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SYNTHESIS OF DERIVATIVES OF METHYL β-SOPHOROSIDE

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ABSTRACT

Selective tritylation of methyl β-sophoroside (**1**) and subsequent acetylation gave the 3,4,2′,3′,4′-penta-*O*-acetyl-6,6′-di-*O*-trityl derivative, which was *O*-detritylated, and the product *p*-toluenesulfonylated, to give methyl 3,4,2′,3′,4′-penta-*O*-acetyl-6,6′-di-*O*-*p*-tolylsulfonyl-β-sophoroside (**4**) in 63% net yield. Compound **4** was also obtained in 69% yield by *p*-toluenesulfonylation of **1**, followed by acetylation. Several 6,6′-disubstituted derivatives of **1** were synthesized by displacement reactions of **4** with various nucleophiles. Treatment of **4** with sodium methoxide afforded methyl 3,6:3′,6′-dianhydro-β-sophoroside. Several 6- and 6′-monosubstituted derivatives of **1** were prepared, starting from the 4,6-*O*-benzylidene derivative of **1**.

INTRODUCTION

Sophorose (2-*O*-β-D-glucopyranosyl-D-glucose) is either the sole or the major repeating-unit of some bacterial[1–6] polysaccharides and of a synthetic polysaccharide[7]. We have synthesized several sophorose derivatives which may serve as models for solvolytic and displacement reactions of higher members of sophoro-oligo-[3] and -poly-saccharides[1–7] that contain (1→2)-β-D-glucosidic linkages exclusively. The synthesis is now described of several 6,6′-disubstituted derivatives of methyl β-sophoroside[8] (**1**) by displacement reactions of the sulfonyloxy groups of methyl 3,4,2′,3′,4′-penta-*O*-acetyl-6,6′-di-*O*-*p*-tolylsulfonyl-β-sophoroside (**4**) with various nucleophiles, and the preparation of methyl 6- (**28**) and 6′-deoxy-β-sophoroside (**39**), methyl 6-acetamido-6-deoxy- (**31**) and 6′-acetamido-6′-deoxy-β-sophoroside (**41**), and methyl 3,6:3′,6′-dianhydro-β-sophoroside (**44**). The transformation of **1** into methyl 2-*O*-β-D-glucopyranosyl-β-D-allopyranoside (**47**) is also included.

RESULTS AND DISCUSSION

In order to synthesize **4**, the key intermediate in the synthesis of a homologous series of 6,6′-disubstituted derivatives of **1**, two routes were employed. In the first, tritylation of **1** with 2.5 mol. equiv. of chlorotriphenylmethane in pyridine, followed by acetylation, and purification of the products by column chromatography, gave, in 83% yield, the per-*O*-acetyl-6,6′-di-*O*-trityl derivative **2** as an amorphous powder,

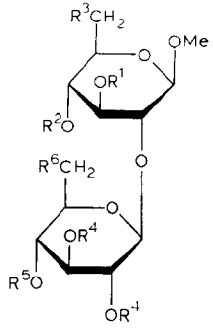
which was *O*-detritylated with aqueous acetic acid to afford, in 81% yield after column chromatography, the 3,4,2′,3′,4′-penta-*O*-acetyl derivative **3** as an amorphous material having the HO-6 and -6′ groups free. *p*-Toluenesulfonylation of **3** gave **4** in crystalline form in 93% yield. The overall yield of **4** was 63%, based on **1**. In the second route, treatment of **1** with 2.4 mol. equiv. of *p*-toluenesulfonyl chloride in pyridine, and subsequent acetylation, gave a mixture from which **4** was directly obtained in crystalline form in 69% yield. The compounds obtained by the two routes were identical in all respects.

Nucleophilic displacement of **4** with azide, bromide, chloride, iodide, and thioacetate ions in *N*,*N*-dimethylformamide gave high yields of 6,6′-diazido-6,6′-dideoxy (**5**), 6,6′-dibromo-6,6′-dideoxy (**6**), 6,6′-dichloro-6,6′-dideoxy (**7**), 6,6′-dideoxy-6,6′-diiodo (**8**), and 6,6′-di-*S*-acetyl-6,6′-dithio (**9**) derivatives, respectively. Compound **5** was hydrogenated with Raney nickel in the presence of hydrazine hydrate[9,10] and the product acetylated, to afford the 6,6′-diacetamido-6,6′-dideoxy derivative **10**. Reductive dehalogenation[9,10] of **8** gave the 6,6′-dideoxy derivative **11**. *O*-Deacetylation of **6**, **7**, **10**, and **11** with methanolic sodium methoxide furnished methyl 6,6′-dibromo-6,6′-dideoxy-β-sophoroside (**12**), methyl 6,6′-dichloro-6,6′-dideoxy-β-sophoroside (**13**), methyl 6,6′-diacetamido-6,6′-dideoxy-β-sophoroside (**14**), and methyl 6,6′-dideoxy-β-sophoroside (**15**), respectively, all of these compounds being obtained in crystalline form. Compound **12** was also obtained by an alternative route: conventional benzylidenation of **1** with benzaldehyde in the presence of zinc chloride gave, in 82% yield, the crystalline 4,6:4′,6′-di-*O*-benzylidene derivative **16**, which was acetylated to afford the crystalline 3,2′,3′-tri-*O*-acetyl-4,6:4′,6′-di-*O*-benzylidene derivative **17**. Oxidative removal of the benzylidene groups of **17** with *N*-bromosuccinimide[11] yielded the 3,2′,3′-tri-*O*-acetyl-4,4′-di-*O*-benzoyl-6,6′-dibromo-6,6′-dideoxy derivative **18**, which, on *O*-deacylation, gave **12** having physical constants in good agreement with those of the compound prepared from **6**.

Treatment of **4** with sodium methoxide in methanol, followed by acetylation, gave methyl 4,2′,4′-tri-*O*-acetyl-3,6:3,6′-dianhydro-β-sophoroside (**43**), which was *O*-deacetylated to provide **44** in crystalline form. The resistance of this compound to periodate oxidation was consistent with the structure assigned.

