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SYNTHESIS OF DERIVATIVES OF METHYL β-MALTOTRIOSIDE*

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ABSTRACT

Selective *p*-toluenesulfonylation of methyl β-maltotrioside gave methyl 6,6′,6″-tri-*O*-*p*-tolylsulfonyl-β-maltotrioside (**2**) in 67% yield, which on acetylation produced methyl 2,3,2′,3′,2″,3″,4″-hepta-*O*-acetyl-6,6′,6″-tri-*O*-*p*-tolylsulfonyl-β-maltotrioside (**3**). Nucleophilic displacement of **3** with iodide, bromide, thioacetate, chloride, and azide ions afforded the 6,6′,6″-triiodo (**4**), -tribromo (**5**), -tri-*S*-acetyl (**9**), -trichloro (**10**), and -triazido (**12**) derivatives, respectively, of methyl β-maltotrioside heptaacetate. Methyl 2,3,2′,3′,2″,3″,4″-hepta-*O*-acetyl-6,6′,6″-trideoxy-β-maltotrioside (**7**) was prepared by reductive dehalogenation of **4** and **5**. Reduction of **12** followed by acetylation gave methyl 6,6′,6″-triacetamido-2,3,2′,3′,2″,3″,4″-hepta-*O*-acetyl-6,6′,6″-trideoxy-β-maltotrioside (**13**). The 6,6′,6″-tribromo (**6**), -trideoxy (**8**), and -trichloro (**11**) derivatives of methyl β-maltotrioside were obtained by *O*-deacetylation of the corresponding heptaacetates **5**, **7**, and **10**. Treatment of **3** with sodium methoxide gave methyl 3,6:3′,6′:3″,6″-trianhydro-β-maltotrioside (**15**). Reaction of **2** with acetic anhydride and pyridine under controlled conditions led to the formation of **3**, methyl 2,2′,3′,2″,3″,4″-hexa-*O*-acetyl-6,6′,6″-tri-*O*-*p*-tolylsulfonyl-β-maltrotrioside, methyl 2,3,2′,2″,3″,4″-hexa-*O*-acetyl-6,6′,6″-tri-*O*-*p*-tolylsulfonyl-β-maltotrioside, and methyl 2,2′,2″,3″,4″-penta-*O*-acetyl-6,6′,6″-tri-*O*-*p*-tolylsulfonyl-β-maltotrioside.

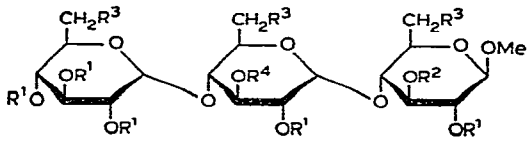
INTRODUCTION

As a further extension of our study of the chemical modification of maltotriose[1–4] we describe the synthesis of several 6,6′,6″-trisubstituted derivatives of methyl β-maltotrioside[2] (**1**) by replacement reactions of the sulfonyloxy groups in methyl 2,3,2′,3′,2″,3″,4″-hepta-*O*-acetyl-6,6′,6″-tri-*O*-*p*-tolylsulfonyl-β-maltotrioside (**3**) with various nucleophiles and the preparation of methyl 3,6:3′,6′:3″,6″-trianhydro-β-maltotrioside (**15**). The acetylation of methyl 6,6′,6″-tri-*O*-*p*-tolylsulfonyl-β-maltotrioside (**2**) with acetic anhydride and pyridine under controlled conditions was also investigated.

*Chemical modification of maltotriose. Part V. For Part IV, see ref. 1.

RESULTS AND DISCUSSION

Selective *p*-toluenesulfonylation of **1** with 4 molar equivalents of reagent in pyridine gave a mixture from which the 6,6′,6″-tri-*p*-toluenesulfonate **2** was directly isolated in crystalline form in 67% yield; the overall yield was 28% based on *β*-maltotriose hendecaacetate. Subsequently, it was found that **2** could be readily prepared from the *β*-hendecaacetate without the isolation of **1**. Thus, sequential



1 $R^1 = R^2 = R^4 = H$, $R^3 = OH$
2 $R^1 = R^2 = R^4 = H$, $R^3 = OTs$
3 $R^1 = R^2 = R^4 = Ac$, $R^3 = OTs$
4 $R^1 = R^2 = R^4 = Ac$, $R^3 = I$
5 $R^1 = R^2 = R^4 = Ac$, $R^3 = Br$
6 $R^1 = R^2 = R^4 = H$, $R^3 = Br$
7 $R^1 = R^2 = R^4 = Ac$, $R^3 = H$
8 $R^1 = R^2 = R^3 = R^4 = H$
9 $R^1 = R^2 = R^4 = Ac$, $R^3 = SAc$
10 $R^1 = R^2 = R^4 = Ac$, $R^3 = Cl$
11 $R^1 = R^2 = R^4 = H$, $R^3 = Cl$
12 $R^1 = R^2 = R^4 = Ac$, $R^3 = N_3$
13 $R^1 = R^2 = R^4 = Ac$, $R^3 = NHAc$
16 $R^1 = R^4 = Ac$, $R^2 = H$, $R^3 = OTs$
17 $R^1 = R^2 = Ac$, $R^3 = OTs$, $R^4 = H$,
18 $R^1 = R^4 = Ac$, $R^2 = Me$, $R^3 = OTs$
19 $R^1 = R^2 = Ac$, $R^3 = OTs$, $R^4 = Me$
20 $R^1 = R^2 = Ac$, $R^2 = Me$, $R^3 = OAc$
21 $R^1 = R^2 = Ac$, $R^3 = OAc$, $R^4 = Me$
22 $R^1 = R^2 = Ac$, $R^2 = Ms$, $R^3 = OTs$
23 $R^1 = R^2 = Ac$, $R^3 = OTs$, $R^4 = Ms$
24 $R^1 = Ac$, $R^2 = R^4 = H$, $R^3 = OTs$
25 $R^1 = Ac$, $R^2 = R^4 = Me$, $R^3 = OTs$
26 $R^1 = Ac$, $R^2 = R^4 = Ms$, $R^3 = OTs$
27 $R^1 = Ac$, $R^2 = R^4 = Me$, $R^3 = OAc$

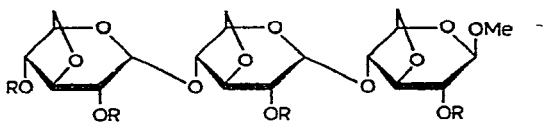
treatment of the *β*-hendecaacetate with hydrogen bromide–acetic acid, methanol–mercuric cyanide, methanolic sodium methoxide, and *p*-toluenesulfonyl chloride–pyridine afforded **2** in an overall yield of 50% without the need for column chromatography at any stage. Subsequent acetylation of **2** with acetic anhydride and pyridine for 40 h at room temperature gave crystalline **3** in 85% yield.

