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Note

Synthesis of derivatives of methyl β-laminarabioside

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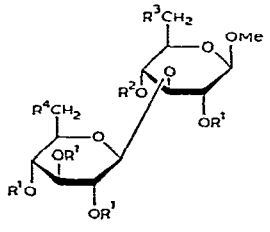
Laminarabiose is either the sole or major repeating unit of many types of polysaccharide[1]. Recently, we reported a convenient synthesis of laminarabiose[2] and some of its glycosides[2–4]. We have synthesized several laminarabiose derivatives which may serve as models for solvolytic and displacement reactions of higher members of laminaradextrins[5] and polysaccharides[1] that contain exclusively (1→3)-β-D-glucosidic linkages. The present paper describes the synthesis of several 6,6′-disubstituted derivatives of methyl β-laminarabioside[2,3] (**1**) by replacement reactions of the sulfonyloxy groups of methyl 2,4,2′,3′,4′-penta-*O*-acetyl-6,6′-di-*O*-*p*-tolylsulfonyl-β-laminarabioside (**4**) with various nucleophiles, and the preparation of methyl 6- (**25**) and 6′-deoxy-β-laminarabioside (**31**). In order to obtain **4**, the key intermediate in the synthesis of a homologous series of 6,6′-disubstituted derivatives of **1**, two routes were studied. In the first, tritylation of **1** with 2.4 mol. equiv. of reagent in pyridine followed by acetylation gave, in 81% yield, the crystalline 6,6′-di-*O*-trityl derivative **2**, which was *O*-detritylated with aqueous acetic acid to afford, in 80%



1 $R^1 = R^2 = H, R^3 = R^4 = OH$
2 $R^1 = R^2 = Ac, R^3 = R^4 = OTr$
3 $R^1 = R^2 = Ac, R^3 = R^4 = OH$
4 $R^1 = R^2 = Ac, R^3 = R^4 = OTs$
5 $R^1 = R^2 = H, R^3 = OTr, R^4 = OH$
6 $R^1 = R^2 = H, R^3 = OH, R^4 = OTr$
7 $R^1 = R^2 = H, R^3 = OTs, R^4 = OH$
8 $R^1 = R^2 = H, R^3 = OH, R^4 = OTs$
9 $R^1 = R^2 = Ac, R^3 = R^4 = I$
10 $R^1 = R^2 = Ac, R^3 = R^4 = Br$
11 $R^1 = R^2 = Ac, R^3 = R^4 = Cl$
12 $R^1 = R^2 = Ac, R^3 = R^4 = SAc$
13 $R^1 = R^2 = Ac, R^3 = R^4 = N_3$
14 $R^1 = R^2 = Ac, R^3 = R^4 = H$
15 $R^1 = R^2 = Ac, R^3 = R^4 = NHAc$
16 $R^1 = R^2 = H, R^3 = R^4 = Br$
17 $R^1 = R^2 = H, R^3 = R^4 = Cl$
18 $R^1 = R^2 = R^3 = R^4 = H$
19 $R^1 = R^2 = H, R^3 = R^4 = NHAc$
20 $R^1 = Ac; R^2, R^3 = PhCHO; R^4 = OAc$
21 $R^1 = Ac, R^2 = Bz, R^3 = Br, R^4 = OAc$
22 $R^1 = R^2 = H, R^3 = Br, R^4 = OH$
23 $R^1 = R^2 = Ac, R^3 = Br, R^4 = OAc$
24 $R^1 = R^2 = Ac, R^3 = H, R^4 = OAc$
25 $R^1 = R^2 = R^3 = H, R^4 = OH$
26 $R^1 = H; R^2, R^3 = PhCHO; R^4 = OH$
27 $R^1 = Ac; R^2, R^3 = PhCHO; R^4 = OTs$
28 $R^1 = Ac; R^2, R^3 = PhCHO; R^4 = I$
29 $R^1 = R^2 = Ac, R^3 = OAc, R^4 = I$
30 $R^1 = R^2 = Ac, R^3 = OAc, R^4 = H$
31 $R^1 = R^2 = R^4 = H, R^3 = OH$