Attempted regioselective tritylation and *p*-toluenesulfonylation of **1** with 1.1 mol. equiv. of each of the reagents in pyridine, with the aim of obtaining the 6- (**19**) and 6′-monotrityl (**20**) ethers, and the 6- (**21**) and 6′-*O*-*p*-tolylsulfonyl (**22**) derivatives, respectively, as starting materials for chemical modification at the 6- and 6′-positions in **1**, were not successful, because each of the reactions gave a mixture that was inseparable by column chromatography and fractional recrystallization. This observation agrees with the results obtained for preferential tritylation and *p*-toluenesulfonylation of methyl β-glycosides of laminarabiose[10] and cellobiose[12].

Reaction of methyl 2′,3′,4′,6′-tetra-*O*-acetyl-4,6-*O*-benzylidene-β-sophoroside[8] (**23**) with *N*-bromosuccinimide[11] afforded the 2′,3′,4′,6′-tetra-*O*-acetyl-4-*O*-benzoyl-6-bromo-6-deoxy derivative **24**, which was *O*-deacylated to give crystalline methyl 6-bromo-6-deoxy-β-sophoroside (**25**). Acetylation of **25** yielded the 6-bromo-6-



1 $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = R^6 = OH$

2 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = R^6 = OTr$

3 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = R^6 = OH$

4 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = R^6 = OTs$

5 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = R^6 = N_3$

6 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = R^6 = Br$

7 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = R^6 = Cl$

8 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = R^6 = I$

9 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = R^6 = SAc$

10 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = R^6 = NHAc$

11 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = R^6 = H$

12 $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = R^6 = Br$

13 $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = R^6 = Cl$

14 $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = R^6 = NHAc$

15 $R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H$

16 $R^1 = R^4 = H$; $R^2,R^3 = R^5,R^6 = PhCHO$

17 $R^1 = R^4 = Ac$; $R^2,R^3 = R^5,R^6 = PhCHO$

18 $R^1 = R^4 = Ac$, $R^2 = R^5 = Bz$, $R^3 = R^6 = Br$

19 $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = OTr$, $R^6 = OH$

20 $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = OH$, $R^6 = OTr$

21 $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = OTs$, $R^6 = OH$

22 $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = OH$, $R^6 = OTs$

23 $R^1 = H$, $R^2,R^3 = PhCHO$; $R^4 = R^5 = Ac$, $R^6 = OAc$

24 $R^1 = H$, $R^2 = Bz$, $R^3 = Br$, $R^4 = R^5 = Ac$, $R^6 = OAc$

25 $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = Br$, $R^6 = OH$

26 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = Br$, $R^6 = OAc$

27 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = H$, $R^6 = OAc$

28 $R^1 = R^2 = R^3 = R^4 = R^5 = H$, $R^6 = OH$

29 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = N_3$, $R^6 = OAc$

30 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = NHAc$, $R^6 = OAc$

31 $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = NHAc$, $R^6 = OH$

32 $R^1 = R^4 = R^5 = H$, $R^2,R^3 = PhCHO$; $R^6 = OH$

33 $R^1 = R^4 = R^5 = Ac$; $R^2,R^3 = PhCHO$, $R^6 = OTs$

34 $R^1 = R^4 = R^5 = Ac$, $R^2,R^3 = PhCHO$, $R^6 = I$

35 $R^1 = R^4 = R^5 = Ac$, $R^2,R^3 = PhCHO$; $R^6 = N_3$

36 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = OAc$, $R^6 = I$

37 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = OAc$, $R^6 = N_3$

38 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = OAc$, $R^6 = H$

39 $R^1 = R^2 = R^4 = R^5 = R^6 = H$, $R^3 = OH$

40 $R^1 = R^2 = R^4 = R^5 = Ac$, $R^3 = OAc$, $R^6 = NHAc$

41 $R^1 = R^2 = R^4 = R^5 = H$, $R^3 = OH$, $R^6 = NHAc$

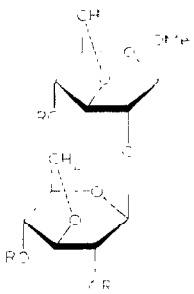
42 $R^1 = Ms$, $R^2,R^3 = PhCHO$; $R^4 = R^5 = Ac$, $R^6 = OAc$

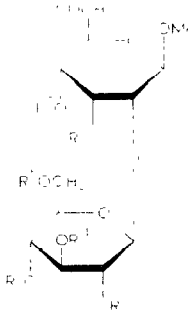
deoxy derivative **26**, which, when reductively dehalogenated, gave the 6-deoxy derivative **27**. *O*-Deacetylation of **27** produced **28** in crystalline form. Treatment of **26** with sodium azide in *N*,*N*-dimethylformamide gave the 6-azido-6-deoxy derivative **29**, which was reduced and the product acetylated, to afford the 6-acetamido-6-deoxy derivative **30**. This was *O*-deacetylated to give **31** in crystalline form.

Selective *p*-toluenesulfonylation of methyl 4,6-*O*-benzylidene-β-sophoroside[8] (**32**) with 1.5 mol. equiv. of reagent in pyridine, followed by acetylation, afforded the crystalline 3,2′,3′,4′-tetra-*O*-acetyl-4,6-*O*-benzylidene-6′-*O*-*p*-tolylsulfonyl derivative **33** in 74% yield. Displacement of the tosyloxy group of **33** with iodide and azide

ions, respectively, in *N*,*N*-dimethylformamide gave the 3,2′,3′,4′-tetra-*O*-acetyl-4,6-*O*-benzylidene-6′-deoxy-6′-iodo (**34**) and 3,2′,3′,4′-tetra-*O*-acetyl-6′-azido-4,6-*O*-benzylidene-6′-deoxy (**35**) derivatives, respectively, which were converted by sequential debenzylidenation and acetylation into the 6′-deoxy-6′-iodo (**36**) and 6′-azido-6′-deoxy (**37**) derivatives, respectively. Reductive dehalogenation of **36** gave the 6′-deoxy derivative **38**, which was *O*-deacetylated to provide **39** in crystalline form. On successive reduction and acetylation, **37** afforded the 6′-acetamido-6′-deoxy derivative **40**, which was *O*-deacetylated to **41**, obtained in crystalline form.

