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Synthesis and reactions of leucrose and its exocyclic glycal*

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ABSTRACT

5-*O*-α-D-Glucopyranosyl-β-D-fructopyranose (leucrose, **1**) was transformed into 3,4-di-*O*-acetyl-1-*O*-methanesulfonyl-5-*O*-(2,3,4-tri-*O*-acetyl-6-*O*-methanesulfonyl-α-D-glucopyranosyl)-β-D-fructopyranosyl bromide (**3**) and 1,3,4-tri-*O*-benzoyl-5-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-β-D-fructopyranosyl bromide (**8**), which were converted into derivatives (**8** and **9**) of 2,6-anhydro-1-deoxy-5-*O*-α-D-glucopyranosyl-D-*arabino*-hex-1-enitol. Hydrogenation of **8** and **9** gave the corresponding anhydroalditol derivatives. *N*-Iodosuccinimide-mediated glycosylation of **9** with 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose gave 1,2,3,4-tetra-*O*-acetyl-6-*O*-[3,4-di-*O*-benzoyl-1-deoxy-1-iodo-5-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-β-D-fructopyranosyl]-β-D-glucopyranose (**12**). Some amino, acetylated, and isopropylidene derivatives of leucrose have been prepared and characterised.

INTRODUCTION

Following its biotechnological preparation[1], leucrose (**1**, 5-*O*-α-D-glucopyranosyl-β-D-fructopyranose) has become of interest as a non-cariogenic, fully digestable sweetening agent, and chemical modifications have been described[2]. Owing to the (1→5) linkage, the fructose residue can adopt only the pyranose or acyclic forms.

Unsaturated carbohydrate derivatives are attractive intermediates for the synthesis of deoxy and allylic-substituted glycosides. The potential in synthesis of glycals derived from aldoses has been discussed[3] but those from keto sugars have been studied little. The *N*-iodosuccinimide-mediated glycosylation procedure[4] has been applied to an α-ketogluconic acid in work related to *N*-acetylneuraminic acid[5] and some corresponding model compounds[6], but not hitherto to 1,2-unsaturated derivatives of ketoses. We now report the synthesis of exocyclic vinyl ethers (glycals) of leucrose and some reactions thereof.

On heating, the leucrose in foods is assumed to undergo Maillard reactions[7] with amines and generate aroma components as well as brown melanoids which determine smell and taste. Glycosylamines are precursors for Amadori and Heyns rearrangements, and their formation from leucrose has been studied. Various esters and cyclic acetals of leucrose are reported also.

* Dedicated to Professor Leslie Hough in the year of his 65th birthday.

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RESULTS AND DISCUSSION

1,2-Unsaturated ketoses[8,9] and acyclic sugar derivatives or hexopyranosides[10] with isolated double bonds in terminal positions can be obtained by elimination reactions of α-halogenomesylates. Reductive elimination of benzoylated leucrosyl bromide with reactive zinc species has been used to obtain the exocyclic vinyl ethers. A similar approach was reported by Lichtenthaler *et al.*[11] for the synthesis of glycals of fructose.

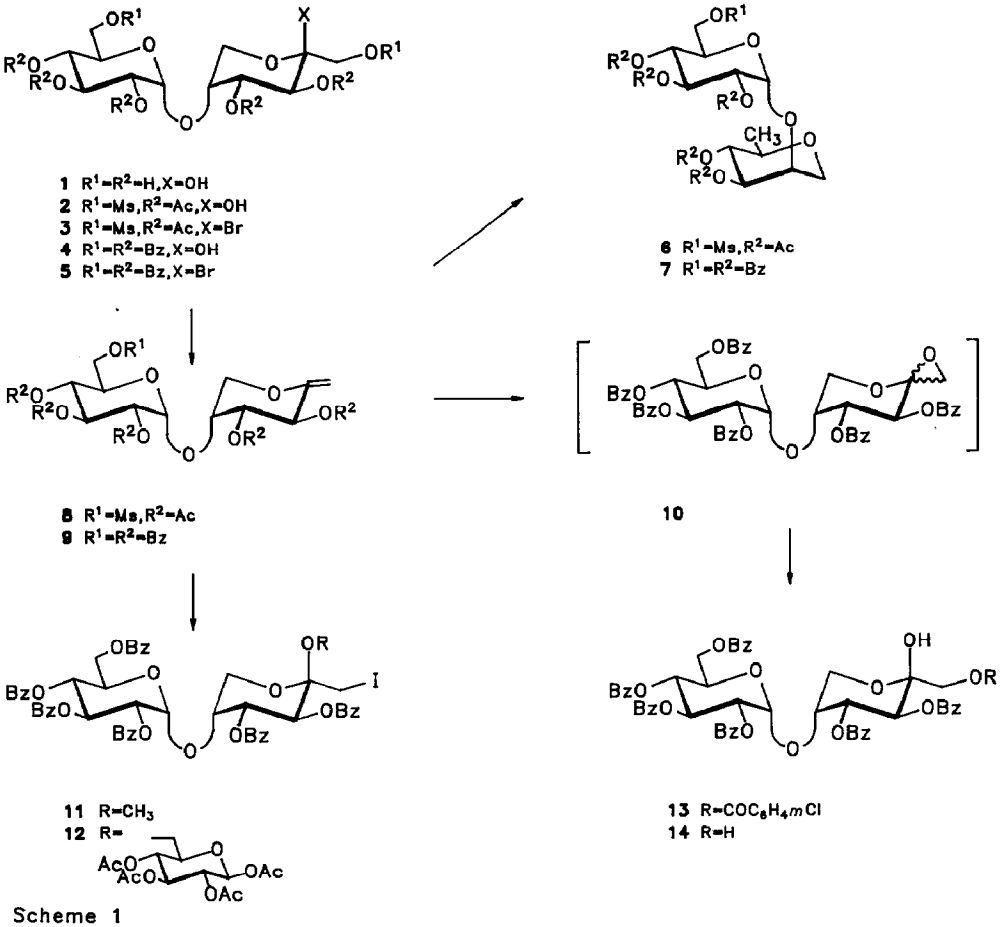
Reaction of leucrose (**1**) with mesyl chloride in pyridine at low temperature selectively sulfonylated HO-1 and HO-6'. The product was not isolated but acetylated to give the dimesylate **2** (33% after chromatography). The $^3J_{H,H}$ values of **2** revealed $^2C_5$(D) and $^4C_1$(D) conformations of the fructose and glucose rings, respectively.

Treatment of **2** with hydrogen bromide–acetic acid gave 72% of the glycosyl bromide **3**. It was not necessary to acylate HO-2' in **2**, as described for the preparation of D-fructo- and L-sorbo-pyranosyl bromides. The structure of **3** was assigned fully by ^{1}H-n.m.r. spectroscopy. Reaction of **3** with sodium iodide in anhydrous acetone gave the exocyclic vinyl ether **8** (50%). Although the chemical shifts of the resonances of H-1a,1b in **3** (δ 4.48 and 4.71) and **8** (δ 4.50 and 4.76) were similar, the $J_{1a,1b}$ values were markedly different (**3** 12.0 Hz, **8** 2.2 Hz) and there were long-range couplings in **8** ($J_{1a,3}$ 1.4, $J_{1b,3}$ 1.2 Hz). The remaining J values indicated a $^2C_5$(D) conformation for the fructopyranose ring in the bromide **3**.