yield, the crystalline 2,4,2′,3′,4′-penta-*O*-acetyl derivative **3** having free OH-6 and -6″ groups. *p*-Toluenesulfonylation of **3** gave **4** in crystalline form in 91% yield. The overall yield of **4** was 59%, based on **1**. In a second study, treatment of **1** with 2.3 mol. equiv. of *p*-toluenesulfonyl chloride in pyridine at −20° and subsequent acetylation gave a mixture from which **4** was directly isolated in crystalline form in 70% yield. The compounds obtained by both routes were shown to be identical by comparison of their m.p., optical rotation, n.m.r. spectra, and behavior in t.l.c. Attempted regioselective tritylation and *p*-toluenesulfonylation of **1** with 1.1 mol. equiv. of reagents in pyridine, with a view to obtaining the 6- (**5**) and 6′-monotrityl (**6**) ethers, and the 6- (**7**) and 6′-*O*-*p*-tolylsulfonyl (**8**) derivatives, respectively, as the starting materials for the chemical modification of the 6- and 6′-positions in **1**, were not successful, because each of the reactions gave a mixture that was difficult to separate by chromatography and fractional crystallization.

Nucleophilic displacement of **4** with iodide, bromide, chloride, thioacetate, and azide ions in *N*,*N*-dimethylformamide afforded 6,6′-dideoxy-6,6′-diiodo (**9**), 6,6′-dibromo-6,6′-dideoxy (**10**), 6,6′-dichloro-6,6′-dideoxy (**11**), 6,6′-di-*S*-acetyl-6,6′-dithio (**12**) and 6,6′-diazido-6,6′-dideoxy (**13**) derivatives, respectively, of methyl β-laminarabioside pentaacetate in high yields. Reductive dehalogenation of **9** with Raney nickel in the presence of hydrazine[6] gave the 6,6′-dideoxy derivative **14**. In the n.m.r. spectrum of **14** in chloroform-*d*, the signals due to CH_3-5 and -5′ overlapped at δ 1.24 as a doublet (J 6.0 Hz). Compound **13** was successively hydrogenated and acetylated to give the 6,6′-diacetamido-6,6′-dideoxy derivative **15**. *O*-Deacetylation of **10**, **11**, **14**, and **15** furnished methyl 6,6′-dibromo-6,6′-dideoxy-β-laminarabioside (**16**), methyl 6,6′-dichloro-6,6′-dideoxy-β-laminarabioside (**17**), methyl 6,6′-dideoxy-β-laminarabioside (**18**), and methyl 6,6′-diacetamido-6,6′-dideoxy-β-laminarabioside (**19**), respectively, all the compounds being obtained in crystalline form.

Oxidative removal of the benzylidene group of methyl 2,2′,3′,4′,6′-penta-*O*-acetyl-4,6-*O*-benzylidene-β-laminarabioside[3] (**20**) with *N*-bromosuccinimide[7] gave the 2,2′,3′,4′,6′-penta-*O*-acetyl-4-*O*-benzoyl-6-bromo-6-deoxy derivative **21**, which on *O*-deacylation afforded methyl 6-bromo-6-deoxy-β-laminarabioside (**22**). Acetylation of **22** gave the 6-bromo-6-deoxy derivative **23**, which was reductively dehalogenated to provide the 6-deoxy derivative **24**. This was *O*-deacetylated to furnish **25** in crystalline form.

Selective *p*-toluenesulfonylation of methyl 4,6-*O*-benzylidene-β-laminarabioside[3] (**26**) with 1.5 mol. equiv. of reagent in pyridine, followed by acetylation afforded the crystalline 2,2′,3′,4′-tetra-*O*-acetyl-4,6-*O*-benzylidene-6′-*O*-*p*-tolylsulfonyl derivative **27** in 80% yield. Displacement of the tosyloxy group of **27** with iodide ion in *N*,*N*-dimethylformamide gave the 2,2′,3′,4′-tetra-*O*-acetyl-4,6-*O*-benzylidene-6′-deoxy-6′-iodo derivative **28**, which was converted by sequential debenzylidenation and acetylation into the 6′-deoxy-6′-iodo derivative **29**. Reductive dehalogenation of **29** produced the 6′-deoxy derivative **30**, which was *O*-deacetylated to provide **31** in crystalline form.

