Carbohydrate Research, 107 (1982) 71–90
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

CHEMICAL MODIFICATION OF METHYL β-CELLOBIOSIDE

KEN'ICHI TAKEO*, TOSHIYA FUKATSU, AND TETSUSHI YASATO
Department of Agricultural Chemistry, Kyoto Prefectural University, Shimogamo, Kyoto 606 (Japan)
(Received January 27th, 1982; accepted for publication, February 18th, 1982)

ABSTRACT

Treatment of methyl β-cellobioside (**1**) with α,α-dimethoxytoluene in *N,N*-dimethylformamide in the presence of *p*-toluenesulfonic acid gave a high yield of methyl 4′,6′-*O*-benzylidene-β-cellobioside (**6**), which was transformed into methyl 2,3,2′,3′,4′,6′-hexa-*O*-acetyl-6-*O*-*p*-tolylsulfonyl- (**4**) and methyl 2,3,6,2′,3′,4′-hexa-*O*-acetyl-6′-*O*-*p*-tolylsulfonyl-β-cellobioside (**5**). Several 6- and 6′-monosubstituted derivatives of **1** were synthesized by displacement reactions of **4** and **5** with various nucleophiles. Treatment of **4** and **5** with sodium methoxide gave methyl 3,6-anhydro- and methyl 3′,6′-anhydro-β-cellobioside, respectively. The synthesis and catalytic hydrogenation of the 5- and 5′-ene derivatives of **1** are described. Conversion of **1** into methyl 4-*O*-β-D-allopyranosyl-β-D-allopyranoside and methyl 4-*O*-β-D-amicetosyl-β-D-amicetoside was undertaken, using **6** as the key intermediate.

INTRODUCTION

Cello-oligosaccharides are important model compounds for studies of various properties of cellulose. Our continued interest in the chemistry of cello-oligosaccharides[1–3] led us to investigate the chemical modification of methyl β-cellobioside (**1**). As to specifically substituted derivatives of **1**, a number of the disubstituted derivatives, namely, the 6,6′-di-*O*-trityl[4,5], -di-*O*-sulfonyl[6–9], -dideoxydihalo[4,6,9,10], -dideoxy[6,9], -diazidodideoxy[10], and -dialdehyde[10] derivatives, and the 5,5′-diene[4] have been synthesized. Synthesis of the 3,6:3′,6′-dianhydro derivative[8] of **1**, and conversion of methyl β-lactoside *via* the 4′,6′-di-*O*-(methylsulfonyl) derivative into the 4′,6′-di(acetamido)-4′,6′-dideoxy derivative[11] of **1** have been reported. However, only a few studies have been conducted on the synthesis of specifically monosubstituted derivatives of **1**; the 3-*O*-(methylsulfonyl) derivative[1] and the 6- and 6′-monotrityl ethers[5] have been prepared. Recently, reaction of **1** in *N,N*-dimethylformamide with triphenylphosphine and *N*-bromosuccinimide, followed by acetylation, was reported to give methyl 2,3,2′,3′,4′,6′-hexa-*O*-acetyl-6-bromo-6-deoxy- (**13**) and methyl 2,3,6,2′,3′,4′-hexa-*O*-acetyl-6′-bromo-6′-deoxy-β-cellobioside (**17**), in addition to the

*To whom enquiries should be addressed.

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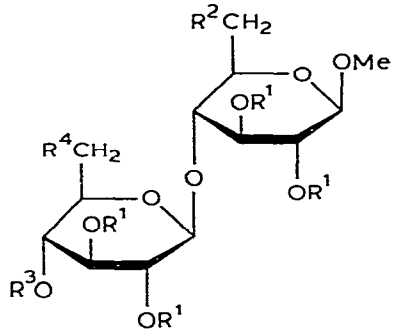
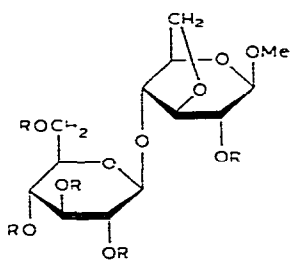
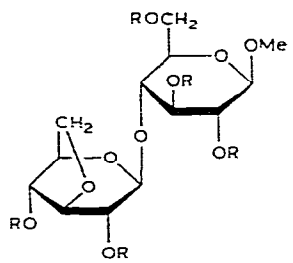


1 $R^1 = R^3 = H, R^2 = R^4 = OH$
2 $R^1 = R^3 = H, R^2 = OTs, R^4 = OH$
3 $R^1 = R^3 = H, R^2 = OH, R^4 = OTs$
4 $R^1 = R^3 = Ac, R^2 = OTs, R^4 = OAc$
5 $R^1 = R^3 = Ac, R^2 = OAc, R^4 = OTs$
6 $R^1 = H, R^2 = OH, R^3, R^4 = PhCHO$
7 $R^1 = Ac, R^2 = OAc; R^3, R^4 = PhCHO$
8 $R^1 = Me, R^2 = OMe; R^3, R^4 = PhCHO$
9 $R^1 = Ac, R^2 = OAc, R^3 = H, R^4 = OH$
10 $R^1 = Ac, R^2 = OAc, R^3 = R^4 = Ms$
11 $R^1 = Ac, R^2 = OTs; R^3, R^4 = PhCHO$
12 $R^1 = R^3 = Ac, R^2 = N_3, R^4 = OAc$
13 $R^1 = R^3 = Ac, R^2 = Br, R^4 = OAc$
14 $R^1 = R^3 = Ac, R^2 = Cl, R^4 = OAc$
15 $R^1 = R^3 = Ac, R^2 = I, R^4 = OAc$
16 $R^1 = R^3 = Ac, R^2 = OAc, R^4 = N_3$
17 $R^1 = R^3 = Ac, R^2 = OAc, R^4 = Br$
18 $R^1 = R^3 = Ac, R^2 = OAc, R^4 = Cl$
19 $R^1 = R^3 = Ac, R^2 = OAc, R^4 = I$
20 $R^1 = R^3 = Ac, R^2 = NHAc, R^4 = OAc$
21 $R^1 = R^3 = Ac, R^2 = OAc, R^4 = NHAc$
22 $R^1 = R^3 = Ac, R^2 = H, R^4 = OAc$
23 $R^1 = R^3 = Ac, R^2 = OAc, R^4 = H$
24 $R^1 = R^3 = H, R^2 = Br, R^4 = OH$
25 $R^1 = R^3 = H, R^2 = Cl, R^4 = OH$
26 $R^1 = R^3 = H, R^2 = OH, R^4 = Br$
27 $R^1 = R^3 = H, R^2 = OH, R^4 = Cl$
28 $R^1 = R^3 = H, R^2 = NHAc, R^4 = OH$
29 $R^1 = R^3 = H, R^2 = OH, R^4 = NHAc$
30 $R^1 = R^2 = R^3 = H, R^4 = OH$
31 $R^1 = R^3 = R^4 = H, R^2 = OH$
32 $R^1 = Ac, R^2 = OAc, R^3 = Bz, R^4 = Br$
33 $R^1 = Ac, R^2 = OAc, R^3 = Bz, R^4 = H$
34 $R^1 = Ms, R^2 = OMs; R^3, R^4 = PhCHO$
35 $R^1 = Ac, R^2 = I; R^3, R^4 = PhCHO$
36 $R^1 = Ac, R^2 = H, R^3, R^4 = PhCHO$
37 $R^2 = R^2 = H; R^3, R^4 = PhCHO$
38 $R^1 = Ms, R^2 = H; R^3, R^4 = PhCHO$



39 R = Ac
40 R = H



41 R = Ac
42 R = H

penta-*O*-acetyl-6,6′-dibromo-6,6′-dideoxy derivative, but the physical properties of **13** and **17** were not described[9].

We report here the synthesis of several 6- and 6′-monosubstituted derivatives of **1** by displacement reactions of the sulfonyloxy groups of methyl 2,3,2′,3′,4′,6′-hexa-*O*-acetyl-6-*O*-*p*-tolylsulfonyl- (**4**) and methyl 2,3,6,2′,3′,4′-hexa-*O*-acetyl-6′-*O*-*p*-tolylsulfonyl-β-cellobioside (**5**), respectively, with various nucleophiles, and the preparation of methyl 3,6-anhydro- (**40**) and methyl 3′,6′-anhydro-β-cellobioside (**42**). The synthesis and catalytic hydrogenation of methyl 2,3-di-*O*-acetyl-6-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-*xylo*-hex-5-enopyranoside (**43**)

and methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4-tri-*O*-acetyl-6-deoxy-β-D-*xylo*-hex-5-enopyranosyl)-β-D-glucopyranoside (**44**), and the transformation of **1** into methyl 4-*O*-β-D-allopyranosyl-β-D-allopyranoside (**52**) and methyl 2,3,6-trideoxy-4-*O*-(2,3,6-trideoxy-β-D-*erythro*-hexopyranosyl)-β-D-*erythro*-hexopyranoside (methyl 4-*O*-β-D-amicetosyl-β-D-amicetoside, **58**), starting from methyl 4′,6′-*O*-benzylidene-β-cellobioside (**6**), are also described.

RESULTS AND DISCUSSION

Attempted regioselective *p*-toluenesulfonylation of **1** with 1.1 mol. equiv. of reagent in pyridine, with a view to obtaining the 6- (**2**) and 6′-*O*-*p*-tolylsulfonyl (**3**) derivatives, respectively, as starting materials for the chemical modification of the 6- and 6′-positions of **1**, were not successful, because the reaction gave a mixture that was difficult to separate by column chromatography and fractional recrystallization. Therefore, on the basis of our previous studies on the chemical modification of methyl β-glycosides of maltose[12], laminarabiose[13], and sophorose[14], in which the mono-*O*-benzylidene derivatives were used as the starting materials, we attempted the synthesis of the hexa-*O*-acetyl-6- (**4**) and -6′-*O*-*p*-tolylsulfonyl (**5**) derivatives, respectively, starting from **6** and methyl 2,3,6,2′,3′-penta-*O*-acetyl-4′,6′-*O*-benzylidene-β-cellobioside (**7**). Recently, Bock *et al.* reported, in a short communication[15], that benzylidenation of **1** with benzal halide in pyridine and subsequent acetylation give **7** in 34% yield, together with three isomeric tri-*O*-acetyl-di-*O*-benzylidene derivatives; however, the details of the isolation of these compounds, as well as the physical constants of **7**, have not yet been reported.

