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PARTIALLY ESTERIFIED SUCROSE DERIVATIVES: SYNTHESIS OF 6-*O*-ACETYL-2,3,4-TRI-*O*-[(*S*)-3-METHYLPENTANOYL]SUCROSE, A NATURALLY OCCURRING FLAVOUR PRECURSOR OF TOBACCO

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ABSTRACT

Sucrose esters, *O*-acylated in the glucopyranosyl group, occur as flavour precursors in various tobaccos. In order to obtain such esters, a sucrose derivative, namely, 6-*O*-acetyl-3-*O*-allyl-1′,3′,4′,6′-tetra-*O*-benzyl-2-*O*-(4-methoxybenzyl)sucrose was synthesised with a substitution pattern which allows the preparation of derivatives having other acyl groups at positions 2, 3, or 4. The title compound was prepared from this derivative and shown to be identical to a naturally occurring sucrose ester.

INTRODUCTION

Sucrose esters, which occur as flavour precursors in various tobaccos[1], contain a 6-*O*-acetylglucosyl group with various fatty acid residues in the secondary positions. In order to assign unambiguously the structures of these natural products, a number of sucrose esters are being made which will be compared to those isolated from tobacco[1,2]. A sucrose derivative was therefore needed carrying persistent blocking groups in the fructose moiety, a 6-*O*-acetyl group, and a substitution pattern in the glucose moiety that allows sequential regioselective introduction of various acyl groups.

RESULTS AND DISCUSSION

3,3′,4′,6′-Tetra-*O*-acetyl-2,1′:4,6-di-*O*-isopropylidenesucrose[4] was partially *O*-deacetylated by treatment with methanolic sodium methoxide to yield the 3-*O*-acetylated derivative **1**[5], which was treated with benzyl bromide and silver oxide[6] in *N*,*N*-dimethylformamide to give the 3′,4′,6′-tri-*O*-benzyl derivative **2**.

The 3-*O*-acetyl group in **2** was exchanged for an allyl group by first *O*-deacetylating **2** and then allylating the product to obtain **3**. Hydrolysis of **3** gave 3-*O*-allyl-3′,4′,6′-tri-*O*-benzylsucrose (**4**) which was converted into the 4,6-*O*-(4-methoxybenzylidene) acetal **5**. Partial phase-transfer alkylation of **5** with 4-

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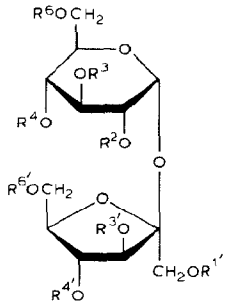
methoxybenzyl bromide gave **6** with preferential 2-substitution, probably due to HO-2 being more acidic than HO-1′. The position of the 4-methoxybenzyl group was determined by ^{13}C-n.m.r. spectroscopy since the signal of the non-alkylated C-1′ was recognised easily at 63–64 p.p.m. Alkylation of HO-1′ in **6** gives the expected downfield shift, and moves the C-1′ signal to the region for secondary ring carbons. Compound **6** does not show this downfield shift of the signal for C-1′, but its regioisomer (and also **7**, see below) does. The 1′-position was then benzylated to give the fully substituted derivative **7**, which was hydrolysed with acid to give **8** with HO-4,6 unsubstituted. Compound **8** was converted into the 4,6-methoxy-

TABLE I

^{13}C-N.M.R. CHEMICAL SHIFT DATA AND ASSIGNMENTS FOR THE RING CARBONS OF **13**

Compound	*Carbon atom*											
	1	*2*	*3*	*4*	*5*	*6*	*1′*	*2′*	*3′*	*4′*	*5′*	*6′*
13[a]	89.2	70.5	69.3	67.7	68.7	61.6	64.5	104.7	78.4	73.6	82.1	60.7
13[b]	89.2	70.6	69.2	67.7	68.9	61.6	64.8	104.8	78.8	73.7	82.0	60.5
13[c]	89.3	70.6	69.4	68.0	68.6	61.8	63.0	104.3	77.8	74.1	82.2	61.4

[a]Synthetic product. [b]Ref. 2. [c]Ref. 1.



