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SYNTHESIS OF THE REPEATING UNITS OF SCHIZOPHYLLAN

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ABSTRACT

The tetrasaccharides β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-D-Glc*p*, β-D-Glc*p*-(1→3)-[β-D-Glc*p*-(1→6)]-β-D-Glc*p*-(1→3)-D-Glc*p*, and β-D-Glc*p*-(1→6)-β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→3)-D-Glc*p*, corresponding to the three possible repeating-units of Schizophyllan, have been synthesised by silver trifluoromethanesulfonate-promoted Koenigs–Knorr type condensations, using 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl bromide as the key intermediate.

INTRODUCTION

Schizophyllan, a polysaccharide produced extracellularly by the fungus *Schizophyllum commune* Fries, contains[1] a main chain of (1→3)-linked β-D-glucopyranosyl residues with side chains of single, (1→6)-linked β-D-glucopyranosyl residues for every three D-glucosyl residues in the backbone. Polysaccharides having a similar, (1→6)-branched, (1→3)-β-D-glucan structure are also prominent products elaborated by several fungi[2].

We now report the synthesis of D-glucotetrasaccharides having the structures *O*-β-D-glucopyranosyl-(1→3)-*O*-β-D-glucopyranosyl-(1→3)-*O*-[β-D-glucopyranosyl-(1→6)]-D-glucopyranose (**1**), *O*-β-D-glucopyranosyl-(1→3)-*O*-[β-D-glucopyranosyl-(1→6)]-*O*-β-D-glucopyranosyl-(1→3)-D-glucopyranose (**2**), and *O*-β-D-glucopyranosyl-(1→6)-*O*-β-D-glucopyranosyl-(1→3)-*O*-β-D-glucopyranosyl-(1→3)-D-glucopyranose (**3**), which correspond to the three possible repeating-units of Schizophyllan. Recently, Ogawa and Kaburagi[3] reported the synthesis of **1** by a reaction sequence alternative to that now described, and Ueno and Abe[4] isolated **2** in crystalline form from the partial acid hydrolysate of a polysaccharide from the sclerotia of *Sclerotinia sclerotiorum* (Lib.).

RESULTS AND DISCUSSION

The strategy employed for the synthesis of the tetrasaccharides **1–3** was based

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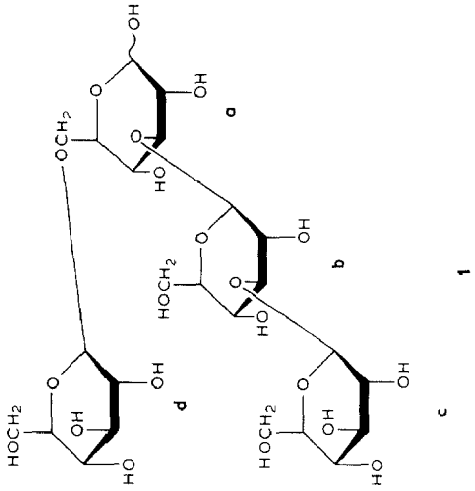

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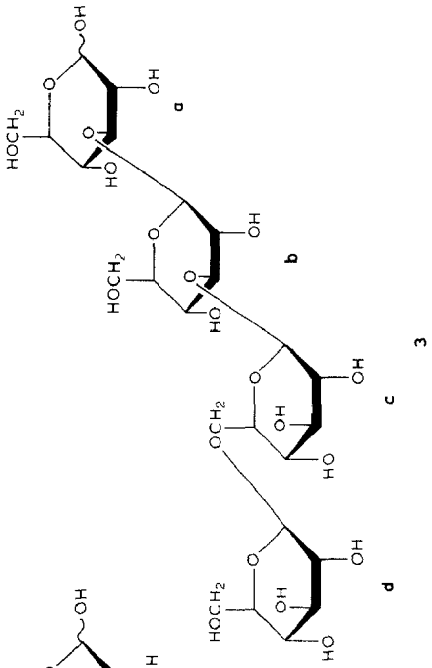

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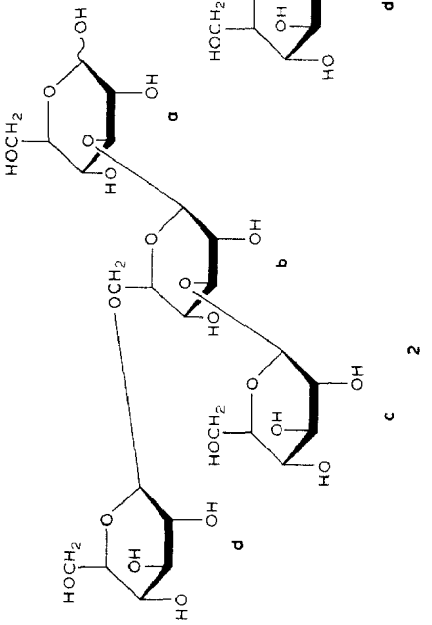
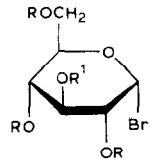


2

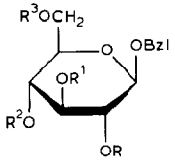
on the synthesis of suitably benzylated mono- and di-saccharide derivatives to serve as the glycosyl acceptors, and the use of a combination of silver trifluoromethanesulfonate[5] (triflate) as catalyst and molecular sieve as proton acceptor[6] for all the glycosylation steps, except for the preparation of benzyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-D-glucopyranoside (**6**).

The glucosyl acceptors, benzyl 3-*O*-allyl-2,4-di-*O*-benzyl- (**10**), benzyl 2,4-di-*O*-benzyl- (**11**), and benzyl 2,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**13**), were prepared from the easily obtainable[7] 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl bromide (**4**). Condensation of **4** with benzyl alcohol in benzene–ether in the presence of silver carbonate gave 80% of **6**. One of the acetyl groups in **6**, probably[7] AcO-2, was not affected by methanol containing a catalytic amount of sodium methoxide at room temperature, but was removed[7] with boiling methanolic sodium methoxide to afford benzyl 3-*O*-allyl-β-D-glucopyranoside (**7**). Treatment of **7** with benzaldehyde–zinc chloride gave the 4,6-*O*-benzylidene derivative **8** which, with benzyl bromide and sodium hydride in *N*,*N*-dimethylformamide[8], gave the 3-*O*-allyl-2-*O*-benzyl-4,6-*O*-benzylidene derivative **9**. The benzylidene group of **9** was selectively cleaved by treatment with lithium aluminium hydride and aluminium chloride[9] to give 83% of **10**, the ^{13}C-n.m.r. spectrum of which contained a signal for C-6 at 61.9 p.p.m., confirming[10] that HO-6 was unsubstituted. The allyl group in **10** was removed by rearrangement first to the propenyl ether with tris(triphenylphosphine)rhodium(I) chloride[11], followed by hydrolysis[12] with dilute acid, to give **11**. Benzylation of **7** afforded the 3-*O*-allyl-2,4,6-tri-*O*-benzyl derivative **12**, which was *O*-deallylated, as above, to provide **13**.