Treatment of **1** with 1.5 mol. equiv. of α,α-dimethoxytoluene in *N*,*N*-dimethylformamide in the presence of *p*-toluenesulfonic acid under essentially the same conditions as those reported[16] for the benzylidenation of methyl α- and β-D-glucopyranoside gave a mixture from which **6** was directly isolated in crystalline form in 75% yield. Methylation of **6** afforded the 4′,6′-*O*-benzylidene-2,3,6,2′,3′-penta-*O*-methyl derivative **8**, which, on successive hydrolysis, reduction with sodium borohydride, and acetylation, gave a 1 : 1 mixture of the peracetates of 2,3-di- and 2,3,6-tri-*O*-methyl-D-glucitol (g.l.c.), confirming the structure of **6**. During the course of this work, conventional benzylidenation of **1** with benzaldehyde in the presence of zinc chloride was reported to give **6** in 47% yield, but the optical rotation value for **6** was not given[5]. Acetylation of **6** afforded crystalline **7**, which was *O*-debenzylidenated to give the 2,3,6,2′,3′-penta-*O*-acetyl derivative **9** in crystalline form. Methanesulfonylation of **9** gave the crystalline 2,3,6,2′,3′-penta-*O*-acetyl-4′,6′-di-*O*-(methylsulfonyl) derivative **10**.

Selective *p*-toluenesulfonylation of **6** with 2 mol. equiv. of the reagent in pyridine at −20°, followed by acetylation, gave the crystalline 2,3,2′,3′-tetra-*O*-acetyl-4′,6′-*O*-benzylidene-6-*O*-*p*-tolylsulfonyl derivative **11**, which was sequentially *O*-debenzylidenated, and the product acetylated, to afford **4** in crystalline form. Similarly, selective *p*-toluenesulfonylation of **9** and subsequent acetylation provided **5** in crystal-

line form. Thus, compounds **4** and **5** were obtained in 60 and 56% yield, respectively, based on **6**, without resort to column chromatography at any stage.

Nucleophilic displacement of the sulfonyloxy group of **4** with azide, bromide, chloride, and iodide ions in *N*,*N*-dimethylformamide afforded the 6-azido-6-deoxy (**12**), 6-bromo-6-deoxy (**13**), 6-chloro-6-deoxy (**14**), and 6-deoxy-6-iodo (**15**) derivatives, respectively, in high yields. Compound **5** underwent similar displacement reactions, to give the 6′-azido-6′-deoxy (**16**), 6′-bromo-6′-deoxy (**17**), 6′-chloro-6′-deoxy (**18**), and 6′-deoxy-6′-iodo (**19**) derivatives, respectively. Compounds **12** and **16** were successively hydrogenated and acetylated, to give the 6-acetamido-6-deoxy (**20**) and 6′-acetamido-6′-deoxy (**21**) derivatives, respectively. Reductive dehalogenation of **15** and **19** with Raney nickel in the presence of hydrazine hydrate[17] afforded the 6-deoxy (**22**) and 6′-deoxy (**23**) derivatives, respectively. In the n.m.r. spectra of **22** and **23** in chloroform-*d*, the signals due to the C-5 and -5′ methyl groups appeared at δ 1.36 and 1.24 as doublets (J 6.0 Hz), respectively.

O-Deacetylation of **13**, **14**, **17**, **18**, and **20**–**23** with methanolic sodium methoxide furnished methyl 6-bromo-6-deoxy-β-cellobioside (**24**), methyl 6-chloro-6-deoxy-β-cellobioside (**25**), methyl 6′-bromo-6′-deoxy-β-cellobioside (**26**), methyl 6′-chloro-6′-deoxy-β-cellobioside (**27**), methyl 6-acetamido-6-deoxy-β-cellobioside (**28**), methyl 6′-acetamido-6′-deoxy-β-cellobioside (**29**), methyl 6-deoxy-β-cellobioside (**30**), and methyl 6′-deoxy-β-cellobioside (**31**), respectively, all of the compounds being obtained in crystalline form. Compounds **26** and **31** were also obtained by an alternative route: oxidative removal of the benzylidene group of **7** with *N*-bromosuccinimide[18] afforded the 2,3,6,2′,3′-penta-*O*-acetyl-4′-*O*-benzoyl-6′-bromo-6′-deoxy derivative **32**, which was reductively dehalogenated to give the 2,3,6,2′,3′-penta-*O*-acetyl-4′-*O*-benzoyl-6′-deoxy derivative **33**. *O*-Deacylation of **32** and **33** gave **26** and **31**, respectively.

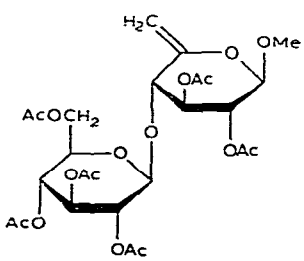
Treatment of **4** and **5** with sodium methoxide in methanol followed by acetylation gave methyl 2,2′,3′,4′,6′-penta-*O*-acetyl-3,6-anhydro- (**39**) and methyl 2,3,6,2′,4′-penta-*O*-acetyl-3′,6′-anhydro-β-cellobioside (**41**), respectively, which were *O*-deacetylated to afford **40** and **42**, respectively. On periodate oxidation[19], **40** and **42** consumed 1.89 and 0.96 mol. equiv. of periodate, respectively, consistent with the structure assigned. The n.m.r. spectrum of **40** in deuterium oxide showed the H-1 resonance at δ 4.83 as a doublet ($J_{1,2}$ 1.5 Hz), whereas that of **42** in deuterium oxide exhibited the H-1′ resonance at δ 4.99 as a doublet ($J_{1',2'}$ 1.0 Hz). The small coupling constants observed suggest that the D-glucopyranoside residue in **40** and the methyl D-glucopyranosyl group in **42** adopt the expected $^1C_4$(D) conformation[20].

Treatment[21] of **4** and **5** with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in *N*,*N*-dimethylformamide afforded the 5- (**43**) and 5′-ene (**44**) derivatives in 72 and 75% yield, respectively. Catalytic hydrogenation of **43** over palladium-on-charcol gave, after column chromatography, the 6-deoxy derivative **22** and methyl 6-deoxy-4-*O*-β-D-glucopyranosyl-α-L-idopyranoside hexaacetate (**45**) in 88 and 6% yield, respectively, whereas similar catalytic hydrogenation of **44** over palladium-on-charcol led to exclusive formation of the 6′-deoxy derivative **23** (95%). When hydro-

genation of **43** was performed over Raney nickel, it gave, after column chromatography, the D-*gluco* (**22**) and L-*ido* (**45**) isomers in 17 and 75% yield, respectively, whereas analogous catalytic hydrogenation (over Raney nickel) of **44** produced exclusively the D-*gluco* isomer **23** (94%). Goto *et al.*[22] recently studied the effects of catalysts and solvents in the catalytic hydrogenation of the 5-ene derivatives of reducing disaccharides.

Methanesulfonylation of **6** gave the 4′,6′-*O*-benzylidene-2,3,6,2′,3′-penta-*O*-(methylsulfonyl) derivative **34**. In view of the steric and polar factors influencing the feasibility of SN2 reactions[23], a displacement reaction with a benzoate ion should occur readily at C-3 and -3′, with inversion of the configurations, as well as at C-6 of **34**, whereas the sulfonyloxy groups at C-2 and -2′ in **34** should not be readily replaced, because of the electron-withdrawing, inductive effect of the anomeric center and the unfavorable dipolar interactions in the transition state[23]. As a pilot experiment, when treated with sodium benzoate in *N*,*N*-dimethylformamide, methyl 4,6-*O*-benzylidene-2,3-di-*O*-(methylsulfonyl)-β-D-glucopyranoside[24] (**46**) underwent ready replacement of the sulfonyloxy group at C-3, with inversion of configuration, to give methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-*O*-(methylsulfonyl)-β-D-allopyranoside (**47**) in 89% yield. Treatment of **47** with lithium aluminum hydride in 1,4-dioxane simultaneously removed the methylsulfonyloxy group, with splitting of the O–S bond[25], and the benzoyl group, to afford methyl 4,6-*O*-benzylidene-β-D-allopyranoside[26] (**48**) in 81% yield.