Methanesulfonylation of **23** afforded the 2′,3′,4′,6′-tetra-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(methylsulfonyl) derivative **42**, which was transformed, by displacement with benzoate ion in *N*,*N*-dimethylformamide, into methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-allopyranoside (**45**) in 68% yield. *O*-Deacylation of **45** gave crystalline methyl 4,6-*O*-benzylidene-2-*O*-β-D-glucopyranosyl-β-D-allopyranoside (**46**), which was debenzylidenated to furnish amorphous **47**. G.l.c. examination of the methanolyzate as the *O*-(trimethylsilyl) derivatives showed the presence of methyl α,β-D-allopyranoside and methyl α,β-D-glucopyranoside in the ratio of 1 : 1, which confirmed the structure assigned to **47**.





43 R = Ac
44 R = H

45 R = Bz R, R = PhCH R = Ac
46 R = R′ = R″ = H R′ = Ac
47 R = R′ = R″ = R‴ = H

EXPERIMENTAL

General methods. — Unless stated otherwise, the general experimental conditions were the same as those described previously[12]. Gas–liquid chromatography was performed with a Hitachi gas chromatograph 063, using a column (2.5 × 200 mm) of 5% of Silicone SE-30 on Chromosorb W (80–100 mesh) at an operating temperature of 185°, with nitrogen as the carrier gas, and a flame-ionization detector. Retention times for the per-*O*-(trimethylsilyl) derivatives of the methyl D-glycosides are given relative to that for that of methyl β-D-glucopyranoside as unity. The following solvent systems (v/v) were used: (*1*) 4 : 1 and (*2*) 1 : 1 benzene–ethyl acetate, and (*3*) 4 : 1 benzene–ethanol.

*Methyl 3,4-di-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-*D*-glucopyranosyl)-6-*O*-trityl-β-*D*-glucopyranoside* (**2**). — A solution of **1** (2.05 g, 5.75 mmol) and chlorotriphenylmethane (4.01 g, 14.4 mmol) in anhydrous pyridine (20 mL) was stirred with exclusion of moisture for 48 h at room temperature, cooled to 0°, treated with acetic anhydride (15 mL), and then kept overnight at room temperature. The solution was poured into ice–water, and the precipitate that separated was filtered off, washed with water, dried, dissolved in the minimal volume of chloroform, and fractionated on a column of silica gel with solvent *1*. The initial fraction from the column gave **2** as an amorphous powder (5.02 g, 83%); $[\alpha]_D^{22}$ +44.6° (*c* 1.3, chloroform); t.l.c. (solvent *1*): R_F 0.45; n.m.r. data (chloroform-*d*): δ 7.60–7.20 (m, 30 H, aryl H), 3.52 (s, 3 H, OMe), and 2.07, 2.02, 1.97, 1.75, and 1.72 (s, each 3 H, 5 OAc).

Anal. Calc. for $C_{61}H_{62}O_{16}$: C, 69.70; H, 5.95. Found: C, 69.91; H, 5.89.

*Methyl 3,4-di-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**3**). — A solution of **2** (4.85 g) in 80% aqueous acetic acid (150 mL) was stirred for 2.5 h at 70°. Removal of the solvents by codistillation with toluene gave a syrup, which was eluted from a column of silica gel with solvent *3*, to afford **3** as an amorphous powder (2.12 g, 81%); $[\alpha]_D^{22}$ −5.0° (*c* 1.2, chloroform); t.l.c. (solvent *3*): R_F 0.50.

Anal. Calc. for $C_{23}H_{34}O_{16}$: C, 48.76; H, 6.05. Found: C, 48.91; H, 5.92.

*Methyl 3,4-di-*O*-acetyl-6-*O*-p-tolylsulfonyl-2-*O*-(2,3,4-tri-*O*-acetyl-6-*O*-p-tolylsulfonyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**4**). — (*a*) A solution of **3** (1.84 g) in pyridine (20 mL) was treated with *p*-toluenesulfonyl chloride (1.86 g) at −10°, and kept overnight at room temperature. The solution was poured into ice–water, and the precipitate formed was filtered off, washed with water, dried, and recrystallized from ethanol–chloroform, to give **4** (2.64 g, 93%); m.p. 162–163°, $[\alpha]_D^{24}$ +17.8° (*c* 1.7, chloroform); n.m.r. data (chloroform-*d*): δ 7.87–7.29 (m, 8 H, aryl H), 3.44 (s, 3 H, OMe), 2.46 (s, 6 H, 2 aryl-CH_3), 2.03 (s, 3 H, OAc), 2.00 (s, 3 H, OAc), 1.19 (s, 3 H, OAc), and 1.96 (s, 6 H, 2 OAc).

Anal. Calc. for $C_{37}H_{46}O_{20}S_2$: C, 50.80; H, 5.30; S, 7.33. Found: C, 50.62; H, 5.38; S, 7.48.

(*b*) To a stirred solution of **1** (5.01 g, 14.1 mmol) in anhydrous pyridine (50 mL), maintained at −20°, was added portionwise *p*-toluenesulfonyl chloride (6.43 g, 33.7 mmol) during 1 h. The mixture was further stirred for 1 h at −20°, stored overnight at 0°, treated with acetic anhydride (35 mL), and then kept overnight at room temperature. The mixture was processed, as described in method *a*, to give **4** (8.48 g, 69%); m.p. and mixed m.p. 162–163°, $[\alpha]_D^{20}$ +17.6° (*c* 1.0, chloroform); the n.m.r. spectrum was identical with that of the compound prepared by method *a*.

