-dimethylaminopyridine (catalytic amount) in CCl_4. The mixture was stirred for 16 h at room temperature, then filtered, and concentrated. Column chromatography (iso-octane–ethyl acetate 4:1) of the residue gave 2,1',3',4',6'-penta-*O*-benzyl-6-*O*-decanoyl-4-O-isobutyryl-3-O-[(*S*)-2-methylbutyryl]sucrose (**10**; 28 mg, 95%), $[\alpha]_D$ +60° (*c* 1.4 chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 11.6 (CH_3CH_2CH), 14.1 [$CH_3(CH_2)_8$], 16.5 (CH_3CH), 18.7, 18.9 [2 (CH_3)$_2$CH], 22.7, 24.7, 26.5, 29.1, 29.3, 29.5, 31.9 [$CH_3(CH_2)_7CH_2$,CH_3CH_2CH], 33.9, 34.0 [$(CH_3)_2CH$, $CH_3(CH_2)_7CH_2$], 41.0 (CH_3CH_2CH), 61.5 (C-6), 67.7, 67.8, 70.3, 71.3, 71.4, 71.8, 72.6, 73.2, 73.4, 76.5, 79.4, 81.0, 83.9 (C-1',3',4',5',6',2,3,4,5,6, PhCH_2), 88.8 (C-1), 104.5 (C-2'), 127.5–128.4 (aromatic C), 137.7, 137.8, 138.1 (aromatic C-1), 173.4, 175.5, 175.7 (carbonyl C).

A solution of **10** (110 mg) in ethyl acetate–methanol–water (80:15:5, 4 mL) was hydrogenolyzed over Pd–C (10%, 10 mg) at 400 kPa for 16 h, then filtered, and concentrated. Column chromatography (14:1 chloroform–methanol) of the residue yielded **11** (54 mg, 85%), $[\alpha]_D$ +72° (*c* 1.1, chloroform). N.m.r. data ($CDCl_3$–CD_3OD, 1:1): ^{13}C, δ 11.6 (CH_3CH_2CH), 14.2 [$CH_3(CH_2)_8$], 16.7 (CH_3CH), 18.9, 19.0 [2 (CH_3)$_2$ CH], 23.1, 25.2, 27.0, 29.6, 29.7, 29.9, 32.4 [$CH_3(CH_2)_7CH_2$,CH_3CH_2CH], 34.4, 34.5 [$(CH_3)_2CH$, $CH_3(CH_2)_7CH_2$], 41.6 (CH_3CH_2CH), 174.6, 176.4, 177.4 (carbonyl C); ^{1}H, δ 0.85–0.95 (6 H), 1.11 (d, 3 H, *J* 7.1 Hz), 1.13 (d, 3 H, *J* 7.0 Hz), 1.14 (d, 3 H, *J* 7.0 Hz), 1.22–1.77 (16 H), 2.32–2.44 (3 H), 2.51 [sep, *J* 7.0 Hz (CH_3)$_2$C*H*], 3.68–3.83 (m, 3 H, H-2,6'), 4.03–4.16 (m, 2 H, H-3,4').

Anal. Calc. for $C_{31}H_{54}O_{14}$: C, 57.2; H, 8.4. Found: C, 57.5; H, 8.6.

3-O-Allyl-2,1',3',4',6'-penta-O-benzyl-6-O-(4-methoxylbenzyl)sucrose (**12**). — A

solution of trifluoroacetic acid (156 μL) in *N,N*-dimethylformamide (1.2 mL) at 0° was added dropwise to a stirred solution containing **1** (200 mg), sodium cyanoborohydride (66 mg), and 3 Å molecular sieves in *N,N*-dimethylformamide (1.6 mL). The mixture was stirred for 16 h at room temperature, then filtered through Celite, and poured into ice-cold saturated aqueous sodium hydrogencarbonate. The aqueous phase was extracted with dichloromethane, and the combined extracts were washed with saturated aqueous sodium hydrogencarbonate, dried, filtered, and concentrated. Column chromatography (toluene–ethyl acetate, 6:1) of the residue yielded **12** (147 mg, 74%), $[\alpha]_D$ +30° (*c* 1.2, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 55.1 (CH_3O), 69.4, 70.2, 71.0, 71.2, 71.4, 72.0, 72.6, 72.9, 73.1, 73.2, 73.4, 74.0, 79.3, 79.6, 81.0, 82.4, 83.8 (C-1′,3′,4′,5′,6′,2,3,4,5,6 PhCH_2, CH_2=$CHCH_2$), 90.0 (C-1), 104.5 (C-2′), 113.7 ($CH_3OC_6H_4CH_2$), 116.8 (CH_2=CH), 127.6–130.1 (aromatic C), 135.3 (CH_2=CH 137.9, 138.2 (aromatic C-1), 159.1 (C-1 in *p*-methoxybenzyl).