1 R^3 = Ac, $R^{1'}$, R^2 = R^4, R^6 = $(CH_3)_2C$, $R^{3'}$ = $R^{4'}$ = $R^{6'}$ = H

2 R^3 = Ac, $R^{1'}$, R^2 = R^4, R^6 = $(CH_3)_2C$, $R^{3'}$ = $R^{4'}$ = $R^{6'}$ = Bzl

3 R^3 = CH_2=$CHCH_2$, $R^{1'}$, R^2 = R^4, R^6 = $(CH_3)_2C$, $R^{3'}$ = $R^{4'}$ = $R^{6'}$ = Bzl

4 $R^{1'}$ = R^2 = R^4 = R^6 = H, R^3 = CH_2=$CHCH_2$, $R^{3'}$ = $R^{4'}$ = $R^{6'}$ = Bzl

5 $R^{1'}$ = R^2 = H, R^3 = CH_2=$CHCH_2$, R^4, R^6 = *p*-$MeOC_6H_4CH$, $R^{3'}$ = $R^{4'}$ = $R^{6'}$ = Bzl

6 $R^{1'}$ = H, R^2 = *p*-$MeOC_6H_4CH_2$, R^3 = CH_2=$CHCH_2$, R^4, R^6 = *p*-$MeOC_6H_4CH$, $R^{3'}$ = $R^{4'}$ = $R^{6'}$ = Bzl

7 R^2 = *p*-$MeOC_6H_4CH_2$, R^3 = CH_2=$CHCH_2$, R^4, R^6 = *p*-$MeOC_6H_4CH$, $R^{1'}$ = $R^{3'}$ = $R^{4'}$ = $R^{6'}$ = Bzl

8 R^4 = R^6 = H, R^2 = *p*-$MeOC_6H_4CH_2$, R^3 = CH_2=$CHCH_2$, $R^{1'}$ = $R^{3'}$ = $R^{4'}$ = $R^{6'}$ = Bzl

9 R^4 = H, R^2 = *p*-$MeOC_6H_4CH_2$, R^3 = CH_2=$CHCH_2$, R^6 = Ac, $R^{1'}$ = $R^{3'}$ = $R^{4'}$ = $R^{6'}$ = Bzl

10 R^3 = R^4 = H, R^2 = *p*-$MeOC_6H_4CH_2$, R^6 = Ac, $R^{1'}$ = $R^{3'}$ = $R^{4'}$ = $R^{6'}$ = Bzl

11 R^2 = R^3 = R^4 = H, R^6 = Ac, $R^{1'}$ = $R^{3'}$ = $R^{4'}$ = $R^{6'}$ = Bzl

12 R^2 = R^3 = R^4 = $CH_3CH_2CH(CH_3)CH_2CO$, R^6 = Ac, $R^{1'}$ = $R^{3'}$ = $R^{4'}$ = $R^{6'}$ = Bzl

13 R^2 = R^3 = R^4 = $CH_3CH_2CH(CH_3)CH_2CO$, R^6 = Ac, $R^{1'}$ = $R^{3'}$ = $R^{4'}$ = $R^{6'}$ = H

14 R^2 = R^3 = R^4 = $CH_3CH_2CH(CH_3)CH_2CO$, R^6 = $R^{1'}$ = $R^{3'}$ = $R^{4'}$ = $R^{6'}$ = Ac

ethylidene derivative which was then treated under mildly acidic conditions to give a mixture of the 4- and 6-acetates. The mixture was treated under conditions for acyl migration with aqueous pyridine to give 6-*O*-acetyl-3-*O*-allyl-1′,3′,4′,6′-tetra-*O*-benzyl-2-*O*-(4-methoxybenzyl)sucrose (**9**) in good overall yield. This compound is a key intermediate for the synthesis of sucrose esters with varying substituent patterns in the 2-, 3-, and 4-positions.

In order to make the title compound, the 2- and 3-substituents of **9** were removed. The allyl group was removed by isomerisation into the 1-propenyl group with tris(triphenyl)rhodium(I) chloride, followed by mild acid treatment to give **10**. The 4-methoxybenzyl group of **10** was then removed by mild oxidation with cerium(IV)ammonium nitrate. Acylation of the product (**11**) with (*S*)-3-methylpentanoyl chloride then gave **12**, catalytic hydrogenolysis of which gave the title compound **13**. The ^{13}C-n.m.r. spectrum of **13** showed slight discrepancies in comparison with that published for the natural product[1,2] especially in the fructose moiety (see Table I) probably due to solubility problems of amphotheric **13** in chloroform. Acetylation of **13** gave the penta-acetate **14**, which was indistinguishable from the acetylated natural product[2].

