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SYNTHESIS OF KOJITETRAOSE AND KOJIPENTAOSE

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ABSTRACT

Kojitriose [α-D-Glc*p*-(1→2)-α-D-Glc*p*-(1→2)-D-Glc*p*], kojitetraose, and kojipentaose have been synthesised by silver perchlorate-promoted Koenigs–Knorr type condensations, using 3,4,6-tri-*O*-acetyl-2-*O*-allyl-β-D-glucopyranosyl chloride and hepta-*O*-acetyl-β-kojibiosyl chloride as the key intermediates. The synthesis of α-D-Glc*p*-(1→2)-α-D-Glc*p*-(1→3)-D-Glc*p* is also described.

INTRODUCTION

Oligosaccharides having (1→2)-α-D-glucosidic linkages have rarely been found in Nature. The isolation of kojibiose (2-*O*-α-D-glucopyranosyl-D-glucopyranose, **1**) and kojitriose [*O*-α-D-glucopyranosyl-(1→2)-O-α-D-glucopyranosyl-(1→2)-D-glucopyranose, **2**] from natural products has been reviewed[1,2]. Kojihexaose has been isolated[2] as an extracellular oligosaccharide from *Rhizobium japonicum* strain 561. Evidence has also been presented[3] that **2**, kojitetraose (**3**), and kojipentaose (**4**) occur as non-reducing α-D-glucopyranosyl α-D-glucosides in small quantities in the cyclic (1→2)-β-D-glucan preparation from *Rhizobium meliloti* J 7017. However, no systematic approach to the synthesis of a homologous series of lower koji-oligosaccharides has been reported. The disaccharide **1** has been synthesised as the α-octa-acetate **34** (1.5–47%) by condensation of 1,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose (**6**) with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide[4,5], 3,4,6-tri-*O*-acetyl-2-*O*-nitro-β-D-glucopyranosyl chloride[6], or 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-β-D-glucopyranosyl chloride[7]. Recently, an improved synthesis of **34** (62–69%) by reaction of **6** with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride or an imidate has been developed[8]. The trisaccharide **2** has been prepared[9] (21%) by a non-specific route from **6** and hepta-*O*-acetyl-α-kojibiosyl bromide (**37**).

We now report the first syntheses of **3** and **4** as well as an improved preparation of **2**. Also described is the synthesis of *O*-α-D-glucopyranosyl-(1→2)-*O*-α-D-glucopyranosyl-(1→3)-D-glucopyranose (**5**), corresponding to the outer trisaccharide unit of the lipid-linked oligosaccharide chain which is involved in the biosynthesis of asparagine-linked glycopeptides[10].

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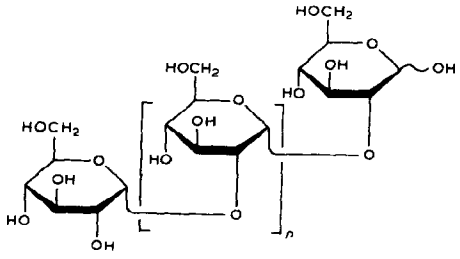
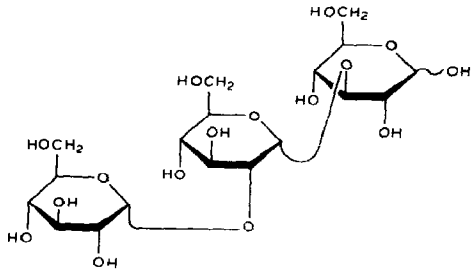


1 $n = 0$
2 $n = 1$
3 $n = 2$
4 $n = 3$



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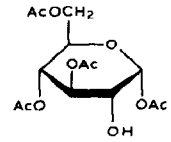
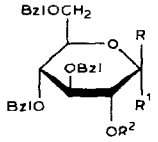
RESULTS AND DISCUSSION

2-*O*-Allyl-3,4,6-tri-*O*-benzyl-D-glucopyranose[11] (**9**), in which the 2-*O*-allyl group should serve as a non-participant in 1,2-*cis*-glycoside synthesis[12], was considered first as a suitable intermediate for a stepwise synthesis of **2**, **3**, and **4**. As the previous[11] synthesis of **9**, starting from 3-*O*-benzyl-D-glucose, was multi-stage and gave a low yield (17%), we sought an alternative synthesis of **9**. Reaction of the easily accessible[13] methyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (**7**) with allyl bromide and sodium hydride in *N*,*N*-dimethylformamide[14] and hydrolysis of the product[13,15] **8** with dilute acid gave **9** (67% from **7**), whose physical properties agreed with those reported[11]. However, the derived 1-*p*-nitrobenzoate **10** (70%) had physical constants (m.p. 130°, $[\alpha]_D + 63°$) that were very different from those (m.p. 88°, $[\alpha]_D$ −12.4°) reported[11]. The n.m.r. signal of H-1 of **10** in $CDCl_3$ was a doublet having a small coupling constant (δ 6.61, $J_{1,2}$ 3.3 Hz) consistent with the α configuration at C-1, suggesting that the previous compound[11] was the corresponding β anomer **11** on the basis of its optical rotation.





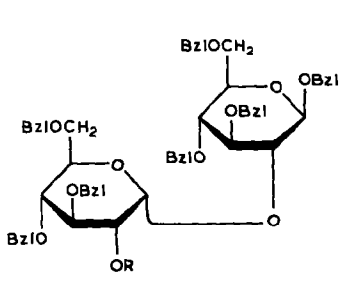
6

7 R = R^2 = H, R^1 = OMe
8 R = H, R^1 = OMe, R^2 = Allyl
9 R, R^1 = H, OH; R^2 = Allyl
10 R = H, R^1 = ONBz, R^2 = Allyl
11 R = ONBz, R^1 = H, R^2 = Allyl
NBz = $COC_6H_4NO_2$ (*p*)

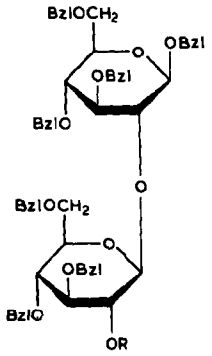
12 R = H, R^1 = Br, R^2 = Allyl
13 R = H, R^1 = Cl, R^2 = Allyl
14 R = OC(Me)=NMe, R^1 = H, R^2 = Allyl
15 R = H, R^1 = Br, R^2 = Ac
16 R = OBzl, R^1 = R^2 = H

Compound **10** was converted into the corresponding α-bromide **12** with hydrogen bromide–dichloromethane and into the α-chloride **13** with oxalyl chloride–dichloromethane in the presence of a catalytic amount of *N,N*-dimethylformamide[16]. Treatment of **13** with *N*-methylacetamide, silver oxide, di-isopropylethylamine, and molecular sieve in benzene[17] gave the imidate **14**. Condensation of benzyl 3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**16**) [prepared (78%) by reaction of 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl bromide[18] (**15**) with benzyl alcohol in benzene–ether in the presence of silver carbonate, followed by *O*-deacetylation] with **12**, **13**, or **14** was then examined.