The exocyclic glycal **8** was stable at room temperature, and hydrogenation (Pd–C) resulted in stereospecific reduction to give 3,4-di-*O*-acetyl-1,5-anhydro-6-deoxy-2-*O*-(2,3,4-tri-*O*-acetyl-6-*O*-methanesulfonyl-α-D-glucopyranosyl)-D-mannitol (**6**). In the ^{1}H-n.m.r. spectrum of **6**, the signals for H-6,6,6 appeared at δ 1.22 ($J_{5,6}$ 6.2 Hz) and the $J_{4,5}$ value of 9.2 Hz indicated H-4,5 to be *trans*-diaxial. This and the remaining J values supported the *manno* configuration of the anhydroalditol moiety and a $^4C_1$(D) conformation. Thus, the hydrogenation of **8** involved exclusive approach of hydrogen from the less hindered side of the double bond[12].

Base-catalysed benzoylation of leucrose (**1**) gave the heptabenzoate **4** (76%), treatment of which with hydrogen bromide–acetic acid yielded the glycosyl bromide **5**. Reductive elimination of **5** with copper sulfate-activated zinc dust gave the exocyclic glycal **9** (65% from **4**). Alternatively, **5** could be reacted with the activated zinc–graphite reagent[13,14] in anhydrous tetrahydrofuran. Although this reaction had a better work-up procedure, the overall yield was 42%. As found for **8**, the $J_{1a,1b}$ value for **9** was small (1.5 Hz) and there were long-range couplings ($J_{1a,3} = J_{1b,3} = 1.3$ Hz). Hydrogenation of **9** proceeded stereospecifically to give the dideoxy derivative **7**.

Reaction of **9** with 3-chloroperoxybenzoic acid in anhydrous dichloromethane did not give the expected mixture of diastereomeric spiro-epoxides **10**, but 77% of **13** was formed with HO-2 unsubstituted and HO-1 3-chlorobenzoylated. The ^{1}H-n.m.r. spectrum of **13** was almost identical to that of the heptabenzoate **4**. It is assumed that **13** was formed by the reaction of **10** with 3-chlorobenzoic acid. Alternatively, the isomeric



Scheme 1

epoxide may have been opened at C-1 with subsequent anomerisation. Work-up of the reaction mixture in the presence of water gave the 1,2-diol **14** (73%).

The stereospecific glycosylation of ketoses remains a problem[15]. Thus, it was of interest to apply *N*-iodosuccinimide-mediated glycosylation to **9**. A mechanism similar to that for endocyclic glycals would be expected[16] and, in fact, reaction of **9** with methanol and *N*-iodosuccinimide gave ~60% of the crystalline glycoside **11**. In the ^{1}H-n.m.r. spectrum of **11**, there was a signal for OMe (δ 3.32) and the signals for H-1a,1b were shifted considerably upfield (δ 3.24 and 3.68) with a $J_{1a,1b}$ value of 11.2 Hz. The other *J* values indicated $^2C_5$(D) and $^4C_1$(D) conformations for the pyranose rings.

N-Iodosuccinimide-mediated glycosylation of **9** with 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose[17,18] gave ~50% of the crystalline trisaccharide derivative **12**, the structure of which was established by ^{1}H-n.m.r. and 2D-COSY experiments. Again, the resonances of H-1'a,1'b appeared ~1.00 p.p.m. upfield in comparison with those of **9**, and the $J_{1'a,1'b}$ value was 11.3 Hz. The n.m.r. data indicated the reducing pyranose ring to have a chair conformation.

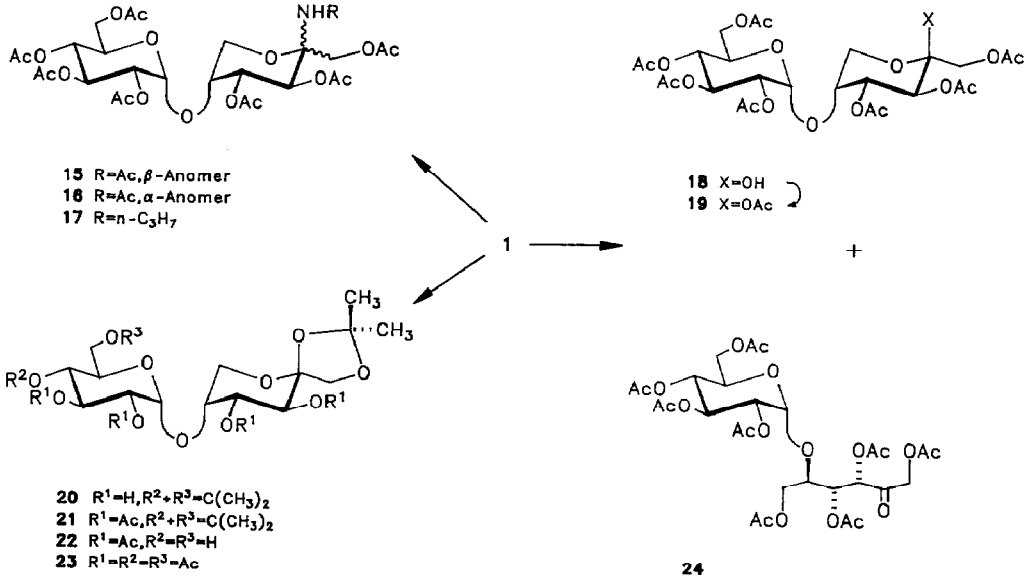
Treatment of leucrose (**1**) with amines generally produces a change in colour from yellow to brown, which is characteristic of Maillard reactions. Only after the reactions of **1** with liquid ammonia or propylamine and subsequent acetylation could products be obtained. The equilibrium between the acyclic and pyranose forms of **1** could be shifted by adding ammonium chloride, as demonstrated by Heyns *et al.*[19] on treatment of fructose with liquid ammonia. Thus, the anomeric acetylated leucrosylamines **15** and **16** were obtained. The yield could not be enhanced above ~30% and the α,β-ratio was ~1:1.

The reaction of **1** with propylamine gave a single product (**17**) in low yield (3%).

The resonance of C-2 of the fructose residue of **15** (or **16**, δ 85.51), **16** (or **15**, δ 86.19), and **17** (δ 86.91) occurred at markedly lower and characteristic field, in contrast to that (δ 102.65) of C-2 of leucrose octa-acetate (**19**). Although the other n.m.r. data indicated both rings in **15–17** to have chair conformations, the configuration at the anomeric centre could not be established.

Treatment of leucrose (**1**) with alanine or glycine in methanol, following work in the fructose series[20], gave typical yellow–brown products only on heating and these could not be isolated.

The tendency of fructose to form acyclic derivatives[21,22] was paralleled by leucrose (**1**). Acetylation of **1** with zinc chloride–acetic anhydride in the cold gave 91% of a 1:3 mixture, from which the syrupy cyclic (**9**) and the crystalline acyclic (**24**) octa-acetates were isolated. With pyridine–acetic anhydride in the cold, **1** gave 74% of the crystalline hepta-acetate **18** but, when a catalytic amount of 4-dimethylaminopyridine was added,



Scheme 2

the octa-acetates **19** and **24** were obtained in the ratio 1:3. The acyclic structure of **24** was deduced from the characteristic resonance of C-2 at δ 197.8

The acid-catalysed reaction of leucrose (**1**) with 2,2-dimethoxypropane[23,34] at room temperature gave the crystalline 1,2:4′,6′-di-*O*-isopropylidene derivative **20**, characterised as the tetra-acetate **21**. The 1,2- and 4′,6′-*O*-isopropylidene groups were indicated by the upfield shifts of the resonances of H-1a,1b,6′a,6′b by 0.5–1.0 p.p.m. compared to those of **19**. Similarly, H-4′ resonated at δ 3.63 (*cf.* δ 5.34 in **19**). Assignment of the isopropylidene group in the fructose moiety to the 1,2-position was supported by the chemical shift (δ 5.67) of the H-3 resonance in **21**.