*Methyl 3,4-di-*O*-acetyl-6-azido-6-deoxy-2-*O*-(2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**5**). — A solution of **4** (1.51 g) in *N*,*N*-dimethylformamide (30 mL) was stirred with sodium azide (3 g) for 3 h at 100°. The mixture was evaporated to dryness, and the residue was extracted with chloroform. The extract was washed with water, dried (sodium sulfate), and evaporated.

Crystallization from ethanol gave **5** (0.93 g, 88%); m.p. 159–160°, $[\alpha]_D^{25}$ +1.8 (*c* 1.1, chloroform); ν_{max} 2100 cm^{-1} (N_3).

Anal. Calc. for $C_{23}H_{32}N_6O_{14}$: C, 44.81; H, 5.23; N, 13.63. Found: C, 44.88; H, 5.34; N, 13.50.

Methyl 3,4-di-O-acetyl-6-bromo-6-deoxy-2-O-(2,3,4-tri-O-acetyl-6-bromo-6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (**6**). — A solution of **4** (0.82 g) in *N,N*-dimethylformamide (16 mL) containing sodium bromide (1.7 g) was stirred for 3 h at 100°. The mixture was processed as just described, to give **6** (0.58 g, 89%); m.p. 145–146° (ether–petroleum ether), $[\alpha]_D^{25}$ +12.5 (*c* 1.0, chloroform).

Anal. Calc. for $C_{23}H_{32}Br_2O_{14}$: C, 39.90; H, 4.66; Br, 23.08. Found: C, 40.14; H, 4.57; Br, 22.90.

Methyl 3,4-di-O-acetyl-6-chloro-6-deoxy-2-O-(2,3,4-tri-O-acetyl-6-chloro-6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (**7**). — A solution of **4** (0.91 g) in *N,N*-dimethylformamide (18 mL) containing lithium chloride (1.8 g) was stirred for 3 h at 100°. The mixture was processed as described for the preparation of **5**, to give **7** (0.53 g, 84%): m.p. 110–112° (ether–petroleum ether), $[\alpha]_D^{25}$ +11.8 (*c* 1.7, chloroform).

Anal. Calc. for $C_{23}H_{32}Cl_2O_{14}$: C, 45.78; H, 5.35; Cl, 11.75. Found: C, 45.93; H, 5.44; Cl, 11.48.

Methyl 3,4-di-O-acetyl-6-deoxy-6-iodo-2-O-(2,3,4-tri-O-acetyl-6-deoxy-6-iodo-β-D-glucopyranosyl)-β-D-glucopyranoside (**8**). — A solution of **4** (1.57 g) in *N,N*-dimethylformamide (30 mL) was stirred with sodium iodide (3 g) for 3 h at 100°. The mixture was evaporated to dryness, and the residue was extracted with chloroform. The extract was washed successively with water, 3% sodium thiosulfate, and water, dried (sodium sulfate), and evaporated to give a solid, which was recrystallized from ethanol to afford **8** (1.24 g, 88%); m.p. 159–160°, $[\alpha]_D^{24}$ +9.8° (*c* 1.6, chloroform).

Anal. Calc. for $C_{23}H_{32}I_2O_{14}$: C, 35.13; H, 4.10; I, 32.28. Found: C, 35.01; H, 4.04; I, 32.11.

Methyl 3,4-di-O-acetyl-6-S-acetyl-6-thio-2-O-(2,3,4-tri-O-acetyl-6-S-acetyl-6-thio-β-D-glucopyranosyl)-β-D-glucopyranoside (**9**). — A solution of **4** (0.31 g) in *N,N*-dimethylformamide (4 mL) containing potassium thiolacetate (0.16 g) was heated for 20 min at 100°. The precipitate, which separated on addition of ice–water, was filtered off, washed with water, and dried. Crystallization from 2-propanol gave **9** (0.20 g, 83%); m.p. 170–171°, $[\alpha]_D^{25}$ 8.1 (*c* 1.2, chloroform); n.m.r. data (chloroform-*d*): δ 2.38 and 2.36 (s, each 3 H, 2 SAc).

Anal. Calc. for $C_{27}H_{38}O_{16}S_2$: C, 47.50; H, 5.61; S, 9.39. Found: C, 47.42; H, 5.80; S, 9.24.

Methyl 6-acetamido-2-O-(6-acetamido-2,3,4-tri-O-acetyl-6-deoxy-β-D-glucopyranosyl)-3,4-di-O-acetyl-6-deoxy-β-D-glucopyranoside (**10**). Compound **5** (0.66 g) was dissolved in ethanol (25 mL), and a small amount of Raney nickel was added. The mixture was heated to boiling with stirring while hydrazine hydrate (2 mL) was added during 5 min. It was then boiled and stirred for a further 40 min under reflux,

cooled, filtered through a Celite layer, and evaporated to dryness. The residue was acetylated with acetic anhydride (2 mL) and pyridine (3 mL) overnight at room temperature. The solvents were removed by codistillation with toluene, to give a mass which, on recrystallization from 2-propanol–ethanol, afforded **10** (0.56 g, 81%); m.p. 163.5–165°, $[\alpha]_D^{25}$ −4.5° (*c* 2.2, chloroform).

Anal. Calc. for $C_{27}H_{40}N_2O_{16}$: C, 50.00; H, 6.22; N, 4.32. Found: C, 50.24; H, 6.30; N, 4.21.

*Methyl 3,4-di-*O*-acetyl-6-deoxy-2-*O*-(2,3,4-tri-*O*-acetyl-6-deoxy-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**11**). — A solution of **8** (1.01 g) in ethanol (40 mL) was mixed with barium carbonate (5 g) and a small amount of Raney nickel. The mixture was stirred under reflux while hydrazine hydrate (3 mL) was added dropwise during 5 min. The mixture was stirred and boiled for a further 20 min under reflux, cooled, and filtered through a layer of Celite, and the filtrate was evaporated. The residue was processed as described for the preparation of **8**, to give **11** (0.55 g, 80%); m.p. 170–171° (2-propanol), $[\alpha]_D^{24}$ +9.0° (*c* 1.8, chloroform); n.m.r. data (chloroform-*d*): δ 1.25 (d, 3 H, *J* 6.0 Hz, CH_3-5′), and 1.22 (d, 3 H, *J* 6.0 Hz, CH_3-5).