4 R = Ac, R^1 = Allyl

5 R = R^1 = Bz



6 R = R^2 = R^3 = Ac, R^1 = Allyl

7 R = R^2 = R^3 = H, R^1 = Allyl

8 R = H, R^1 = Allyl, R^2, R^3 = PhCH

9 R = Bzl, R^1 = Allyl, R^2, R^3 = PhCH

10 R = R^2 = Bzl, R^1 = Allyl, R^3 = H

11 R = R^2 = Bzl, R^1 = R^3 = H

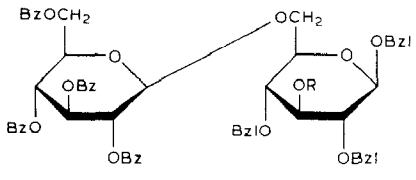
12 R = R^2 = R^3 = Bzl, R^1 = Allyl

13 R = R^2 = R^3 = Bzl, R^1 = H

Condensation[13] of **10** with 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide[14] (**5**) gave a mixture, column chromatography of which afforded 81% of crystalline benzyl 3-*O*-allyl-2,4-di-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranoside (**14**). In the ^{13}C-n.m.r. spectrum of **14**, the signal for C-1′ appeared at 101.2 p.p.m., indicating[10] the configuration at C-1′ to

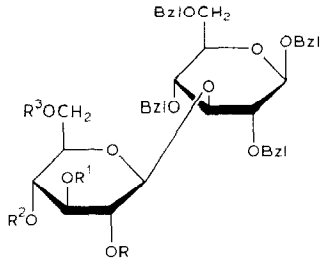
be β. Removal of the allyl group in **14** with palladium chloride[15] in aqueous acetic acid–1,4-dioxane gave the crystalline disaccharide derivative **15** having HO-3 unsubstituted.

Glucosylation of **13** with **4** gave 83% of benzyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-D-glucopyranosyl)-β-D-glucopyranoside (**16**) after column chromatography. The β configuration at C-1′ in **16** was clear[10] from the ^{13}C-n.m.r. signal at 100.3 p.p.m. *O*-Deacetylation of **16** in boiling, methanolic sodium methoxide[7] afforded the crystalline 2′,4′,6′-triol **17** which, with α,α-dimethoxytoluene in acetonitrile in the presence of toluene-*p*-sulfonic acid, gave the 4′,6′-*O*-benzylidene derivative **18**. Benzylation then gave the crystalline 2′-*O*-benzyl derivative **19**. Reductive ring-cleavage of the benzylidene group in **19** with lithium aluminium hydride–aluminium chloride[9] gave 80% of the crystalline 6′-ol **20**, the ^{13}C-n.m.r. spectrum of which contained the signal for C-6′ at 61.7 p.p.m., proving[10] that HO-6′ was unsubstituted. *O*-Deallylation of **20** with palladium chloride in aqueous acetic acid gave the disaccharide derivative **21** having HO-3′,6′ unsubstituted. Benzylation of **17** gave **22**, which was *O*-deallylated, as for **20**, to provide the disaccharide derivative **23** having HO-3′ unsubstituted.



14 R = Allyl

15 R = H



16 R = R^2 = R^3 = Ac, R^1 = Allyl

17 R = R^2 = R^3 = H, R^1 = Allyl

18 R = H, R^1 = Allyl, R^2, R^3 = PhCH

19 R = Bzl, R^1 = Allyl, R^2, R^3 = PhCH

20 R = R^2 = Bzl, R^1 = Allyl, R^3 = H

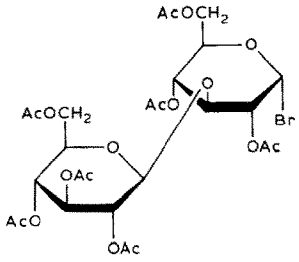
21 R = R^2 = Bzl, R^1 = R^3 = H

22 R = R^2 = R^3 = Bzl, R^1 = Allyl

23 R = R^2 = R^3 = Bzl, R^1 = H

Condensation of **15** with hepta-*O*-acetyl-α-laminarabiosyl bromide[16] (**24**) gave 78% of the tetrasaccharide derivative **25** after column chromatography. *O*-Deacylation of **25** afforded the crystalline 2,4-di-*O*-benzyl-D-glucotetraoside **26** which was hydrogenolysed in acetic acid over Pd/C to furnish known[3] **1**, which was further characterised by conversion (acetic anhydride–sodium acetate[17]) into the crystalline β-tetradeca-acetate **27**.

Reaction of **21** with 3 mol of **5**, followed by *O*-debenzoylation with sodium methoxide (to facilitate the isolation of the tetrasaccharide derivative) and column chromatography, afforded 75% of the partially blocked D-glucotetraoside deriva-



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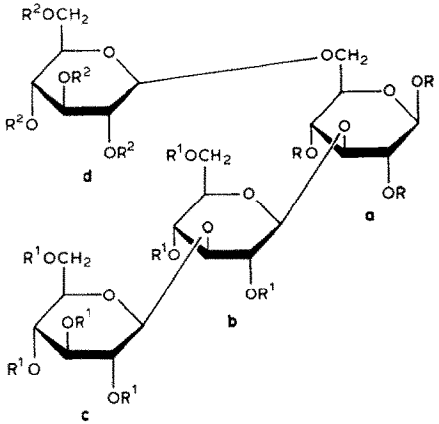
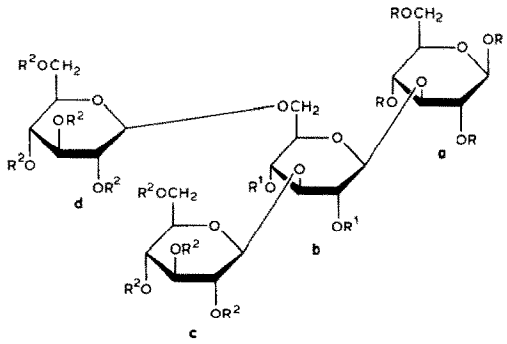
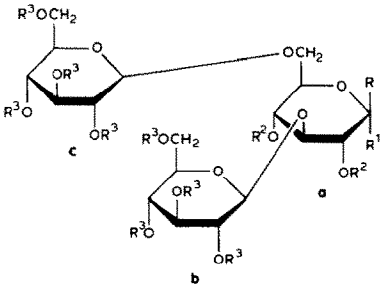