Glucosylation of **16** with **12** in 1,2-dichloroethane-*N,N*-dimethylformamide in the presence of tetraethylammonium bromide[19] and molecular sieve gave benzyl 2-*O*-(2-*O*-allyl-3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**17**, 8%) after column chromatography. In the ^{13}C-n.m.r. spectrum of **17**, the signal for C-1′ appeared at 95.5 p.p.m., indicating[20] the configuration at C-1′ to be α. Removal of the allyl group from **17** with palladium chloride–sodium acetate[21] in aqueous acetic acid afforded the crystalline disaccharide derivative **18** having HO-2′ unsubstituted.



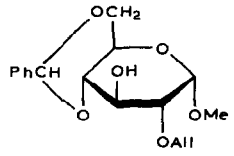
17 R = Allyl
18 R = H



19 R = Allyl
20 R = H

Reaction of **16** with **13** in ether in the presence of silver perchlorate[7] and molecular sieve[22] gave 82% of a mixture of **17** and the β-(1→2)-linked isomer **19** in the ratio 3.8:1, as indicated by ^{13}C-n.m.r. spectroscopy which showed the signals for C-1′ of **17** and **19** at 95.5 and 100.7 p.p.m., respectively. However, difficulties were encountered in the fractionation of the mixture by column chromatography, because **17** and **19** have similar chromatographic mobilities. Compounds **17** and **19** were isolated in yields of 32 and 6%, respectively, after two further fractionations of the mixture by column chromatography. *O*-Deallylation of **19**, as for **17**, afforded the crystalline disaccharide derivative **20** having HO-2′ unsubstituted.

Compound **16** was treated with **14** in benzene in the presence of toluene-*p*-sulfonic acid[17] to give a 4:1 mixture (67%) of **17** and **19** after column chromatography. Two fractionations of the mixture by column chromatography afforded **17** (29%) and **19** (3%).



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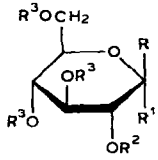
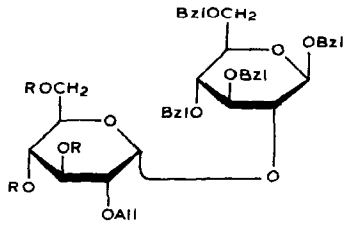
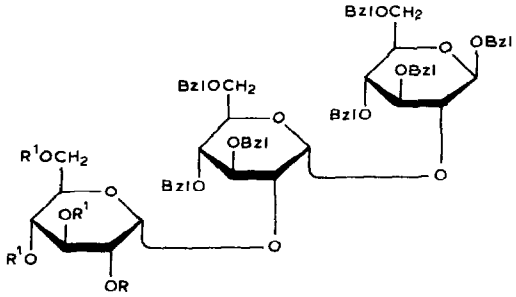


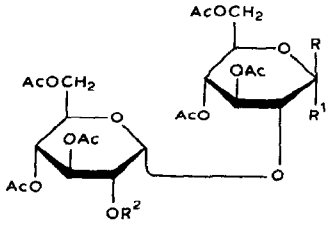
22 R = R^3 = H, R^1 = OMe, R^2 = Allyl
23 R, R^1 = H, OH; R^2 = Allyl, R^3 = H
24 R, R^1 = H, OAc; R^2 = Allyl, R^3 = Ac
25 R = H, R^1 = Br, R^2 = Allyl, R^3 = Ac
26 R = Cl, R^1 = H, R^2 = Allyl, R^3 = Ac



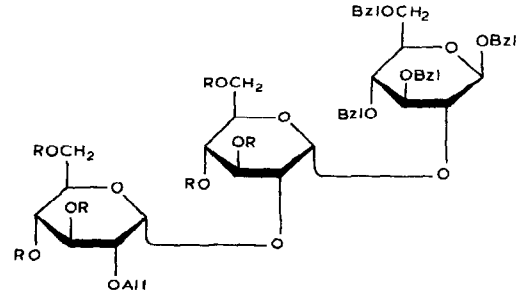
27 R = Ac
28 R = H



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



33 R = H, R^1 = OAc, R^2 = Allyl
34 R = H, R^1 = OAc, R^2 = Ac
35 R = H, R^1 = Br, R^2 = Allyl
36 R = Cl, R^1 = H, R^2 = Allyl
37 R = H, R^1 = Br, R^2 = Ac
38 R = Cl, R^1 = H, R^2 = Ac