Treatment of **3** with sodium iodide in *N*,*N*-dimethylformamide replaced the tosyloxy by iodo groups to give the crystalline 6,6′,6″-trideoxy-6,6′,6″-triiodo derivative **4**, proving that the three sulfonyl groups of **3** were located on the primary hydroxyl groups. The tri-*p*-toluenesulfonate **3** also underwent replacement reaction with sodium bromide in *N*,*N*′,*N*″-hexamethylphosphoric triamide to afford the crystalline 6,6′,6″-tribromo-6,6′,6″-trideoxy derivative **5** which, on *O*-deacetylation with sodium methoxide in methanol, gave methyl 6,6′,6″-tribromo-6,6′,6″-trideoxy-*β*-maltotrioside (**6**) as an amorphous solid. Reductive dehalogenation of **4** and of **5** with Raney nickel and hydrazine[5] gave crystalline methyl 2,3,2′,3′,2″,3″,4″-hepta-*O*-acetyl-6,6′,6″-trideoxy-*β*-maltotrioside (**7**) which was deacetylated to give methyl 6,6′,6″-trideoxy-*β*-maltotrioside (**8**) as an amorphous powder. G.l.c. examination of the methanolizate of **8** as the trimethylsilyl derivatives showed the presence of methyl 6-deoxy-D-glucopyranosides as the sole products, confirming the structure of **8**.

The n.m.r. spectrum of **7** in chloroform-*d* showed three doublets (*J* 6.3 Hz) at high field (τ 8.57, 8.68, and 8.84), which were equal in intensity and together integrated for three protons. The doublets at τ 8.57 and τ 8.84 were assigned to the C-5 and C-5″ methyl groups, respectively, on the basis that the C-5 and C-5″ methyl signals of deca-*O*-acetyl-6-deoxy- and deca-*O*-acetyl-6″-deoxy-β-maltotriose appear at τ 8.54 and τ 8.84, respectively[1,4]. The doublet at τ 8.68 was therefore assigned to the C-5′ methyl. Sleeter and Sinclair[6] reported that, in the n.m.r. spectra of 6-deoxypyranosides, the doublet for the C-5 methyl group of the α anomer is always located at a field higher than that of the doublet of the β anomer. This was also the case for **7**; the C-5′ and C-5″ methyl resonances occured at a field higher than that of the C-5 methyl signal. However, in this case, a significant difference in the chemical shifts between the C-5′ and C-5″ methyl resonances (Δτ 0.16 p.p.m.) was observed. Furthermore, the chemical shift of the C-5′ methyl group in **7** was very similar to that observed for di-*O*-acetyl-6-deoxyamylose[7] (τ 8.65). These observations are indicative of a shielding of the methyl protons of the intermediate 6-deoxy-α-D-glucopyranose residue, which is surrounded in both sides by 6-deoxy-α-D-glucosyl residues.

Displacement of the tosyloxy groups of **3** with the thioacetate ion in *N*,*N*-dimethylformamide afforded the crystalline 6,6′,6″-tri-*S*-acetyl-6,6′,6″-trideoxy derivative **9**. Substitution reaction of **3** with lithium chloride in *N*,*N*′,*N*″-hexamethylphosphoric triamide gave the crystalline 6,6′,6″-trichloro-6,6′,6″-trideoxy derivative **10**, which was also prepared by treatment of **3** with pyridine hydrochloride in *N*,*N*-dimethylformamide. *O*-Deacetylation of **10** afforded methyl 6,6′,6″-trichloro-6,6′,6″-trideoxy-β-maltotrioside (**11**) as an amorphous solid. Hydrolysis of **11** in aqueous sulfuric acid followed by zinc chloride-catalyzed acetylation[8] gave 1,2,3,4-tetra-*O*-acetyl-6-chloro-6-deoxy-α-D-glucopyranose[9], thus confirming the structure of **11**. Displacement of the tosyloxy groups of **3** with the azide ion in *N*,*N*-dimethylformamide gave the crystalline 6,6′,6″-triazido-6,6′,6″-trideoxy derivative **12**, which was successively hydrogenated and acetylated to give the crystalline 6,6′,6″-triacetamido-6,6′,6″-trideoxy derivative **13**.

Treatment of **3** with sodium methoxide in methanol followed by acetylation gave methyl 2,2′,2″,4″-tetra-*O*-acetyl-3,6:3′,6′:3″,6″-trianhydro-β-maltotrioside (**14**)



14 R = Ac
15 R = H

in crystalline form. This was *O*-deacetylated to furnish methyl 3,6:3′,6′:3″,6″-trianhydro-β-maltotrioside (**15**). The resistance of this compound to periodate oxidation was consistent with its assigned structure. In the n.m.r. spectrum of **15** in deuterium oxide, the H-1 resonance occured at τ 5.18 as a doublet ($J_{1,2}$ 1.5 Hz) and

the signals due to other glycosidic protons appeared at τ 4.66 and 4.71 as doublets (J 1.5 Hz). The observed, small coupling-constants suggest that each of the D-glucopyranose rings of **15** adopts the expected $^1C_4$ conformation[10].

When the acetylation of **2** with acetic anhydride and pyridine under the conditions that previously led to the complete formation of **3** was stopped after 3 h, t.l.c. indicated the presence of three components which were separated by column chromatography on silica gel. The first-eluted component was obtained in crystalline form in 25% yield and identified as the heptaacetate **3** by comparison with an authentic specimen obtained previously.