Selective removal of the 4′,6′-*O*-isopropylidene group from **21**, following the method of Kim *et al.*[25] with silica-bound ferric chloride, gave 74% of the diol **22**, which is an important precursor for further modifications of the glucose moiety of leucrose. Acetylation of **22** gave the hexa-acetate **23**.

EXPERIMENTAL

General methods. — Reactions were monitored by t.l.c. on Silica Gel FG_{254} (Merck) with detection by u.v. light or charring with sulfuric acid. Column chromatography was performed on Silica Gel 60 (70–230 mesh, Merck) and flash chromatography on Silica Gel 60 (230–400 mesh). Melting points are uncorrected (Reichert heating microscope). Optical rotations were measured with a Perkin–Elmer polarimeter (1-dm cuvettes) at 589 nm.

The ^{1}H- and ^{13}C-n.m.r. spectra (internal Me_4Si or MeOH) were recorded with a Bruker WM 300 spectrometer at 300 and 75.4 MHz, respectively. Generally, the assignments of ^{1}H signals were supported by spin-decoupling and 2D-COSY experiments (Bruker software 1985, Aspect 300 computer).

Work-up procedures. — (*a*) N-*Iodosuccinimide-mediated glycosylations.* Each reaction mixture was filtered, and concentrated *in vacuo* to dryness, a solution of the residue in dichloromethane was washed with aqueous 10% sodium thiosulfate, the aqueous phase was re-extracted with dichloromethane, and the combined organic phases were dried ($MgSO_4$), filtered, and concentrated *in vacuo* to dryness.

(*b*) *Acetylation.* Each reaction mixture was poured into ice–water, stirred for 10 min, and extracted 3 × with chloroform. The combined extracts were washed with aqueous sodium hydrogensulfate and water, dried ($MgSO_4$), and concentrated, and toluene was distilled several times from the residue in order to remove pyridine.

*3,4-Di-*O*-acetyl-1-*O*-methanesulfonyl-5-*O*-(2,3,4-tri-*O*-acetyl-6-*O*-methanesulfonyl-α-*D*-glucopyranosyl)-β-*D*-fructopyranose* (**2**). — To a suspension of leucrose (**1**; 3.0 g, 8.8 mmol) in anhydrous pyridine (30 mL) at −20° was added methanesulfonyl chloride (456 μL, 5.9 mmol), and the mixture was warmed to room temperature, then cooled again. This procedure was repeated twice more and, after the last addition, stirring was continued for 3 h at −20°. Acetic anhydride (12 mL) was added and the mixture was left overnight after warming to room temperature, and then worked-up. Column chromatography (toluene–ethyl acetate, 2:1) of the product gave **2** (2.2 g, 33%), m.p. 78–80°,

$[\alpha]_D^{20}$ +36° (*c* 1, chloroform). ^{1}H-N.m.r. data (C_6D_6–$CDCl_3$, 1:1): δ 4.05–4.23 (m, 5 H, H-1a,1b,5′,6′a,6′b), 5.49 (d, H-3), 5.31 (dd, H-4), 4.01 (m, H-5), 3.95 (dd, H-6a), 3.73 (dd, H-6b), 5.30 (d, H-1′), 4.82 (dd, H-2′), 5.57 (dd″t″, H-3′), 5.00 (dd″t″, H-4′), 2.61 and 2.92 (2 s, each 3 H, 2 Ms), 1.85–1.96 (5 s, each 3 H, 5 Ac); $J_{3,4}$ 10.4, $J_{4,5}$ 3.0, $J_{5,6a}$ 1.5, $J_{5,6b}$ 2.0, $J_{6a,6b}$ 13.0, $J_{1',2'}$ 4.0, $J_{2',3'}$ 10.4, $J_{3',4'}$ 9.4, $J_{4',5'}$ 10.2 Hz.

Anal. Calc. for $C_{24}H_{36}O_{20}S_2$ (708.7): C, 40.68; H, 5.12. Found: C, 40.63; H, 5.02.

3,4-Di-O-acetyl-1-O-methanesulfonyl-5-O-(2,3,4-tri-O-acetyl-6-O-methanesulfonyl-α-D-glucopyranosyl)-β-D-fructopyranosyl bromide (**3**). — A solution of **2** (1.0 g, 1.4 mmol) in anhydrous dichloromethane (5 mL) was stirred with hydrogen bromide in acetic acid (5 mL, 33%) for 5 h at room temperature. The mixture was concentrated *in vacuo* and the residue was purified quickly by column chromatography (toluene–ethyl acetate, 1:1) to give amorphous **3** (778 mg, 72%), $[\alpha]_D^{20}$ −19° (*c* 0.7, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 4.48 and 4.71 (2 d, 2 H, H-1a,1b), 5.52 (d, H-3), 5.32 (dd, H-4), 4.16–4.31 (m, 6 H, H-5,6a,6b,5′,6′a,6′b), 5.37 (d, H-1′), 4.80 (dd, H-2′), 5.46 (dd″t″; H-3′), 4.98 (dd″t″, H-4′), 3.04 and 3.25 (2 s, 6 H, 2 Ms), 2.03–2.16 (5 s, 15 H, 5 Ac); $J_{1a,1b}$ 12.0, $J_{3,4}$ 10.3, $J_{4,5}$ 3.0, $J_{1',2'}$ 3.8, $J_{2',3'}$ 10.4, $J_{3',4'}$ 9.4, $J_{4',5'}$ 10.2 Hz.

1,3,4-Tri-O-benzoyl-5-O-(2,3,4,6-tetra-O-benzoyl-α-D-glucopyranosyl)-β-D-fructopyranose (**4**). — A solution of leucrose (**1**; 5.0 g, 14.6 mmol) in anhydrous pyridine (100 mL) at 0° was treated dropwise with benzoyl chloride (20 mL, 0.2 mmol). After stirring overnight at room temperature, the mixture was poured into saturated aqueous potassium carbonate (50 mL) and extracted with chloroform (3 × 150 mL). The combined extracts were washed with aqueous sodium hydrogencarbonate and water, dried ($MgSO_4$), and concentrated, and toluene was distilled from the residue. Column chromatography (toluene–ethyl acetate, 7:1) then gave **4** (11.9 g, 76%), m.p. 105°, $[\alpha]_D^{20}$ −13° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 4.53 and 4.70 (ABq, 2 H, H-1a,1b), 6.19 (d, H-3), 5.78 (dd, H-4), 4.50 (m, H-5), 4.37 (bd, H-6a), 4.17 (dd, H-6b), 5.39 (d, H-1′), 5.51 (dd, H-2′), 6.30 (dd″t″, H-3′), 5.69 (dd″t″, H-4′), 4.70 (ddd, H-5′), 4.59 (dd, H-6′a), 4.47 (dd, H-6′b), 6.88–8.19 (m, 35 H, 7 Ph); $J_{1a,1b}$ 12.0, $J_{3,4}$ 10.6, $J_{4,5}$ 3.0, $J_{5,6b}$ 1.4, $J_{6a,6b}$ 13.0, $J_{1',2'}$ 4.0, $J_{2',3'}$ 10.4, $J_{3',4'}$ 9.2, $J_{4',5'}$ 10.6, $J_{5',6'a}$ 2.6, $J_{5',6'b}$ 5.4, $J_{6'a,6'b}$ 12.2 Hz.

Anal. Calc. for $C_{61}H_{50}O_{18}$ (1071.1): C, 68.41; H, 4.71. Found: C, 67.92; H, 4.71.