Anal. Calc. for $C_{23}H_{34}O_{14}$: C, 51.68; H, 6.41. Found: C, 51.81; H, 6.30.

*Methyl 4,6-*O*-benzylidene-2-*O*-(4,6-*O*-benzylidene-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**16**). — A suspension of **1** (2.0 g) and anhydrous powdered zinc chloride (2 g) in freshly distilled benzaldehyde (30 mL) was stirred for 6 h at room temperature. The solution was poured into a mixture of ice–water and petroleum ether, and the resulting precipitate was filtered off, successively washed with cold water and ether, and dried. Crystallization from methanol gave **16** (2.45 g, 82%); m.p. 224–226° (dec.), $[\alpha]_D^{18}$ −72.0° (*c* 1.2, *N*,*N*-dimethylformamide); n.m.r. data (dimethyl sulfoxide-d_6): δ 7.43–7.28 (m, 10 H, 2 Ph), 6.60 (broad s, 2 H, 2 benzylic H), and 3.42 (s, 3 H, OMe).

Anal. Calc. for $C_{27}H_{32}O_{11}$: C, 60.90; H, 6.06. Found: C, 61.08; H, 6.17.

*Methyl 3-*O*-acetyl-4,6-*O*-benzylidene-2-*O*-(2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**17**). — Conventional acetylation of **16** (2.06 g) with 1:1 (v/v) acetic anhydride–pyridine (20 mL) overnight at room temperature gave **17** (2.34 g, 92%); m.p. 241–242° (ethanol–chloroform), $[\alpha]_D^{18}$ −92.4° (*c* 1.2, chloroform); n.m.r. data (chloroform-*d*): δ 7.50–7.23 (m, 10 H, 2 Ph), 5.47 (broad s, 2 H, 2 benzylic H), 3.52 (s, 3 H, OMe), and 2.11, 2.06, and 2.02 (s, each 3 H, 3 OAc).

Anal. Calc. for $C_{33}H_{38}O_{14}$: C, 60.18; H, 5.82. Found: C, 60.32; H, 5.98.

*Methyl 3-*O*-acetyl-4-*O*-benzoyl-6-bromo-6-deoxy-2-*O*-(2,3-di-*O*-acetyl-4-*O*-benzoyl-6-bromo-6-deoxy-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**18**). — A mixture of **17** (1.17 g), barium carbonate (2 g), and *N*-bromosuccinimide (0.67 g) in dry carbon tetrachloride (40 mL) and 1,1,2,2-tetrachloroethane (20 mL) was boiled and stirred for 3 h under reflux. The mixture was filtered through a layer of Celite, and the inorganic solid was washed with chloroform. The filtrate and washings were combined, and evaporated to a syrup which was dissolved in chloroform. The solution was washed with water, dried (sodium sulfate), and evaporated to a solid which was recrystallized from ethanol, to afford **18** (1.20 g, 83%); m.p. 174–175°, $[\alpha]_D^{18}$ −66.0°

(*c* 1.2, chloroform); n.m.r. data (chloroform-*d*): δ 8.07–7.27 (m, 10 H, 2 Ph), 3.64 (s, 3 H, OMe), and 2.03, 1.97, and 1.87 (s, each 3 H, 3 OAc).

Anal. Calc. for $C_{33}H_{36}Br_2O_{14}$: C, 48.55; H, 4.44; Br, 19.57. Found: C, 48.69; H, 4.35; Br, 19.35.

Methyl 6-bromo-2-O-(6-bromo-6-deoxy-β-D-glucopyranosyl)-6-deoxy-β-D-glucopyranoside (**12**), *methyl 6-chloro-2-O-(6-chloro-6-deoxy-β-D-glucopyranosyl)-6-deoxy-β-D-glucopyranoside* (**13**), *methyl 6-acetamido-2-O-(6-acetamido-6-deoxy-β-D-glucopyranosyl)-6-deoxy-β-D-glucopyranoside* (**14**), *and methyl 6-deoxy-2-O-(6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside* (**15**). – *O*-Deacetylation of **6** (0.39 g), **7** (0.35 g), **10** (0.40 g), and **11** (0.36 g) in anhydrous methanol with a catalytic amount of sodium methoxide for 1 h at room temperature, followed by neutralization of the base with Amberlite IR-120 (H^+) ion-exchange resin, gave the corresponding unsubstituted glycosides **12**, **13**, **14**, and **15**, respectively.

Compound **12** (0.23 g, 85%): m.p. 168–169° (dec.) (ethanol–ether), $[\alpha]_D^{17}$ −50.7° (*c* 1.3, water).

Anal. Calc. for $C_{13}H_{22}Br_2O_9$: C, 32.39; H, 4.60; Br, 33.15. Found: C, 32.25; H, 4.49; Br, 32.92.

Compound **12** (0.24 g, 77%) was also obtained from **18** (0.52 g) by a similar *O*-deacylation; m.p. and mixed m.p. 168–169°, $[\alpha]_D^{20}$ 51.2° (*c* 1.1, water).

Compound **13** (0.18 g, 78%): m.p. 212–213° (dec.) (ethanol–ether), $[\alpha]_D^{25}$ −51.9° (*c* 1.0, water).

Anal. Calc. for $C_{13}H_{22}Cl_2O_9$: C, 39.71; H, 5.64; Cl, 18.03. Found: C, 39.95; H, 5.52; Cl, 17.86.

Compound **14** (0.22 g, 81%), m.p. 262–264° (dec.) (aqueous ethanol), $[\alpha]_D^{22}$ −32.9° (*c* 1.0, water); n.m.r. data (dimethyl sulfoxide-d_6): δ 1.85 (s, 6 H, 2 NAc).