The second fraction eluted from the column moved as a single component on t.l.c. in several solvent-systems and was obtained as an amorphous solid in 45% yield. Elementary analysis indicated that it was a hexaacetyl derivative, which subsequently was shown to be a 3:1 mixture of methyl 2,2′,3′,2″,3″,4″-hexa-*O*-acetyl-6,6′,6″-tri-*O*-*p*-tolylsulfonyl-β-maltotrioside (**16**) and methyl 2,3,2′,2″,3″,4″-hexa-*O*-acetyl-6,6′,6″-tri-*O*-*p*-tolylsulfonyl-β-maltotrioside (**17**) by the following sequence of reactions: On methanesulfonylation, the hexaacetyl derivative gave a hexa-*O*-acetyl-mono-*O*-methylsulfonyl-6,6′,6″-tri-*O*-*p*-tolylsulfonyl derivative that was homogeneous on t.l.c. in a variety of solvent systems. However, the n.m.r. spectrum of the methylsulfonylated derivatives in chloroform-*d* exhibited two singlets due to the methylsulfonyl groups at τ 6.90 and τ 6.95 with relative proton intensities of 1:3, which indicates that the hexaacetyl derivative was a 3:1 mixture of two positional isomers. The mixture of the hexaacetates (**16** and **17**) was converted into a mixture of the mono-*O*-methyl-nona-*O*-acetyl derivatives (**20** and **21**) by methylation with diazomethane–boron trifluoride etherate in order to retain the base labile substituents[11] (to give the mixture of mono-*O*-methyl-hexa-*O*-acetyl-6,6′,6″-tri-*O*-*p*-tolylsulfonyl derivatives **18** and **19**), replacement of the tosyloxy groups with benzoate groups in *N*,*N*′,*N*″-hexamethylphosphoric triamide, *O*-deacylation, and acetylation. G.l.c. analysis of the methanolyzate of the mixture of **20** and **21** as the trimethylsilyl ethers showed the presence of methyl D-glucopyranosides and methyl 3-*O*-methyl-D-glucopyranosides in a ratio of 2:1, which indicates that the free hydroxyl group in the mixture of **16** and **17** was located at one of the positions C-3,3′, or 3″. In view of the steric and polar factors influencing SN2 reactions[12], a displacement reaction with the benzoate ion should occur readily at C-3 as well as at C-6, 6′, and 6″ of the hexa-*O*-acetyl-mono-*O*-methylsulfonyl-6,6′,6″-tri-*O*-*p*-tolylsulfonyl derivatives (**22** and **23**), whereas sulfonyloxy groups at C-3′ and C-3″ should not be readily replaced because of the β-*trans*-axial effect. Treatment of the mixture of **22** and **23** with sodium benzoate in *N*,*N*′,*N*″-hexamethylphosphoric triamide for 15 h at 85° resulted in the complete disappearance of the signal of the methylsulfonyl group at τ 6.95, whereas the signal of the methylsulfonyl group at τ 6.90 remained intact. This observation suggests that the signal at τ 6.95 given by the mixture of **22** and **23** was due to the methylsulfonyl group of methyl 2,2′,3′,2″,3″,4″-hexa-*O*-acetyl-3-*O*-methylsulfonyl-6,6′,6″-tri-*O*-*p*-tolylsulfonyl-β-maltotrioside (**22**), which confirms the structure of the hexaacetate **16** having HO-3 free. It follows that the resonance at τ 6.90 was due to the methyl-

sulfonyl group either at C-3′ or C-3″. It has been previously established[13,14] that the 3-hydroxyl group of β-maltose and methyl 6,6′-di-*O*-*p*-tolylsulfonyl-β-maltoside[15] is the most resistant to acylation, which suggests that in the acetylation of **2**, HO-3′ is less reactive rather than HO-3″. Accordingly, the free hydroxyl group in the hexaacetate **17** was assigned to HO-3′, and hence the signal at τ 6.90 in the mixture of **22** and **23** to the methylsulfonyl group of methyl 2,3,2′,2″,3″,4″-hexa-*O*-acetyl-3′-*O*-methylsulfonyl-6,6′,6″-tri-*O*-*p*-tolylsulfonyl-β-maltotrioside (**23**). Repeated fractional crystallization of the mixture of the methylsulfonylated derivatives **22** and **23** gave the 3′-*O*-methylsulfonyl derivative **23** in pure crystalline form, although the total recovery was only 22%. However, an attempt to isolate the 3-*O*-methylsulfonyl derivative **22** from the remainder of **23** was not successful. The n.m.r. spectrum of **23** showed a three-proton singlet at τ 6.90 for the methylsulfonyl group, which survived a further displacement-reaction with the benzoate ion. This supports the structural assignment for the hexaacetate **17** having HO-3′ free.

The third component eluted from the column was obtained as an amorphous powder in 18% yield. Elementary analysis showed it to be a pentaacetyl derivative. The structure of methyl 2,2′,2″,3″,4″-penta-*O*-acetyl-6,6′,6″-tri-*O*-*p*-tolylsulfonyl-β-maltotrioside (**24**) was assigned to this compound on the basis of a reaction sequence similar to that used for the structural elucidation of the hexaacetates **16** and **17**. The pentaacetate **24** was transformed into methyl 2,6,2′,6′,2″,3″,4″,6″-octa-*O*-acetyl-3,3′-di-*O*-methyl-β-maltotrioside (**27**) *via* methyl 2,2′,2″,3″,4″-penta-*O*-acetyl-3,3′-di-*O*-methyl-6,6′,6″-tri-*O*-*p*-tolylsulfonyl-β-maltotrioside (**25**). G.l.c. examination revealed the presence of methyl 3-*O*-methyl-D-glucopyranosides and methyl D-glucopyranosides in the ratio 2:1 in the methanolyzate of **27**, indicating that the two free hydroxyl groups in **24** were located at C-3, 3′, or 3″. In the n.m.r. spectrum of methyl 2,2′,2″,3″,4″-penta-*O*-acetyl-3,3′-di-*O*-methylsulfonyl-6,6′,6″-tri-*O*-*p*-tolylsulfonyl-β-maltotrioside (**26**), the signals of the methylsulfonyl groups appeared at τ 6.88 and τ 6.93 as two three-proton singlets. Nucleophilic displacement of **26** with the benzoate ion caused the disappearance of the signal at τ 6.93 while the resonance at τ 6.88 remained intact. This confirmed that the signal at τ 6.93 in **26** was due to the methylsulfonyl group at C-3. Hence, one of the free hydroxyl groups in **24** was assigned to HO-3. On the basis that the HO-3″ is more reactive toward acetylation rather than the HO-3′, as discussed earlier, the remaining free hydroxyl group of **24** was ascribed to HO-3′, and the signal at τ 6.88 to the methylsulfonyl group at C-3′.

It is noteworthy that seemingly identical secondary hydroxyl groups at C-3 and C-3′ of **2** may well be subjected to different stereo-electronic effects and, in the acetylation with acetic anhydride and pyridine, HO-3 has one-third the relative reactivity of HO-3′, as deduced from the relative proton intensities of the methylsulfonyl groups in the n.m.r. spectrum of the mixture of **22** and **23**.