1,3,4-Tri-O-benzoyl-5-O-(2,3,4,6-tetra-O-benzoyl-α-D-glucopyranosyl)-β-D-fructopyranosyl bromide (**5**). — Compound **4** (7.0 g, 6.5 mmol) was stirred for 5 h at room temperature with hydrogen bromide in acetic acid (60 mL, 33%). The mixture was concentrated in a strong vacuum and toluene was distilled from the residue to remove acetic acid and leave **5** (6.3 g, 86%), m.p. 85–86°, $[\alpha]_D^{20}$ −15° (*c* 0.9, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 4.86 (m, 2 H, H-1a,1b), 6.28 (d, H-3), 5.75 (dd, H-4), 4.59 (m, H-5), 4.54 (dd, H-6a), 4.38 (dd, H-6b), 5.42 (d, H-1′), 5.48 (dd, H-2′), 6.24 (dd″t″, H-3′), 5.66 (dd″t″, H-4′), 4.65 (ddd, H-5′), 4.51 (dd, H-6′a), 4.44 (dd, H-6′b), 6.89–8.25 (m, 35 H, 7 Ph); $J_{3,4}$ 10.4, $J_{4,5}$ 3.2, $J_{5,6a}$ 1.8, $J_{5,6b}$ 1.0, $J_{6a,6b}$ 12.6, $J_{1',2'}$ 3.8, $J_{2',3'}$ 10.2, $J_{3',4'}$ 9.4, $J_{4',5'}$ 10.4, $J_{5',6'a}$ 3.0, $J_{5',6'b}$ 5.2, $J_{6'a,6'b}$ 12.0 Hz.

Anal. Calc. for $C_{61}H_{49}BrO_{17}$ (1134.0): C, 64.61; H, 4.36. Found: C, 64.60; H, 4.67.

3,4-Di-O-acetyl-1,5-anhydro-6-deoxy-2-O-(2,3,4-tri-O-acetyl-6-O-methanesulfonyl-α-D-glucopyranosyl)-D-mannitol (**6**). — A solution of **8** (100 mg, 0.17 mmol) in

anhydrous ethyl acetate (12 mL) was stirred overnight under hydrogen at room temperature in the presence of 10% Pd–C (1.0 g), then filtered, and concentrated to yield **6** (94 mg, 92%), as a colourless syrup, $[\alpha]_D^{20}$ +56° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 3.93 (bd, H-1a), 3.57 (bd, H-1b), 4.05 (m, H-2), 4.92 (dd, H-3), 4.97 (dd″t″, H-4), 3.39 (dq, H-5), 1.22 (d, 3 H, H-6,6,6), 5.24 (d, H-1′), 4.78 (dd, H-2′), 5.56 (dd″t″, H-3′), 5.05 (dd″t″, H-4′), 4.15–4.17 (m, 3 H, H-5′,6′a,6′b), 3.00 (s, 3 H, Ms), 2.00–2.14 (5 s, each 3 H, 5 Ac); $J_{1a,1b}$ 13.0, $J_{2,3}$ 2.5, $J_{3,4}$ 10.2, $J_{4,5}$ 9.2, $J_{5,6}$ 6.2, $J_{1',2'}$ 4.0, $J_{2',3'}$ 10.4, $J_{3',4'}$ 9.2, $J_{4',5'}$ 10.4 Hz.

Anal. Calc. for $C_{23}H_{34}O_{16}S$ (598.6): C, 46.15; H, 5.73. Found: C, 46.01; H, 5.71.

*1,5-Anhydro-3,4-di-*O*-benzoyl-6-deoxy-2-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-*D*-glucopyranosyl)-*D*-mannitol* (**7**). — A solution of **9** (30 mg, 0.03 mmol) in anhydrous ethyl acetate (3 mL) was stirred for 16 h under hydrogen at room temperature with 33% Pd–C (100 mg), then filtered, and concentrated to give **7** (16 mg, 53%), m.p. 90–92°, $[\alpha]_D^{20}$ −12° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 4.32 (dd, H-1a), 3.72 (dd, H-1b), 4.39 (m, H-2), 5.31 (dd, H-3), 5.72 (dd″t″, H-4), 3.67 (dq, H-5), 1.39 (d, 3 H, H-6,6,6), 5.35 (d, H-1′), 5.43 (dd, H-2′), 6.26 (dd″t″, H-3′), 5.67 (dd″t″, H-4′), 4.70 (ddd, H-5′), 4.59 (dd, H-6′a), 4.47 (dd, H-6′b), 6.94–8.04 (m, 30 H, 6 Ph); $J_{1a,1b}$ 12.8, $J_{1a,2}$ 2.0, $J_{1b,2}$ 1.0, $J_{2,3}$ 3.2, $J_{3,4}$ 10.0, $J_{4,5}$ 9.6, $J_{5,6}$ 6.0, $J_{1',2'}$ 3.8, $J_{2',3'}$ 10.4, $J_{3',4'}$ 9.5, $J_{4',5'}$ 10.4, $J_{5',6'a}$ 2.8, $J_{5',6'b}$ 5.2, $J_{6'a,6'b}$ 12.3 Hz.

Anal. Calc for $C_{54}H_{46}O_{15}$ (935.0): C, 69.37; H, 4.96. Found: C, 69.18; H, 5.08.

*3,4-Di-*O*-acetyl-2,6-anhydro-1-deoxy-5-*O*-(2,3,4-tri-*O*-acetyl-6-*O*-methanesulfonyl-α-*D*-glucopyranosyl)-*D*-arabino-hex-1-enitol* (**8**). — A solution of **3** (700 mg, 0.9 mmol) in anhydrous acetone (10 mL) was stirred overnight at room temperature with sodium iodide (700 mg), then concentrated. A solution of the residue in dichloromethane (30 mL) was washed 3 × each with aqueous sodium hydrogencarbonate, aqueous sodium thiosulfate, and water, dried ($MgSO_4$), and concentrated. Column chromatography (toluene–ethyl acetate, 1:1) of the residue gave **8** (297 mg, 50%), m.p. 89°, $[\alpha]_D^{20}$ +47° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 4.50 and 4.76 (ABq, H-1a,1b), 5.67 (dt, H-3), 4.48 (dd, H-4), 4.20 (m, H-5), 4.09 (dd, H-6a), 3.77 (dd, H-6b), 5.29 (d, H-1′), 4.82 (dd, H-2′), 5.52 (dd″t″, H-3′), 4.99 (dd″t″, H-4′), 4.16 (dd, H-5′), 4.25–4.29 (m, 2 H, H-6′a,6′b), 3.04 (s, 3 H, Ms), 2.01–2.54 (5 s, each 3 H, 5 Ac); $J_{1a,1b}$ 2.2, $J_{1a,3}$ 1.4, $J_{1b,3}$ 1.2, $J_{3,4}$ 9.0, $J_{4,5}$ 3.0, $J_{5,6a}$ 4.0, $J_{5,6b}$ 2.0, $J_{6a,6b}$ 12.4, $J_{1',2'}$ 4.0, $J_{2',3'}$ 10.4, $J_{3',4'}$ 9.4, $J_{4',5'}$ 9.6, $J_{5',6'a}$ 5.2, $J_{5',6'b}$ 2.0 Hz.

Anal. Calc. for $C_{23}H_{32}O_{16}S$ (596.6): C, 46.31; H, 5.41. Found: C, 45.83; H, 5.36.

*2,6-Anhydro-3,4-di-*O*-benzoyl-1-deoxy-5-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-*D*-glucopyranosyl)-*D*-arabino-hex-1-enitol* (**9**). — (**a**) A solution of sodium acetate (28.5 g, 0.35 mol) in aqueous 50% acetic acid (110 mL) was stirred vigorously at −10° with zinc dust (34.3 g, 0.52 mol) and an aqueous solution of copper sulfate pentahydrate (3.45 g, 13.8 mmol in 10.8 mL). When the solution was decolourised, a solution of the crude glycosyl bromide **5** (6.3 g) in acetic acid (50 mL) was added dropwise during 20 min. After stirring for a further 3 h at −10°, the suspension was filtered, and the residue was washed twice with cold acetic acid (30 mL). The aqueous phase was extracted with chloroform (3 × 200 mL), the combined extracts were washed successively with water (3 × 200 mL), aqueous sodium hydrogencarbonate (4 × 150 mL), and water (100 mL), dried

($MgSO_4$), and concentrated to dryness. Flash chromatography (toluene–ethyl acetate, 4:1) of the residue gave **9** (2.18 g, 65%).