EXPERIMENTAL

General methods. — These were the same as those previously reported[3], except that the ^{13}C-n.m.r. spectra for **12–14** were obtained with a JEOL GSX 270 spectrometer. Column chromatography was performed on silica gel (0.035–0.070, Amicon; and 0.040–0.063, Merck).

3-O-Acetyl-2,1′:4,6-di-O-isopropylidenesucrose (**1**). — A solution of 3,3′,4′,6′-tetra-*O*-acetyl-2,1′:4,6-di-*O*-isopropylidenesucrose[4] (12.9 g) in methanol (200 mL) was treated at room temperature with sodium methoxide (from 40 mg of sodium metal added to 100 mL of methanol). After ~75 min (t.l.c., chloroform–methanol 5:1), the solution was neutralised with Dowex 50 (H^+) resin. Filtration, concentration, and column chromatography (1:24 toluene–acetone) of the residue then gave **1** (6.9 g, 69%), $[\alpha]_D$ +29° (*c* 0.8, chloroform); lit.[5] $[\alpha]_D$ +28° (chloroform).

3-O-Allyl-3′,4′,6′-tri-O-benzyl-2,1′:4,6-di-O-isopropylidenesucrose (**3**). — Benzyl bromide (15 mL) was added to a solution of **1** (3.0 g) in *N,N*-dimethylformamide followed by silver oxide (20 g) during 1 h at room temperature with stirring. After 16 h, the mixture was filtered, diluted with toluene–ether (9:1), and washed with water, aqueous sodium thiosulfate, and water. Drying (Na_2SO_4), filtering, concentration, and column chromatography (9:1 toluene–ethyl acetate) of the residue then gave 3-*O*-acetyl-3′,4′,6′-tri-*O*-benzyl-2,1′:4,6-di-*O*-isopropylidenesucrose (**2**; 4.3 g, 91%), $[\alpha]_D$ +19° (*c* 1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 21.0 (CH_3CO), 19.0, 23.9, 25.4, 29.0 [$(CH_3)_2CH$], 62.2, 63.6, 65.1, 66.5, 70.9, 71.6, 71.9, 72.1, 72.5, 72.9, 73.3, 80.6, 85.7 (C-2,3,4,5,6,1′,3′,4′,5′,6′ and PhCH_2), 91.1 (C-1), 99.6, 101.1 [$(CH_3)_2CH$], 104.1 (C-2′), 126.9–129.0 (aromatic C), 137.8, 138.0, 138.1 (Ph C-1), 169.9 (carbonyl C).

A solution of **2** (4.2 g) in methanol (50 mL) was treated with sodium methoxide (catalytic amount) overnight at room temperature and then concentrated, and sodium hydride (300 mg) was added to a solution of the product in *N,N*-dimethylformamide (10 mL). After 15 min at room temperature, allyl bromide (1.0 mL) in *N,N*-dimethylformamide was added with stirring. After 2 h, methanol (10 mL) was added and the mixture was concentrated. Column chromatography (12:1 toluene–ethyl acetate) of the residue gave **3** (3.7 g, 89%), $[\alpha]_D$ +6° (*c* 1.7, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 19.1, 23.9, 25.5, 29.2 [$(CH_3)_2CH$], 62.4, 63.5, 66.5, 72.5, 73.4, 73.7, 74.0, 77.5, 80.7, 85.8 (C-2,3,4,5,6,1′,3′,4′,5′,6′, PhCH_2 and CH_2=CH–CH_2, overlap), 91.2 (C-1), 99.3, 101.1 [$(CH_3)_2CH$], 104.0 (C-2′), 115.7 (CH_2=CH–CH_2), 127.7–129.0 (aromatic C), 135.9 (CH_2=CH–CH_2), 138.2 (Ph C-1, overlap).

Anal. Calc. for $C_{42}H_{52}O_{11}$: C, 68.9; H, 7.1. Found: C, 69.0; H, 7.0.

3-O-Allyl-3′,4′,6′-tri-O-benzylsucrose (**4**). — Compound **3** (3.9 g) was treated with aqueous 60% acetic acid (30 mL) for 45 min at 50° (t.l.c., 5:1 chloroform–methanol). The hydrolysate was concentrated and column chromatography (1:2 toluene–ethyl acetate) of the residue gave **4** (2.9 g, 83%), $[\alpha]_D$ +33° (*c* 0.8, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 61.9 (C-6), 64.4 (C-1′), 70.1, 70.5, 70.7, 72.1, 72.3, 72.9, 73.2, 73.9, 80.2, 81.9, 83.6, 85.6 (C-2,3,4,5,3′,4′,5′,6′, PhCH_2 and CH_2=CH–CH_2), 92.1 (C-1), 105.7 (C-2′), 117.2 (CH_2=CH–CH_2), 127.7–128.4 (aromatic C), 135.2 (CH_2=CH–CH_2), 137.8, 137.9, 138.1 (Ph C-1).