EXPERIMENTAL

General methods. — Unless otherwise stated, experimental conditions were as described[5] in Part I. G.l.c. analysis was performed under the same conditions as

described[1] in Part IV. The following solvent systems were used; (*A*) 45:5:3 (v/v) ethyl acetate–ethanol–water, (*B*) 3:2 (v/v) benzene–ethyl acetate, (*C*) 4:1 (v/v) benzene–ethanol, and (*D*) 1:1 (v/v) benzene–ethyl acetate.

Methyl O-(*6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1*→*4*)-O-(*6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1*→*4*)-*6*-O-p-*tolylsulfonyl*-β-D-*glucopyranoside* (**2**). — (*a*). A solution of **1** (1.2 g) in anhydrous pyridine (15 ml) was cooled to −10°, and treated with *p*-toluenesulfonyl chloride (1.76 g, 9.26mM) and kept for 20 h at 5°. Water (2 ml) was added, and the reaction mixture was concentrated to a mobile, thin syrup which was poured into ice–water. The resulting precipitate was filtered off, washed with water, and dried. Crystallization from chloroform–ethanol gave **2** (1.52 g, 67%), m.p. 119–120°, $[\alpha]_D^{15}$ +68.0° (*c* 1.0, chloroform); n.m.r. (dimethyl sulfoxide-d_6): τ 6.67 (s, 3 H, OMe) and 7.59 (s, 9 H, 3 aryl-CH_3).

Anal. Calc. for $C_{40}H_{52}O_{22}S_3$: C, 48.97; H, 5.34; S, 9.81. Found: C, 48.78; H, 5.45; S, 9.68.

(*b*). A solution of β-maltotriose hendecaacetate[3] (15 g) in acetic acid (45 ml) was cooled to 15° and treated with acetic acid (30 ml) that had been saturated with HBr at 0°. The mixture was stirred for 1 h at room temperature and diluted with chloroform. The solution was successively washed with iced water, aqueous $NaHCO_3$ and water, dried ($MgSO_4$), and evaporated to give the α-D-glycosyl bromide[2] (14.5 g). The bromide was dissolved in a mixture of anhydrous methanol (40 ml) and dry benzene (200 ml) containing $Hg(CN)_2$ (3.7 g). The mixture was stirred for 5 h at room temperature and concentrated to a syrup which was dissolved in chloroform. The solution was filtered through a Celite pad, and the filtrate was washed well with water, dried ($MgSO_4$), and concentrated to a syrup (13 g). A solution of the syrup in methanol (120 ml) was treated with methanolic M sodium methoxide (6 ml), and the mixture was kept for 3 h at room temperature, then neutralized with Amberlite IR-120 (H^+) ion-exchange resin, and evaporated. To a solution of the resulting crude **1** (6.7 g) in dry pyridine (80 ml) was added *p*-toluenesulfonyl chloride (9.85 g) at −10°, and the mixture was processed as described in (*a*) to give **2** (7.6 g, 50%), m.p. and mixed m.p. 119–120° (from chloroform–ethanol), $[\alpha]_D^{20}$ +68.5° (*c* 1.2, chloroform); the n.m.r. spectrum was identical with that of the compound prepared with method *a*.

Methyl O-(*2,3,4-tri*-O-*acetyl-6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1*→*4*)-O-(*2,3-di*-O-*acetyl-6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1*→*4*)-*2,3-di*-O-*acetyl-6*-O p-*tolylsulfonyl*-β-D-*glucopyranoside* (**3**). — Compound **2** (10 g) was treated with acetic anhydride (50 ml) and pyridine (50 ml) for 40 h at room temperature. The reaction mixture was poured into ice–water, and the precipitate formed was collected by filtration, washed with water, and dried. Crystallization from methanol–chloroform afforded **3** (11 g, 85%), m.p. 180–181°, $[\alpha]_D^{25}$ +86.1° (*c* 1.5, chloroform); n.m.r. (chloroform-*d*): τ 6.67 (s, 3 H, OMe) and 7.55 (s, 9 H, 3 × aryl-CH_3).

Anal. Calc. for $C_{54}H_{66}O_{29}S_3$: C, 50.86; H, 5.22; S, 3.64. Found: C, 50.80; H, 5.10; S, 3.55.

Methyl O-(*2,3,4-tri*-O-*acetyl-6-deoxy-6-iodo*-α-D-*glucopyranosyl*)-(*1*→*4*)-O-(*2,3-di*-O-*acetyl-6-deoxy-6-iodo*-α-D-*glucopyranosyl*)-(*1*→*4*)-*2,3-di*-O-*acetyl-6-deoxy-6-iodo*-

β-D-glucopyranoside (**4**). — NaI (2 g) was added to a solution of **3** (1.2 g) in *N,N*-dimethylformamide (30 ml), and the mixture was heated for 2.5 h at 100° with stirring. The cooled mixture was poured into ice–water, and the precipitate formed was filtered off and dissolved in chloroform. The solution was successively washed with water, 5% NaS_2O_3, and water, dried (Na_2SO_4), and evaporated to a syrup which crystallized from 2-propanol to give **4** (0.8 g, 80%), m.p. 123–124°, $[\alpha]_D^{25}$ +71.1° (*c* 1.3, chloroform).

Anal. Calc. for $C_{33}H_{45}I_3O_{20}$: C, 34.70; H, 3.97; I, 33.30. Found: C, 34.95; H, 4.13; I, 33.18.

Methyl O-(2,3,4-tri-O-acetyl-6-bromo-6-deoxy-α-D-glucopyranosyl)-(1→4)-O-(2,3-di-O-acetyl-6-bromo-6-deoxy-α-D-glucopyranosyl)-(1→4)-2,3-di-O-acetyl-6-bromo-6-deoxy-β-D-glucopyranoside (**5**). — NaBr (3 g) was added to a solution of **3** (2 g) in *N,N',N''*-hexamethylphosphoric triamide (10 ml), and the mixture was heated for 3 h at 100° with stirring. The cooled mixture was poured into ice–water, and the precipitate was filtered off, washed with water, and dried. Crystallization from 2-propanol gave **5** (1.35 g, 86%), m.p. 114–115°, $[\alpha]_D^{25}$ +79.8° (*c* 1.1, chloroform).

Anal. Calc. for $C_{33}H_{45}Br_3O_{20}$: C, 39.58; H, 4.53; Br, 23.94. Found: C, 39.51; H, 4.74; Br, 23.79.