25 R = Bzl, R^1 = Ac, R^2 = Bz
26 R = Bzl, R^1 = R^2 = H
27 R = R^1 = R^2 = Ac

tive **28**. Acetylation then gave **29**. Hydrogenolysis of **28** produced known[4] **2**, the m.p. of which agreed well with that reported[4] but with different mutarotation {$[\alpha]_D$ $-2° \rightarrow -6°$ (water); *cf.*[4] $+5.7° \rightarrow +1.8°$}. The ^{13}C-n.m.r. spectrum of **2** contained a signal for C-1b,c,d, at 105.4 p.p.m., signals for C-1aβ and C-1aα at 98.3 and 94.6 p.p.m., respectively, and deshielded signals for C-3aβ, C-3b, and C-3aα at 88.0, 86.8, and 85.8 p.p.m., respectively, consistent with the structure assigned. Acetylation of **2** gave the known[4] β-tetradeca-acetate **30**, the physical constants of which were slightly different from those reported[4].



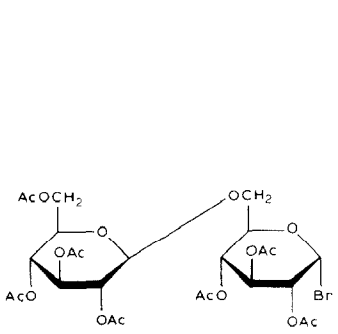
28 R = R^1 = Bzl, R^2 = H
29 R = R^1 = Bzl, R^2 = Ac
30 R = R^1 = R^2 = Ac
31 R = Bzl, R^1 = R^2 = Ac
32 R = Bzl, R^1 = R^2 = H



33 R = OBzl, R^1 = H, R^2 = Bzl, R^3 = Bz
34 R = OBzl, R^1 = R^3 = H, R^2 = Bzl
35 R = OBzl, R^1 = H, R^2 = Bzl, R^3 = Ac
36 R = OAc, R^1 = H, R^2 = R^3 = Ac
37 R = H, R^1 = Br, R^2 = R^3 = Ac

In investigating the above discrepancies, a block synthesis of **2** was explored in which **13** was coupled with the branched-trisaccharide α-glycosyl bromide **37**. Compound **11** was treated with 3 mol of **5** to give 77% of the trisaccharide derivative **33** after column chromatography. That the newly introduced interglucosidic linkages in **33** were β was supported by the ^{13}C-n.m.r. spectrum, which showed signals for C-1c and C-1b at 101.1 and 100.5 p.p.m., respectively. Compound **33** was converted into crystalline **37** by a reaction sequence involving *O*-debenzoylation (→ **34**), acetylation (→ **35**), hydrogenolysis followed by acetylation (→ **36**), and treatment with hydrogen bromide in acetic acid and dichloromethane. Compound **36** had previously been obtained[18] as a crystalline α,β-mixture. Glycosylation of **13** with **37** gave 72% of the D-glucotetraoside derivative **31** after column chromatography. *O*-Deacetylation then afforded **32** which was hydrogenolysed to furnish **2**, characterised as **30**. The physical properties of **2** and **30** were in good agreement* with those of the compound obtained by the reaction of **21** with **5**.

Coupling of **23** with hepta-*O*-acetyl-α-gentiobiosyl bromide[19] (**38**) gave 80% of the D-glucotetraoside derivative **39** after column chromatography. *O*-Deacetylation then gave **40**, hydrogenolysis of which furnished amorphous **3**. The ^{13}C-n.m.r. spectrum of **3** contained signals for C-1b,c,d at 105.5 and 105.3 p.p.m., signals for C-1aβ and C-1aα at 98.3 and 94.6 p.p.m., respectively, and deshielded signals for C-3b, C-3aβ, and C-3aα at 87.7, 87.3, and 85.0 p.p.m., respectively, in accord with the structure assigned. The tetrasaccharide **3** was further characterised as the crystalline β-tetradeca-acetate **41**.



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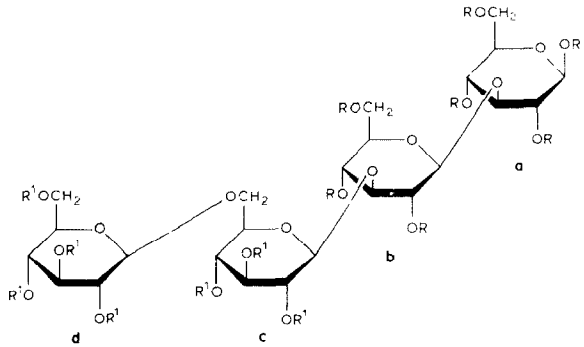

39 R = Bzl, R' = Ac
40 R = Bzl, R' = H
41 R = R' = Ac

*After this work had been completed, Dr. Y. Ueno informed us that the $[\alpha]_D^{20}$ value reported[4] previously for **2** was erroneous and should be −2.0° (2 min) → −5.9° (final, *c* 0.4, water). There was no depression of m.p. on admixture of **2** with an authentic specimen kindly provided by Dr Ueno The ^{13}C-n m r spectra of the two compounds were identical.

EXPERIMENTAL

General methods. — Unless stated otherwise, these were the same as those described previously[20]. N.m.r. spectra (^{1}H, 90 MHz; ^{13}C, 22.6 MHz) were recorded with a Hitachi R-90H spectrometer for solutions in $CDCl_3$ (internal Me_4Si) or D_2O (internal sodium 4,4-dimethyl-4-silapentanoate-d_4). The following solvent systems were used for chromatography, hexane–ethyl acetate (*1*, 1:1; *2*, 2:1; *3*, 4:1), benzene–ethyl acetate (*4*, 20:1; *5*, 4:1), and benzene–ethanol (*6*, 9:1).

*Benzyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-*D*-glucopyranoside* (**6**). — A mixture of benzyl alcohol (25 mL), silver carbonate (30 g), and Drerite (20 g) in dry ether–benzene (1:1, 240 mL) was stirred for 2 h at room temperature in the dark with exclusion of moisture, and a solution of **4** (40.2 g) in ether (100 mL) was added dropwise during 1 h. The mixture was stirred overnight at room temperature, and insoluble material was collected on a bed of Celite and washed with benzene. The combined filtrate and washings were concentrated, and the remaining benzyl alcohol was removed by repeated coevaporation with water. The resulting syrup was crystallised from ether–light petroleum and recrystallised from hexane–ether to give **6** (34.3 g, 80%), m.p. 62–63°, $[\alpha]_D^{26}$ −57° (*c* 2.5, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.31 (s, 5 H, Ph), 5.92–5.57 (m, 1 H, -CH=), and 2.01, 1.99, and 1.98 (3 s, each 3 H, 3 OAc).

Anal. Calc. for $C_{22}H_{28}O_9$: C, 60.54; H, 6.47. Found: C, 60.60; H, 6.54.

*Benzyl 3-*O*-allyl-β-*D*-glucopyranoside* (**7**). — A solution of **6** (31.2 g) in anhydrous methanol (250 mL) and methanolic M sodium methoxide (10 mL) was boiled under reflux for 1 h, then cooled, neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. The residue was recrystallised from ether–light petroleum to afford **7** (20.4 g, 92%), m.p. 82–83°, $[\alpha]_D^{26}$ −68° (*c* 1.4, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 135.1 and 117.0 (CH_2=CH), 101.9 (C-1), 84.3 (C-3), and 61.9 (C-6).

Anal. Calc. for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 61.95; H, 7.11.

*Benzyl 3-*O*-allyl-4,6-*O*-benzylidene-β-*D*-glucopyranoside* (**8**). — A suspension of **7** (8.6 g) and powdered, anhydrous zinc chloride (8.5 g) in freshly distilled benzaldehyde (45 mL) was stirred overnight at room temperature, and then poured into a mixture of light petroleum and ice–water. The precipitate was collected, washed with cold water and then light petroleum, and dried. Crystallisation from ethanol gave **8** (9.5 g, 86%), m.p. 137–138°, $[\alpha]_D^{20}$ −69° (*c* 1.6, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.55–7.31 (m, 10 H, 2 Ph), 7.08–5.73 (m, 1 H, -CH=), and 5.54 (s, 1 H, PhC*H*).

Anal. Calc. for $C_{23}H_{26}O_6$: C, 69.33; H, 6.58. Found: C, 69.45; H, 6.66.

*Benzyl 3-*O*-allyl-2-*O*-benzyl-4,6-*O*-benzylidene-β-*D*-glucopyranoside* (**9**). — A solution of **8** (7.1 g) in *N,N*-dimethylformamide (80 mL) was stirred with sodium hydride (1.6 g; 50% mineral oil) for 1 h at room temperature and then cooled to 0°. Benzyl bromide (3 mL) was added dropwise and the mixture was stirred for 5 h at room temperature. Methanol was then added to decompose the excess of

hydride, most of the solvent was evaporated, and a solution of the residue in dichloromethane was washed with water, dried, and concentrated. The residue was recrystallised from ethanol to give **9** (7.4 g, 85%), m.p. 117–118°, $[\alpha]_D^{26}$ −54.5° (*c* 1.4, chloroform).

Anal. Calc. for $C_{30}H_{32}O_6$: C, 73.75; H, 6.60. Found: C, 73.66; H, 6.65.

*Benzyl 3-O-allyl-2,4-di-O-benzyl-β-*D*-glucopyranoside* (**10**). — To a stirred solution of **9** (7.0 g) in dry ether–dichloromethane (1:1, 140 mL) was added lithium aluminium hydride (2.7 g), and the mixture was heated to reflux. A solution of aluminium chloride (6 g) in dry ether (90 mL) was added dropwise during 20 min, and stirring was continued under reflux for 2 h. The mixture was then cooled, the excess of reagent was decomposed with ethyl acetate (20 mL), and water (30 mL) was added. Insoluble material was collected on a Celite pad and washed with dichloromethane, and the combined filtrate and washings were washed with water, dried, and concentrated. The residue was recrystallised from ethanol to give **10** (5.8 g, 83%), m.p. 116–117°, $[\alpha]_D^{20}$ −16° (*c* 1.1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 135.0 and 116.5 (CH_2=CH), 102.7 (C-1), and 61.9 (C-6).

Anal. Calc. for $C_{30}H_{34}O_6$: C, 73.45; H, 6.99. Found: C, 73.53; H, 7.10.

*Benzyl 2,4-di-O-benzyl-β-*D*-glucopyranoside* (**11**). — A mixture of **10** (5.1 g), tris(triphenylphosphine)rhodium(I) chloride (0.4 g), and 1,4-diazabicyclo[2.2.2]-octane (2 g) in ethanol–toluene–water (8:3:1, 150 mL) was boiled under reflux for 6 h and then concentrated. A solution of the residue in dichloromethane was washed successively with cold M hydrochloric acid, aqueous sodium hydrogencarbonate, and water, dried, and concentrated. A solution of the residue in acetone–M hydrochloric acid (10:1, 110 mL) was boiled under reflux for 15 min, then cooled, neutralised with aqueous sodium hydrogencarbonate, and concentrated, and the residue was extracted with dichloromethane. The extract was washed with water, dried, and concentrated. Column chromatography (solvent *1*) of the syrupy residue gave **11** (4.0 g, 85%), m.p. 84–85° (from methanol), $[\alpha]_D^{20}$ +1° (*c* 1.4, chloroform).

Anal. Calc. for $C_{27}H_{30}O_6$: C, 71.98; H, 6.71. Found: C, 71.86; H, 6.78.

*Benzyl 3-O-allyl-2,4,6-tri-O-benzyl-β-*D*-glucopyranoside* (**12**). — A solution of **7** (11.7 g) in *N,N*-dimethylformamide (150 mL) was treated with sodium hydride (8 g; 50% mineral oil), followed by benzyl bromide (20 mL) as described for **9**, to give **12** (19.3 g, 83%), m.p. 92–93° (from ethanol), $[\alpha]_D^{26}$ −13° (*c* 1.6, chloroform).

Anal. Calc. for $C_{37}H_{40}O_6$: C, 76.53; H, 6.94. Found: C, 76.65; H, 6.81.