Anal. Calc. for $C_{58}H_{64}O_{12}$: C, 73.1; H, 6.8. Found: C, 73.6; H, 7.0.

6-O-Decanoyl-3-O-isobutyryl-4-O-[(S)-2-methylbutyryl]sucrose (**18**). — Compound **12** (44 mg) was acylated with (*S*)-2-methylbutyric acid (8 μL), as described for **9**, to give 3-*O*-allyl-2,1′,3′,4′,6′-penta-*O*-benzyl-6-*O*-(4-methoxybenzyl)-4-*O*-[(*S*)-2-methylbutyryl]sucrose (**13**; 44 mg, 92%), $[\alpha]_D$ +36° (*c* 0.9, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 11.7 (CH_3CH_2), 16.4 (CH_3CH), 26.6 (CH_3CH_2CH), 41.2 (CH_3CH), 55.1 (CH_3O), 68.6, 69.3, 69.7, 71.3, 71.6, 72.4, 72.6, 72.9, 73.1, 73.2, 73.4, 73.7, 78.9, 79.3, 79.8, 82.6, 84.0 (C-1′,3′,4′,5′,6′,2,3,4,5,6, PhCH_2, CH_2=$CHCH_2$), 89.8 (C-1), 104.5 (C-2′), 113.6 ($CH_3OC_6H_4CH_2$), 116.3 (CH_2=CH), 127.6–130.0 (aromatic C), 135.0 (CH_2=CH), 138.0–138.3 (aromatic C-1), 159.1 (C-1 in *p*-methoxybenzyl), 175.2 (carbonyl C).

Compound **13** (314 mg) was deallylated, as described above for **3**, to give, after column chromatography (6:1 toluene–ethyl acetate), 2,1′,3′,4′,6′-penta-*O*-benzyl-6-*O*-(4-methoxybenzyl)-4-*O*-[(*S*)-2-methylbutyryl]sucrose (**14**, 290 mg) of ~90% purity. An analytical sample had $[\alpha]_D$ +44° (*c* 1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 11.6 (CH_3CH_2), 16.5 (CH_3CH), 26.6 (CH_3CH_2CH), 41.3 (CH_3CH), 55.1 (CH_3O), 68.2, 68.9, 70.4, 71.2, 71.5, 72.0, 72.6, 73.1, 73.2, 73.5, 78.9, 79.7, 82.2, 84.1 (C-1′,3′,4′,5′,6′,2,3,4,5,6, PhCH_2, CH_2=$CHCH_2$), 89.2 (C-1), 104.5 (C-2′), 113.7 ($CH_3OC_6H_4CH_2$); 127.6–130.0 (aromatic C), 137.8, 137.9, 138.2 (aromatic C-1), 159.1 (C-1 in *p*-methoxybenzyl), 176.0 (carbonyl C).

Compound **14** (174 mg) was acylated with isobutyryl chloride (55 μL), as described for **4**. Column chromatography (4:1 iso-octane–ethyl acetate) of the product gave 2,1′,3′,4′,6′-penta-*O*-benzyl-3-*O*-isobutyryl-6-*O*-(4-methoxybenzyl)-4-*O*-[(*S*)-2-methylbutyryl]sucrose (**15**; 172 mg, 92%), $[\alpha]_D$ +58° (*c* 0.8, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 11.6 (CH_3CH_2), 16.2 (CH_3CH), 18.9 [$(CH_3)_2CH$], 26.3 (CH_3CH_2CH), 34.0 [$(CH_3)_2CH$], 40.8 (CH_3CH), 55.1 (CH_3O), 67.9, 68.3, 68.8, 71.4, 71.7, 72.6, 73.1, 73.2, 73.4, 76.7, 79.8, 82.2, 84.1 (C-1′,3′,4′,5′,6′,2,3,4,5,6, PhCH_2), 89.3 (C-1), 104.6 (C-2′), 113.6 ($CH_3OC_6H_4CH_2$), 127.4–129.9 (aromatic C), 137.8–138.2 (aromatic C-1), 159.1 (C-1 in *p*-methoxybenzyl), 175.2, 176.1 (carbonyl C).