39 R = Ac
40 R = H

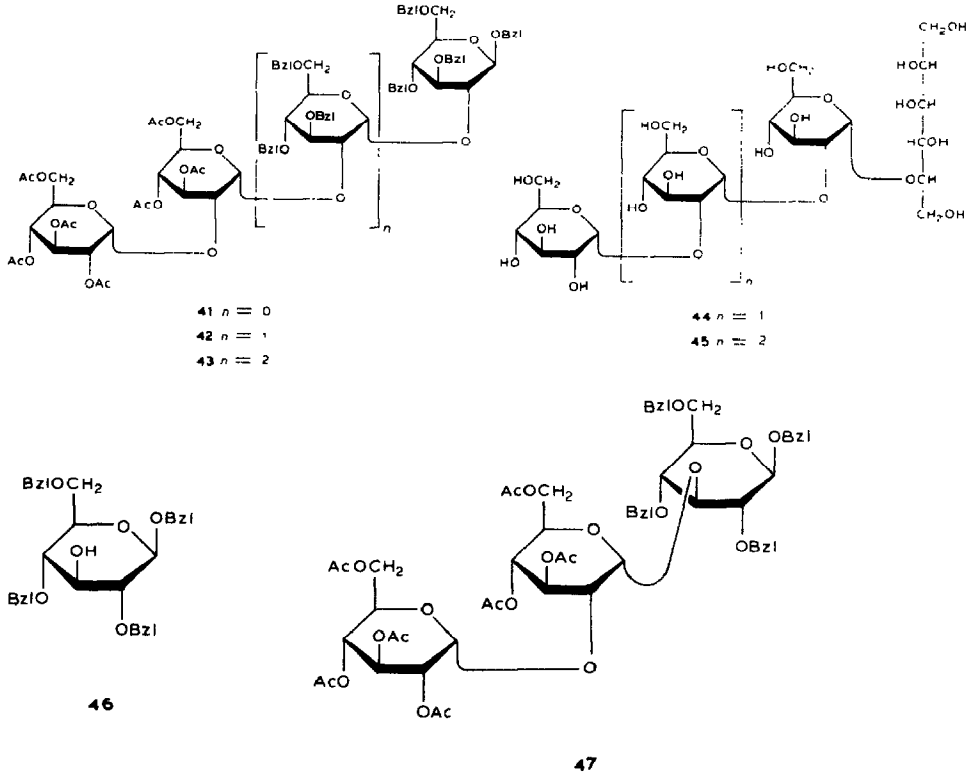
In view of the low isolated yield of **17**, this route was abandoned and an alternative approach to **2**, **3** and **4** was investigated. Removal of the benzylidene group of methyl 2-*O*-allyl-4,6-*O*-benzylidene-α-D-glucopyranoside[15] (**21**) with aqueous acetic acid afforded crystalline methyl 2-*O*-allyl-α-D-glucopyranoside (**22**). Hydrolysis of **22** with dilute acid gave crystalline 2-*O*-allyl-D-glucopyranose (**23**, 81%), which was acetylated to afford, 1,3,4,6-tetra-*O*-acetyl-2-*O*-allyl-D-glucopyranose (**24**). Treatment of **24** with hydrogen bromide in acetic acid and dichloromethane gave the α-bromide **25** which, with tetraethylammonium chloride[23] in acetonitrile, gave the β-chloride **26**. Glucosylation of **16** with **26** in ether in the presence of silver perchlorate and molecular sieve gave benzyl 2-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-allyl-α-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**27**, 75%). The α configuration at C-1′ in **27** was apparent[20] from the ^{13}C-n.m.r. signal for C-1′ at 95.0 p.p.m. *O*-Deacetylation of **27**, benzylation[14] of the crystalline product **28** (→**17**), and then deallylation[21] gave **18**, identical with the compound obtained by way of the reaction of **16** with **12**. Condensation of **18** with **26** in ether–1,2-dimethoxyethane[22] in the presence of silver perchlorate and molecular sieve gave the trisaccharide derivative **29** (71%), the ^{13}C-n.m.r. spectrum of which contained signals for C-1′ and C-1″ at 93.0 and 92.7 p.p.m. *O*-Deacetylation of **29** (→**30**), benzylation (→**31**), and *O*-deallylation[21] afforded the trisaccharide derivative **32** having HO-2″ unsubstituted.

In an attempt to obtain **32** more conveniently, an alternative route to **31** was explored. Coupling of **6** with **26** in ether–1,2-dimethoxyethane in the presence of silver perchlorate and molecular sieve afforded crystalline 1,3,4,6-tetra-*O*-acetyl-2-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-allyl-α-D-glucopyranosyl)-α-D-glucopyranose (**33**, 71%). *O*-Deallylation[21] of **33**, followed by acetylation, gave known[4] **34** (82%). Compound **33** was transformed[23], *via* α-bromide **35**, into the β-chloride **36**, which was condensed with **16** to provide the trisaccharide derivative **39** (68% based on **16**), the ^{13}C-n.m.r. spectrum of which showed the signals for C-1′ and C-1″ at 96.2 and 93.8 p.p.m. *O*-Deacetylation of **39** then afforded **40**. However, attempts to benzylate **40** under the conditions[14] that were satisfactorily employed for the benzylation of **28** were unsuccessful; a mixture of partially benzylated derivatives was obtained, and recovery and re-benzylation of the products did not result in the formation of **31**.

Glycosylation of **16**, **18**, and **32** with hepta-*O*-acetyl-β-kojibiosyl chloride (**38**), prepared[24] from **34** *via* **37**, in ether–1,2-dimethoxyethane in the presence of silver perchlorate and molecular sieve gave the tri- (**41**), tetra- (**42**), and penta-saccharide derivative **43** in yields of 70, 59, and 39%, respectively. *O*-Deacetylation of **41**, **42**, and **43**, followed by catalytic hydrogenolysis in acetic acid over Pd/C, furnished **2** (ref. 9), **3**, and **4**, in yields of 84, 73, and 66%, respectively. The sequence **16**+**38**→**41**→**2**, giving **2** in 59% yield (based on **16**) is clearly superior to the synthesis[9] from **6** and **37**. Compounds **3** and **4** were homogeneous by h.p.l.c. Reduction of **3** and **4** with sodium borohydride afforded kojitetraitol (**44**) and kojipentaitol (**45**), respectively. In the ^{13}C-n.m.r. spectrum of **3**, seven signals for four anomeric carbon atoms appeared at 98.9, 98.4, 96.4, 96.1, 95.4, 94.9, and 91.8

p.p.m., whereas, in that of **44**, three signals for the anomeric carbon atoms appeared at 98.6, 96.9, and 96.6 p.p.m., in accord[20] with the α configuration at each anomeric carbon atom in **3**. The ^{13}C-n.m.r. spectrum of **4** contained seven signals for five anomeric carbon atoms at 99.2, 97.6, 96.4, 96.1, 94.9, 93.3, and 91.4 p.p.m., whereas that of **45** contained three signals for the anomeric carbon atoms at 98.1, 97.2, and 95.4 (2C) p.p.m., supporting[20] the α configuration at each anomeric centre in **4**.

Glycosylation of benzyl 2,4,6-tri-*O*-benzyl-α-D-glucopyranoside[25] (**46**) with **38**, as above, gave the trisaccharide derivative **47** (72%) which, on successive *O*-deacetylation and hydrogenolysis, furnished **5**. The ^{13}C-n.m.r. spectrum of **5** contained signals for C-1β and C-1α at 99.0 and 94.0 p.p.m., respectively, and a signal for C-1′ and C-1″ at 98.6 p.p.m.



EXPERIMENTAL

General. — Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Optical rotations were determined with an Applied Electronic automatic polarimeter Model MP-IT. 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_4 Si) or D_2O (internal sodium 4,4-dimethyl-4-sila-

pentanoate-d_4). H.p.l.c. was performed with a JASCO trirotar V provided with a RID-300 detector (JASCO) and a column of Finepac Sil NH_2 (10 μm, 250 × 4.6 mm i.d, JASCO). Elementary analyses were not obtained for syrupy products, but they were shown to be pure by chromatography and n.m.r. spectroscopy. Organic solutions were dried over anhydrous sodium sulfate or magnesium sulfate. Solutions were concentrated at a temperature $<50°$ under diminished pressure. T.l.c. was performed on Silica Gel 60 (No. 7734, Merck) with detection by charring with sulfuric acid. Column chromatography was performed on Silica Gel 60 (No. 9385, Merck). The following solvent systems (v/v) were used: hexane–ethyl acetate (*1*, 4:1; *2*, 2:1, *3*, 1:1; *4*, 2:3) and chloroform–methanol (*5*, 5:1).