*Benzyl 2,4,6-tri-O-benzyl-β-*D*-glucopyranoside* (**13**). — A solution of **12** (15.0 g) in ethanol–toluene–water (8:3:1, 375 mL) containing tris(triphenylphosphine)rhodium(I) chloride (0.5 g) and 1,4-diazabicyclo[2.2.2]octane (2.5 g) was boiled under reflux for 5 h. The mixture was processed and the product was hydrolysed with acetone–M hydrochloric acid (10:1, 220 mL), as described for **11**. Column chromatography (solvent *3*) of the product gave **9** (11.6 g, 83%), m.p. 30–35° (from ethanol), $[\alpha]_D^{20}$ −3° (*c* 2.6, chloroform).

Anal. Calc. for $C_{34}H_{36}O_6$: C, 75.53; H, 6.71. Found: C, 75.58; H, 6.79.

Benzyl 3-O-allyl-2,4-di-O-benzyl-6-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranoside (**14**). — A solution of **5** (6.55 g, 9.9 mmol) in toluene–nitromethane (1:1, 40 mL) was added dropwise during 25 min, with exclusion of moisture and light, to a stirred solution at −15° of **10** (3.75 g, 7.6 mmol) in toluene–nitromethane (1:1, 30 mL) containing silver triflate (3.06 g, 11.9 mmol) and powdered molecular sieve Type 4A (3 g). The mixture was allowed to attain 0° gradually, and then stirred at 0° for 30 min. Insoluble material was collected on a layer of Celite and washed with toluene, and the combined filtrate and washings were washed successively with aqueous sodium hydrogencarbonate and water, dried, and concentrated. Column chromatography (solvent *4*) of the residue gave **14** (6.62 g, 81%), m.p. 144–145° (from ethanol), $[\alpha]_D^{20}$ −2° (*c* 1.1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 102.2 (C-1) and 101.2 (C-1′).

Anal. Calc. for $C_{64}H_{60}O_{15}$: C, 71.90; H, 5.66. Found: C, 71.76; H, 5.74.

Benzyl 2,4-di-O-benzyl-6-O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-β-D-glucopyranoside (**15**). — A mixture of **14** (3.72 g), palladium chloride (0.67 g), and sodium acetate (3.1 g) in acetic acid–1,4-dioxane–water (20:10:1, 62 mL) was stirred at room temperature for 6 h. Insoluble material was collected on a Celite pad and washed with methanol, and the combined filtrate and washings were concentrated. Column chromatography (solvent *4*) of the syrupy residue gave **15** (2.82 g, 79%), m.p. 124–126° (from ethanol), $[\alpha]_D^{20}$ +7° (*c* 1.8, chloroform).

Anal. Calc. for $C_{61}H_{56}O_{15}$: C, 71.19; H, 5.48. Found: C, 71.26; H, 5.61.

Benzyl 2,4,6-tri-O-benzyl-3-O-(2,4,6-tri-O-acetyl-3-O-allyl-β-D-glucopyranosyl)-β-D-glucopyranoside (**16**). — To a stirred mixture of **13** (17.4 g, 32.2 mmol), silver triflate (12.7 g, 49 mmol), powdered molecular sieve Type 4A (15 g), and 1,2-dichloroethane (100 mL) at −20° was added dropwise a solution of **4** (18.4 g, 45 mmol) in 1,2-dichloroethane (50 mL). The mixture was stirred at 0° for 2 h, and then processed as described for the preparation of **14**. Column chromatography (solvent *1*) of the syrupy residue gave amorphous **16** (23.2 g, 83%), $[\alpha]_D^{20}$ −3° (*c* 1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 170.4, 168.9, and 168.6 (3 C=O), 134.2 and 116.8 (CH_2=CH), 101.9 (C-1), 100.3 (C-1′), and 21.0, 20.7, and 20.6 (3 $COCH_3$).

Anal. Calc. for $C_{49}H_{56}O_{14}$: C, 67.73; H, 6.50. Found: C, 67.80; H, 6.61.

Benzyl 3-O-(3-O-allyl-β-D-glucopyranosyl)-2,4,6-tri-O-benzyl-β-D-glucopyranoside (**17**). — A solution of **16** (20.7 g) in methanol (200 mL) containing M sodium methoxide (10 mL) was boiled under reflux for 1 h. Processing of the mixture, as described for **7**, gave **17** (16.6 g, 94%), m.p. 147–148° (from ethanol–hexane), $[\alpha]_D^{20}$ −18° (*c* 1.1, chloroform).

Anal. Calc. for $C_{43}H_{50}O_{11}$: C, 69.52; H, 6.78. Found: C, 69.59; H, 6.86.

Benzyl 3-O-(3-O-allyl-4,6-O-benzylidene-β-D-glucopyranosyl)-2,4,6-tri-O-benzyl-β-D-glucopyranoside (**18**). — A mixture of **17** (9.6 g), α,α-dimethoxytoluene (6 mL), toluene-*p*-sulfonic acid (0.1 g), and acetonitrile (50 mL) was stirred at room temperature for 5 h, then neutralised with triethylamine, and concentrated. A solution of the residue in dichloromethane was washed with water, dried, and

concentrated. Crystallisation of the residue from methanol afforded **18** (9.3 g, 87%), m.p. 156–157°, $[\alpha]_D^{20}$ −17° (*c* 1.2, chloroform).^{1}H-N.m.r. data ($CDCl_3$): δ 5.42 (s, 1 H, PhC*H*).

Anal. Calc. for $C_{50}H_{54}O_{11}$: C, 72.27; H, 6.55. Found: C, 72.13; H, 6.72.

*Benzyl 3-O-(3-O-allyl-2-O-benzyl-4,6-O-benzylidene-β-*D*-glucopyranosyl)-2,4,6-tri-O-benzyl-β-*D*-glucopyranoside* (**19**). — Compound **18** (7.0 g) was treated in *N,N*-dimethylformamide (50 mL) with sodium hydride (0.9 g; 50% mineral oil), followed by benzyl bromide (1.5 mL), as described for the preparation of **9**, to give **19** (7.0 g, 90%), m.p. 134–135° (from ethanol), $[\alpha]_D^{20}$ −3° (*c* 1.6, chloroform).

Anal. Calc. for $C_{77}H_{60}O_{11}$: C, 74.33; H, 6.57. Found: C, 74.45; H, 6.48.