Methyl O-(6-bromo-6-deoxy-α-D-glucopyranosyl)-(1→4)-O-(6-bromo-6-deoxy-α-D-glucopyranosyl)-(1→4)-6-bromo-6-deoxy-β-D-glucopyranoside (**6**). — A solution of **5** (0.3 g) in dry methanol (5 ml) was treated with methanolic M sodium methoxide (0.1 ml). The solution was kept for 1 h at room temperature, and then neutralized with Amberlite IR-120 (H^+) ion-exchange resin and evaporated to give **6** as an amorphous solid (190 mg, 90%), $[\alpha]_D^{25}$ +81.5° (*c* 1.9, water); t.l.c.: R_F 0.38 (solvent *A*); n.m.r. (deuterium oxide): τ 4.57 (d, 2 H, $J_{1',2'}$ and $J_{1'',2''}$ 3.0 Hz, H-1′ and H-1″), 5.58 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), and 6.44 (s, 3 H, OMe).

Anal. Calc. for $C_{19}H_{31}Br_3O_{13}$: C, 32.27; H, 4.42; Br, 33.90. Found: C, 32.12; H, 4.68; Br, 33.71.

Methyl O-(2,3,4-tri-O-acetyl-6-deoxy-α-D-glucopyranosyl)-(1→4)-O-(2,3-di-O-acetyl-6-deoxy-α-D-glucopyranosyl)-(1→4)-2,3-di-O-acetyl-6-deoxy-β-D-glucopyranoside (**7**). — (*a*). A solution of **4** (0.7 g) in ethanol (20 ml) was mixed with $BaCO_3$ (2 g) and heated to boiling with stirring. A small amount of Raney Ni (one spatulaful) was then added to the mixture and, after 5 min, hydrazine hydrate (2 ml) was added dropwise during 5 min. The reaction mixture was boiled for 30 min under reflux, and then filtered through a Celite pad, and the filtrate was evaporated to dryness. The residue was dissolved in chloroform, and the solution was successively washed with water, 5% $Na_2S_2O_3$ and water, dried (Na_2SO_4) and evaporated to a syrup which was purified by elution from a short column of silica gel with solvent *B* to give **7** (420 mg, 89%), m.p. 108–110° (from 2-propanol), $[\alpha]_D^{25}$ +71.2° (*c* 1.1, chloroform).

Anal. Calc. for $C_{33}H_{48}O_{20}$: C, 51.83; H, 6.33. Found: C, 51.72; H, 6.50.

(*b*). A mixture of **5** (0.9 g), $BaCO_3$ (2.5 g), and Raney Ni (one spatulaful) in ethanol (25 ml) was treated with hydrazine hydrate (3 ml), as described in (*a*), and

purification of the product by column chromatography on silica gel with solvent *B* gave **7** (590 mg, 86%), m.p. and mixed m.p. 108–110° (from 2-propanol), $[\alpha]_D^{22}$ +71.5° (*c* 1.0, chloroform); the n.m.r. spectrum was identical with that of the compound obtained with method *a*.

Methyl O-(*6-deoxy-α-*D-*glucopyranosyl*)-(*1→4*)-O-(*6-deoxy-α-*D-*glucopyranosyl*)-(*1→4*)-*6-deoxy-β-*D-*glucopyranoside* (**8**). — Treatment of **7** (500 mg) with sodium methoxide in methanol, as described for the preparation of **6**, afforded **8** as an amorphous powder (280 mg, 91%), $[\alpha]_D^{25}$ +108.2° (*c* 1.2, water); t.l.c.: R_F 0.15 (solvent *A*); n.m.r. (deuterium oxide): τ 4.71 (d, 2 H, $J_{1',2'}$ and $J_{1'',2''}$ 4.0 Hz, H-1′ and H-1″), 5.65 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 6.46 (s, 3 H, OMe), 8.67 (d, 3 H, *J* 6.0 Hz, CH_3-5), 8.70 (d, 3 H, *J* 6.0 Hz, CH_3-5′), and 8.72 (d, 3 H, *J* 6.0 Hz, CH_3-5″).

Anal. Calc. for $C_{19}H_{34}O_{13}$: C, 48.51; H, 7.28. Found: C, 48.43; H, 7.41.

Methanolysis of **8** (30 mg; 1% methanolic HCl, 5 ml; reflux, 20 h) and g.l.c. of the resulting methyl glycosides as their per-*O*-(trimethylsilyl) derivatives gave peaks corresponding to methyl 6-deoxy-D-glucopyranosides (7.1 and 8.3 min). No other peaks were detected.

Methyl O-(*2,3,4-tri-*O-*acetyl-6-*S-*acetyl-6-thio-α-*D-*glucopyranosyl*)-(*1→4*)-O-(*2,3-di-*O-*acetyl-6-*S-*acetyl-6-thio-α-*D-*glucopyranosyl*)-(*1→4*)-*2,3-di-*O-*acetyl-6-*S-*acetyl-6-thio-β-*D-*glucopyranoside* (**9**). — A solution of **3** (500 mg) in *N,N*-dimethylformamide (8 ml) containing potassium thioacetate (360 mg) was heated for 30 min at 100°. The reaction mixture was processed in the usual way and the resulting, dried precipitate was crystallized from 2-propanol to give **9** (345 mg, 89%), m.p. 162–163°, $[\alpha]_D^{25}$ +97.1° (*c* 1.5, chloroform); n.m.r. (chloroform-*d*): τ 6.53 (s, 3 H, OMe) and 7.63, 7.68 (s, 9 H, 3 × SAc).

Anal. Calc. for $C_{39}H_{54}O_{23}S_3$: C, 47.46; H, 5.51; S, 9.75. Found: C, 47.71; H, 5.45; S, 9.69.

Methyl O-(*2,3,4-tri-*O-*acetyl-6-chloro-6-deoxy-α-*D-*glucopyranosyl*)-(*1→4*)-O-(*2,3-di-*O-*acetyl-6-chloro-6-deoxy-α-*D-*glucopyranosyl*)-(*1→4*)-*2,3-di-*O-*acetyl-6-chloro-6-deoxy-β-*D-*glucopyranoside* (**10**). — (*a*). A solution of **3** (1.25 g) in *N,N′,N″*-hexamethylphosphoric triamide (6 ml) was heated with LiCl (1.7 g) for 4 h at 100°. The reaction mixture was poured into ice–water, and the precipitate was filtered off, washed with water, dried, and crystallized from ethanol to afford **10** (780 mg, 91%), m.p. 114–116°, $[\alpha]_D^{25}$ +78.7° (*c* 1.2, chloroform).