A solution of **15** (86 mg) and cerium(IV) ammonium nitrate (120 mg) in acetonitrile–water (9:1, 4 mL) was stirred for 1 h at room temperature, then diluted with

dichloromethane, and extracted with saturated aqueous sodium hydrogen carbonate. The organic phase was washed with water, dried, filtered, and concentrated. Column chromatography (toluene–ethyl acetate, 14:1) of the residue gave 2',1',3',4',6'-penta-*O*-benzyl-3-*O*-isobutyryl-4-*O*-[(*S*)-2-methylbutyryl]sucrose (**16**; 57 mg, 74%), $[\alpha]_D$ +61° (*c* 1.1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 11.6 (CH_3CH_2), 16.5 (CH_3CH), 18.9 [$(CH_3)_2CH$], 26.4 (CH_3CH_2CH), 34.0 [$(CH_3)_2CH$], 40.9 (CH_3CH), 61.0 (C-6), 68.7, 69.7, 69.9, 70.9, 71.4, 71.9, 72.7, 73.2, 73.3, 73.4, 76.5, 79.2, 80.6, 83.7 (C-1',3',4',5',6',2,3,4,5, $PhCH_2$), 88.5 (C-1), 104.3 (C-2'), 127.5–128.3 (aromatic C), 137.7, 138.0, 138.1 (aromatic C-1), 175.9, 176.6 (carbonyl C).

Decanoyl chloride (25 μL) was added to a solution of **16** (57 mg) in pyridine (0.5 mL). After stirring for 3 h, methanol was added and the mixture was concentrated. Column chromatography (6:1 iso-octane–ethyl acetate) of the residue yielded 2,1',3',4', 6'-penta-*O*-benzyl-6-*O*-decanoyl-3-*O*-isobutyryl-4-*O*-[(*S*)-2-methylbutyryl]sucrose (**17**; 56 mg, 85%), $[\alpha]_D$ +61° (*c* 1.2, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 11.5 (CH_3CH_2CH), 14.1 [$CH_3(CH_2)_8$], 16.3 (CH_3CH), 18.9 [$(CH_3)_2CH$], 22.6, 24.7, 26.3, 29.2, 29.3, 29.4, 31.9 [$CH_3(CH_2)_7CH_2$,CH_3CH_2CH], 34.0 [$(CH_3)_2CH$, CH_2CO], 40.8 (CH_3CH), 61.7 (C-6), 67.7, 67.8, 70.4, 71.5, 71.8, 72.6, 73.2, 73.4, 73.5, 79.4, 81.1, 83.9 (C-1',3',4',5',6',2,3,4,5, $PhCH_2$), 88.8 (C-1), 104.5 (C-2'), 127.4–129.9 (aromatic C), 137.8, 138.2 (aromatic C-1), 173.4, 175.1, 176.0 (carbonyl C).

Compound **17** (56 mg) was debenzylated, as described above for **10**, to give **18** (18 mg, 54%), $[\alpha]_D$ +71° (*c* 0.9, chloroform). N.m.r. data ($CDCl_3$–CD_3OD, 1:1): ^{13}C, δ 11.7 (CH_3CH_2CH), 14.2 [$CH_3(CH_2)_8$], 16.6 (CH_3CH), 19.1 [$(CH_3)_2CH$], 23.1, 25.2, 26.8, 29.6, 29.7, 29.9, 32.4 [$CH_3(CH_2)_7CH_2$,CH_3CH_2CH], 34.4, 34.6 [$(CH_3)_2CH$, CH_2CO], 41.5 (CH_3CH), 174.6, 176.0, 177.8, (carbonyl C); ^{1}H, δ 0.85–0.92 (6 H), 1.10 (d, 3 H, *J* 7.1 Hz), 1.14 (d, 3 H, *J* 7.1 Hz), 1.16 (d, 3 H, *J* 7.1 Hz), 1.23–1.75 (16 H), 2.26–2.41 (3 H), 2.57 [sep, *J* 7.1 Hz, $(CH_3)_2CH$], 3.70–3.80 (m, 2 H, H-3',4').

Anal. Calc. for $C_{31}H_{54}O_{14}\cdot H_2O$: C, 55.7; H, 8.4 Found: C, 55.6; H, 8.1.

6-O-Decanoyl-3,4-di-O-[(S)-2-methylbutyryl]sucrose (**23**). — The allyl group was removed from **12** (75 mg) as described above for **3**, to give, after column chromatography (6:1 toluene–ethyl acetate), 2,1',3',4',6'-penta-*O*-benzyl-6-*O*-(4-methoxybenzyl)-sucrose (**19**; 54 mg, 75%), $[\alpha]_D$ +38° (*c* 0.9, chloroform). ^{13}C-N.m.r. ($CDCl_3$): δ 55.1 (CH_3O), 69.3, 69.9, 71.0, 71.3, 71.4, 71.6, 72.6. 72.8, 73.1, 73.2, 73.4, 78.5, 79.4, 81.9, 83.8 (C-1',3',4',5',6',2,3,4,5,6, $PhCH_2$), 89.2 (C-1), 104.4 (C-2'), 113.7 ($CH_3OC_6H_4CH_2$), 127.5–130.1 (aromatic C), 137.9, 138.1, 138.1 (aromatic C-1), 159.2 (C-1 in *p*-methoxybenzyl).