*Benzyl 3-O-(3-O-allyl-2,4-di-O-benzyl-β-*D*-glucopyranosyl)-2,4,6-tri-O-benzyl-β-*D*-glucopyranoside* (**20**). — Treatment of **19** (6.0 g) in ether–dichloromethane (1:1, 180 mL) containing lithium aluminium hydride (2.3 g) with aluminium chloride (6.9 g) in ether (60 mL), as described for the preparation of **10**, followed by column chromatography (solvent *2*) of the product gave **20** (4.8 g, 80%), m.p. 99–100° (from hexane), $[\alpha]_D^{20}$ +10° (*c* 1.2, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 102.5 (C-1'), 102.2 (C-1), and 61.7 (C-6).

Anal. Calc. for $C_{57}H_{62}O_{11}$: C, 74.16; H, 6.67. Found: C, 74.02; H, 6.65.

*Benzyl 2,4,6-tri-O-benzyl-3-O-(2,4-di-O-benzyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**21**). — A mixture of **20** (3.80 g), palladium chloride (0.8 g), and sodium acetate (3.7 g) in acetic acid–water (20:1, 60 mL) was stirred for 8 h at room temperature, and then processed as described for the preparation of **15**. Column chromatography (solvent *5*) of the product gave **21** as a syrup (2.76 g, 76%), $[\alpha]_D^{20}$ +11.5° (*c* 1, chloroform).

Anal. Calc. for $C_{54}H_{58}O_{11}$: C, 73.45; H, 6.62. Found: C, 73.63; H, 6.76.

*Benzyl 3-O-(3-O-allyl-2,4,6-tri-O-benzyl-β-*D*-glucopyranosyl)-2,4,6-tri-O-benzyl-β-*D*-glucopyranoside* (**22**). — Treatment of **17** (2.63 g) in *N,N*-dimethylformamide (30 mL) with sodium hydride (1.5 g, 50% mineral oil) and benzyl bromide (3.7 mL), as described for the preparation of **9**, followed by chromatography (solvent *3*) of the product, gave **22** as a syrup (2.94 g, 82%), $[\alpha]_D^{20}$ +16° (*c* 1.6, chloroform).

Anal. Calc. for $C_{64}H_{68}O_{11}$: C, 75.87; H, 6.76. Found: C, 75.99; H, 6.90.

*Benzyl 2,4,6-tri-O-benzyl-3-O-(2,4,6-tri-O-benzyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**23**). — Compound **22** (3.26 g) was treated in acetic acid–water (20:1, 50 mL) with palladium chloride (0.63 g) and sodium acetate (2.9 g) for 7 h at room temperature. The mixture was processed as described for the preparation of **15**. Column chromatography (solvent *3*) of the product gave **23** as a syrup (2.44 g, 78%), $[\alpha]_D^{20}$ +12° (*c* 2.3, chloroform).

Anal. Calc. for $C_{61}H_{64}O_{11}$: C, 75.29; H, 6.63. Found: C, 75.42; H, 6.70.

*Benzyl O-(2,3,4,6-tetra-O-acetyl-β-*D*-glucopyranosyl)-(1→3)-O-(2,4,6-tri-O-acetyl-β-*D*-glucopyranosyl)-(1→3)-O-[2,3,4,6-tetra-O-benzoyl-β-*D*-glucopyranosyl-(1→6)]-2,4-di-O-benzyl-β-*D*-glucopyranoside* (**25**). — A mixture of **15** (2.02 g, 2 mmol), silver triflate (1.21 g, 4.7 mmol), and powdered molecular sieve Type 4A

(2 g) in 1,2-dichloroethane (20 mL) was treated with a solution of **24** (2.06 g, 3 mmol) in 1,2-dichloroethane (20 mL), as described for the preparation of **16**. Column chromatography (solvent *5*) of the product gave **25** (2.51 g, 78%), $[\alpha]_D^{20}$ −4° (*c* 1.3, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 101.0, 100.8, 100.2, and 99.8 (C-1a,b,c,d).

Anal. Calc. for $C_{87}H_{90}O_{32}$: C, 63.42; H, 5.51. Found: C, 63.51; H, 5.75.

Benzyl O-*β*-D-*glucopyranosyl-(1→3)*-O-*β*-D-*glucopyranosyl-(1→3)-O*-[*β*-D-*glucopyranosyl-(1→6)*]-*2,4-di*-O-*benzyl*-*β*-D-*glucopyranoside* (**26**). — A solution of **25** (2.30 g) in dry methanol (30 mL) and dichloromethane (10 mL) was treated with M sodium methoxide (1 mL) at room temperature for 5 h, and then processed as described for the preparation of **7**. Crystallisation of the product from ethanol–ether gave **26** (1.21 g, 92%), m.p. 176.5–178°, $[\alpha]_D^{20}$ −3° (*c* 0.9, chloroform).

Anal. Calc. for $C_{45}H_{60}O_{21}$: C, 57.69; H, 6.45. Found: C, 57.80; H, 6.57.

O-*β*-D-*Glucopyranosyl-(1→3)*-O-*β*-D-*glucopyranosyl-(1→3)*-O-[*β*-D-*glucopyranosyl-(1→6)*]-D-*glucopyranose* (**1**). — A solution of **26** (1.09 g) in acetic acid (15 mL) was hydrogenated in the presence of 10% Pd/C (1.0 g) at normal pressure overnight at room temperature. Insoluble material was collected on a Celite pad and washed with methanol, and the combined filtrate and washings were concentrated. The residue was purified by precipitation from methanol with ether to afford **1** (0.65 g, 80%), $[\alpha]_D^{20}$ −3° (*c* 1.5, water); lit.[3] $[\alpha]_D$ −0.3° (*c* 0.5, water). ^{13}C-N.m.r. data (D_2O): δ 105.5 and 105.2 (C-1b,c,d), 98.4 (C-1a*β*), 94.7 (C-1a*α*), 87.5 (C-3a*β*), 87.1 (C-3b), and 84.8 (C-3a*α*).

O-*(2,3,4,6-Tetra*-O-*acetyl*-*β*-D-*glucopyranosyl)-(1→3)*-O-*(2,4,6-tri*-O-*acetyl*-*β*-D-*glucopyranosyl)-(1→3)*-O-[*2,3,4,6-tetra*-O-*acetyl*-*β*-D-*glucopyranosyl-(1→6)*]-*1,2,4-tri*-O-*acetyl*-*β*-D-*glucopyranose* (**27**). — Compound **1** (0.32 g) was acetylated[17] with acetic anhydride (7 mL) and sodium acetate (0.4 g) under reflux for 30 min. Crystallisation of the product from ethanol gave **27** (0.46 g, 80%), m.p. 120–122°, $[\alpha]_D^{20}$ −32° (*c* 1.4, chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 5.58 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1); ^{13}C, δ 100.9, 100.8, and 100.6 (C-1b,c,d), and 91.5 (C-1a).