(*b*) Under a stream of argon, graphite (1.55 g, 0.13 mmol) was heated to 140–150° and stirred vigorously with potassium (0.66 g, 0.02 mmol). After the bronze-coloured product was formed, the mixture was cooled to room temperature, and anhydrous tetrahydrofuran (15 mL) was added, followed by zinc chloride (1.0 g, 0.01 mmol) and silver acetate (100 mg, 0.6 mmol). The mixture was heated under reflux for 30 min, cooled to −20°, and treated dropwise with a solution of the glycosyl bromide **5** (600 mg, 0.5 mmol) in anhydrous tetrahydrofuran (5 mL). The mixture was warmed gradually to room temperature overnight, filtered, and concentrated, and the residue was purified as in (*a*) to give **9** (208 mg, 42%), m.p. 87–89°, $[\alpha]_D^{20}$ −6.7° (*c*, 0.9, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 4.65 and 4.85 (2 dd″t″, 2 H, H-1a,1b), 6.17 (bd, H-3), 5.47 (dd, H-4), 4.58 (ddd, H-5), 4.46 (dd, H-6a), 4.01 (dd, H-6b), 5.52 (d, H-1′), 5.40 (dd, H-2′), 6.22 (dd″t″, H-3′), 5.68 (dd″t″, H-4′), 4.65 (ddd, H-5′), 4.61 (dd, H-6′a), 4.52 (dd, H-6′b), 7.06–8.08 (m, 30 H, 6 Ph), $J_{1a,1b}$ 1.3, $J_{1a,3}$ 1.3, $J_{1b,3}$ 1.3, $J_{3,4}$ 9.0, $J_{4,5}$ 3.0, $J_{5,6a}$ 5.0, $J_{5,6b}$ 2.2, $J_{6a,6b}$ 12.1, $J_{1',2'}$ 4.0, $J_{2',3'}$ 10.4, $J_{3',4'}$ 9.2, $J_{4',5'}$ 10.6, $J_{5',6'a}$ 2.6, $J_{5',6'b}$ 5.8, $J_{6'a,6'b}$ 12.5 Hz.

Anal. Calc. for $C_{54}H_{44}O_{15}$ (932.9): C, 69.52; H, 4.57. Found: C, 69.31; H, 4.62.

*Methyl 3,4-di-*O*-benzoyl-1-deoxy-1-iodo-5-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-*D*-glucopyranosyl)-β-*D*-fructopyranoside* (**11**). — A solution of **9** (300 mg, 0.3 mmol) in anhydrous acetonitrile (3 mL) and methanol (1 mL) was stirred for 30 min at room temperature in the presence of molecular sieves (3A, 100 mg). *N*-Iodosuccinimide (550 mg, 2.45 mmol) was added, stirring was continued for 72 h, and the mixture was worked-up. Flash chromatography (toluene–ethyl acetate, 15:1) of the product gave **11** (193 mg, 59%), m.p. 105°, $[\alpha]_D^{20}$ −36° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$); δ 3.24 and 3.68 (ABq, 2 H, H-1a,1b), 6.50 (d, H-3), 5.50 (dd, H-4), 4.41 (m, H-5), 4.26 (dd, H-6a), 3.82 (dd, H-6b), 5.44 (d, H-1′), 5.38 (dd, H-2′), 6.46 (dd″t″, H-3′), 5.71 (dd″t″, H-4′), 5.03 (ddd, H-5′), 4.69 (dd, H-6′a), 4.49 (dd, H-6′b), 3.32 (s, 3 H, OMe), 6.87–8.11 (m, 30 H, 6 Ph); $J_{1a,1b}$ 11.2, $J_{3,4}$ 10.4, $J_{4,5}$ 3.0, $J_{5,6a}$ 2.0, $J_{5,6b}$ 1.2, $J_{6a,6b}$ 12.6, $J_{1',2'}$ 3.8, $J_{2',3'}$ 10.2, $J_{3',4'}$ 9.6, $J_{4',5'}$ 10.4, $J_{5',6'a}$ 2.6, $J_{5',6'b}$ 5.4, $J_{6'a,6'b}$ 12.4 Hz, C.i. (NH_3)-mass spectrum: *m/z* 1108 $(M + NH_4)^+$.

*1,2,3,4-Tetra-*O*-acetyl-6-*O*-[3,4-di-*O*-benzoyl-1-deoxy-1-iodo-5-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-*D*-glucopyranosyl)-β-*D*-fructopyranosyl]-β-*D*-glucopyranose* (**12**). — A solution of **9** (100 mg, 0.11 mmol) and 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose[17,18] (40 mg, 0.11 mmol) in anhydrous acetonitrile (1 mL) was stirred under argon for 30 min at room temperature in the presence of molecular sieves (3A, 100 mg). The mixture was then stirred with *N*-iodosuccinimide (500 mg, 2.23 mmol) for 16 h at room temperature, and worked-up. Flash chromatography (toluene–ethyl acetate, 10:1) of the product gave **12** (73 mg, 47%), m.p. 110–112°, $[\alpha]_D^{20}$ −18.5° (*c* 1.3, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 5.74 (d, H-1), 5.16 (dd″t″, H-2), 5.23 (dd″t″, H-3), 5.26 (dd″t″, H-4), 3.83 (ddd″dt″,H-5), 3.64 (dd, H-6a), 3.55 (dd, H-6b), 3.21 and 3.55 (ABq, 2 H, H-1′a,1′b), 6.52 (d, H-3′), 5.37 (dd, H-4′), 4.48 (m, H-5′), 4.21 (dd, H-6′a), 3.95 (bd, H-6′b), 5.74 (d, H-1″), 5.36 (dd, H-2″), 6.45 (dd″t″, H-3″), 5.70 (dd″t″, H-4″), 4.98 (ddd, H-5″), 4.70 (dd, H-6″a); 4.46 (dd, H-6″b), 2.02–2.11 (4 s, 12 H, 4 Ac), 6.89–8.11 (m, 30 H, 6 Ph); $J_{1,2}$ 8.0,

$J_{2,3}$ 9.6, $J_{3,4}$ 9.6, $J_{4,5}$ 10.2, $J_{5,6a}$ 4.0, $J_{5,6b}$ 2.2, $J_{6a,6b}$ 11.2, $J_{1'a,1'b}$ 11.3, $J_{3',4'}$ 10.4, $J_{4',5'}$ 3.0, $J_{5',6'a}$ 2.2, $J_{5',6'b}$ 1.0, $J_{6'a,6'b}$ 12.5, $J_{1'',2''}$ 3.8, $J_{2'',3''}$ 10.2, $J_{3'',4''}$ 9.6, $J_{4'',5''}$ 10.2, $J_{5'',6''a}$ 2.6, $J_{5'',6''b}$ 5.2, $J_{6''a,6''b}$ 12.4 Hz. C.i. (NH_3)-mass spectrum: *m/z* 1425 $(M + NH_4)^+$.