EXPERIMENTAL

General methods. — The general experimental conditions were the same as those described previously[3].

*Methyl 2,4-di-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-*D*-glucopyranosyl)-6-*O*-trityl-β-*D*-glucopyranoside* (**2**). — A solution of **1** (867 mg, 2.4 mmol) and chlorotriphenylmethane (1.629 g, 5.8 mmol) in anhydrous pyridine (10 mL) was stirred for 48 h at room temperature with exclusion of moisture, cooled to 0°, treated with acetic anhydride (8 mL), and then kept overnight at room temperature. The solution was poured into ice–water, and the resulting precipitate was filtered off, washed with water, and dried. Crystallization from ethanol and recrystallization from ethanol–chloroform gave **2** (2.071 g, 81%), m.p. 211–212°, $[\alpha]_D^{22}$ +2.3° (*c* 1.7, chloroform); n.m.r. (chloroform-*d*): δ 7.59–7.18 (m, 30 H, aryl-H), 3.56 (s, 3 H, OMe), 2.15, 2.11, 2.00, 1.73, and 1.58 (s, each 3 H, 5 OAc); t.l.c.: R_F 0.58 (2:1, v/v, benzene–ethyl acetate).

Anal. Calc. for $C_{61}H_{62}O_{16}$: C, 69.70; H, 5.95. Found: C, 69.77; H, 6.03.

*Methyl 2,4-di-*O*-acetyl-3-*O*-(2,3,4-tri-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**3**). — A solution of **2** (1.0 g) in 80% aqueous acetic acid (35 mL) was stirred for 2.5 h at 70°. Removal of the solvents by co-distillation with toluene gave a crystalline mass that was recrystallized twice from ethanol to afford **3** (431 mg, 80%), m.p. 190–192°, $[\alpha]_D^{22}$ −47.3° (*c* 1.3, chloroform).

Anal. Calc. for $C_{23}H_{34}O_{16}$: C, 48.76; H, 6.05. Found: C, 48.70; H, 6.12.

*Methyl 2,4-di-*O*-acetyl-6-*O*-p-tolylsulfonyl-3-*O*-(2,3,4-tri-*O*-acetyl-6-*O*-p-tolylsulfonyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**4**). — (*a*) A solution of **3** (381 mg) in dry pyridine (5 mL) was treated with *p*-toluenesulfonyl chloride (384 mg) at −10° and kept overnight at room temperature. The reaction mixture was poured into ice–water, and the precipitate formed was filtered off, washed with water, dried, and crystallized from ethanol–chloroform to give **4** (535 mg, 91%), m.p. 174–175°, $[\alpha]_D^{24}$ −4.3° (*c* 1.9, chloroform); n.m.r. (chloroform-*d*): δ 7.85–7.27 (m, 8 H, aryl-H), 3.40 (s, 3 H, OMe), 2.47 (s, 6 H, 2 aryl-CH_3), 2.10, 1.98, 1.95, 1.93, and 1.90 (s, each 3 H, 5 OAc); t.l.c.: R_F 0.40 (3:2, v/v, ethyl acetate–benzene).

Anal. Calc. for $C_{37}H_{46}O_{20}S_2$: C, 50.80; H, 5.30; S, 7.33. Found: C, 50.87; H, 5.34; S, 7.24.