Anal. Calc. for $C_{52}H_{70}O_{35}$: C, 49.76; H, 5.62. Found: C, 49.80; H, 5.71.

Benzyl O-*β*-D-*glucopyranosyl-(1→3)*-O-[*β*-D-*glucopyranosyl-(1→6)*]-O-*(2,4-di*-O-*benzyl*-*β*-D-*glucopyranosyl)-(1→3)-2,4,6-tri*-O-*benzyl*-*β*-D-*glucopyranoside* (**28**). — A mixture of **21** (2.05 g, 2.3 mmol), silver triflate (2.14 g, 8.3 mmol), and molecular sieve Type 4A (3 g) in toluene–nitromethane (1:1, 25 mL) was treated with **5** (4.60 g, 7 mmol) in toluene–nitromethane (1:1, 50 mL), as described for the preparation of **14**, followed by *O*-debenzoylation as described for **25**. Column chromatography (solvent *6*) of the product gave amorphous **28** (2.09 g, 75%), $[\alpha]_D^{20}$ −3° (*c* 0.9, chloroform).

Anal. Calc. for $C_{66}H_{78}O_{21}$: C, 65.66; H, 6.51. Found: C, 65.87; H, 6.60.

Benzyl O-*(2,3,4,6-tetra*-O-*acetyl*-*β*-D-*glucopyranosyl)-(1→3)*-O-[*2,3,4,6-tetra*-O-*acetyl*-*β*-D-*glucopyranosyl-(1→6)*]-O-*(2,4-di*-O-*benzyl*-*β*-D-*glucopyranosyl)-(1→3)-2,4,6-tri*-O-*benzyl*-*β*-D-*glucopyranoside* (**29**). — Conventional treatment of **28** (0.15 g) with acetic anhydride–pyridine (1:1, 3 mL), followed by column

chromatography (solvent 5) of the product, gave **29** (0.18 g, 95%), $[\alpha]_D^{20}$ −4° (*c* 1.3, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 101.0, 100.8, 100.2, and 99.9 (C-1a,b,c,d).

Anal. Calc. for $C_{82}H_{94}O_{29}$: C, 63.80; H, 6.14. Found: C, 63.71; H, 6.01.

O-β-D-Glucopyranosyl-(1→3)-O-[β-D-glucopyranosyl-(1→6)]-O-β-D-glucopyranosyl-(1→3)-D-glucopyranose (**2**). — Hydrogenolysis of **28** (1.80 g), as described for **26**, gave **2** (0.84 g, 85%), m.p. 199–200° (from aqueous ethanol), $[\alpha]_D^{20}$ −2° (2 min) → −6° (24 h, constant; *c* 0.8, water); lit.[4] m.p. 199–200°, $[\alpha]_D^{20}$ +5.7° (2 min) → +1.8° (final; *c* 1, water).

Anal. Calc. for $C_{24}H_{42}O_{21}$: C, 43.24; H, 6.35. Found: C, 43.15; H, 6.55.

O-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-(1→3)-O-[2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-(1→6)]-O-(2,4-di-O-acetyl-β-D-glucopyranosyl)-(1→3)-1,2,4,6-tetra-O-acetyl-β-D-glucopyranose (**30**). — Acetylation of **2** (0.24 g), as described for **1**, gave **30** (0.37 g, 82%), m.p. 157–158° (from ethanol), $[\alpha]_D^{18}$ −32° (*c* 1.3, chloroform); lit.[4] m.p. 149–150° (from ethanol–light petroleum), $[\alpha]_D^{20}$ −27.7° (chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 5.64 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1a); ^{13}C, δ 100.9 and 100.3 (C-1b,c,d), and 91.6 (C-1a).

Anal. Calc. for $C_{52}H_{70}O_{35}$: C, 49.76; H, 5.62. Found: C, 49.80; H, 5.68.

Benzyl O-(2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl)-(1→3)-O-[2,3,4,6-tetra-O-benzoyl-β-D-glucopyranosyl-(1→6)]-2,4-di-O-benzyl-β-D-glucopyranoside (**33**). — The product obtained by treatment of a mixture of **11** (2.90 g, 6.4 mmol), silver triflate (5.96 g, 23.2 mmol), and molecular sieve Type 4A (5 g) in toluene–nitromethane (1:1, 40 mL) with **5** (12.74 g, 19.4 mmol) in toluene–nitromethane (1:1, 70 mL), as described for the preparation of **14**, was subjected to column chromatography (solvent 4) to give **33** (7.97 g, 77%), $[\alpha]_D^{20}$ +7° (*c* 3.1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 101.7 (C-1a), 101.1 (C-1c), and 100.5 (C-1b).

Anal. Calc. for $C_{95}H_{82}O_{24}$: C, 70.97; H, 5.14. Found: C, 71.17; H, 5.30.

Benzyl O-β-D-glucopyranosyl-(1→3)-O-[β-D-glucopyranosyl-(1→6)]-2,4-di-O-benzyl-β-D-glucopyranoside (**34**). — *O*-Debenzoylation of **33** (8.02 g), as described for **25**, gave **34** (3.48 g, 90%), m.p. 112–113° (from ethanol), $[\alpha]_D^{20}$ −35.5° (*c* 1.1, *N,N*-dimethylformamide).

Anal. Calc. for $C_{39}H_{50}O_{16}$: C, 60.46; H, 6.50. Found: C, 60.58; H, 6.61.

Benzyl O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-(1→3)-O-[2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→6)]-2,4-di-O-benzyl-β-D-glucopyranoside (**35**). — Acetylation of **34** (3.13 g), as described for **28**, gave **35** (4.08 g, 91%), m.p. 154–156° (from ethanol), $[\alpha]_D^{20}$ −27° (*c* 1, chloroform).

Anal. Calc. for $C_{55}H_{66}O_{24}$: C, 59.45; H, 5.99. Found: C, 59.38; H, 6.16.