*3,4-Di-*O*-benzoyl-1-*O*-(3-chlorobenzoyl)-5-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-*D*-glucopyranosyl)-β-*D*-glucopyranose* (**13**). — A solution of **9** (100 mg, 0.1 mmol) in 1,2-dichloromethane (10 mL) was stirred with anhydrous 3-chloroperoxybenzoic acid (52 mg, 0.3 mmol) for 48 h at room temperature. The mixture was extracted with 0.1M sodium hydroxide (2 × 20 mL) and water (3 × 20 mL), dried ($MgSO_4$), and concentrated to dryness. Flash chromatography (toluene–ethyl acetate, 4:1) of the residue gave **13** (79.6 mg, 72%), m.p. 96–99°, $[\alpha]_D^{20}$ −14° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 4.49 and 4.69 (ABq, 2 H, H-1a,1b), 6.13 (d, H-3), 5.73 (dd, H-4), 4.48 (m, H-5), 4.34 (dd, H-6a), 4.14 (dd, H-6b), 5.37 (d, H-1'), 5.48 (dd, H-2'), 6.26 (dd″t″, H-3'), 5.66 (dd″t″, H-4'), 4.67 (ddd, H-5'), 4.58 (dd, H-6'a), 4.47 (dd, H-6'b), 3.75 (bs, HO-2), 6.89–8.02 (m, 34 H, aryl H); $J_{1a,1b}$ 12.0, $J_{3,4}$ 10.5, $J_{4,5}$ 3.2, $J_{5,6a}$ 1.0, $J_{5,6b}$ 1.6, $J_{6a,6b}$ 12.3, $J_{1',2'}$ 3.8, $J_{2',3'}$ 10.3, $J_{3',4'}$ 9.6, $J_{4',5'}$ 10.4, $J_{5',6'a}$ 3.0, $J_{5',6'b}$ 5.5, $J_{6'a,6'b}$ 12.3 Hz, C.i. (NH_3)-mass spectrum: *m/z* 1123 $(M + NH_4)^+$.

*3,4-Di-*O*-benzoyl-5-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-*D*-glucopyranosyl)-β-*D*-fructopyranose* (**14**). — Compound **9** was treated with 3-chloroperoxybenzoic acid as in the previous experiment. Water (10 μL) was added to the mixture which, after 35 h, was worked-up, as described above, to give **14** (71 mg, 73%), m.p. 94–97°, $[\alpha]_D^{20}$ −36° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 3.53 and 3.84 (ABq, 2 H, H-1a,1b), 5.92 (d, H-3), 5.72 (dd, H-4), 4.43 (m, H-5), 4.19 (dd, H-6a), 4.13 (dd, H-6b), 5.36–5.42 (m, 2 H, H-1',2'), 4.65 (dd, H-6'a), 4.47 (dd, H-6'b), 6.94–8.14 (m 30 H, 6 Ph); $J_{1a,1b}$ 12.0, $J_{3,4}$ 5.0, $J_{4,5}$ 3.2, $J_{5,6a}$ 1.0, $J_{5,6b}$ 1.4, $J_{6a,6b}$ 12.0, $J_{1',2'}$ 4.0, $J_{2',3'}$ 9.6, $J_{3',4'}$ 9.4, $J_{4',5'}$ 10.3, $J_{5',6'a}$ 3.2, $J_{5',6'b}$ 5.8, $J_{6'a,6'b}$ 11.8 Hz.

Anal. Calc for $C_{54}H_{46}O_{17}$ (967.0): C, 67.08; 4.80. Found: C, 66.64; H, 4.89.

N-*Acetyl-1,3,4-tri-*O*-acetyl-5-*O*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-β-*D*-fructopyranosylamine* (**16**). — To a solution of leucrose (**1**; 1.0 g, 2.9 mmol) in anhydrous liquid ammonia (60 mL) was added ammonium chloride (100 mg). The mixture was stirred for 8 days at −50°, then warmed to room temperature, the ammonia was evaporated, and to a solution of the residue in anhydrous pyridine (10 mL) was added acetic anhydride dropwise at 0°. After work-up, column chromatography (toluene–ethyl acetate, 1:10) of the product gave, first, **15** and then **16** (combined yield, 570 mg, 29%) in the ratio 1:1.

Compound **15** (or **16**) had m.p. 91–94°, $[\alpha]_D^{20}$ +69° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 4.62 and 4.89 (ABq, 2 H, H-1a,1b), 5.30 (bd, H-3), 5.24 (dd, H-4), 4.05 (m, H-5), 3.86–3.88 (m, 2 H, H-6a,6b), 5.17 (d, H-1'), 4.81 (dd, H-2'), 5.46 (dd″t″, H-3'), 4.98 (dd″t″, H-4'), 4.03 (ddd, H-5'), 4.18 (dd, H-6'a), 4.07 (dd, H-6'b), 6.20 (bs, NH), 2.00–2.10 (7 s, 24 H, 8 Ac); $J_{1a,1b}$ 12.0, $J_{3,4}$ 7.0, $J_{4,5}$ 3.0, $J_{1',2'}$ 3.8, $J_{2',3'}$ 10.5, $J_{3',4'}$ 9.4, $J_{4',5'}$ 10.2, $J_{5',6'a}$ 5.4, $J_{5',6'b}$ 2.4, $J_{6'a,6'b}$ 12.2 Hz; ^{13}C, δ 60.18, 61.19, and 61.89 (C-1,6,6'), 85.51 (C-2), 67.84, 67.94, 68.48, 69.00, 69.43, 70.18, and 70.63 (C-3,4,5,2',3',4',5'), 95.74 (C-1'), 168.89–170.48 (8 $COCH_3$), 20.40–24.28 (8 $COCH_3$).

Anal. Calc. for $C_{28}H_{39}NO_{18}$ (677.6): C, 49.63, H, 5.80; N, 2.07. Found: C, 50.23; H,

5.84. N, 2.01.

Compound **16** (or **15**) was a colourless oil, $[\alpha]_D^{20}$ +19° (*c* 1.3, chloroform). N.m.r. data ($CDCl_3$): δ 4.70 (ABq, 2 H, H-1a), 4.16–4.25 (m, 3 H, H-1b,5',6'a), 5.64 (d, H-3), 5.09 (dd, H-4), 4.04 (m, H-5), 3.93 (dd, H-6a), 3.83 (dd, H-6b), 5.26 (d, H-1'), 4.77 (dd, H-2'), 5.53 (dd"t", H-3'), 5.01 (dd"t", H-4'), 4.07 (dd, H-6'b), 5.81 (bs, NH), 1.99–2.15 (8 s, each 3 H, 8 Ac); $J_{1a,1b}$ 12.0, $J_{3,4}$ 10.6, $J_{4,5}$ 3.0, $J_{5,6a}$ 1.4, $J_{5,6b}$ 1.0, $J_{1',2'}$ 4.0, $J_{2',3'}$ 10.4, $J_{3',4'}$ 9.4, $J_{4',5'}$ 10.3, $J_{5',6'b}$ 3.0, $J_{6'a,6'b}$ 12.8 Hz; ^{13}C, δ 61.83, 62.24, and 62.79 (C-1,6,6'), 86.19 (C-2), 66.05, 67.74, 68.45, 69.46, 70.15, 70.76, 73.65 (C-3,4,5,2',3',4',5'), 96.36 (C-1'), 168.18–170.55 (8 $COCH_3$), 20.33–20.51 (8 $COCH_3$).

Anal. Found: C, 49.42; H, 5.67; N, 2.01.