(*b*) To a stirred solution of **1** (2.988 g, 8.4 mmol) in anhydrous pyridine (30 mL), cooled to −20°, was added portionwise *p*-toluenesulfonyl chloride (3.667 g, 19.3 mmol). The mixture was further stirred for 1 h at −20°, stored overnight at 0°, treated with acetic anhydride (20 mL), and then kept overnight at room temperature. The reaction mixture was processed, as described in method *a*, to give **4** (5.135 g, 70%), m.p. 174–175°, $[\alpha]_D^{22}$ −4.4° (*c* 2.2, chloroform); the n.m.r. spectrum and the mobility in t.l.c. were identical with those of the compound prepared by method *a*.

*Methyl 2,4-di-*O*-acetyl-6-deoxy-6-iodo-3-*O*-(2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**9**). — A solution of **4** (1.335 g) in *N*,*N*-dimethylformamide (25 mL) containing sodium iodide (2 g) was heated for 2 h at

100°. The mixture was concentrated to dryness and the residue was extracted with chloroform. The extract was washed extensively with water, dried (sodium sulfate), and evaporated. Crystallization from ethanol gave **9** (1.032 g, 86%), m.p. 220–221°, $[\alpha]_D^{24}$ −7.2° (*c* 2.2, chloroform).

Anal. Calc. for $C_{23}H_{32}I_2O_{14}$: C, 35.13; H, 4.10; I, 32.28. Found: C, 35.21; H, 4.06; I, 32.17.

Methyl 2,4-di-O-acetyl-6-bromo-6-deoxy-3-O-(2,3,4-tri-O-acetyl-6-bromo-6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (**10**). — Sodium bromide (800 mg) was added to a solution of **4** (635 mg) in *N,N*-dimethylformamide (12 mL). The mixture was heated for 2 h at 100° with stirring, and then processed as just described. The residue was crystallized from ethanol to afford **10** (440 mg, 88%), m.p. 242–243°, $[\alpha]_D^{25}$ −27.8° (*c* 1.6, chloroform).

Anal. Calc. for $C_{23}H_{32}Br_2O_{14}$: C, 39.90; H, 4.66; Br, 23.08. Found: C, 39.81; H, 4.75; Br, 23.20.

Methyl 2,4-di-O-acetyl-6-chloro-6-deoxy-3-O-(2,3,4-tri-O-acetyl-6-chloro-6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (**11**). — A solution of **4** (719 mg) and lithium chloride (0.9 g) in *N,N*-dimethylformamide (14 mL) was heated for 3 h at 100°. The product was isolated, as described for the preparation of **9**, to give **11** (431 mg, 87%), m.p. 244–245° (ethanol), $[\alpha]_D^{25}$ −29.5° (*c* 1.1, chloroform).

Anal. Calc. for $C_{23}H_{32}Cl_2O_{14}$: C, 45.78; H, 5.35; Cl, 11.75. Found: C, 45.86; H, 5.44; Cl, 11.26.

Methyl 2,4-di-O-acetyl-6-S-acetyl-6-thio-3-O-(2,3,4-tri-O-acetyl-6-S-acetyl-6-thio-β-D-glucopyranosyl)-β-D-glucopyranoside (**12**). — A solution of **4** (300 mg) in *N,N*-dimethylformamide (4 mL) containing potassium thioacetate (211 mg) was heated for 20 min at 100°. The cooled mixture was poured into ice–water, and the precipitate was filtered off, washed with water, and dried. Crystallization from ether–petroleum ether gave **12** (206 mg, 88%), m.p. 149–150°, $[\alpha]_D^{25}$ −42.2° (*c* 1.0, chloroform); n.m.r. (chloroform-*d*): δ 2.35 and 2.33 (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, 47.57; H, 5.58; S, 9.26.

Methyl 2,4-di-O-acetyl-6-azido-6-deoxy-3-O-(2,3,4-tri-O-acetyl-6-azido-6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (**13**). — A solution of **4** (1.240 g) and sodium azide (1.5 g) in *N,N*-dimethylformamide (14 mL) was heated for 3 h at 100°. The mixture was processed, as described for the preparation of **9**, to give **13** (760 mg, 87%), m.p. 189–191° (ethanol–chloroform), $[\alpha]_D^{25}$ −56.3° (*c* 1.3, chloroform).