Compound **19** (54 mg) was acylated with (*S*)-2-methylbutyric acid (14 μL), as described above for **9**, to yield, after column chromatography (iso-octane–ethyl acetate, 3:1), 2,1',3',4',6'-penta-*O*-benzyl-6-*O*-(4-methoxybenzyl)-3,4-di-*O*-[(*S*)-2-methylbutyryl]-sucrose (**20**; 58 mg, 90%), $[\alpha]_D$ +58° (*c* 1.2, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 11.5, 11.6 (2 CH_3CH_2), 16.0, 16.4 (2 CH_3CH), 26.3, 26.4, (2 CH_3CH_2CH), 40.8, 40.9 (2 *C*HCO), 55.1 (CH_3O), 67.9, 68.4, 68.8, 71.3, 71.4, 71.6, 71.6, 72.6, 73.1, 73.2, 73.4, 79.8, 82.1, 84.1 (C-1',3',4',5',6',2,3,4,5,6, $PhCH_2$), 89.2 (C-1), 104.6 (C-2'), 113.6 ($CH_3OC_6H_4CH_2$), 127.4–129.9 (aromatic C), 137.8–138.3 (aromatic C-1), 159.1 (C-1 in *p*-methoxybenzyl), 175.2, 175.7 (carbonyl C).

The 4-methoxybenzyl group was removed from **20** (55 mg), as described above for **15**, to give 2,1′,3′,4′,6′-penta-*O*-benzyl-3,4-di-*O*-[(S)-2-methylbutyryl]sucrose (**21**; 39 mg, 80%), $[\alpha]_D$ +61° (c 0.8 chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 11.6 (CH_3CH_2), 16.2, 16.4 (2 CH_3CH), 26.4, 26.5 (2 CH_3CH_2), 40.9, 41.0 (2 *C*HCO), 61.1 (C-6), 68.9, 69.8, 69.9, 70.9, 71.3, 72.0, 72.7, 73.3, 73.4, 73.5, 76.6, 79.2, 80.6, 83.8 (C-1′,3′,4′,5′,6′,2,3,4,5, PhCH_2), 88.5 (C-1), 104.4 (C-2′), 127.5–128.4 (aromatic C), 137.7–138.1 (aromatic C-1), 175.6, 176.6 (carbonyl C).

Compound **21** (39 mg) was acylated, as described above for **16**, to yield, after column chromatography (14:1 toluene–ethyl acetate), 2,1′,3′,4′,6′-penta-*O*-benzyl-6-*O*-decanoyl-3,4-di-*O*-[(*S*)-2-methylbutyryl]sucrose (**22**; 41 mg, 90%), $[\alpha]_D$ +54° (*c* 0.8 chloroform). ^{13}C-N.m.r. data ($CDCl_3$):δ 11.5, 11.6 (2 CH_3CH_2), 14.1 [$CH_3(CH_2)_8$], 16.1, 16.3 (2 CH_3CH), 22.7, 24.8, 26.3, 26.5, 29.2, 29.3, 29.5, 31.9 [$CH_3(CH_2)_7CH_2$, CH_3CH_2CH], 34.0 (CH_2CO), 40.8, 40.9 (2 *C*HCO), 61.7 (C-6), 67.7, 67.9, 70.3, 71.4, 71.8, 72.7, 73.2, 73.5, 73.5, 76.6, 79.4, 81.0, 84.0 (C-1′,3′,4′,5′,6′,2,3,4,5, PhCH_2), 88.7 (C-1), 104.5 (C-2′), 127.5–128.4 (aromatic C), 137.8, 137.9, 138.2 (aromatic C-1), 173.4, 175.1, 175.7 (carbonyl C).

Compound **22** (22.6 mg) was hydrogenolyzed, as described above for **10**, to give **23** (10.4 mg, 77%), $[\alpha]_D$ +75° (*c* 1, chloroform), after column chromatography (9:1 chloroform–methanol). N.m.r. data ($CDCl_3$–CD_3OD, 1:1): ^{13}C, δ 11.6, 11.7 (2 CH_3CH_2), 14.2 [$CH_3(CH_2)_8$], 16.6 (CH_3CH), 23.1, 25.2, 26.8, 27.1, 29.6, 29.8, 29.9, 32.4 [$CH_3(CH_2)_7CH_2$,CH_3CH_2CH], 34.4 (CH_2CO), 41.5 (*C*HCO), 174.7, 176.1, 177.4 (carbonyl C); ^{1}H, δ 0.85–0.96 (9 H), 1.09 (d, 3 H, *J* 7.1 Hz), 1.12 (d, 3 H, *J* 7.1 Hz), 1.25–1.77 (18 H), 2.27–2.44 (4 H), 3.68–3.80 (m, 2 H, H-6′,6′).

Anal. Calc. for $C_{32}H_{56}O_{14}$: C, 57.8; H, 8.5. Found: C, 58.0; H, 8.2.

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