Anal. Calc. for $C_{36}H_{44}O_{11}$: C, 66.3; H, 6.7. Found: C, 65.5; H, 6.8.

3-O-Allyl-3′,4′,6′-tri-O-benzyl-4,6-O-(4-methoxybenzylidene)sucrose (**5**). — A solution of **4** (3.4 g) in *N,N*-dimethylformamide was stirred with 4-methoxybenzaldehyde dimethyl acetal (1.1 g, 1.1 equiv.) and toluene-4-sulfonic acid monohydrate (60 mg) for 5 min, then concentrated, and neutralised with triethylamine. After two co-concentrations with toluene, column chromatography (3:1 toluene–ethyl acetate) of the residue gave **5** (3.6 g, 86%), which crystallised from toluene–light petroleum (b.p. 40–60°) and had m.p. 98–99°, $[\alpha]_D$ +32° (*c* 0.8, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 55.3 (CH_3O), 63.6 (C-6), 64.6 (C-1′), 69.0, 70.7, 72.1, 72.4, 73.1, 73.5, 73.8, 80.7, 82.2, 84.0, 86.0 (C-2,3,4,5,3′,4′,5′,6′, PhCH_2 and CH_2=CH–CH_2, overlap), 92.2 (C-1), 101.4 (MeOPhCH), 106.1 (C-2′), 113.7 (MeOPh C-3,5), 117.3 (CH_2=CH–CH_2), 127.6–130.3 (aromatic C), 135.2 (CH_2=CH–CH_2), 138.0, 138.2, 138.5 (Ph C-1), 160.2 (MeOPh C-4).

Anal. Calc. for $C_{44}H_{50}O_{12}$: C, 68.9; H, 6.7. Found: C, 68.9; H, 6.6.

3-O-Allyl-3′,4′,6′-tri-O-benzyl-2-O-(4-methoxybenzyl)-4,6-O-(4-methoxybenzylidene)sucrose (**6**). — Aqueous sodium hydroxide (5%, 4 mL) was added with stirring at room temperature to a solution of **5** (0.95 g) in dichloromethane (20 mL) containing 2,4,6-trimethylpyridine (150 μL), 4-methoxybenzyl bromide (300 μL), and tetrabutylammonium hydrogen sulfate (100 mg). After 20 h, the organic phase was separated, basified with triethylamine, and concentrated. Column chromatography [first with 4:1:1 light petroleum (b.p. 40–60°)–chloroform–ethyl acetate to separate regioisomers, then with 3:1 toluene–ethyl acetate to remove 2,4,6-tri-

methylpyridine and 4-methoxybenzyl alcohol] of the residue gave **6** (0.89 g, 73%), $[\alpha]_D$ −8° (*c* 1.3, chloroform), and also 3-*O*-allyl-3′,4′,6′-tri-*O*-benzyl-1′-*O*-(4-methoxybenzyl)-4,6-*O*-(4-methoxybenzylidene)sucrose (0.2 g, 17%), $[\alpha]_D$ +30° (*c* 1.3, chloroform). ^{13}C-N.m.r. data ($CDCl_3$) for **6**: δ 55.1 (CH_3O, overlap), 63.2 (C-6), 64.4 (C-1′), 68.8, 70.5, 72.1, 72.9, 73.3, 73.9, 74.5, 77.8, 78.6, 80.6, 82.4, 84.0, 86.1 (C-2,3,4,5,3′,4′,5′,6′, PhCH_2, MeOPhCH_2, and CH_2=CH–CH_2), 91.3 (C-1), 101.3 (MeOPh*C*H), 106.2 (C-2′), 113.6, 114.0 (MeOPh C-3,5), 116.7 (*C*H_2=CH–CH_2), 127.5–130.4 (aromatic C), 135.2 (CH_2=*C*H–CH_2), 137.9, 138.1, 138.5 (Ph C-1), 159.8, 160.1 (MeOPh C-4).