Anal. Calc. for $C_{33}H_{45}Cl_3O_{20}$: C, 45.66; H, 5.23; Cl, 12.25. Found: C, 45.49; H, 5.37; Cl, 12.17.

(*b*). A solution of **3** (1 g) in *N,N*-dimethylformamide (20 ml) containing pyridine hydrochloride (730 mg) was heated for 4 h at 100°. The reaction mixture was processed as described in (*a*) to give **10** (580 mg, 85%), m.p. and mixed m.p. 114–116° (from ethanol), $[\alpha]_D^{25}$ +78.2° (*c* 1.2, chloroform); the n.m.r. spectrum was identical with that of the compound prepared with method *a*.

Methyl O-(*6-chloro-6-deoxy-α-*D-*glucopyranosyl*)-(*1→4*)-O-(*6-chloro-6-deoxy-α-*D-*glucopyranosyl*)-(*1→4*)-*6-chloro-6-deoxy-β-*D-*glucopyranoside* (**11**). — *O*-Deacetylation of **10** (1 g), as described for **5**, gave **11** (0.6 g, 90%) as an amorphous solid, $[\alpha]_D^{25}$

+96.0° (*c* 1.4, water); t.l.c.: R_F 0.27 (solvent *A*); n.m.r. (deuterium oxide): τ 4.56 (d, 1 H, $J_{1',2'}$ 3.0 Hz, H-1'), 4.58 (d, 1 H, $J_{1'',2''}$ 3.0 Hz, H-1''), 5.59 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1), and 6.45 (s, 3 H, OMe).

Anal. Calc. for $C_{19}H_{31}Cl_3O_{13}$: C, 39.77; H, 5.45; Cl, 18.54. Found: C, 39.61; H, 5.62; Cl, 18.43.

Hydrolysis of **11** (200 mg) in aqueous H_2SO_4, followed by acetylation[8] with acetic anhydride and $ZnCl_2$, gave 1,2,3,4-tetra-*O*-acetyl-6-chloro-6-deoxy-α-D-glucopyranose (280 mg, 73%), m.p. 162–163° (from ether), $[\alpha]_D^{15}$ +119.0° (*c* 0.8, chloroform); lit.[9]: m.p. 164°, $[\alpha]_D^{25}$ +120° (*c* 1.0, chloroform).

Methyl O-(*2,3,4-tri*-O-*acetyl-6-azido-6-deoxy*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,3-di*-O-*acetyl-6-azido-6-deoxy*-α-D-*glucopyranosyl*)-(*1→4*)-*2,3-di*-O-*acetyl-6-azido-6-deoxy*-β-D-*glucopyranoside* (**12**). — A solution of **3** (2.0 g) in *N,N*-dimethylformamide (70 ml) containing sodium azide (3 g) was stirred for 2.5 h at 100°. The reaction mixture was poured into ice–water, and the precipitate formed was filtered off, dried, and crystallized from 2-propanol to give **12** (1.1 g, 78%), m.p. 93–95°, $[\alpha]_D^{25}$ +73.5° (*c* 1.6, chloroform); i.r.: ν_{max}^{KBr} 2100 cm^{-1} (N_3).

Anal. Calc. for $C_{33}H_{45}N_9O_{20}$: C, 44.65; H, 5.11; N, 14.20. Found: C, 44.48; H, 5.17; N, 14.06.

Methyl O-(*6-acetamido-2,3,4-tri*-O-*acetyl-6-deoxy*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*6-acetamido-2,3-di*-O-*acetyl-6-deoxy*-α-D-*glucopyranosyl*)-(*1→4*)-*6-acetamido-2,3-di*-O-*acetyl-6-deoxy*-β-D-*glucopyranoside* (**13**). — $BaCO_3$ (2.4 g) was added to a boiling solution of **12** (0.8 g) in ethanol (20 ml). The addition of Raney Ni (one spatulaful) was followed by the dropwise addition of hydrazine hydrate (2 ml), and the mixture was boiled for 50 min under reflux while being stirred. The hot reaction mixture was filtered through a Celite pad, and the filtrate was concentrated to a syrup, which was dissolved in a mixture of acetic anhydride (3 ml) and pyridine (7 ml). The mixture was kept overnight at room temperature and then concentrated to dryness. The residue was eluted from a column of silica gel with solvent *B* to give **13** (0.8 g, 77%), m.p. 135–137° (from ether), $[\alpha]_D^{25}$ +56.5° (*c* 1.0, chloroform).

Anal. Calc. for $C_{39}H_{57}N_3O_{23}$: C, 50.05; H, 6.14; N, 4.49. Found: C, 49.88; H, 6.29; N, 4.32.

Methyl O-(*2,4-di*-O-*acetyl-3,6-anhydro*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2*-O-*acetyl-3,6-anhydro*-α-D-*glucopyranosyl*)-(*1→4*)-*2*-O-*acetyl-3,6-anhydro*-β-D-*glucopyranoside* (**14**). — A mixture of **3** (2.5 g), dry methanol (50 ml), and M sodium methoxide (30 ml) was stirred for 18 h at room temperature. The reaction mixture was neutralized with acetic acid and concentrated to dryness. The residue was acetylated with acetic anhydride (20 ml) and pyridine (30 ml). After storage for 20 h at room temperature, the mixture was poured into ice–water, and the resulting precipitate was filtered off, washed with water, and dried. Crystallization from chloroform gave **14** (1.1 g, 89%), m.p. 265–266°, $[\alpha]_D^{25}$ +20.2° (*c* 0.9, chloroform); n.m.r. (chloroform-*d*): τ 6.57 (s, 3 H, OMe) and 7.83, 7.89, 8.80 (s, 12 H, 4×OAc).

Anal. Calc. for $C_{27}H_{36}O_{17}$: C, 51.27; H, 5.74. Found: C, 51.29; H, 5.89.

Methyl O-(*3,6-anhydro*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*3,6-anhydro*-α-D-*gluco-*

pyranosyl)-(*1→4*)-*3,6-anhydro-β*-D-*glucopyranoside* (**15**). — *O*-De acetylation of **14** (1 g), as described for **5**, gave **15** (780 mg, 90%) as an amorphous solid, $[\alpha]_D^{25}$ −46.5° (*c* 1.0, water); t.l.c.: R_F 0.26 (solvent *C*).