Similarly, **34** reacted with sodium benzoate in *N*,*N*-dimethylformamide to give, in 74% yield, methyl 3,6-di-*O*-benzoyl-4-*O*-[3-*O*-benzoyl-4,6-*O*-benzylidene-2-*O*-(methylsulfonyl)-β-D-allopyranosyl]-2-*O*-(methylsulfonyl)-β-D-glucopyranoside (**49**)



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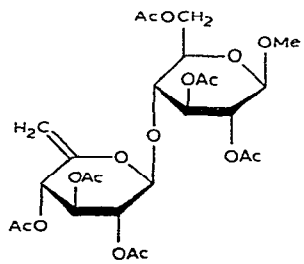

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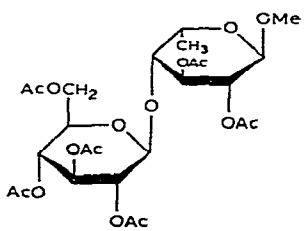

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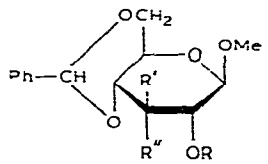
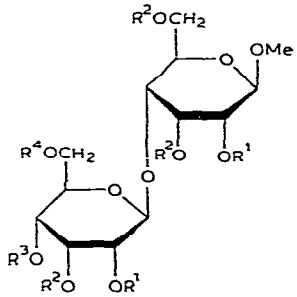
as amorphous material, after column chromatography. The n.m.r. spectrum of **49** in chloroform-*d* showed the H-3′ and -3 resonances at δ 6.21 and 6.06, respectively, as two triplets, both having spacings of 3.0 Hz, in accord with the *allo*, *allo* configuration of **49**. Successive treatment of **49** with lithium aluminum hydride in 1,4-dioxane and acetic anhydride in pyridine gave methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-allopyranosyl)-β-D-allopyranoside (**50**), which was *O*-deacetylated to afford methyl 4-*O*-(4,6-*O*-benzylidene-β-D-allopyranosyl)-β-D-allopyranoside (**51**). This was *O*-debenzylidenated to furnish crystalline **52**. G.l.c. examination of the *O*-(trimethylsilyl) derivatives of the methanolyzate of **52** showed the presence of methyl α,β-D-allopyranoside as the sole product, which confirmed the structure of **52**. Acetylation of **52** gave **53** in crystalline form.



46 R = Ms, R′ = OMs, R″ = H
47 R = Ms, R′ = H, R″ = OBz
48 R = R′ = H, R″ = OH

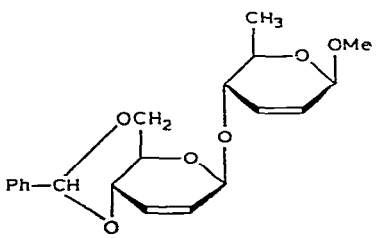


49 R^1 = Ms, R^2 = Bz; R^3, R^4 = PhCH
50 R^1 = R^2 = Ac; R^3, R^4 = PhCH
51 R^1 = R^2 = H; R^3, R^4 = PhCH
52 R^1 = R^2 = R^3 = R^4 = H
53 R^1 = R^2 = R^3 = R^4 = Ac

Reaction of **11** with sodium iodide in *N*,*N*-dimethylformamide gave the 2,3,2′,3′-tetra-*O*-acetyl-4′,6′-*O*-benzylidene-6-deoxy-6-iodo derivative **35**, which was reductively dehalogenated with Raney nickel and hydrazine, without hydrogenolysis of the benzylidene group, to afford the 2,3,2′,3′-tetra-*O*-acetyl-4′,6′-*O*-benzylidene-6-deoxy derivative **36**. The latter was *O*-deacetylated to give the 4′,6′-*O*-benzylidene-6-deoxy derivative **37**, which, on methanesulfonylation, produced the 4′,6′-*O*-benzylidene-6-deoxy-2,3,2′,3′-tetra-*O*-(methylsulfonyl)derivative **38**. The Tipson–Cohen reaction[27,28] of **38** by treatment with sodium iodide and zinc dust in *N*,*N*-dimethylformamide gave the crystalline 4′,6′-*O*-benzylidene-2,3,6,2′,3′-pentadeoxy-2,2′-diene derivative **54** in 69% yield, after column chromatography. Hydrogenation of **54** over palladium-on-charcol could be readily terminated at the point of saturation of the 2,3 and 2′,3′ double bonds, with no detectable hydrozinolysis of the benzylidene group, to give the crystalline, saturated 4′,6′-*O*-benzylidene acetal **55**. This behavior agrees with that of methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside, which underwent selective saturation of the double bond on hydrogenation over palladium-on-charcol[29], but contrasts with that of the palladium-catalyzed hydrogenolysis of the 4,6:4′,6′-di-*O*-benzylidene-2,3,2′,3′-tetradeoxy-2,2′-diene

derivative of α,α-trehalose, which reduced the double bonds and removed the benzylidene groups simultaneously[30].

Treatment[18] of **55** with *N*-bromosuccinimide in carbon tetrachloride gave the 4′-*O*-benzoyl-6′-bromo-2,3,6,2′,3′,6′-hexadeoxy derivative **56** as a chromatographically homogeneous powder, after column chromatography. Compound **56** is very labile, and tends to decompose on storage, so that it was immediately used for the next step. Reductive debromination of **56** with Raney nickel and hydrazine afforded the 4′-*O*-benzoyl-2,3,6,2′,3′,6′-hexadeoxy derivative **57**, which was *O*-debenzoylated to methyl 4-*O*-β-D-amicetoxyl-β-D-amicetoside (**58**), obtained in crystalline form. The n.m.r. spectrum of **58** in chloroform-*d* showed a broad, 1-proton singlet at δ 2.07 for a hydroxyl group, and two 3-proton doublets (*J* 6.0 Hz) at δ 1.28 and 1.27 for methyl groups at C-5 and -5′. Treatment[29,31] of **58** with (2,4-dinitrophenyl)hydrazine in 2M hydrochloric acid gave, with concomitant cleavage of the inter-sugar glycosidic linkage, an 80% yield of 2,3,6-trideoxy-D-erythrose (2,4-dinitrophenyl)hydrazone[29,31], which established the structure of **58**.



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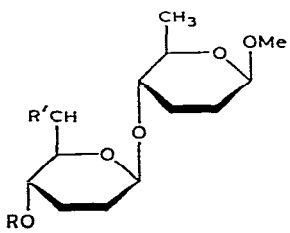

55 R, R′ = PhCHO
56 R = Bz, R′ = Br
57 R = Bz, R′ = H
58 R = R′ = H

EXPERIMENTAL

General methods. — Organic solutions were generally dried with anhydrous sodium sulfate. Solutions were evaporated, at a temperature <40°, under diminished pressure. Melting points were determined with a Yanagimoto micro hot-stage apparatus and are uncorrected. Optical rotations were measured with an Applied Electronic automatic polarimeter, Model MP-1T, and i.r. spectra were recorded with a Shimadzu IR-2C spectrometer for potassium bromide pellets. N.m.r. spectra were recorded with a Varian A-60A spectrometer; tetramethylsilane (in chloroform-*d*, acetone-d_6, and dimethyl sulfoxide-d_6) and sodium 4,4-dimethyl-4-silapentane-1-sulfonate (in deuterium oxide) were the internal standards. Gas–liquid chromatography was performed with a Hitachi gas chromatograph 063, using the following columns: (*A*) 3% of ECNSS-M on 80–100 mesh Gas-Chrom Q (operating temperature, 180°) and (*B*) 5% of silicone SE-30 on 80–100 mesh Chromosorb W (operating temperature, 190°), with nitrogen as the carrier gas, and a flame-ionization detector. Retention

times are given, relative to that of 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methyl-D-glucitol as unity for *O*-acetyl-*O*-methyl-D-alditols, and to methyl α-D-glucopyranoside for methyl D-glycosides. T.l.c. was performed on Silica gel No. 7731 (Merck); spots were made visible by spraying the plates with 5% sulfuric acid in ethanol, followed by heating. Column chromatography was performed on Silica gel No. 7734 (Merck). The following solvent combinations (v/v) were used: (*1*) 2:3, (*2*) 3:2, and (*3*) 4:1 benzene–ethyl acetate.

*Methyl 4-*O*-(4,6-*O*-benzylidene-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**6**). — Compound **1** (31.0 g, 87 mmol), α,α-dimethoxytoluene (20.0 g, 131 mmol), *p*-toluenesulfonic acid monohydrate (1.0 g), and anhydrous *N*,*N*-dimethylformamide (150 mL) were placed in a 1-L, round-bottomed flask; this was then attached to an evaporator, and rotated for 2 h at a bath temperature of ~50° under diminished pressure (~30 torr). The mixture was cooled, the acid neutralized with Amberlite IR-400 (OH^-) ion-exchange resin, and the resin filtered off and washed with methanol. The filtrate and washings were combined, and evaporated, to give a white, crystalline mass which was recrystallized twice from ethanol to give **6** (29.1 g, 75%); m.p. 151–152° [lit.[5] m.p. 154–155° (ethanol)], $[\alpha]_D^{17}$ −37.0° (*c* 1.9, *N*,*N*-dimethylformamide); n.m.r. data (dimethyl sulfoxide-d_6): δ 7.38 (s, 5 H, Ph), 5.58 (s, 1 H, benzylic-H), 4.55 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.15 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), and 3.33 (s, 3 H, OMe).

Anal. Calc. for $C_{20}H_{28}O_{11}$: C, 54.05; H, 6.35. Found: C, 54.12; H, 6.48.

*Methyl 4-*O*-(4,6-*O*-benzylidene-2,3-di-*O*-methyl-β-*D*-glucopyranosyl)-2,3,6-tri-*O*-methyl-β-*D*-glucopyranoside* (**8**). — Sodium hydride (0.9 g) was added to a solution of **6** (0.76 g) in *N*,*N*-dimethylformamide (40 mL). The mixture was stirred for 1 h, and then cooled to 0°, methyl iodide (5 mL) was added during 10 min, and the mixture was stirred, with cooling, for 1 h, and for 16 h at room temperature. Methanol (2 mL) was added to decompose the excess of the hydride, the mixture was filtered, and the filtrate was evaporated to dryness. The residue was extracted with chloroform, and the extract was washed successively with water, 5% sodium thiosulfate, and water, dried, and evaporated. Crystallization from ether–petroleum ether gave **8** (0.88 g, 81%); m.p. 134–136°, $[\alpha]_D^{17}$ −34.9° (*c* 1.8, chloroform); n.m.r. data (chloroform-*d*): δ 7.55–7.17 (m, 5 H, Ph), 5.53 (s, 1 H, benzylic-H), 4.53 (d, 1 H, $J_{1',2'}$ 7.5 Hz, H-1'), 4.17 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), and 3.64–3.40 (singlets, 18 H, 6 OMe).