The ^{13}C-n.m.r. spectrum of the regioisomer showed a downfield shift of the C-1′ signal due to alkylation, thereby confirming the identity of the two regioisomers.

Anal. Calc. for $C_{52}H_{56}O_{13}$: C, 70.3; H, 6.3. Found: C, 70.0; H, 6.4.

3-O-Allyl-1′,3′,4′,6′-tetra-O-benzyl-2-O-(4-methoxybenzyl)-4,6-O-(4-methoxybenzylidene)sucrose (**7**). — Sodium hydride (100 mg) was added to a solution of **6** (0.78 g) in *N*,*N*-dimethylformamide at room temperature. After 15 min, benzyl bromide (0.3 mL) in *N*,*N*-dimethylformamide was added, and, after 1 h at room temperature, methanol (5 mL) was added dropwise. Concentration and column chromatography [4:1:1 light petroleum (b.p. 40–60°)–chloroform–ethyl acetate] of the residue gave **7** (0.75 g, 87%), $[\alpha]_D$ +34° (*c* 1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 55.1 (CH_3O, overlap), 62.7 (C-6), 68.8, 70.8, 71.5, 72.9, 73.1, 73.3, 73.7, 78.2, 78.7, 79.4, 81.5, 82.1, 83.7 (C-2,3,4,5,1′,3′,4′,5′,6′, PhCH_2, MeOPhCH_2, and CH_2=CH–CH_2, overlap), 90.6 (C-1), 101.1 (MeOPh*C*H), 104.5 (C-2′), 113.6 (MeOPh C-3,5, overlap), 116.1 (*C*H_2=CH–CH_2), 127.5–130.4 (aromatic C), 135.5 (CH_2=*C*H–CH_2), 138.0, 138.1 (Ph C-1, overlap), 159.1, 159.9 (MeOPh C-4).

Anal. Calc. for $C_{59}H_{64}O_{13}$: C, 72.2; H, 6.5. Found: C, 72.3; H, 6.7.

3-O-Allyl-1′,3′,4′,6′-tetra-O-benzyl-2-O-(4-methoxybenzyl)sucrose (**8**). — Aqueous acetic acid (80%, 2 mL) was added to a solution of **7** (0.60 g) in acetonitrile (1 mL). After 3 h at room temperature, the solution was concentrated and column chromatography (2:1 toluene–ethyl acetate) of the residue gave **8** (0.49 g, 93%), $[\alpha]_D$ +40° (*c* 0.7 chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 55.1 (CH_3O), 62.4 (C-6), 70.3, 71.6, 72.6, 73.0, 73.2, 73.4, 74.0, 79.2, 81.1, 81.3, 83.6 (C-2,3,4,5,1′,3′,4′,5′,6′, PhCH_2, MeOPhCH_2, and CH_2=CH–CH_2, overlap), 89.6 (C-1), 104.6 (C-2′), 113.7 (MeOPh C-3,5), 116.5 (*C*H_2=CH–CH_2), 127.6–130.5 (aromatic C), 135.5 (CH_2=*C*H–CH_2), 138.0, 138.1, 138.2 (Ph C-1, overlap), 159.2 (MeOPh C-4).

Anal. Calc. for $C_{51}H_{58}O_{12}$: C, 71.0; H, 6.7. Found: C, 71.1; H, 6.7.

6-O-Acetyl-3-O-allyl-1′,3′,4′,6′-tetra-O-benzyl-2-O-(4-methoxybenzyl)sucrose (**9**). — Trimethyl orthoacetate (0.15 mL) and toluene-4-sulfonic acid monohydrate (catalytic amount) were added with stirring to a solution of **8** (0.43 g) in acetonitrile (5 mL). After 5 min at room temperature, the solution was concentrated, aqueous trifluoroacetic acid (90%, 0.1 mL) was added to a solution of the residue in acetonitrile, and, after 5 min, the solution was concentrated. A solution of the

residue in dichloromethane was washed twice with aqueous sodium hydrogencarbonate, dried (Na_2SO_4), and concentrated. The residue was dissolved in pyridine (5 mL) and water (4 mL). After 3 days, the solution was concentrated and co-concentrated twice with toluene. Column chromatography (9:1 toluene–ethyl acetate) of the residue gave **9** (0.34 g, 76%), $[\alpha]_D$ +29° (*c* 1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 20.9 (CH_3CO), 55.1 (CH_3O), 63.4 (C-6), 69.9, 70.9, 72.0, 72.6, 73.2, 73.3, 74.2, 79.4, 79.6, 80.9, 82.0, 84.0 (C-2,3,4,5,1',3',4',5',6', $PhCH_2$, $MeOPhCH_2$, and CH_2=CH–CH_2, overlap), 90.0 (C-1), 104.8 (C-2'), 113.8 (MeOPh C-3,5), 116.8 (CH_2=CH–CH_2), 127.7–130.0 (aromatic C), 135.4 (CH_2=CH–CH_2), 138.3 (Ph C-1, overlap), 159.4 (MeOPh C-4), 171.3 (CH_3CO).