Anal. Calc. for $C_{23}H_{32}N_6O_{14}$: C, 44.81; H, 5.23; N, 13.63. Found: C, 44.89; H, 5.19; N, 12.84.

Methyl 2,4-di-O-acetyl-6-deoxy-3-O-(2,3,4-tri-O-acetyl-6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (**14**). — A solution of **9** (971 mg) in methanol (40 mL) was mixed with barium carbonate (3 g) and heated to boiling with stirring. A small amount of Raney nickel was added to the mixture, and, after 5 min, hydrazine hydrate (2 mL) was added dropwise during 5 min. The mixture was boiled for 20 min under reflux, then filtered through a Celite pad, and the filtrate was evaporated. The residue

was dissolved in chloroform, and the solution was washed successively with water, 5% sodium thiosulfate, and water, dried (sodium sulfate), and evaporated to a solid which was recrystallized from ethanol to give **14** (548 mg, 83%), m.p. 220–222°, $[\alpha]_D^{24}$ −34.9° (*c* 1.4, chloroform).

Anal. Calc. for $C_{23}H_{34}O_{14}$: C, 51.68; H, 6.41. Found: C, 51.76; H, 6.33.

*Methyl 6-acetamido-3-*O*-(6-acetamido-2,3,4-tri-*O*-acetyl-6-deoxy-β-*D*-glucopyranosyl)-2,4-di-*O*-acetyl-6-deoxy-β-*D*-glucopyranoside* (**15**). — Compound **13** (511 mg) was dissolved in methanol (30 mL), and a small amount of Raney nickel was added. The mixture was heated to boiling while hydrazine hydrate (1 mL) was added dropwise during 5 min. It was then heated for a further 40 min under reflux, filtered through a Celite layer, and evaporated to dryness. The residue was acetylated with acetic anhydride (2 mL) and pyridine (4 mL) overnight at room temperature. The solution was evaporated to a syrup which crystallized from 2-propanol to give **15** (433 mg, 80%), m.p. 126–128°, $[\alpha]_D^{26}$ −28.4° (*c* 2.0, chloroform).

Anal. Calc. for $C_{27}H_{40}N_2O_{16}$: C, 50.00; H, 6.22; N, 4.32. Found: C, 49.89; H, 6.29; N, 4.25.

*Methyl 6-bromo-3-*O*-(6-bromo-6-deoxy-β-*D*-glucopyranosyl)-6-deoxy-β-*D*-glucopyranoside* (**16**), *methyl 6-chloro-3-*O*-(6-chloro-6-deoxy-β-*D*-glucopyranosyl)-6-deoxy-β-*D*-glucopyranoside* (**17**), *methyl 6-deoxy-3-*O*-(6-deoxy-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**18**), *and methyl 6-acetamido-3-*O*-(6-acetamido-6-deoxy-β-*D*-glucopyranosyl)-6-deoxy-β-*D*-glucopyranoside* (**19**). — Compounds **10**, (335 mg), **11** (316 mg), **14** (431 mg), and **15** (220 mg) were each treated with a catalytic amount of sodium methoxide in anhydrous methanol in the usual way to give the corresponding unsubstituted glycosides **16**, **17**, **18**, and **19**, respectively.

Compound **16** (212 mg, 91%): m.p. 191–192° (dec.) (ethanol), $[\alpha]_D^{25}$ −46.6° (*c* 1.0, methanol).

Anal. Calc. for $C_{13}H_{22}Br_2O_9$: C, 32.39; H, 4.60; Br, 33.15. Found: C, 32.47; H, 4.67; Br, 33.07.

Compound **17** (187 mg, 91%): m.p. 200–201° (dec.) (ethanol–ether), $[\alpha]_D^{24}$ −58.4° (*c* 0.8, methanol).

Anal. Calc. for $C_{13}H_{22}Cl_2O_9$: C, 39.71; H, 5.64; Cl, 18.03. Found: C, 39.80; H, 5.71; Cl, 17.92.