Anal. Calc. for $C_{19}H_{28}O_{13}$: C, 49.14; H, 6.08. Found: C, 48.96; H, 6.25.

Treatment of **2** *with acetic anhydride and pyridine under controlled conditions.* — To a solution of **2** (9.2 g) in pyridine (46 ml) was added acetic anhydride (46 ml), and the mixture was kept for 3 h at room temperature. T.l.c. (solvent *B*) showed the product to be composed of three components having R_F values of 0.75 (**3**), 0.51 (**16** and **17**), and 0.21 (**24**), respectively. The solution was poured into ice–water, and the precipitate formed was collected by filtration, washed with water, dried, and then fractionated on a column of silica gel (600 g) with solvent *B*.

The first fraction gave **3** (2.9 g, 25%), m.p. and mixed m.p. 180–181° (from methanol-chloroform), $[\alpha]_D^{20}$ +86.0° (*c* 1.0, chloroform).

The second component from the column gave a mixture of methyl *O*-(2,3,4-tri-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-α-D-glucopyranosyl)-(1→4)-*O*-(2,3-di-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-α-D-glucopyranosyl)-(1→4)-2-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-β-D-glucopyranoside (**16**) and methyl *O*-(2,3,4-tri-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-α-D-glucopyranosyl)-(1→4)-(2-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-α-D-glucopyranosyl)-(1→4)-2,3-di-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-β-D-glucopyranoside (**17**) (5.25 g, 45%), $[\alpha]_D^{25}$ +77.2° (*c* 1.0, chloroform); n.m.r. (chloroform-*d*): τ 6.63 (s, 3 H, OMe), 7.54 (s, 9 H, 3 × aryl-CH_3), and 7.93–8.03 (s, 18 H, 6 × OAc).

Anal. Calc. for $C_{52}H_{64}O_{28}S_3$: C, 50.64; H, 5.23; S, 7.80. Found: C, 50.71; H, 5.29; S, 7.67.

The third component from the column gave methyl *O*-(2,3,4-tri-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-α-D-glucopyranosyl)-(1→4)-*O*-(2-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-α-D-glucopyranosyl)-(1→4)-2-*O*-acetyl-6-*O*-*p*-tolylsulfonyl-β-D-glucopyranoside (**24**) as an amorphous powder (1.96 g, 18%), $[\alpha]_D^{25}$ +75.6° (*c* 0.9, chloroform); n.m.r. (chloroform-*d*): τ 6.63 (s, 3 H, OMe), 7.57 (s, 9 H, 3 × aryl-CH_3), and 7.91–8.04 (s, 15 H, 5 × OAc).

Anal. Calc. for $C_{50}H_{62}O_{27}S_3$: C, 50.42; H, 5.25; S, 8.08. Found: C, 50.65; H, 5.20; S, 8.14.

Mixture of methyl O-(*2,3,4-tri*-O-*acetyl-6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,3-di*-O-*acetyl-6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1→4*)-*2*-O-*acetyl-3*-O-*methyl-6*-O-p-*tolylsulfonyl*-β-D-*glucopyranoside* (**18**) *and methyl* O-(*2,3,4-tri*-O-*acetyl-6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2*-O-*acetyl-3*-O-*methyl-6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1→4*)-*2,3-di*-O-*acetyl-6*-O-p-*tolylsulfonyl*-β-D-*glucopyranoside* (**19**). — Diazomethane in dichloromethane was gradually added to a cooled solution of the mixture of **16** and **17** (1.2 g) in dichloromethane (8 ml) containing BF_3 etherate (0.1 ml) until a pale yellow color persisted. Polymethylene was filtered off, and the solution was washed successively with water, aqueous $NaHCO_3$ and water, and dried (Na_2SO_4). Evaporation of the solvent gave a mixture of **18** and **19** as a crystalline mass (948 mg, 78%), m.p. 150–153°, $[\alpha]_D^{25}$ +81.1°

(*c* 1.0, chloroform); n.m.r. (chloroform-*d*): τ 6.58 (s, 1 H, OMe-3'), 6.65 (s, 3 H, OMe), 6.68 (s, 2 H, OMe-3), and 7.93–8.00 (s, 18 H, 6 × OAc).

Anal. Calc. for $C_{53}H_{66}O_{28}S_3$: C, 51.04; H, 5.33; S, 7.71. Found: C, 51.25; H, 5.24; S, 7.84.

Mixture of methyl O-(*2,3,4,6-tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,3,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-*2,6-di*-O-*acetyl-3*-O-*methyl*-β-D-*glucopyranoside* (**20**) *and methyl* O-(*2,3,4,6-tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,6-di*-O-*acetyl-3*-O-*methyl*-α-D-*glucopyranosyl*)-(*1→4*)-*2,3,6-tri*-O-*acetyl*-β-D-*glucopyranoside* (**21**). — A solution of a mixture of **18** and **19** (844 mg) in *N,N',N''*-hexamethylphosphoric triamide (5 ml) containing sodium benzoate (1 g) was heated for 20 h at 90°. The cooled solution was poured into ice–water, and the precipitate formed was filtered off and dissolved in chloroform. The solution was washed with water, dried ($MgSO_4$), and concentrated to a syrup which was treated with methanolic M sodium methoxide (1 ml) in methanol (10 ml). The mixture was kept overnight at room temperature, neutralized with Amberlite IR-120 (H^+) ion-exchange resin, and evaporated to dryness. The residue was acetylated with acetic anhydride (4 ml) and pyridine (5 ml) overnight at room temperature, and the reaction mixture was processed in the usual way to give a mixture of **20** and **21** as an amorphous powder (475 mg, 77%), $[\alpha]_D^{25}$ +89.9° (*c* 1.1, chloroform); t.l.c.: R_F 0.61 (solvent *D*); n.m.r. (chloroform-*d*): τ 6.53 (s, 3 H, OMe), 6.55 (s, 1 H, OMe-3'), 6.60 (s, 2 H, OMe-3), and 7.86–7.99 (s, 27 H, 9 × OAc).

Anal. Calc. for $C_{38}H_{54}O_{25}$: C, 50.11; H, 5.98. Found: C, 49.99; H, 6.14.

Methanolysis of the mixture of **20** and **21** under the same conditions as for **8** and g.l.c. of the methanolyzate as the per(trimethylsilyl) ethers gave peaks corresponding to methyl 3-*O*-methyl-D-glucopyranosides (7.5 and 7.9 min, 33%) and methyl D-glucopyranosides (13.8 and 15.2 min, 67%).