Methyl 2-O-allyl-3,4,6-tri-O-benzyl-α-D-glucopyranoside (**8**). — A solution of **7** (18.4 g) in *N,N*-dimethylformamide (250 ml) was stirred with sodium hydride (3.8 g; 50% mineral oil) for 1 h at room temperature and then cooled to 0°. Allyl bromide (6.5 mL) was added dropwise and the mixture was stirred for 3 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 successively with water, dilute hydrochloric acid, and water, dried, and concentrated. Purification of the product by column chromatography (solvent *1*) gave **8** (18.5 g, 93%), $[\alpha]_D^{20}$ +44.5° (*c* 1.2, chloroform); lit.[15] +44.2° (*c* 1.59, chloroform).

2-O-Allyl-3,4,6-tri-O-benzyl-D-glucopyranose (**9**). – M Hydrochloric acid (100 mL) was added dropwise with stirring to a boiling solution of **8** (24.2 g) in acetic acid (400 mL) during 30 min. The mixture was further stirred for 2 h at 100°, then cooled, and concentrated to one-fifth of the original volume. The resulting white solid was collected by filtration, washed with cold water, and dissolved in dichloromethane. The solution was washed successively with water, aqueous sodium hydrogencarbonate, and water, dried, and concentrated. The residue was recrystallised twice from methanol to give **9** (16.9 g, 72%), m.p. 134–136°, $[\alpha]_D^{19}$ +28° (*c* 1.8, chloroform); lit.[11] m.p. 137–139°, $[\alpha]_D$ +25.7° (*c* 0.9, chloroform).

2-O-Allyl-3,4,6-tri-O-benzyl-1-O-p-nitrobenzoyl-α-D-glucopyranose (**10**). — *p*-Nitrobenzoyl chloride (1.9 g) was added at 0° to a stirred solution of **9** (3.3 g) in dichloromethane (20 mL) and pyridine (1.1 mL), and the mixture was kept overnight at room temperature. Water (2 mL) was added, and the solution was stirred for 1 h, washed successively with dilute hydrochloric acid, aqueous sodium hydrogencarbonate, and water, dried, and concentrated. Recrystallisation of the residue from ethanol afforded **10** (3.0 g, 70%), m.p. 128–130°, $[\alpha]_D^{20}$ +63° (*c* 2.4, chloroform); lit.[11] m.p. 86–88°, $[\alpha]_D$ −12.4° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): 6.61 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1) and 6.09–5.66 (m, 1 H, –CH=)

Anal. Calc. for $C_{37}H_{37}NO_9$: C, 69.47; H, 5.83; N, 2.19. Found: C, 69.32; H, 5.90; N, 2.24.

Benzyl 3,4,6-tri-O-benzyl-β-D-glucopyranoside (**16**). — A mixture of benzyl alcohol (10 mL), silver carbonate (15 g), and Drierite (20 g) in ether–benzene (1:1, 130 mL) was stirred at room temperature for 3 h in the dark with exclusion of

moisture, and a solution of **15** (19.5 g) in ether (50 mL) was added dropwise during 2 h. The mixture was stirred overnight at room temperature, and insoluble material was collected on a layer of Celite and washed with benzene. The combined filtrate and washings were concentrated, the remaining benzyl alcohol was removed by repeated co-evaporation with water, and the residue was dissolved in dichloromethane. The solution was washed with water, dried, and concentrated. A solution of the residue in methanol (200 mL) containing M sodium methoxide (5 mL) was kept at room temperature for 6 h, neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. The resulting solid was recrystallised thrice from ethanol to give **16** (15.7 g, 78%), m.p. 87–88°, $[\alpha]_D^{20}$ −25° (*c* 1.2, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 101.5 (C-1).

Anal. Calc. for $C_{34}H_{36}O_6$: C, 75.53; H, 6.71. Found: C, 75.67; H, 6,76.

Benzyl 2-O-(2-O-allyl-3,4,6-tri-O-benzyl-α- and -β-D-glucopyranosyl)-3,4,6-tri-O-benzyl-β-D-glucopyranoside (**17** *and* **19**). — (*a*) To a solution of **10** (2.10 g) in dichloromethane (5 mL) was added a saturated (at 0°) solution of hydrogen bromide in dichloromethane (40 mL). After 5 min at room temperature, the precipitated *p*-nitrobenzoic acid was removed by filtration, and the filtrate was concentrated to give 2-*O*-allyl-3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl bromide (**12**) as a syrup (1.71 g, 94%), $[\alpha]_D^{24}$ +106° (*c* 1.3, dichloromethane). ^{1}H-N.m.r. data ($CDCl_3$): δ 6.55 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1) and 6.14–5.71 (m, 1 H, –CH=).

A solution of **16** (0.75 g, 1.4 mmol) and **12** (1.53 g, 2.8 mmol) in 1,2-dichloroethane (10 mL) and *N*,*N*-dimethylformamide (2 mL) was stirred with tetraethylammonium bromide (0.58 g) and molecular sieve Type 4A (2 g) at room temperature for 6 days. Insoluble material was collected on a layer of Celite and washed with dichloromethane, and the combined filtrate and washings were washed with water, dried, and concentrated. Column chromatography (solvent *1*) of the residual oil gave **17**, isolated as a syrup (0.11 g, 8%), $[\alpha]_D^{20}$ +30° (*c* 1.6, chloroform); t.l.c. (solvent *1*): R_F 0.22. ^{13}C-N.m.r. data ($CDCl_3$): δ 134.5 and 117.3 ($CH{=}CH_2$), 102.8 (C-1), and 95.5 (C-1′).

(*b*) A solution of oxalyl chloride (1.3 mL) in dichloromethane (5 mL) was added dropwise at 0° to a solution of **9** (2.51 g) in dichloromethane (20 mL) containing *N*,*N*-dimethylformamide (0.1 mL). The mixture was kept at room temperature for 1 h and then concentrated. A solution of the residue in hexane–ethyl acetate (1:1, 20 mL) was filtered through a layer of silica gel (5 g), and the layer was washed with hexane–ethyl acetate (1:1, 15 mL). The combined filtrate and washings were concentrated to give 2-*O*-allyl-3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl chloride (**13**) as a syrup (2.39 g, 92%), $[\alpha]_D^{24}$ +86° (*c* 2.2, dichloromethane). N.m.r. data ($CDCl_3$): ^{1}H, δ 6.19 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1) and 6.10–5.72 (m, 1 H, –CH=); ^{13}C, δ 134.0 and 118.0 ($CH{=}CH_2$) and 93.5 (C-1).