Anal. Calc. for $C_{53}H_{60}O_{13}$: C, 70.4, H, 6.6. Found: C, 69.8; H, 6.7.

The structure of **9** was confirmed as follows: **11** (below) was methylated with methyl triflate[7,8] to give a product containing one OAc (δ 2.01, s, 3 H) and 3 OMe (δ 3.28, 3.47, and 3.57, 3 s, each 3 H). The sucrose derivative was hydrolysed, reduced, and acetylated. G.l.c.[9,10] of the products revealed 1,5,6-tri-*O*-acetyl-2,3,4-tri-*O*-methylglucitol by comparison with an authentic standard.

6-O-Acetyl-1',3',4',6'-tetra-O-benzyl-2-O-(4-methoxybenzyl)sucrose (**10**). — A solution of **9** (250 mg) and tris(triphenyl)rhodium(I) chloride (100 mg) in 6:3:1 ethanol–toluene–water (20 mL) was boiled under reflux for 3 h and then cooled to room temperature. Mercury(II) bromide (200 mg) was added, and the mixture was stirred for 3 h, then filtered, and concentrated. Column chromatography (3:1 toluene–ethyl acetate) of the residue gave **10** (199 mg, 82%), $[\alpha]_D$ +37° (*c* 0.9, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 20.8 (CH_3CO), 55.2 (CH_3O), 63.2 (C-6), 69.7, 70.4, 71.2, 71.5, 72.6, 73.2, 73.4, 78.4, 79.2, 81.3, 83.7 (C-2,3,4,5,-1',3',4',5',6', $PhCH_2$ and $MeOPhCH_2$, overlap), 89.1 (C-1), 104.4 (C-2'), 113.8 (MeOPh C-3,5), 127.5–129.8 (aromatic C), 137.9, 138.1 (Ph C-1, overlap), 159.3 (MeOPh C-4), 171.4 (CH_3CO).

Anal. Calc. for $C_{50}H_{56}O_{13}$: C, 69.4; H, 6.5. Found: C, 69.3; H, 6.7.

6-O-Acetyl-1',3',4',6'-tetra-O-benzylsucrose (**11**). — Cerium(IV) ammonium nitrate (200 mg) was added to a solution of **10** (150 mg) in 9:1 acetonitrile–water (10 mL). The mixture was stirred for 40 min, then diluted with dichloromethane, washed with aqueous sodium hydrogencarbonate and water, dried (Na_2SO_4), filtered, and concentrated. Column chromatography (1:2 toluene–ethyl acetate) of the residue gave **11** (123 mg, 95%), $[\alpha]_D$ +16° (*c* 1.2, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 20.8 (CH_3CO), 63.3 (C-6), 69.6, 70.0, 70.4, 71.4, 72.1, 72.4, 73.0, 73.2, 73.6, 74.6, 79.7, 82.9, 84.9 (C-2,3,4,5,1',3',4',5',6', $PhCH_2$), 92.4 (C-1), 104.5 (C-2'), 127.7–128.3 (aromatic C), 137.0, 137.7, 137.9 (Ph C-1, overlap), 171.4 (CH_3CO).

Anal. Calc. for $C_{42}H_{48}O_{12}$: C, 67.7; H, 6.5. Found: C, 67.4; H, 6.6.