Mixture of methyl O-(*2,3,4-tri*-O-*acetyl-6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,3-di*-O-*acetyl-6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1→4*)-*2*-O-*acetyl-3*-O-*methylsulfonyl-6*-O-p-*tolylsulfonyl*-β-D-*glucopyranoside* (**22**) *and methyl* O-(*2,3,4-tri*-O-*acetyl-6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2*-O-*acetyl-3*-O-*methylsulfonyl-6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1→4*)-*2,3-di*-O-*acetyl-6*-O-p-*tolylsulfonyl*-β-D-*glucopyranoside* (**23**). — Conventional methanesulfonylation of a mixture of **16** and **17** (1.65 g) with methanesulfonyl chloride (1 ml) in pyridine (8 ml) overnight at 0° afforded a 3:1 mixture of **22** and **23** (1.6 g, 91%), $[\alpha]_D^{25}$ +78.2° (*c* 1.0, chloroform); t.l.c.: R_F 0.58 (solvent *D*).

Anal. Calc. for $C_{53}H_{66}O_{30}S_4$: C, 48.54; H, 5.07; S, 9.87. Found: C, 48.49; H, 5.00; S, 9.98.

Six crystallizations of the mixture of **22** and **23** (1 g) from methanol gave pure **23** (210 mg), m.p. 221–222°, $[\alpha]_D^{25}$ +77.8° (*c* 0.9, chloroform).

A solution of the mixture of **22** and **23** (500 mg) in *N,N',N''*-hexamethylphosphoric triamide (4 ml) containing sodium benzoate (800 mg) was heated for 15 h at 85°. The mixture was poured into ice–water, and the precipitate was filtered off, washed with water, and dried. The compound (280 mg) showed $[\alpha]_D^{20}$ +88.0° (*c* 0.7,

chloroform); t.l.c.: R_F 0.79 (solvent *D*); n.m.r. (chloroform-*d*): τ 6.53 (s, 3 H, OMe) and 6.90 (s, 3 H, $MeSO_2$-3′).

In a similar manner, treatment of **23** (100 mg) with sodium benzoate (100 mg) in *N,N′,N″*-hexamethylphosphoric triamide (0.5 ml) for 15 h at 85° gave a compound showing $[\alpha]_D^{24}$ +86.0° (*c* 1.0, chloroform); t.l.c.: R_F 0.75 (solvent *D*); n.m.r. (chloroform-*d*): τ 6.53 (s, 3 H, OMe) and 6.90 (s, 3 H, $MeSO_2$-3′).

Methyl O-(*2,3,4-tri*-O-*acetyl-6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2*-O-*acetyl-3*-O-*methyl-6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1→4*)-*2*-O-*acetyl-3*-O-*methyl-6*-O-p-*tolylsulfonyl*-β-D-*glucopyranoside* (**25**). — Treatment of **24** (600 mg) with diazomethane–BF_3 etherate in dichloromethane, as described previously, afforded **25** (436 mg, 71%), m.p. 146–147° (from methanol), $[\alpha]_D^{25}$ +88.1° (*c* 1.0, chloroform); n.m.r. (chloroform-*d*): τ 6.58 (s, 3 H, OMe-3′), 6.64 (s, 3 H, OMe), 6.68 (s, 3 H, OMe-3), and 7.91–8.02 (s, 15 H, 5 × OAc).

Anal. Calc. for $C_{37}H_{54}O_{24}$: C, 50.34; H, 6.17. Found: C, 50.45; H, 6.08.

Methyl O-(*2,3,4,6-tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,6-di*-O-*acetyl-3*-O-*methyl*-α-D-*glucopyranosyl*)-(*1→4*)-*2,6-di*-O-*acetyl-3*-O-*methyl*-β-D-*glucopyranoside* (**27**). — Sequential treatment of **25** (592 mg) with sodium benzoate (600 mg) in *N,N′,N″*-hexamethylphosphoric triamide (4 ml), methanolic M sodium methoxide (1 ml) in methanol (10 ml), and acetic anhydride (3 ml) and pyridine (4 ml), as described previously, gave **27** (309 mg, 72%), $[\alpha]_D^{20}$ +88.9° (*c* 0.9, chloroform); t.l.c.: R_F 0.52 (solvent *D*); n.m.r. (chloroform-*d*): τ 6.53 (s, 3 H, OMe), 6.55 (s, 3 H, OMe-3′), 6.60 (s, 3 H, OMe-3), and 7.88–7.98 (s, 24 H, 8 × OAc).

Anal. Calc. for $C_{37}H_{54}O_{24}$: C, 50.34; H, 6.17. Found: C, 50.52; H, 6.06.

Methanolysis of **27** under the same conditions as for **8** and g.l.c. of the methanolyzate as the per-*O*-(trimethylsilyl) derivatives gave peaks corresponding to methyl 3-*O*-methyl-D-glucopyranosides (7.5 and 7.9 min, 67%) and methyl D-glucopyranosides (13.8 and 15.2 min, 33%).

Methyl O-(*2,3,4-tri*-O-*acetyl-6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2*-O-*acetyl-3*-O-*methylsulfonyl-6*-O-p-*tolylsulfonyl*-α-D-*glucopyranosyl*)-(*1→4*)-*2*-O-*acetyl-3*-O-*methylsulfonyl-6*-O-p-*tolylsulfonyl*-β-D-*glucopyranoside* (**26**). — Conventional methanesulfonylation of **24** (500 mg) with methanesulfonyl chloride (0.4 ml) in pyridine (2.5 ml) overnight at 0° afforded **26** (490 mg, 87%), m.p. 178–179° (from ethanol), $[\alpha]_D^{25}$ +71.4° (*c* 1.2, chloroform).

Anal. Calc. for $C_{52}H_{66}O_{31}S_5$: C, 46.35; H, 4.94; S, 11.90. Found: C, 46.45; H, 4.84; S, 12.04.

Treatment of **26** (200 mg) with sodium benzoate (200 mg) in *N,N′,N″*-hexamethylphosphoric triamide (1 ml), as described previously, gave a compound (97 mg), that showed $[\alpha]_D^{20}$ +87.0° (*c* 0.7, chloroform); t.l.c.: R_F 0.79 (solvent *D*); n.m.r. (chloroform-*d*): τ 6.53 (s, 3 H, OMe) and 6.89 (s, 3 H, $MeSO_2$-3′).

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