Anal. Calc. for $C_{17}H_{30}N_2O_{11}$: C, 46.57; H, 6.90; N, 6.39. Found: C, 46.41; H, 6.84; N, 6.28.

Compound **15** (0.18 g, 82%): m.p. 200–202° (ethanol–ether), $[\alpha]_D^{24}$ −59.1 (*c* 0.8, water); n.m.r. data (dimethyl sulfoxide-d_6): δ 1.18 (d, 6 H, *J* 6.0 Hz, CH_3-5 and -5′).

Anal. Calc. for $C_{13}H_{24}O_9$: C, 48.14; H, 7.46. Found: C, 47.94; H, 7.57.

Methyl 4-O-acetyl-3,6-anhydro-2-O-(2,4-di-O-acetyl-3,6-anhydro-β-D-glucopyranosyl)-β-D-glucopyranoside (**43**). – To a solution of **4** (1.50 g) in methanol (20 mL) was added methanol (20 mL) containing sodium (1 g). The mixture was kept overnight at room temperature, the base neutralized with acetic acid, and the solution evaporated to dryness. The residue was treated with acetic anhydride (10 mL) and pyridine (15 mL), and the mixture was kept overnight at room temperature, and poured into ice–water. The precipitate formed was filtered off, washed with water, and dried. Crystallization from ethanol gave **43** (0.61 g, 79%): 147–148°, $[\alpha]_D^{26}$ 56.2° (*c* 1.8, chloroform); n.m.r. data (chloroform-*d*): δ 3.46 (s, 3 H, OMe), 2.14 (s, 6 H, 2 OAc), and 2.05 (s, 3 H, OAc).

Anal. Calc. for $C_{19}H_{26}O_{12}$: C, 51.12; H, 5.87. Found: C, 51.26; H, 5.99.

Methyl 3,6-anhydro-2-O-(3,6-anhydro-β-D-glucopyranosyl)-β-D-glucopyranoside

(**44**). — *O*-Deacetylation of **43** (0.49 g), as described earlier, gave **44** (0.31 g, 89%); m.p. 137–138° (ethanol), $[\alpha]_D^{26}$ −153.4° (*c* 2.2, water); n.m.r. data (deuterium oxide): δ 5.01 (d, 2 H, $J_{1,2} = J_{1',2'} = 1.5$ Hz, H-1,1'), and 3.47 (s, 3 H, OMe).

Anal. Calc. for $C_{13}H_{20}O_9$: C, 48.75; H, 6.29. Found: C, 48.60; H, 6.37.

*Methyl 4-*O*-benzoyl-6-bromo-6-deoxy-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**24**). — Compound **23** (3.02 g), *N*-bromosuccinimide (0.93 g), and barium carbonate (7 g) were suspended in carbon tetrachloride (130 mL) and 1,1,2,2-tetrachloroethane (80 mL). The mixture was stirred for 2 h under reflux, filtered through a Celite pad, and the filtrate evaporated. The residue was processed as described for the preparation of **8**, to give **24** (2.73 g, 80%); m.p. 91–93° (ether–petroleum ether), $[\alpha]_D^{15}$ −6.0° (*c* 1.6, chloroform); n.m.r. data (chloroform-*d*): δ 8.12–7.42 (m, 5 H, Ph), 3.62 (s, 3 H, OMe), 3.07 (broad s, 1 H, disappeared on deuteration, HO-3), and 2.07, 2.03, 2.02, and 1.98 (s, each 3 H, 4 OAc).

Anal. Calc. for $C_{28}H_{35}BrO_{15}$: C, 48.64; H, 5.10; Br, 11.56. Found: C, 48.71; H, 5.01; Br, 11.42.

*Methyl 6-bromo-6-deoxy-2-*O*-β-*D*-glucopyranosyl-β-*D*-glucopyranoside* (**25**). — *O*-Deacetylation of **24** (2.55 g) gave **25** (1.32 g, 85%); m.p. 195–197° (dec.) (methanol), $[\alpha]_D^{22}$ −65.1° (*c* 1.6, water).

Anal. Calc. for $C_{13}H_{23}BrO_{10}$: C, 37.25; H, 5.53; Br, 19.06. Found: C, 37.41; H, 5.45; Br, 18.92.

*Methyl 3,4-di-*O*-acetyl-6-bromo-6-deoxy-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**26**). — Acetylation of **25** (1.18 g) with 1:1 (v/v) acetic anhydride–pyridine (15 mL) gave **26** (1.77 g, 94%); m.p. 176–177° (ethanol), $[\alpha]_D^{22}$ +11.1° (*c* 1.4, chloroform).

Anal. Calc. for $C_{25}H_{35}BrO_{16}$: C, 44.72; H, 5.25; Br, 11.90. Found: C, 44.84; H, 5.37; Br, 11.76.

*Methyl 3,4-di-*O*-acetyl-6-deoxy-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**27**). — Treatment of **26** (0.65 g), in methanol (50 mL) containing barium carbonate (2 g) and a small amount of Raney nickel, with hydrazine hydrate (2 mL), as described for the preparation of **11**, gave **27** (0.51 g, 89%); m.p. 147–148° (ethanol), $[\alpha]_D^{15}$ +5.1° (*c* 1.2, chloroform); n.m.r. data (chloroform-*d*): δ 1.22 (d, 3 H, *J* 6.0 Hz, CH_3-5).

Anal. Calc. for $C_{25}H_{36}O_{16}$: C, 50.67; H, 6.12. Found: C, 50.90; H, 6.14.

*Methyl 6-deoxy-2-*O*-β-*D*-glucopyranosyl-β-*D*-glucopyranoside* (**28**). — *O*-Deacetylation of **27** (0.31 g) gave **28** (0.15 g, 83%); m.p. 185–187° (ethanol), $[\alpha]_D^{22}$ −52.4° (*c* 0.9, water); n.m.r. data (dimethyl sulfoxide-d_6): δ 1.18 (d, 3 H, *J* 6.0 Hz, CH_3-5).