Compound **18** (240 mg, 92%): m.p. 211–213° (ether), $[\alpha]_D^{25}$ −29.5° (*c* 1.0, methanol); n.m.r. (dimethyl sulfoxide-d_6): δ 1.19 (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, 48.21; H, 7.40.

Compound **19** (134 mg, 90%): m.p. 278–280° (ethanol), $[\alpha]_D^{22}$ −23.8° (*c* 0.8, methanol); n.m.r. (dimethyl sulfoxide-d_6): δ 7.75 (broad s, 2 H, 2 NH) and 1.83 (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, 46.64; H, 6.95; N, 6.26.

*Methyl 2-*O*-acetyl-4-*O*-benzoyl-6-bromo-6-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**21**). — A mixture of **20** (2.0 g), barium carbonate (4 g), and *N*-bromosuccinimide (654 mg) in anhydrous carbon tetra-

chloride (50 mL) and 1,1,2,2-tetrachloroethane (30 mL) was heated for 3 h, while being stirred. The mixture was filtered, and the inorganic precipitate was washed with chloroform. The combined filtrates were evaporated to a syrup which was dissolved in chloroform. The solution was washed with water, dried (sodium sulfate), and evaporated to dryness. The residue was crystallized from chloroform–ethanol to give **21** (1.815 g, 81%), m.p. 258–259°, $[\alpha]_D^{22}$ −88.4° (*c* 1.6, chloroform); n.m.r. (chloroform-*d*): δ 8.13–7.28 (m, 5 H, aryl-H), 3.53 (s, 3 H, OMe), 2.15 (s, 3 H, OAc), 2.02 (s, 6 H, 2 OAc), 1.94 (s, 6 H, OAc), and 1.90 (s, 3 H, OAc).

Anal. Calc. for $C_{30}H_{37}BrO_{16}$: C, 49.12; H, 5.08; Br, 10.89. Found: C, 49.24; H, 5.02; Br, 10.76.

*Methyl 6-bromo-6-deoxy-3-*O*-β-*D*-glucopyranosyl-β-*D*-glucopyranoside* (**22**). — A solution of **21** (1.751 g) in dry methanol (20 mL) and anhydrous chloroform (10 mL) was treated with M sodium methoxide (1 mL) for 2 h at room temperature, neutralized with Amberlite IR-120 (H^+) ion-exchange resin, filtered, and evaporated to give **22** (950 mg, 95%) as an amorphous powder, $[\alpha]_D^{24}$ −24.5° (*c* 2.0, water).

Anal. Calc. for $C_{13}H_{23}BrO_{10}$: C, 37.25; H, 5.53; Br, 19.06. Found: C, 37.41; H, 5.46; Br, 19.16.

*Methyl 2,4-di-*O*-acetyl-6-bromo-6-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**23**). — Conventional acetylation of **22** (760 mg) with 1 : 1 (v/v) acetic anhydride–pyridine (8 mL) overnight at room temperature gave **23** (1.119 g, 92%), m.p. 207–209° (ethanol–chloroform), $[\alpha]_D^{22}$ −41.0° (*c* 1.4, chloroform).

Anal. Calc. for $C_{25}H_{35}BrO_{16}$: C, 44.72; H, 5.25; Br, 11.90. Found: C, 44.82; H, 5.32; Br, 11.77.

*Methyl 2,4-di-*O*-acetyl-6-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**24**). — Treatment of **23** (1.015 g) in methanol (100 mL) with barium carbonate (4 g), a small amount of Raney nickel, and hydrazine hydrate (2 mL), as described for the preparation of **14**, gave **24** (738 mg, 82%), m.p. 198–199° (ethanol), $[\alpha]_D^{22}$ −47.2° (*c* 1.1, chloroform); n.m.r. (chloroform-*d*): δ 1.24 (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, 50.78; H, 6.18.