Anal. Calc. for $C_{25}H_{38}O_{11}$: C, 58.35; H, 7.44. Found: C, 58.16; H, 7.36.

Hydrolysis of a portion (20 mg) of **8** with 0.5M sulfuric acid (3 mL) for 6 h at 100°, followed by reduction with sodium borohydride, and acetylation, gave compounds that had the retention times of the peracetates of 2,3,6-tri-*O*-methyl-D-glucitol (*T* 2.49, 50%) and 2,3-di-*O*-methyl-D-glucitol (*T* 5.38, 50%) on column *A*.

*Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**7**). — Conventional acetylation of **6** (12.5 g) with 1:1 (v/v) acetic anhydride–pyridine (180 mL) overnight at room temperature, and isolation in the usual way, gave **7** (16.9 g, 92%); m.p. 240–241° (ethanol), $[\alpha]_D^{17}$ −52.2° (*c* 2.0, chloroform), lit.[5] m.p. 241°, $[\alpha]_D^{21}$ −40° (*c* 1.0, chloroform); n.m.r. data (chloroform-*d*): δ 3.37 (s, 5 H, Ph), 5.48 (s, 1 H, benzylic-H), 3.47 (s, 3 H,

OMe), 2.12 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), 2.03 (s, 6 H, 2 OAc), and 2.01 (s, 3 H, OAc).

Anal. Calc. for $C_{30}H_{38}O_{16}$: C, 55.04; H, 5.85. Found: C, 54.92; H, 5.74.

*Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3-di-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**9**). — A solution of **7** (11.58 g) in acetic acid (120 mL) was heated at 100°, and water (80 mL) was added in small portions during 15 min. After heating for 20 min at 100°, the solvents were removed by repeated codistillation with toluene, to give a solid, which was recrystallized from 2-propanol to afford **9** (10.02 g, 86%); m.p. 174–175°, $[\alpha]_D^{17}$ −34.0° (*c* 2.0, chloroform).

Anal. Calc. for $C_{23}H_{34}O_{16}$: C, 48.76; H, 6.05. Found: C, 48.58; H, 5.91.

*Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3-di-*O*-acetyl-4,6-di-*O*-(methylsulfonyl)-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**10**). — A solution of **9** (0.52 g) in dry pyridine (5 mL) was cooled to −10°, treated with methanesulfonyl chloride (0.8 mL), and kept overnight at 0°. The solution was poured into ice–water, and the precipitate formed was filtered off, washed with water, and dried. Recrystallization from ethanol–chloroform gave **10** (0.60 g, 91%); m.p. 215–216° (dec.), $[\alpha]_D^{17}$ −21.3° (*c* 1.0, chloroform); n.m.r. data (chloroform-*d*): δ 3.13 and 3.08 (s, each 3 H, 2 OMs), 2.13 (s, 3 H, OAc), 2.07 (s, 6 H, 2 OAc), and 2.03 (s, 6 H, 2 OAc).

Anal. Calc. for $C_{25}H_{30}O_{20}S_2$: C, 41.55; H, 5.30; S, 8.87. Found: C, 41.39; H, 5.48; S, 8.68.

*Methyl 2,3-di-*O*-acetyl-4-*O*-(2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-*D*-glucopyranosyl)-6-*O*-p-tolylsulfonyl-β-*D*-glucopyranoside* (**11**). — To a stirred solution of **6** (9.45 g) in anhydrous pyridine (100 mL), cooled to −20°, was added portionwise *p*-toluenesulfonyl chloride (8.11 g, 2.0 mol. equiv.). The mixture was further stirred for 1 h at −20° and for 15 h at 0°, treated with acetic anhydride (60 mL), and then kept for 5 h at room temperature. The solution was poured into ice–water, and the resulting precipitate was filtered off, washed extensively with water, and dried. Crystallization from ethanol, and recrystallization from ethanol–chloroform gave **11** (11.73 g, 72%); m.p. 172–173°, $[\alpha]_D^{17}$ −32.9° (*c* 2.2, chloroform); n.m.r. data (chloroform-*d*): δ 5.47 (s, 1 H, benzylic-H), 3.37 (s, 3 H, OMe), 2.45 (s, 3 H, aryl-CH_3), 2.05 (s, 3 H, OAc), 2.02 (s, 6 H, 2 OAc), and 1.99 (s, 3 H, OAc).

Anal. Calc. for $C_{35}H_{42}O_{17}S$: C, 54.83; H, 5.52; S, 4.18. Found: C, 54.99; H, 5.40; S, 4.02.

*Methyl 2,3-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-6-*O*-p-tolylsulfonyl-β-*D*-glucopyranoside* (**4**). — A solution of **11** (12.95 g) in acetic acid (130 mL) was treated with water (87 mL) for 20 min at 100°, as described for the preparation of **9**, and the solvents were removed by codistillation with toluene, to give a solid which was treated with 1:1 (v/v) acetic anhydride–pyridine (100 mL), and kept overnight at room temperature. The mixture was poured into ice–water, and the precipitate that separated was filtered off, washed with water, and dissolved in chloroform. The solution was washed with water, dried, and evaporated. The residue crystallized from ethanol and was recrystallized from ethanol–chloroform, to afford **4** (10.82 g, 84%); m.p. 188–189°, $[\alpha]_D^{17}$ −16.1° (*c* 2.0, chloroform); n.m.r.

data (chloroform-*d*): δ 2.48 (s, 3 H, aryl-CH_3), and 3.74–3.14 (singlets, 18 H, 6 OAc).

Anal. Calc. for $C_{32}H_{42}O_{19}S$: C, 50.39; H, 5.55; S, 4.20. Found: C, 50.20; H, 5.61; S, 4.38.

*Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4-tri-*O*-acetyl-6-*O*-p-tolylsulfonyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**5**). — *p*-Toluenesulfonyl chloride (7.40 g, 2.0 mol. equiv.) was added portionwise to a stirred solution of **9** (10.99 g) in dry pyridine (110 mL), cooled to −20°. After being kept for 1 h at −20°, the mixture was allowed to warm to 0°, and kept at this temperature for 15 h, treated with acetic anhydride (66 mL), and kept for 4 h at room temperature. The mixture was poured into ice–water, and the precipitate formed was filtered off, washed with water, and dissolved in chloroform. The solution was washed with water, dried, and evaporated to a solid, which was recrystallized twice from ethanol, to give **5** (10.51 g, 71%); m.p. 176–177°, $[\alpha]_D^{17}$ −4.0° (*c* 2.0, chloroform); n.m.r. data (chloroform-*d*): δ 2.47 (s, 3 H, aryl-CH_3) and 2.17–1.92 (singlets, 18 H, 6 OAc).

Anal. Calc. for $C_{32}H_{42}O_{19}S$: C, 50.39; H, 5.55; S, 4.20. Found: C, 50.50; H, 5.44; S, 4.05.

*Methyl 2,3-di-*O*-acetyl-6-azido-6-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**12**). — A solution of **4** (2.11 g) in *N*,*N*-dimethylformamide (40 mL) containing sodium azide (3.5 g) was heated for 3 h at 100°. The mixture was cooled, and evaporated to dryness, and the residue was extracted with chloroform. The extract was washed with water, dried, and evaporated. Crystallization from ethanol gave **12** (1.60 g, 91%); m.p. 179–180°, $[\alpha]_D^{17}$ −5.9° (*c* 2.0, 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, 47.50; H, 5.68; N, 6.51.

*Methyl 2,3-di-*O*-acetyl-6-bromo-6-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**13**). — Sodium bromide (1.8 g) was added to a solution of **4** (0.97 g) in *N*,*N*-dimethylformamide (20 mL), The mixture was stirred for 5 h at 100°, and then processed as just described. The residue crystallized from ethanol, to give **13** (0.73 g, 86%); m.p. 174–175°, $[\alpha]_D^{17}$ −32.5° (*c* 2.0, chloroform).

Anal. Calc. for $C_{25}H_{35}BrO_{16}$: C, 44.72; H, 5.25; Br, 11.90. Found: C, 44.48; H, 5.32; Br, 12.17.

*Methyl 2,3-di-*O*-acetyl-6-chloro-6-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**14**). — A solution of **4** (1.11 g) in *N*,*N*-dimethylformamide (20 mL) containing lithium chloride (2.0 g) was stirred for 5 h at 100°. The mixture was processed as described for the preparation of **12**, to give **14** (1.11 g, 88%); m.p. 165–167° (2-propanol), $[\alpha]_D^{17}$ −38.3° (*c* 2.0, chloroform).

Anal. Calc. for $C_{25}H_{35}ClO_{16}$: C, 47.89; H, 5.63; Cl, 5.65. Found: C, 47.70; H, 5.53; Cl, 5.50.

*Methyl 2,3-di-*O*-acetyl-6-deoxy-6-iodo-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**15**). — A solution of **4** (2.82 g) and sodium iodide (5 g) in *N*,*N*-dimethylformamide (40 mL) was stirred 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, 5% sodium thiosulfate, and water, dried, and evaporated. Crystallization from ethanol afforded **15** (2.31 g, 87%); m.p. 213–214°, $[\alpha]_D^{17}$ −22.8° (*c* 2.0, chloroform).

Anal. Calc. for $C_{25}H_{35}IO_{16}$: C, 41.79; H, 4.91; I, 17.66. Found: C, 41.85; H, 5.03; I, 17.81.

*Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4-tri-*O*-acetyl-6-azido-6-deoxy-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**16**). — A solution of **5** (1.98 g) in *N,N*-dimethylformamide (40 mL) was stirred with sodium azide (3 g) for 3 h at 100°. The mixture was processed as described for the preparation of **12**, to give **16** (1.53 g, 93%); m.p. 162–163° (ethanol), $[\alpha]_D^{17}$ −20.9° (*c* 2.0, 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, 47.48; H, 5.50; N, 6.46.

*Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4-tri-*O*-acetyl-6-bromo-6-deoxy-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**17**). — A solution of **5** (1.20 g) in *N,N*-dimethylformamide (24 mL) was stirred with sodium bromide (2 g) for 5 h at 100°. The mixture was processed as described for the preparation of **12**, to give **17** (0.82 g, 81%); m.p. 193–194° (ethanol), $[\alpha]_D^{17}$ −15.3° (*c* 2.0, chloroform).

Anal. Calc. for $C_{25}H_{35}BrO_{16}$: C, 44.72; H, 5.25; Br, 11.90. Found: C, 44.61; H, 5.19; Br, 11.77.

*Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4-tri-*O*-acetyl-6-chloro-6-deoxy-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**18**). — Compound **5** (0.86 g) was heated in *N,N*-dimethylformamide (17 mL) with lithium chloride (1.3 g) for 5 h at 100°. Processing of the mixture, as described for the preparation of **12**, gave **18** (0.64 g, 90%); m.p. 205–206° (ethanol), $[\alpha]_D^{17}$ −16.1° (*c* 2.0, chloroform).

Anal. Calc. for $C_{25}H_{35}ClO_{16}$: C, 47.89: H, 5.63; Cl, 5.65. Found: C, 47.70; H, 5.71; Cl, 5.81.

*Methyl 2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4-tri-*O*-acetyl-6-deoxy-6-iodo-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**19**). — Compound **5** (3.01 g) was heated in *N,N*-dimethylformamide (60 mL) with sodium iodide (4.5 g) for 3 h at 100°. The mixture was processed as described for the preparation of **15**, to give **19** (2.45 g, 86%); m.p. 172–173° (ethanol), $[\alpha]_D^{17}$ −10.5° (*c* 2.1, chloroform).

Anal. Calc. for $C_{25}H_{35}IO_{16}$: C, 41.79; H, 4.91; I, 17.66. Found: C, 41.88; H, 4.87; I, 17.45.

*Methyl 6-acetamido-2,3-di-*O*-acetyl-6-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**20**). — Compound **12** (1.31 g) was dissolved in methanol (70 mL), and a small amount of Raney nickel was added. The mixture was heated to boiling while hydrazine hydrate (3 mL) was added dropwise during 5 min. It was then boiled for a further 40 min under reflux, filtered through a layer of Celite, and the filtrate evaporated to dryness. The residue was acetylated with 1:1 (v/v) acetic anhydride–pyridine (18 mL) overnight at room temperature. The solution was evaporated, and a trace of solvent coevaporated with toluene, to give a solid which was recrystallized from ethanol, to afford **20** (1.05 g, 78%); m.p. 217–218°, $[\alpha]_D^{20}$ −67.1° (*c* 2.0, chloroform).

Anal. Calc. for $C_{27}H_{39}NO_{17}$: C, 49.92; H, 6.05; N, 2.16. Found: C, 50.20; H, 6.10; N, 2.07.

Methyl 4-O-(6-acetamido-2,3,4-tri-O-acetyl-6-deoxy-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranoside (**21**). — Treatment of **16** (1.10 g) in methanol containing a small amount of Raney nickel with hydrazine hydrate (3 mL), and subsequent acetylation with 1:1 (v/v) acetic anhydride–pyridine (16 mL), as just described, gave **21** (0.94 g, 83%): m.p. 108–110° (ether–petroleum ether), $[\alpha]_D^{18}$ −23.1° (*c* 2.0, chloroform).

Anal. Calc. for $C_{27}H_{39}NO_{17}$: C, 49.92; H, 6.05; N, 2.16. Found: C, 49.82; H, 5.97; N, 2.08.

Methyl 2,3-di-O-acetyl-6-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-β-D-glucopyranoside (**22**). — A solution of **15** (1.31 g) in methanol (150 mL) was mixed with barium carbonate (5 g), and heated to boiling with stirring. A small amount of Raney nickel was added to the mixture, and, after 5 min, hydrazine hydrate (3 mL) was added dropwise during 5 min. The mixture was boiled for 20 min under reflux, and then filtered through a Celite pad, and the filtrate evaporated. The residue was dissolved in chloroform, and the solution was processed as described for the preparation of **15**, to give **22** (0.86 g, 80%): m.p. 175–176° (ethanol), $[\alpha]_D^{17}$ −42.2° (*c* 2.0, chloroform); n.m.r. data (chloroform-*d*): δ 1.36 (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, 50.50; H, 6.19.

Methyl 2,3,6-tri-O-acetyl-4-O-(2,3,4-tri-O-acetyl-6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (**23**). — Treatment of **19** (1.21 g) in methanol (100 mL) containing barium carbonate (5 g) and a small amount of Raney nickel with hydrazine hydrate (3 mL), as just described, gave **23** (0.78 g, 78%); m.p. 186–187° (ether–petroleum ether), $[\alpha]_D^{17}$ −12.9° (*c* 2.0, chloroform); n.m.r. data (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, 50.75; H, 6.23.

Methyl 2,3,6-tri-O-acetyl-4-O-(2,3-di-O-acetyl-4-O-benzoyl-6-bromo-6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (**32**). — A mixture of **7** (2.50 g), *N*-bromosuccinimide (0.75 g), and barium carbonate (6 g) in anhydrous carbon tetrachloride (60 mL) and 1,1,2,2-tetrachloroethane (40 mL) was boiled and stirred for 2 h under reflux. The mixture was filtered through a bed 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, and evaporated to a solid which was recrystallized from ethanol, to give **32** (2.24 g, 80%); m.p. 154–155°, $[\alpha]_D^{17}$ −46.5° (*c* 2.0, chloroform); n.m.r. data (chloroform-*d*): δ 8.08–7.43 (m, 5 H, Ph), 3.48 (s, 3 H, OMe), 2.14 (s, 3 H, OAc), 2.12 (s, 3 H, OAc), 2.03 (s, 6 H, 2 OAc), and 1.88 (s, 3 H, OAc).

Anal. Calc. for $C_{30}H_{37}BrO_{16}$: C, 49.12; H, 5.08; Br, 10.89. Found: C, 49.30; H, 5.15; Br, 10.74.

Methyl 2,3,6-tri-O-acetyl-4-O-(2,3-di-O-acetyl-4-O-benzoyl-6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside (**33**). — Treatment of **32** (1.59 g) with hydrazine

hydrate (2 mL) in methanol (70 mL) containing barium carbonate (7 g) and a small amount of Raney nickel, as described for the preparation of **22**, gave **33** (1.21 g, 85%); m.p. 203–204° (ethanol), $[\alpha]_D^{18}$ −49.3° (*c* 2.0, chloroform); n.m.r. data (chloroform-*d*): δ 8.07–7.42 (m, 5 H, Ph), 3.48 (s, 3 H, OMe), 2.13 (s, 3 H, OAc), 2.03 (s, 9 H, 3 OAc), 1.87 (s, 3 H, OAc), and 1.29 (d, 3 H, *J* 6.0 Hz, CH_3-5′).

Anal. Calc. for $C_{30}H_{38}O_{16}$: C, 50.04; H, 5.85. Found: C, 49.82; H, 5.97.

Methyl 6-bromo-6-deoxy-4-O-β-D-glucopyranosyl-β-D-glucopyranoside (**24**), *methyl 6-chloro-6-deoxy-4-O-β-D-glucopyranosyl-β-D-glucopyranoside* (**25**), *methyl 4-O-(6-bromo-6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside* (**26**), *methyl 4-O-(6-chloro-6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside* (**27**), *methyl 6-acetamido-6-deoxy-4-O-β-D-glucopyranosyl-β-D-glucopyranoside* (**28**), *methyl 4-O-(6-acetamido-6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside* (**29**), *methyl 6-deoxy-4-O-β-D-glucopyranosyl-β-D-glucopyranoside* (**30**), *and methyl 4-O-(6-deoxy-β-D-glucopyranosyl)-β-D-glucopyranoside* (**31**). — *O*-Deacetylation of **13** (0.51 g), **14** (0.84 g), **17** (0.61 g), **18** (0.49 g), **20** (0.73 g), **21** (0.75 g), **22** (0.57 g), and **23** (0.66 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 **24**, **25**, **26**, **27**, **28**, **29**, **30**, and **31**, respectively.

Compound **24** (0.26 g, 81%): m.p. 143–145° (ethanol–ether), $[\alpha]_D^{15}$ −13.9° (*c* 0.9, water).

Anal. Calc. for $C_{13}H_{23}BrO_{10}$: C, 37.25; H, 5.53; Br, 19.06. Found: C, 37.11; H, 5.60; Br, 18.74.

Compound **25** (0.45 g, 90%): m.p. 124–125° (ethanol–ether), $[\alpha]_D^{15}$ −24.5° (*c* 0.7, water).

Anal. Calc. for $C_{13}H_{23}ClO_{10}$: C, 41.66; H, 6.19; Cl, 9.46. Found: C, 41.55; H, 6.13; Cl, 9.27.

Compound **26** (0.33 g, 87%): m.p. 181–182° (dec.) (ethanol), $[\alpha]_D^{15}$ −31.3° (*c* 0.9, water).

Anal. Calc. for $C_{13}H_{23}BrO_{10}$: C, 37.25; H, 5.53; Br, 19.06. Found: C, 37.51; H, 5.64; Br, 18.80.

Compound **26** (0.13 g, 76%) was also obtained from **32** (0.29 g) by a similar *O*-deacylation; m.p. and mixed m.p. 181–182°, $[\alpha]_D^{15}$ −31.1° (*c* 1.0, water).

Compound **27** (0.25 g, 85%): m.p. 184–185° (dec.) (ethanol), $[\alpha]_D^{15}$ −28.6° (*c* 1.0, water).

Anal. Calc. for $C_{13}H_{23}ClO_{10}$: C, 41.66; H, 6.19; Cl, 9.46. Found: C, 41.79; H, 6.15; Cl, 9.32.