Anal. Calc. for $C_{13}H_{24}O_{10}$: C, 45.88; H, 7.11. Found: C, 45.70; H, 7.18.

*Methyl 6-acetamido-2,3-di-*O*-acetyl-6-deoxy-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**30**). — Treatment of **29** (0.54 g), in ethanol (20 mL) containing a small amount of Raney nickel, with hydrazine hydrate (1 mL), followed by acetylation with 1:1 (v/v) acetic anhydride–pyridine (8 mL), as described

for the preparation of **10**, gave **30** (0.45 g, 82%); m.p. 166–167° (ethanol), $[\alpha]_D^{17}$ −11.3° (*c* 1.2, chloroform).

Anal. Calc. for $C_{27}H_{39}NO_{17}$: C, 49.92; H, 6.05; N, 2.16. Found: C, 50.16; H, 6.14; N, 2.05.

*Methyl 6-acetamido-6-deoxy-2-O-β-*D*-glucopyranosyl-β-*D*-glucopyranoside* (**31**). — *O*-Deacetylation of **30** (0.32 g) gave **31** (0.16 g, 80%); m.p. 254–255° (ethanol), $[\alpha]_D^{18}$ −36.4° (*c* 1.2, water); n.m.r. data (dimethyl sulfoxide-d_6) δ 1.84 (s, 3 H, NAc).

Anal. Calc. for $C_{15}H_{27}NO_{11}$: C, 45.34; H, 6.85; N, 3.52. Found: C, 45.27; H, 6.72; N, 3.60.

*Methyl 3-O-acetyl-4,6-O-benzylidene-2-O-(2,3,4-tri-O-acetyl-6-O-p-tolylsulfonyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**33**). — Sequential treatment of **32** (2.93 g, 6.6 mmol) in pyridine (30 mL) with *p*-toluenesulfonyl chloride (1.89 g, 9.9 mmol), and then with acetic anhydride (20 mL), as described for the preparation of **4** (method *b*), gave **33** (3.74 g, 74%); m.p. 140–141° (ethanol), $[\alpha]_D^{15}$ −30.3° (*c* 1.6, chloroform); n.m.r. data (chloroform-*d*): δ 7.88–7.23 (m, 9 H, aryl H), 5.48 (s, 3 H, benzylic H), 3.50 (s, 3 H, OMe), 2.46 (s, 3 H, aryl-CH_3), 2.10 (s, 3 H, OAc), 2.03 (s, 3 H, OAc), and 1.97 (s, 6 H, 2 OAc).

Anal. Calc. for $C_{35}H_{42}O_{17}S$: C, 54.83; H, 5.52; S, 4.18. Found: C, 54.74; H, 5.59; S, 4.27.

*Methyl 3-O-acetyl-4,6-O-benzylidene-2-O-(2,3,4-tri-O-acetyl-6-iodo-6-deoxy-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**34**). — A solution of **33** (1.50 g) in *N*,*N*-dimethylformamide (30 mL) containing sodium iodide (3 g) was stirred for 3 h at 100°. Processing of the mixture, as described for the preparation of **8**, gave **34** (1.22 g, 87%); m.p. 178–179° (2-propanol–ethanol), $[\alpha]_D^{15}$ −37.2° (*c* 1.7, chloroform).

Anal. Calc. for $C_{28}H_{33}IO_{14}$: C, 46.55; H, 4.88; I, 17.57. Found: C, 46.66; H, 4.82; I, 17.41.

*Methyl 3-O-acetyl-4,6-O-benzylidene-2-O-(2,3,4-tri-O-acetyl-6-azido-6-deoxy-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**35**). — A solution of **33** (1.66 g) in *N*,*N*-dimethylformamide (17 mL) was stirred with sodium azide (3.2 g) for 2 h at 100°. The product was isolated, as described for the preparation of **5**, to give **35** (1.16 g, 84%); m.p. 162–163° (ethanol), $[\alpha]_D^{17}$ +13.7° (*c* 1.3, chloroform), ν_{max} 2100 cm^{-1} (N_3).

Anal. Calc. for $C_{28}H_{33}N_3O_{14}$: C, 52.75; H, 5.53; N, 6.59. Found: C, 52.86; H, 5.46; N, 6.65.

*Methyl 3,4,6-tri-O-acetyl-2-O-(2,3,4-tri-O-acetyl-6-deoxy-6-iodo-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**36**). — A solution of **34** (1.11 g) in 60% acetic acid (17 mL) was heated for 20 min at 100°, and the solvents were removed by codistillation with toluene. The residue was acetylated with 1:1 (v/v) acetic anhydride–pyridine (15 mL) overnight at room temperature. Isolation in the usual way gave **36** (0.98 g, 89%); m.p. 139–140° (ethanol), $[\alpha]_D^{15}$ 0° (*c* 1.8, chloroform).

Anal. Calc. for $C_{28}H_{35}IO_{16}$: C, 41.79; H, 4.91; I, 17.66. Found: C, 41.62; H, 4.83; I, 17.50.

*Methyl 3,4,6-tri-O-acetyl-2-O-(2,3,4-tri-O-acetyl-6-azido-6-deoxy-β-*D*-glucopy-*

ranosyl)-β-D-glucopyranoside (**37**). — Treatment of **35** (0.94 g) in 60% acetic acid (17 mL) at 100°, followed by acetylation with 1:1 (v/v) acetic anhydride–pyridine (10 mL) as just described, gave **37** (0.77 g, 83%); m.p. 138–139° (ethanol), $[\alpha]_D^{17}$ +8.9° (*c* 1.3, chloroform); ν_{max} 2100 cm^{-1} (N_3).

Anal. Calc. for $C_{25}H_{35}N_3O_{16}$: C, 47.39; H, 5.57; N, 6.63. Found: C, 47.31; H, 5.69; N, 6.72.