6-O-Acetyl-1',3',4',6'-tetra-O-benzyl-2,3,4-tri-O-[(S)-3-methylpentanoyl]sucrose (**12**). — A solution of (*S*)-3-methylpentanoic acid (130 mg), prepared *via* a Grignard reaction on the bromide with carbon dioxide[11], and thionyl chloride (0.075 mL) in dichloromethane (1 mL) was stirred for 1 h. A solution of **11** (90 mg)

in pyridine (2 mL) was added dropwise, the mixture was stirred for 2 h, a few drops of methanol were added, and the mixture was concentrated. Column chromatography (4:1 iso-octane–ethyl acetate) of the residue gave **12** (104 mg, 82%), $[\alpha]_D$ +49° (*c* 0.5, chloroform). ^{13}C-n.m.r. data ($CDCl_3$): δ 11.1, 11.3 [$CH_3CH_2CH(CH_3)CH_2CO$, overlap], 19.1, 19.2, 19.2 [$CH_3CH_2CH(CH_3)CH_2CO$], 20.7 (CH_3CO), 29.2 [$CH_3CH_2CH(CH_3)CH_2CO$, overlap], 31.5, 31.5, 31.7 [$CH_3CH_2CH(CH_3)CH_2CO$], 41.1, 41.2 [$CH_3CH_2CH(CH_3)CH_2CO$, overlap], 61.7 (C-6), 67.7, 67.9, 69.8, 70.3, 70.3, 71.5, 72.7, 73.3, 73.5, 73.7, 79.4, 81.5, 83.7 (C-2,3,4,5,1′,3′,4′,5′,6′, $PhCH_2$), 88.9 (C-1), 104.5 (C-2′), 127.5–128.4 (aromatic C), 137.9, 137.9, 138.1, 138.3 (Ph C-1), 170.6, 171.8, 172.1, 172.2 (carbonyl C).

Anal. Calc. for $C_{60}H_{78}O_{15}$: C, 69.4; H, 7.5. Found: C, 69.4; H, 7.8.

*6-O-Acetyl-2,3,4-tri-*O-[(S)-*3-methylpentanoyl]sucrose* (**13**). — A solution of **12** (37 mg) in ethanol (2 mL) was hydrogenolysed over 10% Pd/C in a Parr apparatus for two days. Filtration, concentration, and column chromatography (1:3 toluene–ethyl acetate) of the residue gave **13** (13 mg, 54%), $[\alpha]_D$ +70° (*c* 0.4, ethanol). ^{13}C-N.m.r. data ($CDCl_3$): δ 11.2 [$CH_3CH_2CH(CH_3)CH_2CO$, overlap], 19.2 [$CH_3CH_2CH(CH_3)CH_2CO$, overlap], 20.7 (CH_3CO), 29.1, 29.2 [$CH_3CH_2CH(CH_3)CH_2CO$, overlap], 31.5 [$CH_3CH_2CH(CH_3)CH_2CO$, overlap], 40.9, 40.9, 41.1 [$CH_3CH_2CH(CH_3)CH_2CO$], 60.7, 61.6, 64.5 (C-6,1′,6′), 67.7, 68.7, 69.3, 70.5, 73.6, 78.4, 82.1 (C-2,3,4,5,3′,4′,5′), 89.2 (C-1), 104.7 (C-2′), 170.8, 171.8, 172.7, 173.0 (carbonyl C).

Anal. Calc. for $C_{32}H_{54}O_{15}$: C, 56.6; H, 8.0. Found: C, 56.4; H, 8.0.

*6,1′,3′,4′,6′-Penta-*O-*acetyl-2,3,4-tri-*O-[(S)-*3-methoxypentanoyl]sucrose* (**14**). — Compound **13** (8 mg) was treated with acetic anhydride–pyridine conventionally to give, after work-up, **14** (9 mg, 91%), $[\alpha]_D$ +53° (*c* 0.4, ethanol; lit.[2] $[\alpha]_D$ +46° (ethanol). ^{13}C-N.m.r. data ($CDCl_3$): δ 11.2 [$CH_3CH_2CH(CH_3)CH_2CO$, overlap], 19.2 [$CH_3CH_2CH(CH_3)CH_2CO$, overlap], 20.7 (CH_3CO, overlap), 29.2 [$CH_3CH_2CH(CH_3)CH_2CO$, overlap], 31.5 [$CH_3CH_2CH(CH_3)CH_2CO$ overlap], 40.8, 41.0, 41.1 [$CH_3CH_2CH(CH_3)CH_2CO$], 61.8, 63.1, 63.4 (C-6,1′,6′), 67.8, 68.7, 69.0, 70.2, 74.6, 75.4, 79.0 (C-2,3,4,5,3′,4′,5′), 89.8 (C-1), 103.8 (C-2′), 169.7, 169.9, 170.0, 170.5, 170.7, 171.7, 172.1, 172.4 (carbonyl C).

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