A mixture of **16** (1.46 g, 2.7 mmol), silver perchlorate (0.92 g, 4.4 mmol), and powdered molecular sieve Type 4A (5 g) in ether (50 mL) was stirred at room temperature for 2 h with exclusion of moisture and light, and then cooled to −10°. A solution of **13** (2.06 g, 4 mmol) in ether (20 mL) was added dropwise during 30 min,

and the mixture was allowed to attain 0° gradually and then stirred at 0° for 1 h. Insoluble material was collected on a pad of Celite and washed with ether, and the combined filtrate and washings were washed successively with water, aqueous sodium hydrogencarbonate, and water, dried, and concentrated. The residue was subjected to column chromatography (solvent *1*), to give a disaccharide fraction [2.25 g, 82%; ^{13}C-n.m.r. data ($CDCl_3$): δ 100.7 (C-1′ in **19**) and 95.5 (C-1′ in **17**) in the ratio 3.8:1]. Column chromatography (twice) of this fraction afforded **17** (0.88 g, 32%) and **19** as a syrup (0.16 g, 6%).

Compound **19** had $[\alpha]_D^{20}$ −5° (*c* 1.7, chloroform); t.l.c. (solvent *1*): R_F 0.24. ^{13}C-N.m.r. data ($CDCl_3$): δ 135.0 and 116.1 ($CH=CH_2$), 102.2 (C-1), and 100.6 (C-1′).

(*c*) A mixture of **13** (1.98 g), *N*-methylacetamide (0.4 mL), silver oxide (2.0 g), di-isopropylethylamine (1.22 mL), and molecular sieve Type 4A (3 g) in benzene (60 mL) was stirred overnight at room temperature. Insoluble material was removed by passing the mixture through a short column of neutral aluminium oxide, and the column was then eluted with benzene containing 0.1% of triethylamine to give 2-*O*-allyl-3,4,6-tri-*O*-benzyl-1-*O*-(*N*-methylacetamidoyl)-β-D-glucopyranose (**14**) as a syrup (1.76 g, 83%), $[\alpha]_D^{24}$ +17° (*c* 1.6, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 159.5 (C=N), 135.0 and 116.5 ($CH=CH_2$), 93.7 (C-1), 35.9 (N-CH_3), and 14.5 (C-CH_3).

A solution of **14** (1.60 g, 2.9 mmol) and **16** (1.05 g, 1.9 mmol) in benzene (40 mL) was stirred under dry nitrogen at room temperature for 5 days in the presence of anhydrous toluene-*p*-sulfonic acid (0.25 g) and molecular sieve Type 4A (1 g). The mixture was filtered and the filtrate was washed successively with aqueous sodium hydrogencarbonate and water, dried, and concentrated. Column chromatography (solvent *1*) of the product gave a mixture (1.32 g, 67%) of **17** and **19** in the ratio 4:1 (from the ^{13}C-n.m.r. spectrum). Column chromatography (twice) of this fraction afforded **17** (0.57 g, 29%) and **19** (60 mg, 3%).

Benzyl 3,4,6-tri-O-*benzyl-2*-O-(*3,4,6-tri*-O-*benzyl*-α-D-*glucopyranosyl*)-β-D-*glucopyranoside* (**18**). — A mixture of **17** (0.86 g), palladium chloride (0.17 g), and sodium acetate (0.5 g) in acetic acid–water (20:1, 4 mL) was stirred overnight at room temperature. Insoluble material was collected on a Celite pad and washed with methanol, and the combined filtrate and washings were concentrated. A solution of the residue in dichloromethane was washed with water, dried, and concentrated. Column chromatography (solvent *2*) of the residue gave **18** (0.71 g, 86%), m.p. 120–120.5° (from ethanol), $[\alpha]_D^{20}$ +40° (*c* 1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 101.6 (C-1) and 98.8 (C-1′).

Anal Calc. for $C_{61}H_{64}O_{11}$: C, 75.29; H, 6.63. Found: C, 75.36; H, 6.69.

Benzyl 3,4,6-tri-O-*benzyl-2*-O-(*3,4,6-tri*-O-*benzyl*-β-D-*glucopyranosyl*)-β-D-*glucopyranoside* (**19**). — A mixture of **18** (90 mg), palladium chloride (20 mg), and sodium acetate (30 mg) in acetic acid–water (20:1, 1 mL) was stirred overnight at room temperature, and then processed as described for **18**. Column chromatography (solvent *2*) of the product afforded **19** (76 mg, 81%), m.p. 147–148° (from ethanol),

$[\alpha]_D^{20}$ −15° (*c* 0.4, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 104.1 (C-1′) and 101.7 (C-1).

Anal. Calc. for $C_{61}H_{64}O_{11}$: C, 75.29; H, 6.63. Found: C, 75.40; H, 6.70.

Methyl 2-O-allyl-α-D-glucopyranoside (**22**). — A solution of **21** (25.5 g) in acetic acid (120 mL) was heated to 100°, water (80 mL) was added in small portions, and the mixture was stirred for 15 min and then concentrated; the last traces of the solvents were removed by repeated co-evaporation of toluene. The residue was recrystallised from chloroform–hexane to give **22** (17.0 g, 92%), m.p. 129–131°, $[\alpha]_D^{19}$ +140° (*c* 1.6, methanol).

Anal. Calc. for $C_{10}H_{18}O_6$: C, 51.27; H, 7.75. Found: C, 51.20; H, 7.86.

2-O-Allyl-D-glucopyranose (**23**). — A solution of **22** (15.3 g) in M sulfuric acid (250 mL) was stirred at 100° for 16 h, then cooled, neutralised with barium carbonate, filtered, and concentrated. Column chromatography (solvent *5*) of the product gave **23** (11.7 g, 81%), m.p. 130–145°, $[\alpha]_D^{19}$ +49 (2 min) → +58° (24 h, constant; *c* 1.2, water).

Anal. Calc for $C_9H_{16}O_6$: C, 49.09; H, 7.32. Found; C, 50.15; H, 7.40.

1,3,4,6-Tetra-O-acetyl-2-O-allyl-D-glucopyranose (**24**). — Conventional acetylation of **23** (11.5 g) with acetic anhydride–pyridine (1:1, 100 mL) gave amorphous **24** (19.2 g, 95%), $[\alpha]_D^{17}$ +39° (*c* 2, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 170.3–168.5 (C=O) 134.0 and 117.2 ($CH{=}CH_2$ for β anomer), 135.7 and 117.9 ($CH{=}CH_2$ for α anomer), 93.6 (C-1β), 89.3 (C-1α), and 20.9, 20.7, 20.6, and 20.55 ($COCH_3$).