*1,3,4-Tri-*O*-acetyl-*N*-propyl-5-*O*-(2,3,4,6-tetra-*O*-acetyl-*α*-*D*-glucopyranosyl)-*α*,*β*-*D*-fructopyranosylamine* (**17**). — A solution of leucrose (**1**; 1.0 g, 2.9 mmol) in propylamine (25 mL) was stirred with ammonium chloride (100 mg) for 3 days at room temperature, then concentrated. The residue was dried in a strong vacuum, and to a solution in anhydrous pyridine (5 mL) was added acetic anhydride (3 mL) dropwise at 0°, and stirring was continued overnight. Work-up followed by column chromatography (touene–ethyl acetate, 1:1) of the product gave **17** (59 mg, 3%), isolated as a colourless syrup, $[\alpha]_D^{20}$ +27.5° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 4.15–4.36 (m, 5 H, H-1a,1b,5',6'a,6'b), 5.89 (d, H-3), 5.41 (dd, H-4), 3.74 (m, H-5), 3.78 (dd, H-6a), 3.55 (dd, H-6b), 5.34 (d, H-1'), 4.98 (dd, H-2'), 5.91 (dd"t", H-3'), 5.33 (dd"t", H-4'), 3.00 (m, NH), 2.32 (m, CH_2N), 1.18 (m, CH_2CH_2N), 0.77 (t, $CH_3CH_2CH_2N$), 1.62–2.07 (7 s, each 3 H, 7 Ac); $J_{3,4}$ 10.4, $J_{4,5}$ 3.0, $J_{5,6a}$ 1.0, $J_{5,6b}$ 2.0, $J_{6a,6b}$ 12.2, $J_{1',2'}$ 4.0, $J_{2',3'}$ 10.3, $J_{3',4'}$ 9.4, $J_{4',5'}$ 10.0, J_{CH_3,CH_2} 7.4, J_{CH_2,CH_2} 7.0 Hz; ^{13}C, δ 61.73, 61.82, and 64.02 (C-1,6,6'), 86.91 (C-2), 67.47, 68.11, 68.55, 69.60, 70.68, 70.93 (C-3,4.2',3',4',5'), 74.03 (C-5), 41.12 (CH_2N), 23.94 (NCH_2CH_2), 11.73 ($NCH_2CH_2CH_3$), 168.77–170.73 (7 $COCH_3$), 20.26–20.64 (7 $COCH_3$).

Anal. Calc. for $C_{29}H_{43}NO_{17}$ (677.7): C, 51.40; H, 6.40; N, 2.07. Found: C, 51.09; H, 6.32; N, 2.04.

*1,3,4-Tri-*O*-acetyl-5-*O*-(2,3,4,6-tetra-*O*-acetyl-*α*-*D*-glucopyranosyl)-*β*-*D*-fructopyranose* (**18**). — A solution of leucrose (**1**; 9.0 g, 26.3 mmol) in anhydrous pyridine (53 mL) was treated dropwise with acetic anhydride (40 mL) at 0° and then stirred overnight at room temperature. Work-up and column chromatography (toluene–ethyl acetate, 1:2) of the product gave **18** (12.39 g, 74%), m.p. 144°, $[\alpha]_D^{20}$ +38° (*c* 1, chloroform). ^1H-N.m.r. data (C_6D_6): δ 4.20 (ABq, 2 H, H-1a,1b), 5.76 (d, H-3), 4.78 (dd, H-4), 3.85 (m, H-5), 3.85 (dd, H-6a), 3.63 (dd, H-6b), 5.34 (H-1'), 4.98 (dd, H-2'), 5.88 (dd, H-3'), 5.30 (dd, H-4'), 4.21 (ddd, H-5'), 4.26 (dd, H-6'a), 4.12 (dd, H-6'b), 1.67–2.07 (7 s, each 3 H, 7 Ac); $J_{1a,1b}$ 11.8, $J_{3,4}$ 10.4, $J_{4.5}$ 3.0, $J_{5,6a}$ 1.0, $J_{5,6b}$ 2.2, $J_{6a,6b}$ 12.8, $J_{1',2'}$ 4.0, $J_{2',3'}$ 10.4, $J_{3',4'}$ 9.8, $J_{4',5'}$ 9.8, $J_{5',6'a}$ 4.4, $J_{5',6'b}$ 2.2 Hz.

Anal. Calc. for $C_{26}H_{36}O_{18}$ (636.6): C, 49.02; H, 5.70. Found: C, 49.64; H, 5.97.

*1,2,3,4-Tetra-*O*-acetyl-5-*O*-(2,3,4,6-tetra-*O*-acetyl-*α*-*D*-glucopyranosyl)-*β*-*D*-fructopyranose* (**19**) *and 1,3,4,6-tetra-*O*-acetyl-5-*O*-(2,3,4,6-tetra-*O*-acetyl-*α*-*D*-glucopyranosyl)-*D*-fructose* (**24**). — (*a*) A solution of **18** (4.0 g, 6.3 mmol) in anhydrous pyridine (4 mL) was treated with 4-dimethylaminopyridine (20 mg) and dropwise with acetic

anhydride (2 mL) at 0°. After stirring for 12 h at room temperature, the mixture was worked-up. Column chromatography (toluene–ethyl acetate, 2:1) of the product gave a 1:3 mixture (3.88 g, 91%), of **19** and **24**.

(*b*) A solution of leucrose (**1**; 2.0 g, 5.8 mmol) in acetic anhydride (25 mL) was treated with zinc chloride at 0°. After stirring for 5 h at room temperature, the mixture was poured into ice–water, neutralised with solid sodium hydrogencarbonate, and extracted with chloroform (3 × 100 mL). The combined extracts were washed successively with saturated aqueous sodium hydrogencarbonate and water, dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Column chromatography of the solid residue, as in (*a*), gave a 1:3 mixture (3.0 g, 76%) of **19** and **24**.

Compound **19** was a colourless oil, $[\alpha]_D^{20}$ +60° (*c* 1, chloroform). N.m.r. data: ^1H (C_6D_6), δ 5.19 and 4.95 (ABq, 2 H, H-1a,1b), 6.08 (d, H-3), 5.40 (dd, H-4), 3.87 (m, H-5), 3.82 (dd, H-6a), 3.46 (dd, H-6b), 5.39 (d, H-1′), 5.01 (dd, H-2′), 5.96 (dd, H-3′), 4.24–4.35 (m, 3 H, H-5′,6′a,6′b), 1.68–2.14 (8 s, each 3 H, 8 Ac); $J_{1a,1b}$ 11.8, $J_{3,4}$ 10.4, $J_{4,5}$ 2.8, $J_{5,6a}$ 1.0, $J_{5,6b}$ 2.0, $J_{6a,6b}$ 11.8, $J_{1',2'}$ 4.0, $J_{2',3'}$ 10.4, $J_{3',4'}$ 9.5, $J_{4',5'}$ 10.2 Hz; ^{13}C ($CDCl_3$), δ 61.83, 61.89, and 64.04 (C-1,6,6′), 102.65 (C-2), 65.82, 67.78, 68.44, 69.39, 70.08, and 70.64 (C-3,4,2′,3′,4′,5′), 73.34 (C-5), 96.41 (C-1′), 167.85–170.60 (8 *C*OCH$_3$), 20.34–21.40 (8 CO*C*H$_3$).

Anal. Calc. for $C_{28}H_{38}O_{19}$ (678.3): C, 49.53; H, 5.65. Found: C, 49.86; H, 5.60.

Compound **24** had m.p. 135°, $[\alpha]_D^{20}$ +90.5° (*c* 1, chloroform). N.m.r. data: ^1H (C_6D_6), δ 4.73 (ABq, 2 H, H-1a,1b), 5.74 (d, H-3), 5.85 (dd, H-4), 3.85 (ddd, H-5), 4.32 (dd, H-6a), 4.28 (dd, H-6b), 4.99 (d, H-1′), 5.09 (dd, H-2′), 5.78 (dd, H-3′), 5.24 (dd, H-4′), 4.39 (ddd, H-5′), 4.37 (dd, H-6′a), 4.24 (dd, H-6′b), 1.63–2.03 (8 s, each, 3 H, 8 Ac); $J_{3,4}$ 1.8, $J_{4,5}$ 8.8, $J_{5,6a}$ 2.5, $J_{5,6b}$ 2.5, $J_{6a,6b}$ 11.0, $J_{1',2'}$ 4.0, $J_{2',3'}$ 10.4, $J_{3',4'}$ 10.4, $J_{5',6'a}$ 2.6, $J_{5',6'b}$ 5.9, $J_{6'a,6'b}$ 12.5 Hz; ^{13}C ($CDCl_3$), δ 76.73 (C-1), 197.79 (C-2), 66.58, 67.52, 68.08, 68.31, 69.69, and 70.01 (C-3,4,2′,3′,4′,5′), 61.88, 62.04 (C-6,6′), 73.79 (C-5), 98.38 (C-1′), 169.41–170.46 (8 *C*OCH$_3$), 20.22–20.70 (8 CO*C*H$_3$).