Compound **28** (0.41 g, 91%): m.p. 252–253° (ethanol), $[\alpha]_D^{15}$ −19.0° (*c* 1.1, water); n.m.r. data (dimethyl sulfoxide-d_6): δ 1.85 (s, 3 H, NAc).

Anal. Calc. for $C_{15}H_{27}O_{11}$: C, 45.34; H, 6.85; N, 3.52. Found: C, 45.50; H, 6.90; N, 3.67.

Compound **29** (0.42 g, 91%): m.p. 230–231° (ethanol), $[\alpha]_D^{15}$ −21.2° (*c* 1.0, chloroform); n.m.r. data (dimethyl sulfoxide-d_6): δ 1.87 (s, 3 H, NAc).

Anal. Calc. for $C_{15}H_{27}NO_{11}$: C, 45.34; H, 6.85; N, 3.52. Found: C, 45.21; H, 6.72; N, 3.45.

Compound **30** (0.31 g, 94%): m.p. 196–197° (ethanol–ether), $[\alpha]_D^{15}$ −21.4° (*c* 0.7, water): n.m.r. data (dimethyl sulfoxide-d_6): δ 1.28 (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, 45.99; H, 7.16.

Compound **31** (0.33 g, 87%): m.p. 197–198° (ethanol), $[\alpha]_D^{15}$ −28.6° (*c* 1.0, 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, 45.72; H, 7.20.

Compound **31** (0.24 g, 80%) was also obtained from **33** (0.57 g) by *O*-deacylation; m.p. and mixed m.p. 197–198°, $[\alpha]_D^{15}$ −28.3° (*c* 0.4, water).

Methyl 2-O-acetyl-3,6-anhydro-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-β-D-glucopyranoside (**39**). — To a solution of **4** (2.28 g) in dry methanol (30 mL) was added anhydrous methanol (10 mL) containing sodium (0.4 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 (7 mL) and pyridine (10 mL), and the mixture was kept overnight at room temperature, and evaporated to a syrup which was eluted from a column of silica gel with solvent *1* to give **39** as an amorphous powder (1.27 g, 77%): $[\alpha]_D^{17}$ −97.5° (*c* 2.0, chloroform): n.m.r. data (chloroform-*d*): δ 3.43 (s, 3 H, OMe), 2.05 (s, 6 H, 2 OAc), 2.08 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), and 2.01 (s, 3 H, OAc); t.l.c.: R_F 0.38 (solvent *1*).

Anal. Calc. for $C_{23}H_{32}O_{15}$: C, 50.37; H, 5.88. Found: C, 50.25; H, 5.97.

Methyl 3,6-anhydro-4-O-β-D-glucopyranosyl-β-D-glucopyranoside (**40**). — A solution of **39** (0.98 g) in dry methanol (10 mL) was treated with M methanolic sodium methoxide (0.1 mL). The solution was kept for 1 h at room temperature, made neutral with Amberlite IR-120 (H^+) ion-exchange resin, the suspension filtered, and the filtrate evaporated, to give **40** as an amorphous powder, $[\alpha]_D^{15}$ −98.2° (*c* 1.0, chloroform): n.m.r. data (deuterium oxide): δ 4.83 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1).

Anal. Calc. for $C_{13}H_{22}O_{10}$: C, 46.15; H, 6.55. Found: C, 46.28; H, 6.69.

A weighed amount (6 mg) of **40** consumed 1.89. equiv. of periodate after 20 h, the oxidation being monitored by a spectrophotometric method[19]. Methyl α-D-glucopyranoside consumed 1.95 mol. equiv. of periodate when oxidized under identical conditions.

Methyl 2,3,6-tri-O-acetyl-4-O-(2,4-di-O-acetyl-3,6 anhydro-β-D-glucopyranosyl)-β-D-glucopyranoside (**41**). — A solution of **5** (2.15 g) in dry methanol (30 mL) was treated with methanol (10 mL) containing sodium (0.4 g), and the product acetylated with acetic anhydride (7 mL) and pyridine (10 mL). The mixture was evaporated to dryness, and the residue was extracted with chloroform. The solution was washed with water, dried, and evaporated to a solid, which, on recrystallization from ethanol, gave **41** (1.16 g, 75%); m.p. 175–176°, $[\alpha]_D^{17}$ −51.4° (*c* 2.0, chloroform); n.m.r. data (chloroform-*d*): δ 3.49 (s, 3 H, OMe), 2.13 (s, 3 H, OAc), 2.08 (s, 3 H, OAc), 2.03 (s, 6 H, 2 OAc), and 2.02 (s, 3 H, OAc).

Anal. Calc. for $C_{23}H_{32}O_{15}$: C, 50.37; H, 5.88. Found: C, 50.50; H, 5.96.

Methyl 4-O-(3,6-anhydro-β-D-glucopyranosyl)-β-D-glucopyranoside (**42**). — *O*-

Deacetylation of **41** (0.86 g), as described for **39**, gave **42** (0.47 g, 89%); m.p. 205–206° (ethanol), $[\alpha]_D^{17}$ −108.2° (*c* 1.1, water); n.m.r. data (deuterium oxide): δ 4.99 (d, 1 H, $J_{1',2'}$ 1.0 Hz, H-1').

Anal. Calc. for $C_{13}H_{22}O_{10}$: C, 46.15; H, 6.55. Found: C, 46.07; H, 6.50.

Compound **42** (15 mg) was oxidized[19] by periodate, with an uptake of 0.96 mol. equiv. of periodate after 20 h.

Methyl 2,3-di-O-acetyl-6-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-β-D-xylo-hex-5-enopyranoside (**43**). — A solution of **15** (2.15 g) in *N*,*N*-dimethylformamide (20 mL) containing DBU (0.88 mL) was stirred for 2 h at 50°. The mixture was diluted with water (20 mL), and extracted with chloroform (3 × 60 mL). The extracts were washed successively with cold 5% hydrochloric acid, water, aqueous sodium hydrogencarbonate, and water, dried, and evaporated. Crystallization from ethanol gave **43** (1.27 g, 72%); m.p. 116–117°, $[\alpha]_D^{14}$ −73.9° (*c* 1.2, chloroform); ν_{max} 1675 cm^{-1} (C=C).

Anal. Calc. for $C_{25}H_{34}O_{16}$: C, 50.85; H, 5.80. Found: C, 50.77; H, 5.73.

Methyl 2,3,6-tri-O-acetyl-4-O-(2,3,4-tri-O-acetyl-6-deoxy-β-D-xylo-hex-5-enopyranosyl)-β-D-glucopyranoside (**44**). — Treatment of **19** (2.21 g) in *N*,*N*-dimethylformamide (20 mL) with DBU (0.9 mL) for 2 h at 50°, followed by processing as just described, gave **44** (1.36 g, 75%); m.p. 149–150° (ethanol), $[\alpha]_D^{14}$ −34.9° (*c* 1.0, chloroform); ν_{max} 1675 cm^{-1} (C=C).

Anal. Calc. for $C_{25}H_{34}O_{16}$: C, 50.85; H, 5.80. Found: C, 50.99; H, 5.90.

Hydrogenation of **43** *and* **44** *over palladium-on-charcol.* — Compound **43** (507 mg) was dissolved in 1:1 ethyl acetate–methanol (20 mL), and hydrogenated in the presence of 10% palladium-on-charcol (0.5 g) at atmospheric pressure for 2 h, when t.l.c. (solvent *2*) showed the presence of two components, having R_F values of 0.38 (**22**) and 0.29 (**45**). The catalyst was filtered off through a Celite pad, and washed with chloroform. The filtrate and washings were combined, and evaporated, and the residue was chromatographed on a column of silica gel with solvent *2*. The first fraction gave **22** (519 mg, 88%); m.p. and mixed m.p. 175–176°, $[\alpha]_D^{19}$ −41.3° (*c* 1.0, chloroform); the n.m.r. spectrum was identical with that of the sample of **22** prepared previously.

The second fraction afforded methyl 2,3-di-*O*-acetyl-6-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-L-idopyranoside (**45**) (35 mg, 6%); m.p. 187–188° (ethanol), $[\alpha]_D^{20}$ −68.9° (*c* 0.3, chloroform); n.m.r. data (chloroform-*d*): δ 2.09–1.99 (singlets, 18 H, 6 OAc) and 1.23 (d, 3 H, *J* 6.5 Hz, CH_3-5).

Anal. Calc. for $C_{25}H_{36}O_{16}$: C, 50.67; H, 6.12. Found: C, 50.80; H, 6.19.

A mixture of **44** (220 mg) and palladium-on-charcol (0.2 g) in 1:1 ethyl acetate–methanol (15 mL) was shaken under hydrogen for 2 h at atmospheric pressure; t.l.c. (solvent *2*) then indicated the presence of **23** (R_F 0.38) as the sole product. After removal of the catalyst, the solution was evaporated, to give **23** (210 mg, 95%); m.p. and mixed m.p. 186–187° (ether–petroleum ether), $[\alpha]_D^{19}$ −12.5° (*c* 0.9, chloroform); the n.m.r. spectrum was identical with that of the specimen of compound **23** prepared previously.

Hydrogenation of **43** *and* **44** *over Raney nickel.* — A solution of **43** (428 mg) in 1:1 ethyl acetate–methanol (20 mL) was hydrogenated in the presence of Raney nickel (freshly prepared[32a] from 2 g of alloy) at atmospheric pressure for 2 h. The mixture was processed as just described, and the resulting residue was fractionated on a column of silica gel with solvent *2*. The first fraction gave **22** (73 mg, 17%); m.p. and mixed m.p. 175–176°, $[\alpha]_D^{18}$ −42.0° (*c* 1.4, chloroform).

The next fraction afforded **45** (322 mg, 75%); m.p. 187–188°, $[\alpha]_D^{20}$ −69.1° (*c* 1.1, chloroform).