Anal. Calc. for $C_{17}H_{24}O_{10}$: C, 52.85; H, 6.23. Found: C, 52.75; H, 6.29.

Benzyl 3,4,6-tri-O-benzyl-2-O-(3,4,6-tri-O-acetyl-2-O-allyl-α-D-glucopyranosyl)-β-D-glucopyranoside (**27**). — A saturated (at 0°) solution of hydrogen bromide in acetic acid (15 mL) was added at 0° to a solution of **24** (3.0 g) in dichloromethane (13 mL). The mixture was kept at 0° for 30 min, then diluted with dichloromethane, washed successively with ice–water, aqueous sodium hydrogencarbonate, and water, dried, and concentrated to give 3,4,6-tri-*O*-acetyl-2-*O*-allyl-α-D-glucopyranosyl bromide (**25**) as a syrup (3.0 g, 94%), $[\alpha]_D^{17}$ +159° (*c* 1.2, dichloromethane). ^{1}H-N.m.r. data ($CDCl_3$) δ 6.51 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 6.03–5.66 (m, 1 H, –CH=), and 2.07, 2.05, and 2.04 (3 s, each 3 H, 3 OAc).

A mixture of **25** (2.81 g) in acetonitrile (30 mL) was stirred with tetraethylammonium chloride (2.83 g) at room temperature until the optical rotation reached a minimum (~ 18 min). The mixture was poured into benzene which was washed with water, dried, and concentrated to give 3,4,6-tri-*O*-acetyl-2-*O*-allyl-β-D-glucopyranosyl chloride (**26**) as a syrup (2.20 g, 88%), $[\alpha]_D^{18}$ +83° (*c* 1.2, benzene). ^{1}H-N.m.r. data (C_6D_6): δ 4.94 (d, 1 H, $J_{1,2}$ 8.4 Hz, H-1).

A mixture of **16** (1.96 g, 3.6 mmol), silver perchlorate (1.26 g, 6.1 mmol), and powdered molecular sieve Type 4A (5 g) in ether (70 mL) was stirred at room temperature for 2 h, and then cooled to −10°. A solution of **26** (2.0 g, 5.5 mmol) in ether (20 mL) was added dropwise during 20 min, and the mixture was processed as described for the reaction of **16** with **13**. Column chromatography (solvent *2*) of the

product gave amorphous **27** (2.36 g, 75%), $[\alpha]_D^{17}$ +48° (*c* 1.5, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 5.63 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1) and 1.99 (s, 9 H, 3 OAc); ^{13}C, δ 170.1, 169.6 and 169.2 (3 C=O), 137.7 and 117.3 ($CH=CH_2$), 102.4 (C-1), 95.0 (C-1′), and 20.7, 20.6, and 20.4 (3 $COCH_3$).

Anal. Calc for $C_{49}H_{56}O_{14}$: C, 67.73; H, 6.50. Found; C, 67.81; H, 6.61.

Benzyl 2-O-(2-O-allyl-α-D-glucopyranosyl)-3,4,6-tri-O-benzyl-β-D-glucopyranoside (**28**). — *O*-Deacetylation of **27** (2.15 g), as described for the preparation of **16**, afforded **28** (1.73 g, 94%), m.p. 128–130° (from ethanol), $[\alpha]_D^{18}$ +59° (*c* 0.9, chloroform).

Anal. Calc for $C_{43}H_{50}O_{11}$: C, 69.52; H, 6.78. Found: C, 69.59; H, 6.71.

Compound **28** (2.52 g) was treated with sodium hydride (1.0 g; 50% mineral oil) and benzyl bromide (3 mL) in *N*,*N*-dimethylformamide (30 mL), as described for **7**. Column chromatography (solvent *1*) of the product gave **17** (3.16 g, 92%), $[\alpha]_D^{18}$ +29.5° (*c* 1.1, chloroform).

A mixture of **17** (3.05 g), palladium chloride (0.59 g), and sodium acetate (1.5 g) in acetic acid–water (20:1, 15 mL) was stirred overnight at room temperature, and then processed as described previously, to give **18** (2.58 g, 88%), m.p. and mixture m.p. 120–121°, $[\alpha]_D^{18}$ +39° (*c* 0.8, chloroform).

Benzyl O-(3,4,6-tri-O-acetyl-2-O-allyl-α-D-glucopyranosyl)-(1→2)-O-3,4,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→2)-3,4,6-tri-O-benzyl-β-D-glucopyranoside (**29**). — A mixture of **18** (1.48 g, 1.4 mmol), silver perchlorate (0.53 g, 2.6 mmol), and powdered molecular sieve Type 4A (3 g) in ether (25 mL) and 1,2-dimethoxyethane (12 mL) was treated with a solution of **26** (0.84 g, 2.3 mmol) in ether (10 mL), as described for the preparation of **27**. Column chromatography (solvent *2*) of the product gave amorphous **29** (1.39 g, 71%), $[\alpha]_D^{18}$ +62.5° (*c* 1.1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 170.3, 169.6, and 169.5 (3 C=O), 134.4 and 116.7 ($CH=CH_2$), 101.9 (C-1), 93.0 and 92.7 (C-1′,1″), and 20.8, 20.7, and 20.5 (3 $COCH_3$).

Anal. Calc for $C_{76}H_{84}O_{19}$: C, 70.14; H, 6.51. Found: C, 70.32; H, 6.65.

Benzyl O-(3,4,6-tri-O-benzyl-α-D-glucopyranosyl)-(1→2)-O-(3,4,6-tri-O-benzyl-α-D-glucopyransoyl)-(1→2)-3,4,6-tri-O-benzyl-β-D-glucopyranoside (**32**). — Compound **29** (1.25 g) was *O*-deacetylated, as described for the preparation of **16**, to give benzyl *O*-(2-*O*-allyl-α-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**30**), isolated as a syrup (1.08 g, 96%), $[\alpha]_D^{17}$ +53° (*c* 1, chloroform).

Compound **30** (1.0 g) was treated with sodium hydride (0.25 g; 50% mineral oil) and benzyl bromide (0.8 mL) in *N*,*N*-dimethylformamide (10 mL), as described for **7**, followed by column chromatography (solvent *1*) of the product, to give benzyl *O*-(2-*O*-allyl-3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**31**), isolated as a syrup (1.07 g, 87%), $[\alpha]_D^{20}$ +57° (*c* 1.6, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 134.9 and 116.4 ($CH=CH_2$), 101.5 (C-1), and 93.0 and 92.4 (C-1′,1″).

Treatment of **31** (0.98 g) with palladium chloride (0.14 g) and sodium acetate

(0.35 g) in acetic acid–water (20:1, 5 mL), as described for the preparation of **18**, followed by column chromatography (solvent *2*) of the product, afforded amorphous **32** (0.79 g, 83%), $[\alpha]_D^{20}$ +70° (*c* 1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 102.8 (C-1), and 95.0 and 93.8 (C-1′,1″).