Anal. Found: C, 49.93; H, 5.62.

*1,2-*O*-Isopropylidene-5-*O*-(4,6-*O*-isopropylidene-α-*D*-glucopyranosyl)-β-*D*-fructopyranose* (**20**). — A suspension of leucrose (**1**; 3.0 g, 8.8 mmol) in 2,2-dimethoxypropane (40 mL) was stirred with *p*-toluenesulfonic acid (20 mg) for 65 h at room temperature, then neutralised with aqueous sodium hydrogencarbonate, and concentrated *in vacuo* to dryness. Column chromatography (acetone–dichloromethane, 5:3) of the residue gave **20** (1.7 g, 46%), m.p. 116–119°, $[\alpha]_D^{20}$ −33° (*c* 1, chloroform). ^{13}C-N.m.r. data (D_2O): σ 61.47, 63.92, and 63.99 (C-1,6,6′), 101.79 (C-2), 68.45, 70.51, 71.73, 72.76, 72.33, and 73.92 (C-3,4,2′,3′,4′,5′), 79.85 (C-5), 101.51 (C-1′), 26.01 and 27.23 [each 2 C, C(*C*H$_3$)$_2$], 106.85 and 113.64 (2 *C*Me$_2$).

Anal. Calc. for $C_{18}H_{30}O_{11}$ (422.4): C, 49.85; H, 7.04. Found: C, 49.78; H, 7.10.

*3,4-Di-*O*-acetyl-5-*O*-(2,3-di-*O*-acetyl-4,6-*O*-isopropylidene-α-*D*-glucopyranosyl)-1,2-*O*-isopropylidene-β-*D*-fructopyranose* (**21**). — A solution of **20** (1.0 g, 2.4 mmol) in anhydrous pyridine (3 mL) was treated dropwise with acetic anhydride (2 mL) at 0°, then stirred overnight at room temperature. Work-up and column chromatography (toluene–ethyl acetate, 2:1) of the product gave **21** (1.3 g, 93%), m.p. 98–102°, $[\alpha]_D^{20}$ +8°

(*c* 0.8, chloroform). ^{1}H-N.m.r. data (C_6D_6): δ 3.75 (ABq, 2 H, H-1a,1b), 5.67 (d, H-3), 5.40 (dd, H-4), 3.91 (m, H-5), 3.66 (dd, H-6a), 3.39 (dd, H-6b), 5.39 (d, H-1'), 5.06 (dd, H-2'), 5.98 (dd"t", H-3'), 3.62 (dd"t", H-4'), 4.00 (ddd"dt", H-5'), 3.84 (dd, H-6'a), 3.69 (dd, H-6'b), 1.38–2.18 (8 s, each 3 H, 4 Ac and 2 CMe_2); $J_{3,4}$ 10.5, $J_{4,5}$ 3.2, $J_{5,6a}$ 1.0, $J_{5,6b}$ 2.0, $J_{6a,6b}$ 12.8, $J_{1',2'}$ 4.0, $J_{2',3'}$ 10.2, $J_{3',4'}$ 9.6, $J_{4',5'}$ 10.2, $J_{5',6'a}$ 5.2, $J_{5',6'b}$ 9.0, $J_{6'a,6'b}$ 10.8 Hz.

Anal. Calc. for $C_{26}H_{38}O_{15}$ (590.6): C, 52.88; H, 6.49. Found: C, 53.11; H, 6.40.

*3,4-Di-*O*-acetyl-5-*O*-(2,3-di-*O*-acetyl-α-*D*-glucopyranosyl)-1,2-*O*-isopropylidene-β-*D*-fructopyranose* (**22**). — A solution of **21** (1.0 g, 1.7 mmol) in anhydrous acetone (5 mL) was stirred with ferric chloride–silica gel[25] (100 mg) for 6 h at room temperature, then filtered, and concentrated. Column chromatography (toluene–ethyl acetate, 1:1) of the residue gave **22** (693 mg, 74%), m.p. 94–96°, $[\alpha]_D^{20}$ +17° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 3.92 and 4.05 (ABq, 2 H, H-1a,1b), 5.42 (d, H-3), 5.21 (dd, H-4), 4.14 (m, H-5), 3.76–3.89 (m, 5 H, H-6a,6b,5',6'a,6'b), 5.18 (d, H-1'), 4.74 (dd, H-2'), 5.37 (dd"t", H-3'), 3.65 (dd"t", H-4'), 2.61 (bs, 2 H, HO-4',6'), 1.41 and 1.48 (2 s, each 3 H, CMe_2), 2.02–2.14 (3 s, 12 H, 4 Ac); $J_{1a,1b}$ 9.5, $J_{3,4}$ 10.5, $J_{4,5}$ 3.0, $J_{1',2'}$ 4.0, $J_{2',3'}$ 10.2, $J_{3',4'}$ 9.2, $J_{4',5'}$ 9.0 Hz.

Anal. Calc. for $C_{23}H_{34}O_{15}$ (550.5): C, 50.18; H, 6.23. Found: C, 49.99; H, 6.18.

*3,4-Di-*O*-acetyl-1,2-*O*-isopropylidene-5-*O*-(2,3,4,6-tetra-*O*-acetyl-α-*D*-glucopyranosyl)-β-*D*-fructopyranose* (**23**). — A solution of **22** (500 mg, 0.9 mmol) in anhydrous pyridine was treated dropwise with acetic anhydride (1 mL) at 0°. The mixture was stored overnight at room temperature and then worked-up. Column chromatography (toluene–ethyl acetate, 2:1) of the product gave **23** (553 mg, 97%), as an amorphous solid, $[\alpha]_D^{20}$ +29° (*c* 1, chloroform). ^{1}H-N.m.r. data (C_6D_6): δ 3.78 (ABq, 2 H, H-1a,1b), 5.67 (d, H-3), 5.43 (dd, H-4), 3.92 (m, H-5), 3.76 (dd, H-6a), 3.59 (dd, H-6b), 5.36 (d, H-1'), 5.02 (dd, H-2'), 5.91 (dd"t", H-3'), 5.30 (dd"t", H-4'), 4.19 (ddd, H-5'), 4.27 (dd, H-6'a), 4.13 (dd, H-6'b), 1.65 and 1.67 (2 s, each 3 H, CMe_2), 1.69–1.79 (5 s, 18 H, 6 Ac); $J_{3,4}$ 10.6, $J_{4,5}$ 3.0, $J_{5,6a}$ 1.4, $J_{5,6b}$ 2.0, $J_{6a,6b}$ 13.0, $J_{1',2'}$ 4.0, $J_{2',3'}$ 10.4, $J_{3',4'}$ 9.2, $J_{4',5'}$ 10.2, $J_{5',6'a}$ 4.6, $J_{5',6'b}$ 2.2, $J_{6'a,6'b}$ 11.6 Hz.

Anal. Calc. for $C_{27}H_{38}O_{17}$ (634.6): C, 51.10; H, 6.04. Found: C, 51.09; H, 5.99.

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