A solution of **44** (389 mg) in 1:1 ethyl acetate–methanol (20 mL) was hydrogenated in the presence of Raney nickel, as just described, to give **23** (367 mg, 94%); m.p. and mixed m.p. 186–187°, $[\alpha]_D^{15}$ −12.7° (*c* 1.0, chloroform).

*Methyl 4-*O*-[4,6-*O*-benzylidene-2,3-di-*O*-(methylsulfonyl)-β-*D*-glucopyranosyl]-2,3,6-tri-*O*-(methylsulfonyl)-β-*D*-glucopyranoside* (**34**). — Methanesulfonyl chloride (20 mL) was added, with stirring, to a cooled (−10°) solution of **6** (10 g) in pyridine (100 mL) during 1 h. After being kept overnight at 0°, the mixture was poured into ice–water, and the precipitate was filtered off, washed well with water, dried, and recrystallized twice from acetone–methanol to give **34** (15.2 g, 81%): m.p. 217–218°, $[\alpha]_D^{15}$ −16.3° (*c* 1.1, acetone); n.m.r. data (acetone-d_6): δ 7.60–7.38 (m, 5 H, Ph), 5.77 (s, 1 H, benzylic-H), 3.58 (s, 3 H, OMe), 3.28 (s, 3 H, OMe), 3.23 (s, 3 H, (OMs), 3.20 (s, 6 H, 2 OMs), and 3.10 (s, 3 H, OMs).

Anal. Calc. for $C_{25}H_{38}O_{21}S_5$: C, 35.97; H, 4.59; S, 19.20. Found: C, 35.85; H, 4.48; S, 19.03.

*Methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-*O*-(methylsulfonyl)-β-*D*-glucopyranoside* (**47**). — A solution of **46** (2.91 g) in *N*,*N*-dimethylformamide (100 mL) containing sodium benzoate (3 g) was boiled and stirred for 5 h under reflux. The mixture was cooled, diluted with water (100 mL), and extracted with chloroform (6 × 50 mL). The extracts were combined, extensively washed with water, dried, and evaporated. Crystallization from ethanol, and recrystallization from ethanol–chloroform, gave **47** (2.74 g, 89%); m.p. 177–178°, $[\alpha]_D^{15}$ −24.5° (*c* 1.1, chloroform); n.m.r. data (chloroform-*d*): δ 8.18–7.30 (m, 10 H, 2 Ph), 6.19 (t, 1 H, $J_{3,4}$ 3.0 Hz, H-3), 5.57 (s, 1 H, benzylic-H), 4.91 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.63 (dd, 1 H, $J_{2,3}$ 3.0 Hz, H-2), 3.59 (s, 3 H, OMe), and 3.04 (s, 3 H, OMs).

Anal. Calc. for $C_{22}H_{24}O_9S$: C, 56.89; H, 5.21; S, 6.90. Found: C, 56.78; H, 5.29; S, 6.79.

*Methyl 4,6-*O*-benzylidene-β-*D*-allopyranoside* (**48**). — To a solution of **47** (0.88 g) in dry 1,4-dioxane (30 mL) was added lithium aluminum hydride (0.4 g), and the mixture was stirred for 16 h at 80°. The excess of reagent was decomposed[32b] by cautious addition of water (0.4 mL), and then successive additions of 15% aqueous sodium hydroxide (0.4 mL) and water (1.2 mL) were made. The suspension was filtered off, and the inorganic precipitate was extracted with 1,4-dioxane (3 × 10 mL). The filtrate and washings were combined, and evaporated to a solid which was recrystallized from ethanol, to give **48** (0.43 g, 81%); m.p. 173–174°, $[\alpha]_D^{15}$ −43.0° (*c* 1.0, chloroform); lit.[26] m.p. 176°, $[\alpha]_D^{16}$ −40.0° (*c* 0.8, chloroform).

Methyl 2,6-di-O-benzoyl-4-O-[3-O-benzoyl-4,6-O-benzylidene-2-O-(methylsulfonyl)-β-D-allopyranosyl]-2-O-(methylsulfonyl)-β-D-allopyranoside (**49**). — A solution of **34** (10.50 g) in *N,N*-dimethylformamide (400 mL) was boiled and stirred with sodium benzoate (18 g) under reflux for 5 h. The mixture was processed as described for the preparation of **47**, and the brown, syrupy product was eluted from a column of silica gel with solvent *3* to give **49** as amorphous material (8.50 g, 74%); $[\alpha]_D^{15}$ +9.7° (*c* 1.0, chloroform); n.m.r. data (chloroform-*d*): δ 8.18–7.24 (m, 20 H, 4 Ph), 6.21 (t, 1 H, $J_{3',4'}$ 3.0 Hz, H-3'), 6.06 (t, 1 H, $J_{3,4}$ 3.0 Hz, H-3), 5.39 (s, 1 H, benzylic-H), 5.08 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.86 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 3.53 (s, 3 H, OMe), 3.07 (s, 3 H, OMs), and 2.90 (s, 3 H, OMs); t.l.c.: R_F 0.38 (solvent *3*).

Anal. Calc. for $C_{43}H_{44}O_{18}S_2$: C, 56.57; H, 4.86; S, 7.02. Found: C, 56.66; H, 4.98; S, 6.88.

Methyl 2,3,6-tri-O-acetyl-4-O-(2,3-di-O-acetyl-4,6-O-benzylidene-β-D-allopyranosyl)-β-D-allopyranoside (**50**). — Lithium aluminum hydride (3 g) was added to a solution of **49** (7.97 g) in 1,4-dioxane (200 mL), and the mixture was stirred for 20 h at 80°. The excess of reagent was decomposed[32b] by successive additions of water (3 mL), 15% aqueous sodium hydroxide (3 mL), and water (9 mL). The suspension was filtered, and the granular precipitate was extracted with 1,4-dioxane (4 × 100 mL). The filtrate and washings were combined, and evaporated to dryness, and the residue was acetylated with 1:1 (v/v) acetic anhydride–pyridine (40 mL) overnight at room temperature. The mixture was poured into ice–water, and the precipitate was filtered off, washed with water, and dried. Recrystallization from ethanol gave **50** (4.17 g, 73%); m.p. 211–212°, $[\alpha]_D^{16}$ −36.7° (*c* 1.1, chloroform): n.m.r. data (chloroform-*d*): δ 7.37 (s, 5 H, Ph), 5.75 (t, 2 H, $J_{3,4} = J_{3',4'} = 2.5$ Hz, H-3,3'), 5.50 (s, 1 H, benzylic-H), 3.51 (s, 3 H, OMe), and 2.13–2.03 (singlets, 15 H, 5 OAc).

Anal. Calc. for $C_{30}H_{38}O_{16}$: C, 55.05; H, 5.85. Found: C, 55.30; H, 5.92.

Methyl 4-O-(4,6-O-benzylidene-β-D-allopyranosyl)-β-D-allopyranoside (**51**). — A solution of **50** (1.98 g) in dry chloroform (10 mL) and methanol (15 mL) was treated with M methanolic sodium methoxide (0.3 mL), and the mixture was kept for 1 h at room temperature, and processed as described for the preparation of **40**, to give **51** (1.25 g, 93%); m.p. 227–229°, $[\alpha]_D^{15}$ −41.4° (*c* 1.0, *N,N*-dimethylformamide); n.m.r. data (dimethyl sulfoxide-d_6): δ 7.39 (s, 5 H, Ph), 5.59 (s, 1 H, benzylic-H), 4.73 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.43 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), and 3.37 (s, 3 H, OMe).

Anal. Calc. for $C_{20}H_{28}O_{11}$: C, 54.05; H, 6.35. Found: C, 53.92; H, 6.48.

Methyl 4-O-β-D-allopyranosyl-β-D-allopyranoside (**52**). — Treatment of **51** (1.14 g) with acetic acid (12 mL) and water (8 mL) for 20 min at 100°, as described for the preparation of **9**, gave **52** (0.84 g, 92%); m.p. 206–207°, $[\alpha]_D^{15}$ −18.7° (*c* 1.1, water).

Anal. Calc. for $C_{13}H_{24}O_{11}$: C, 43.82; H, 6.79. Found: C, 43.73; H, 6.92.

Methanolysis of a portion of **52**, and g.l.c. (column *B*) of the resulting methyl glycosides as the per(trimethylsilyl) ethers gave peaks corresponding to methyl α- and β-D-allopyranoside (*T* 0.63 and 0.70). No other peaks were detected.

Methyl 2,3,6-tri-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-allopyranosyl)-β-D-allopyranoside (**53**). — Conventional acetylation of **52** (259 mg) with acetic anhydride–pyridine gave **53** (445 mg, 94%): m.p. 150–151° (ether–petroleum ether), $[\alpha]_D^{15}$ −17.4° (*c* 1.2, chloroform).

Anal. Calc. for $C_{27}H_{38}O_{18}$: C, 49.85; H, 5.89. Found: C, 49.72; H, 5.80.

Methyl 2,3-di-O-acetyl-6-deoxy-4-O-(2,3-di-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl)-6-iodo-β-D-glucopyranoside (**35**). — A solution of **11** (18.1 g) in *N,N*-dimethylformamide (330 mL) was heated and stirred with sodium iodide (36 g) for 4 h at 100°. The mixture was processed as described for the preparation of **15**, to give **35** (15.7 g, 92%); m.p. 268–270° (dec.) (ethanol–chloroform), $[\alpha]_D^{24}$ −47.8° (*c* 1.4, chloroform); n.m.r. data (chloroform-*d*): δ 7.38 (s, 5 H, Ph), 5.50 (s, 1 H, benzylic-H), 3.53 (s, 3 H, OMe), 2.17 (s, 3 H, OAc), 2.02 (s, 6 H, 2 OAc), and 2.00 (s, 3 H, OAc).