Anal. Calc. for $C_{88}H_{92}O_{16}$: C, 75.19; H, 6.60. Found: C, 75.40; H, 6.81.

*1,3,4,6-Tetra-*O*-acetyl-2-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-allyl-*D*-glucopyranosyl)-α-*D*-glucopyranose* (**33**). — A mixture of **6** (6.02 g, 17.3 mmol), silver perchlorate (5.91 g, 28.5 mmol), and powdered molecular sieve Type 4A (20 g) in ether (300 mL) and 1,2-dimethoxyethane (30 mL) was treated with a solution of **26** (9.46 g, 25.9 mmol) in ether (100 mL), as described for the reaction of **16** with **13**. Column chromatography (solvent *3*) of the product gave **33** (8.25 g, 71%), m.p. 102–104° (from ethanol), $[\alpha]_D^{18}$ +145.5° (*c* 1.3, chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 6.38 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.97–5.57 (m, 1 H, –CH=), and 2.17–2.00 (6 s, 21 H, 7 Ac); ^{13}C, δ 170.3–168.9 (C=O), 134.0 and 117.9 ($CH=CH_2$), 96.4 (C-1′), 88.3 (C-1), and 20.8–20.6 ($COCH_3$).

Anal. Calc. for $C_{29}H_{40}O_{18}$: C, 51.48; H, 5.96. Found: C, 51.36; H, 5.92.

A solution of **33** (3.85 g) in acetic acid–water (20:1, 50 mL) was stirred overnight at room temperature with palladium chloride (1.12 g) and sodium acetate (3.8 g). Processing of the mixture, as described for the preparation of **18**, followed by acetylation of the product with acetic anhydride–pyridine (1:1, 30 mL) gave 1,3,4,6-tetra-*O*-acetyl-2-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-glucopyranose (**34**; 3.17 g, 82%), m.p. 167–168°, $[\alpha]_D^{17}$ +152° (*c* 1.5, chloroform); lit.[5] m.p. 168–168.5°, $[\alpha]_D^{18}$ +152.5°.

*Benzyl-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-allyl-α-*D*-glucopyranosyl)-(1→2)-*O*-(3,4,6-tri-*O*-acetyl-α-*D*-glucopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-β-*D*-glucopyranoside* (**39**). — A saturated (at 0°) solution of hydrogen bromide in acetic acid (7.5 mL) was added at 0° to a solution of **33** (1.50 g) in dichloromethane (7.5 mL). The mixture was stirred at 0° for 1.5 h, and then processed, as described for the preparation of **25**, to give 3,4,6-tri-*O*-acetyl-2-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-allyl-α-D-glucopyranosyl)-α-D-glucopyranosyl bromide (**35**) as a syrup (1.42 g, 92%), $[\alpha]_D^{18}$ +152° (*c* 1.3, dichloromethane). N.m.r. data ($CDCl_3$): ^{1}H, δ 6.54 (d, 1 H, $J_{1,2}$ 4.0 Hz); ^{13}C, δ 133.8 and 117.9 ($CH=CH_2$), 97.6 (C-1′), and 87.4 (C-1).

A solution of **35** (1.25 g) in acetonitrile (30 mL) containing tetraethylammonium chloride (0.89 g) was stirred at room temperature until the optical rotation reached a minimum (~20 min). The mixture was processed, as described for the preparation of **26**, to give 3,4,6-tri-*O*-acetyl-2-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-allyl-α-D-glucopyranosyl)-β-D-glucopyranosyl chloride (**36**) as a syrup (1.01 g, 86%), $[\alpha]_D^{18}$ +137° (*c* 1.5, benzene).

A solution of **36** (0.90 g, 1.4 mmol) in ether (5 mL) was added dropwise during 20 min at 0° to a stirred mixture of **16** (0.48 g, 0.9 mmol), silver perchlorate (0.32 g, 1.5 mmol), and powdered molecular sieve Type 4A (2 g) in ether (16 mL). The mixture was allowed to attain room temperature gradually, and then stirred for 3 h at room temperature. Processing of the mixture, as described for the reaction of **16**

with **13**, followed by column chromatography (solvent *3*) gave amorphous **39** (0.70 g, 68%), $[\alpha]_D^{19}$ +98° (*c* 1.2, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 170.2–169.4 (C=O), 134.3 and 117.2 ($CH{=}CH_2$), 102.5 (C-1), 96.2 and 93.8 (C-1′,1″), and 20.7–20.4 ($COCH_3$).

Anal. Calc. for $C_{61}H_{72}O_{22}$: C, 63.31; H, 6.32. Found: C, 63.48; H, 6.42.

O-Deacetylation of **39** (0.65 g), as described for the preparation of **16**, gave benzyl *O*-(2-*O*-allyl-α-D-glucopyranosyl)-(1→2)-*O*-α-D-glucopyranosyl-(1→2)-3,4,6-tri-*O*-benzyl-β-D-glucopyranoside (**40**), isolated as a syrup (0.47 g, 93%), $[\alpha]_D^{17}$ +61° (*c* 1.7, methanol). Attempts to benzylate[14] **40** failed.

Benzyl O-(*2,3,4,6-tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→2*)-O-(*3,4,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→2*)-*3,4,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**41**). — The product obtained by treatment of a mixture of **16** (1.03 g, 1.9 mmol), silver perchlorate (0.74 g, 3.6 mmol), and powdered molecular sieve Type 4A (3 g) in ether (40 mL) with **38** (2.12 g, 3.2 mmol) in ether–1,2-dimethoxyethane (4:1, 30 mL), as described for the preparation of **39**, was subjected to column chromatography (solvent *3*) to give amorphous **41** (1.55 g, 70%), $[\alpha]_D^{20}$ +99° (*c* 1.5, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 170.2–169.2 (C=O), 102.6 (C-1), 93.1 and 92.1 (C-1′,1″), and 20.9–20.0 ($COCH_3$).

Anal. Calc for $C_{60}H_{70}O_{23}$: C, 62.17; H, 6.09. Found: C, 62.31; H, 6.17.

O-α-D-*Glucopyranosyl*-(*1→2*)-O-α-D-*glucopyranosyl*-(*1→2*)-D-*glucopyranose* (**2**). — A solution of **41** (1.40 g) in methanol (10 mL) and dichloromethane (3 mL) was treated with methanolic M sodium methoxide (0.5 mL) at room temperature, and then processed as described for the preparation of **16**. A solution of the residue in acetic acid (30 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 water, and the combined filtrate and washings were concentrated. The residue was crystallised from aqueous methanol to give **2** as the monohydrate[9] (0.53 g, 84%), m.p. 228–230° (dec.), $[\alpha]_D^{20}$ +151° (3 min)→+156° (48 h, constant; *c* 1, water); lit.[9] m.p. 228–230° (dec.), $[\alpha]_D^{25}$ +150.2 (5 min)→+156.1° (48 h, constant; *c* 1.7, water).