*Methyl 6-deoxy-3-*O*-β-*D*-glucopyranosyl-β-*D*-glucopyranoside* (**25**). — *O*-Deacetylation of **24** (533 mg) with methanolic sodium methoxide in methanol in the usual way afforded **25** (281 mg, 92%), m.p. 185–186° (ethanol), $[\alpha]_D^{22}$ −35.8° (*c* 1.7, water); n.m.r. (dimethyl sulfoxide-d_6): δ 1.19 (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, 45.75; H, 7.20.

*Methyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2,3,4-tri-*O*-acetyl-6-*O*-p-tolylsulfonyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**27**). — Sequential treatment of **26** (1.289 g, 2.7 mmol) with *p*-toluenesulfonyl chloride (765 mg, 4.0 mmol) in dry pyridine (25 mL), and then with acetic anhydride (15 mL), as described for the preparation of **4** (method *b*), gave **27** (1.779 g, 80%), m.p. 180–181° (ethanol–chloroform), $[\alpha]_D^{15}$ −25.5° (*c* 1.7, chloroform); n.m.r. (chloroform-*d*): δ 7.82–7.23 (m, 9 H,

aryl H), 5.52 (s, 1 H, benzylic H), 3.48 (s, 3 H, OMe), 2.44 (s, 3 H, aryl-CH_3), 2.12 (s, 3 H, OAc), 2.03 (s, 3 H, OAc), and 1.96 (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, 54.89; H, 5.57; S, 4.09.

Methyl 2-O-acetyl-4,6-O-benzylidene-3-O-(2,3,4-tri-O-acetyl-6-deoxy-6-iodo-β-D-glucopyranosyl)-β-D-glucopyranoside (**28**). — A solution of **27** (1.557 g) in *N,N*-dimethylformamide (15 mL) was stirred with sodium iodide (1.5 g) for 2 h at 100°. The reaction mixture was processed as described earlier to give **28** (1.305 g, 89%), m.p. 209–210° (ethanol), $[\alpha]_D^{14}$ −48.0° (*c* 1.8, chloroform).

Anal. Calc. for $C_{28}H_{35}IO_{14}$: C, 46.55; H, 4.88; I, 17.57. Found: C, 46.71; H, 4.95; I, 17.68.

Methyl 2,4,6-tri-O-acetyl-3-O-(2,3,4-tri-O-acetyl-6-deoxy-6-iodo-β-D-glucopyranosyl)-β-D-glucopyranoside (**29**). — A solution of **28** (1.201 g) in 60% acetic acid (20 mL) was heated for 15 min at 100°, and the solvents were removed by codistillation with toluene. The residue was acetylated with 1 : 1 (v/v) acetic anhydride–pyridine (12 mL) overnight at room temperature. Isolation in the usual way gave **29** (1.042 g, 87%), m.p. 190–191° (ethanol), $[\alpha]_D^{15}$ −19.0° (*c* 1.2, chloroform).

Anal. Calc. for $C_{25}H_{35}IO_{16}$: C, 41.79; H, 4.91; I, 17.66. Found: C, 41.90; H, 4.87; I, 17.50.

Methyl 2,4,6-tri-O-acetyl-3-O-(2,3,4-tri-O-acetyl-6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (**30**). — Treatment of **29** (815 mg) in methanol (40 mL) with barium carbonate (3 g), a small amount of Raney nickel, and hydrazine hydrate (1.5 mL), as described for the preparation of **14**, gave **30** (560 mg, 83%), m.p. 165–166° (ethanol), $[\alpha]_D^{15}$ −37.8° (*c* 1.2, chloroform); n.m.r. (chloroform-*d*): δ 1.24 (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, 50.77; H, 6.20.

Methyl 3-O-(6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (**31**). — *O*-Deacetylation of **30** (426 mg) afforded **31** (227 mg, 93%), m.p. 203–204° (ethanol–ether), $[\alpha]_D^{15}$ −37.5° (*c* 1.3, water); n.m.r. (dimethyl sulfoxide-d_6): δ 1.19 (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, 45.71; H, 7.17.

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