Methyl 3,4,6-tri-O-acetyl-2-O-(2,3,4-tri-O-acetyl-6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (**38**). — Treatment of **36** (0.75 g), in ethanol (20 mL) containing barium carbonate (2 g) and a small amount of Raney nickel, with hydrazine hydrate (2 mL), as described for the preparation of **11**, gave **38** (0.53 g, 85%); m.p. 122–123° (2-propanol), $[\alpha]_D^{14}$ −1.8° (*c* 1.5, chloroform); n.m.r. data (chloroform-*d*): δ 1.25 (d, 3 H, *J* 6.0 Hz, CH_3-5′).

Anal. Calc. for $C_{25}H_{36}O_{16}$: C, 50.67; H, 6.12. Found: C, 50.88; H, 6.05.

Methyl 2-O-(6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (**39**). — *O*-Deacetylation of **38** (0.34 g) gave **39** (0.16 g, 80%); m.p. 209–210° (methanol), $[\alpha]_D^{15}$ −47.8° (*c* 1.2, water); n.m.r. data (dimethyl sulfoxide-d_6): δ 1.15 (d, 3 H, *J* 6.0 Hz, CH_3-5′).

Anal. Calc. for $C_{13}H_{24}O_{10}$: C, 45.88; H, 7.11. Found: C, 50.02; H, 7.19.

Methyl 2-O-(6-acetamido-2,3,4-tri-O-acetyl-6-deoxy-β-D-glucopyranosyl)-3,4,6-tri-O-acetyl-β-D-glucopyranoside (**40**). — Treatment of **37** (0.57 g), in ethanol (20 mL) containing a small amount of Raney nickel, with hydrazine hydrate (1.5 mL), followed by acetylation with 1:1 (v/v) acetic anhydride–pyridine (7 mL), as described for the preparation of **10**, gave a syrupy product, which was eluted from a column of silica gel with solvent *3*, to afford **40** as an amorphous powder (0.45 g, 78%); $[\alpha]_D^{17}$ −6.4° (*c* 1.3, chloroform).

Anal. Calc. for $C_{27}H_{39}NO_{17}$: C, 49.92; H, 6.05; N, 2.16. Found: C, 50.10; H, 6.13; N, 2.04.

Methyl 2-O-(6-acetamido-6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (**41**). — *O*-Deacetylation of **40** (0.26 g) gave **41** (0.14 g, 88%); m.p. 191–193° (ethanol–methanol), $[\alpha]_D^{18}$ −23.0° (*c* 1.3, water); n.m.r. data (dimethyl sulfoxide-d_6): δ 1.80 (s, 3 H, NAc).

Anal. Calc. for $C_{15}H_{27}NO_{11}$: C, 45.34; H, 6.85; N, 3.52. Found: C, 45.22; H, 6.97; N, 3.43.

Methyl 4,6-O-benzylidene-3-O-(methylsulfonyl)-2-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-β-D-glucopyranoside (**42**). — A solution of **23** (2.05 g) in pyridine (20 mL) was cooled to −20°, and treated with methanesulfonyl chloride (3 mL). After being kept overnight at 0°, the solution was poured into ice–water, and the precipitate formed was filtered off, washed with water, and dried. Crystallization from ethanol gave **42** (2.02 g, 87%); m.p. 138–139°, $[\alpha]_D^{20}$ −49.4° (*c* 1.7, chloroform); n.m.r. data (chloroform-*d*): δ 7.38 (broad s, 5 H, Ph), 5.53 (s, 1 H, benzylic H), 3.55 (s, 3 H, OMe), 2.95 (s, 3 H, OMs), 2.08 (s, 6 H, 2 OAc), 2.02 (s, 3 H, OAc), and 2.00 (s, 3 H, OAc).

Anal. Calc. for $C_{29}H_{38}O_{17}S$: C, 50.43; H, 5.55; S, 4.64. Found: C, 50.30; H, 5.42; S, 4.52.

Methyl 3-O-benzoyl-4,6-O-benzylidene-2-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-β-D-glucopyranoside (**45**). — A solution of **42** (1.76 g) in *N,N*-dimethylformamide (50 mL) containing sodium benzoate (2 g) was stirred for 25 h at 90°. The mixture was cooled, diluted with water (100 mL), and extracted with chloroform (4 × 40 mL). The extracts were combined, extensively washed with water, dried (sodium sulfate), and evaporated. The syrupy product was fractionated on a column of silica gel with solvent 2, and the fractions containing the major product were evaporated, to give amorphous **45** (1.24 g, 68%); $[\alpha]_D^{20}$ −38.4° (*c* 0.8, chloroform); t.l.c. (solvent 2): R_1 0.48.

Anal. Calc. for $C_{35}H_{40}O_{16}$: C, 58.66; H, 5.36. Found: C, 58.83; H, 5.79.

Methyl 4,6-O-benzylidene-2-O-β-D-glucopyranosyl-β-D-allopyranoside (**46**). — *O*-Deacetylation of **45** (1.07 g) gave **46** (0.59 g, 89%); m.p. 233–234.5° (ethanol), $[\alpha]_D^{20}$ −97.0° (*c* 0.9, pyridine).

Anal. Calc. for $C_{20}H_{28}O_{11}$: C, 54.05; H, 6.35. Found: C, 54.24; H, 5.23.

Methyl 2-O-β-D-glucopyranosyl-β-D-allopyranoside (**47**). — Treatment of **46** (0.39 g) in 60% acetic acid at 100°, as described for the preparation of **35**, gave amorphous **47** (0.28 g, 90%); $[\alpha]_D^{20}$ −93.0° (*c* 1.2, water).

Anal. Calc. for $C_{13}H_{24}O_{11}$: C, 43.82; H, 6.79. Found: C, 43.98; H, 6.87.

Methanolysis of **47** (20 mg) with 1% methanolic hydrogen chloride (5 mL) under reflux for 15 h, and g.l.c. of the resulting methyl glycosides as the *O*-(trimethylsilyl) derivatives gave peaks corresponding to methyl α,β-D-allopyranoside (*T* 0.57 and 0.63, 50%) and methyl α,β-D-glucopyranoside (*T* 0.91 and 1.00, 50%).

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