Benzyl O-(*2,3,4,6-tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→2*)-O-(*3,4,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→2*)-O-(*3,4,6-tri*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→2*)-*3,4,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**42**). — The product obtained by treatment of a mixture of **18** (1.05 g, 1.1 mmol), silver perchlorate (0.42 g, 2 mmol), and powdered molecular sieve Type 4A (3 g) in ether–1,2-dimethoxyethane (4:1, 25 mL) with **38** (1.20 g, 1.8 mmol) in ether–1,2-dimethoxyethane (4:1, 17 mL), as described for the preparation of **39**, was subjected to column chromatography (solvent *3*) to afford amorphous **42** (1.01 g, 59%), $[\alpha]_D^{20}$ +86° (*c* 1.6, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 170.1–169.2 (C=O), 102.4 (C-1), 93.4, 91.0, and 89.5 (C-1′, 1‴), and 20.9–20.2 ($COCH_3$).

Anal. Calc. for $C_{87}H_{98}O_{28}$: C, 65.25; H, 6.21. Found: C, 65.39; H, 6.33.

O-α-D-*Glucopyranosyl*-(*1→2*)-O-α-D-*glucopyranosyl*-(*1→2*)-O-α-D-*glucopyranosyl*-(1→2)-D-*glucopyranose* (**3**). — Compound **42** (0.88 g) was sequentially

deacetylated and hydrogenolysed as described for **41**, and the residue was eluted from a column of Biogel P-2 (100–200 mesh) with water to give amorphous **3** (0.27 g, 73%; homogeneous by h.p.l.c.), $[\alpha]_D^{22}$ +160.5° (*c* 1.3, water).

Anal. Calc. for $C_{24}H_{42}O_{21}$: C, 43.24; H. 6.35. Found: C, 43.12; H, 6.48.

Compound **3** (91 mg) was reduced with sodium borohydride (7 mg) in water (1 mL) overnight at room temperature. The solution was treated with Amberlite IR-120 (H^+) resin to decompose the excess of the hydride, the resin was filtered off and washed with methanol, and the combined filtrate and washings were concentrated. Repeated evaporation of methanol from the residue gave *O*-α-D-glucopyranosyl-(1→2)-*O*-α-D-glucopyranosyl-(1→2)-*O*-α-D-glucopyranosyl-(1→2)-D-glucitol (**44**) as a syrup (85 mg, 93%), $[\alpha]_D^{21}$ +147° (*c* 0.5, water).

Benzyl O-(*2,3,4,6-tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→2*)-O-(*3,4,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→2*)-O-(*3,4,6-tri*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→2*)-O-(*3,4,6-tri*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→2*)-*3,4,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**43**). — The product obtained by treatment of a mixture of **32** (0.71 g, 0.5 mmol), silver perchlorate (0.25 g, 0.1 mmol), and powdered molecular sieve Type 4A (1 g) in ether (15 mL) with **38** (0.66 g, 0.1 mmol) in ether–1,2-dimethoxyethane (4;1, 10 mL), as described for the preparation of **39**, was subjected to column chromatography (solvent *4*) to give amorphous **43** (0.40 g, 39%), $[\alpha]_D^{21}$ +91° (*c* 0.8, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 170.0–169.1 (C=O), 103.1 (C-1), 93.1, 91.0, 90.1, and 89.2 (C-1′,1″,1‴,1⁗), and 20.9–20.2 ($COCH_3$).

Anal. Calc. for $C_{114}H_{126}O_{33}$: C, 67.74; H, 6.27. Found: C, 67.79; H, 6.41.

O-α-D-*Glucopyranosyl*-(*1→2*)-O-α-D-*glucopyranosyl*-(*1→2*)-O-α-D-*glucopyranosyl*-(*1→2*)-O-α-D-*glucopyranosyl*-(*1→2*)-D-*glucopyranose* (**4**). — *O*-Deacetylation of **43** (350 mg) and hydrogenolysis, as described for **41**, followed by purification of the product, as described for **3**, gave amorphous **4** (95 mg, 66%), homogeneous by h.p.l.c., $[\alpha]_D^{21}$ +167° (*c* 0.5, water).

Anal. Calc. for $C_{30}H_{52}O_{26}$: C, 43.38; H, 6.32. Found: C, 43.60; H, 6.49.

Reduction of **4** (40 mg) with sodium borohydride, as described for **3**, gave *O*-α-D-glucopyranosyl-(1→2)-*O*-α-D-glucopyranosyl-(1→2)-*O*-α-D-glucopyranosyl-(1→2)-*O*-α-D-glucopyranosyl-(1→2)-D-glucitol (**45**), isolated as a syrup (36 mg, 90%), $[\alpha]_D^{26}$ +155° (*c* 0.3, water).

Benzyl O-(*2,3,4,6-tetra*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→2*)-O-(*3,4,6-tri*-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→3*)-*2,4,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**47**). — The product obtained by treatment of a mixture of **46** (0.84 g, 1.6 mmol), silver perchlorate (0.60 g, 2.9 mmol), and powdered molecular sieve Type 4A (3g) in ether (30 mL) with **38** (1.73 g, 2.6 mmol) in ether–1,2-dimethoxyethane (4:1, 25 mL), as described for the preparation of **39**, was subjected to column chromatography (solvent *3*) to give amorphous **47** (1.29 g, 72%), $[\alpha]_D^{17}$ +92° (*c* 1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 170.2–169.2 (C=O), 102.1 (C-1), 96.8 and 95.6 (C-1′,1″), and 20.9–20.6 ($COCH_3$).

Anal. Calc. for $C_{60}H_{70}O_{23}$: C, 62.17; H, 6.09. Found: C, 62.30; H, 6.18.

O-α-D-*Glucopyranosyl*-(*1→2*)-O-α-D-*glucopyranosyl*-(*1→3*)-D-*glucopyrano*-

se (**5**). — *O*-Deacetylation of **47** (0.95 g) and hydrogenolysis, as described for **41**, followed by purification of the product, as described for **3**, gave amorphous **5** (0.35 g, 85%), $[\alpha]_D^{21}$ +159° (*c* 1.2, water).

Anal. Calc for $C_{18}H_{32}O_{16}$: C, 42.86; H, 6.39. Found: C, 42.71; H, 6.50.

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