O-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-(1→3)-O-[2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→6)]-1,2,4-tri-O-acetyl-β-D-glucopyranose (**36**). — Hydrogenolysis of **35** (3.04 g), as described for **26**, followed by acetylation of the product, as described for **1**, gave **36** (2.09 g, 79%), m.p. 244–245° (from ethanol), $[\alpha]_D^{17}$ −21° (*c* 2.4, chloroform); lit.[18] m.p. 237°, $[\alpha]_D^{20}$ −2.56° (*c* 1.33, chloroform) for an α,β-mixture. N.m.r. data ($CDCl_3$): ^{1}H, δ 5.59 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1a);

^{13}C, δ 100.7 (C-1b,c) and 91.5 (C-1a).

Anal. Calc. for $C_{40}H_{54}O_{27}$: C, 49.69; H, 5.63. Found: C, 49.78; H, 5.70.

O-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-(1→3)-O-[2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→6)]-2,4-di-O-acetyl-α-D-glucopyranosyl bromide (**37**). — To a solution of **36** (1.86 g) in anhydrous dichloromethane (6 mL) at 0° was added a saturated (at 0°) solution of hydrogen bromide in acetic acid (3 mL). The mixture was kept for 3 h at room temperature, then diluted with dichloromethane, washed successively with ice–water, aqueous sodium hydrogencarbonate, and water, dried, and concentrated. Crystallisation of the residue from dichloromethane–ether gave **37** (1.52 g, 83%), m.p. 193–195°, $[\alpha]_D^{18}$ +42° (*c* 1.6, dichloromethane). N.m.r. data ($CDCl_3$): ^1H, δ 6.52 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1a); ^{13}C, δ 100.9 and 100.6 (C-1b,c), and 87.2 (C-1a). It was used immediately for the next step.

Benzyl O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-(1→3)-O-[2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl-(1→6)]-O-(2,4-di-O-acetyl-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-O-benzyl-β-D-glucopyranoside (**31**). — The product obtained by treatment of a mixture of **13** (0.50 g, 0.9 mmol), silver triflate (0.41 g, 1.6 mmol), and molecular sieve Type 4A in 1,2-dichloroethane (5 mL) with **37** (1.30 g, 1.3 mmol) in 1,2-dichloroethane (5 mL), as described previously, was subjected to column chromatography (solvent *1*) to give **31** (0.96 g, 72%), $[\alpha]_D^{20}$ −29° (*c* 1.7, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 101.7, 100.9, and 100.0 (C-1a,b,c,d).

Anal. Calc. for $C_{72}H_{86}O_{31}$: C, 59.75; H, 5.99. Found: C, 59.36; H, 6.10.

Benzyl O-β-D-glucopyranosyl-(1→3)-O-[β-D-glucopyranosyl-(1→6)]-O-β-D-glucopyranosyl-(1→3)-2,4,6-tri-O-benzyl-β-D-glucopyranoside (**32**). — *O*-Deacetylation of **31** (1.10 g), as described for **25**, gave **32** (0.73 g, 93%), $[\alpha]_D^{20}$ −32° (*c* 1, water).

Anal. Calc. for $C_{52}H_{66}O_{21}$: C, 60.81; H, 6.48. Found: C, 60.66; H, 6.61.

Hydrogenolysis of **32** (0.55 g), as described previously, afforded **2** (0.29 g, 81%), m.p. (from aqueous ethanol) and mixture m.p. 199–200°, $[\alpha]_D^{20}$ −2° (2 min) → −6° (24 h, constant; *c* 0.6, water). The ^{13}C-n.m.r. spectrum was identical to that of the compound obtained previously.

Acetylation of **2** (0.13 g), as described previously, gave **30** (0.19 g, 79%), m.p. (from ethanol) and mixture m.p. 157–158°, $[\alpha]_D^{18}$ −31° (*c* 1, chloroform).

Benzyl O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-(1→6)-O-(2,3,4-tri-O-acetyl-β-D-glucopyranosyl)-(1→3)-O-(2,4,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-O-benzyl-β-D-glucopyranoside (**39**). — The product obtained by treatment of a mixture of **23** (2.14 g, 2.2 mmol), silver triflate (1.08 g, 4.2 mmol), and molecular sieve Type 4A (1.5 g) in 1,2-dichloroethane (20 mL) with **38** (2.46 g, 3.6 mmol) in 1,2-dichloroethane (15 mL) was subjected to column chromatography (solvent *5*) to give amorphous **39** (2.80 g, 80%), $[\alpha]_D^{20}$ −2° (*c* 1.7, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 102.2, 101.6, 100.4, and 100.2 (C-1a,b,c,d).

Anal. Calc. for $C_{87}H_{98}O_{28}$: C, 65.65; H, 6.21. Found: C, 65.86; H, 6.30.

Benzyl O-β-D-glucopyranosyl-(1→6)-O-β-D-glucopyranosyl-(1→3)-O-(2,4,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→3)-2,4,6-tri-O-benzyl-β-D-glucopyranoside (**40**). — *O*-Deacetylation of **39** (2.43 g), as described previously, gave **40** (1.84 g, 93%), $[\alpha]_D^{20}$ −5° (*c* 1.4, chloroform).

Anal. Calc. for $C_{73}H_{84}O_{21}$: C, 67.58; H, 6.53. Found: C, 67.40; H, 6.59.

O-β-D-Glucopyranosyl-(1→6)-O-β-D-glucopyranosyl-(1→3)-O-β-D-glucopyranosyl-(1→3)-D-glucopyranose (**3**). — Hydrogenolysis of **40** (1.49 g), as described previously, gave amorphous **3** (0.65 g, 82%), $[\alpha]_D^{20}$ −17° (*c* 1.2, water).

Anal. Calc. for $C_{24}H_{42}O_{21} \cdot H_2O$: C, 42.11; H, 6.47. Found: C, 41.83; H, 6.63.

O-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-(1→6)-O-(2,3,4-tri-O-acetyl-β-D-glucopyranosyl)-(1→3)-O-(2,4,6-tri-O-acetyl-β-D-glucopyranosyl)-(1→3)-1,2,4,6-tetra-O-acetyl-β-D-glucopyranose (**41**). — Acetylation of **3** (0.31 g), as described previously, gave **41** (0.46 g, 81%), m.p. 124–125.5° (from ethanol), $[\alpha]_D^{20}$ −24° (*c* 2.0, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.65 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1a); ^{13}C, δ 100.6, 100.3, and 100.2 (C-1b,c,d), and 91.7 (C-1a).

Anal. Calc. for $C_{52}H_{70}O_{35}$: C, 49.76; H, 5.62. Found: C, 49.60; H, 5.53.

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