Anal. Calc. for $C_{28}H_{35}IO_{14}$: C, 46.55; H, 4.88; I, 17.57. Found: C, 46.72; H, 4.96; I, 17.39.

Methyl 2,3-di-O-acetyl-6-deoxy-4-O-(2,3-di-O-acetyl-4,6-O-benzylidene-β-D-glucopyranosyl)-β-D-glucopyranoside (**36**). — Treatment of **35** (15.2 g) with hydrazine (20 mL) in 1:1 (v/v) 1,4-dioxane–methanol (600 mL) containing Raney nickel (freshly prepared from 40 g of alloy) and barium carbonate (60 g), as described for the preparation of **22**, gave **36** (10.7 g, 85%): m.p. 232–233° (ethanol–chloroform), $[\alpha]_D^{24}$ −71.6° (*c* 1.1, chloroform); n.m.r. data (chloroform-*d*): δ 7.38 (s, 5 H, Ph), 5.48 (s, 1 H, benzylic-H), 4.65 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.35 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 3.47 (s, 3 H, OMe), 2.03 (s, 3 H, OAc), 2.01 (s, 6 H, 2 OAc), 1.39 (s, 3 H, OAc), and 1.33 (d, 3 H, *J* 6.0 Hz, CH_3-5).

Anal. Calc. for $C_{28}H_{36}O_{14}$: C, 56.37; H, 6.08. Found: C, 56.27; H, 6.14.

Methyl 4-O-(4,6-O-benzylidene-β-D-glucopyranosyl)-6-deoxy-β-D-glucopyranoside (**37**). — Treatment of **36** (10.1 g) with M sodium methoxide (5 mL) in chloroform (70 mL) and methanol (125 mL) for 2 h at room temperature, as described for **39**, gave **37** (7.3 g, 95%); m.p. 203–204° (ethanol–ether), $[\alpha]_D^{24}$ −47.1° (*c* 1.1, *N,N*-dimethylformamide); n.m.r. data (dimethyl sulfoxide-d_6): δ 7.42 (s, 5 H, Ph), 5.60 (s, 1 H, benzylic-H), 4.72 (d, 1 H, $J_{1',2'}$ 8.0 Hz, H-1'), 4.13 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 3.38 (s, 3 H, OMe), and 1.30 (d, 1 H, *J* 6.0 Hz, CH_3-5).

Anal. Calc. for $C_{20}H_{28}O_{10}$: C, 56.07; H, 6.59. Found: C, 56.20; H, 6.63.

Methyl 4-O-[4,6-O-benzylidene-2,3-di-O-(methylsulfonyl)-β-D-glucopyranosyl]-6-deoxy-2,3-di-O-(methylsulfonyl)-β-D-glucopyranoside (**38**). — To a cooled (−10°) solution of **37** (6.95 g) in pyridine (70 mL) was added methanesulfonyl chloride (15.2 mL), and the mixture was kept overnight at 0°, and processed as described for the preparation of **10**, to give **38** (10.32 g, 86%); m.p. 181–182° (acetone–methanol), $[\alpha]_D^{24}$ −21.4° (*c* 1.1, acetone); n.m.r. data (acetone-d_6): δ 7.65–7.37 (m, 5 H, Ph), 5.75 (s, 1 H, benzylic-H), 3.53 (s, 3 H, OMe), 3.25 (s, 3 H, OMs), 3.22 (s, 3 H, OMs), 3.18 (s, 3 H, OMs), 3.12 (s, 3 H, OMs), and 1.48 (d, 3 H, *J* 5.5 Hz, CH_3-5).

Anal. Calc. for $C_{24}H_{36}O_{18}S_4$: C, 38.91; H, 4.90; S, 17.31. Found: C, 38.74; H, 4.81; S, 17.50.

*Methyl 4-O-(4,6-O-benzylidene-2,3-dideoxy-β-*D*-erythro-hex-2-enopyranosyl)-2,3,6-trideoxy-β-*D*-erythro-hex-2-enopyranoside* (**54**). — A mixture of **38** (8.81 g), dried sodium iodide (69 g), and freshly prepared and dried zinc dust[32c] (31 g) in dry *N,N*-dimethylformamide (300 mL) was vigorously boiled and stirred under reflux for 30 min. The mixture was cooled, diluted with water (300 mL) and chloroform (300 mL), and filtered. The chloroform layer was separated, and the aqueous layer was extracted with chloroform (3 × 100 mL). The chloroform layer and extracts were combined, washed with aqueous sodium chloride (3 × 100 mL), dried, and evaporated. The residue was eluted from a column of silica gel with solvent *3*, to give **54** (2.95 g, 69%); m.p. 125–126° (ethanol), $[\alpha]_D^{22}$ +124.0° (*c* 1.0, chloroform); n.m.r. data (chloroform-*d*): δ 7.63–7.28 (m, 5 H, Ph), 5.60 (s, 1 H, benzylic-H), 6.95 (s, 3 H, OMe), and 1.35 (d, 3 H, *J* 6.0 Hz, CH_3-5).

Anal. Calc. for $C_{20}H_{24}O_6$: C, 66.65; H, 6.71. Found: C, 66.77; H, 6.77.

*Methyl 4-O-(4,6-O-benzylidene-2,3-dideoxy-β-*D*-erythro-hexopyranosyl)-2,3,6-trideoxy-β-*D*-erythro-hexopyranoside* (**55**). — A solution of **54** (2.30 g) in methanol (30 mL) and 1,4-dioxane (20 mL) was hydrogenated in the presence of 10% palladium-on charcol (2 g) until ~2 mol. equiv. of hydrogen had been absorbed. The mixture was processed as described for **43**, to give **55** (2.21 g, 95%); m.p. 127–128° (ethanol), $[\alpha]_D^{22}$ −40.7° (*c* 1.0, chloroform); n.m.r. data (chloroform-*d*): δ 7.53–7.33 (m, 5 H, Ph), 5.52 (s, 1 H, benzylic-H), 3.45 (s, 3 H, OMe), and 1.28 (d, 3 H, *J* 6.0 Hz, CH_3-5).

Anal. Calc. for $C_{20}H_{28}O_6$: C, 65.92; H, 7.74. Found: C, 66.08; H, 7.81.

*Methyl 4-O-(4-O-benzoyl-2,3,6-trideoxy-β-*D*-erythro-hexopyranosyl)-2,3,6-trideoxy-β-*D*-erythro-hexopyranoside* (**57**). — A suspension of **55** (1.01 g), *N*-bromosuccinimide (0.52 g), and barium carbonate (5 g) in carbon tetrachloride (80 mL) was boiled and stirred under reflux for 1 h, when t.l.c. (solvent *3*) showed the disappearance of **55** (R_F 0.45) and the formation of a major product (**56**, R_F 0.54). The suspension was filtered, the solid was washed with hot carbon tetrachloride (50 mL), and the filtrate and washings were combined, and evaporated to dryness. The resulting syrup was dissolved in ether (50 mL), and the solution was washed with water (3 × 10 mL), dried, and evaporated to a syrup which was eluted from a column of silica gel with solvent *3*, to give **56** as an amorphous powder (1.08 g, 88%); $[\alpha]_D^{25}$ +24.4° (*c* 1.4, chloroform). This compound failed to give a satisfactory analysis because of its lability; when kept for 1 day at 0°, it showed a discoloration. Treatment of **56** (1.08 g) with hydrazine hydrate (1 mL) in methanol (40 mL) containing barium carbonate (3 g) and a small amount of Raney nickel, followed by processing as described for the preparation of **22**, gave **57** (0.77 g, 77%); m.p. 124–126° (ethanol), $[\alpha]_D^{25}$ +3.71° (*c* 0.8, chloroform); n.m.r. data (chloroform-*d*): δ 8.12–7.30 (m, 5 H, Ph), 3.47 (s, 3 H, OMe), and 1.30 and 1.28 (s, each 3 H, CH_3-5 and -5′).

Anal. Calc. for $C_{20}H_{28}O_6$: C, 65.92; H, 7.74. Found: C, 65.85; H, 7.84.

*Methyl 2,3,6-trideoxy-4-O-(2,3,6-trideoxy-β-*D*-erythro-hexopyranosyl)-β-*D*-erythro-hexopyranoside* (**58**). — A solution of **57** (620 mg) in methanol (10 mL) was treated with M sodium methoxide (0.2 mL), and the mixture was kept overnight at

room temperature. Processing as described earlier gave **58** (403 mg, 91%); m.p. 131–132° (ether–petroleum ether), $[\alpha]_D^{25}$ −42.0° (*c* 1.2, chloroform); n.m.r. data (chloroform-*d*): δ 3.47 (s, 3 H, OMe), 2.07 (broad s, 1 H, disappeared on deuteration, HO-4'), and 1.28 and 1.27 (s, each 3 H, *J* 6.0 Hz, CH_3-5 and -5').

Anal. Calc. for $C_{13}H_{24}O_5$: C, 59.98; H, 9.29. Found: C, 59.85; H, 9.33.

To a warm solution of (2,4-dinitrophenyl)hydrazine (484 mg, 2.44 mmol) in 2M hydrochloric acid (75 mL) was added **58** (265 mg, 1.02 mmol), and the mixture was heated for 10 min at 90°, kept for 1 h at room temperature, and then cooled for 1 h in an ice-bath. The yellow, crystalline precipitate formed was filtered off, washed with a small amount of cold water, and dried, to give 2,3,6-trideoxy-D-erythrose (2,4-dinitrophenyl)hydrazone (508 mg, 80%); m.p. 154–155° (methanol), $[\alpha]_D^{25}$ −9.8° (*c* 1.4, pyridine); lit. m.p. 154–155.5° (methanol), $[\alpha]_D^{19}$ −9.8° ±1° (*c* 0.4, pyridine)[29]: m.p. 152–153°, $[\alpha]_D^{25}$ −10.0° (*c* 0.86, pyridine)[31].

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