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SYNTHESIS OF THE TRI- AND TETRA-SACCHARIDES RELATED TO THE FINE STRUCTURES OF LICHENAN AND CEREAL β-D-GLUCANS

KEN'ICHI TAKEO* AND YUKIKO SUZUKI
Department of Agricultural Chemistry, Kyoto Prefectural University, Shimogamo, Kyoto 606 (Japan)
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ABSTRACT

Syntheses, based on silver trifluoromethanesulfonate-promoted Koenigs–Knorr type condensations, are described of the D-glucotrioses, β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→4)-D-Glc*p* and β-D-Glc*p*-(1→4)-β-D-Glc*p*-(1→3)-D-Glc*p*, and the D-glucotetraoses, β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→4)-β-D-Glc*p*-(1→4)-D-Glc*p*, β-D-Glc*p*-(1→4)-β-D-Glc*p*-(1→3)-β-D-Glc*p*-(1→4)-D-Glc*p*, and β-D-Glc*p*-(1→4)-β-D-Glc*p*-(1→4)-β-D-Glc*p*-(1→3)-D-Glc*p*, corresponding to the tri- and tetra-saccharide units in the linear chains of (1→4)- and (1→3)-linked β-D-glucopyranosyl residues of lichenan, and of oat and barley β-D-glucans.

INTRODUCTION

Lichenan, a polysaccharide occurring in Iceland moss *(Cetraria islandica)*, is an unbranched β-D-glucan containing mainly a tetrasaccharide repeating-unit, in which a single (1→3) bond alternates with two consecutive (1→4) bonds[1,2], and occasionally a pentasaccharide unit, in which a (1→3) linkage alternates with three consecutive (1→4) linkages[2]. Polysaccharides having a similar (1→4)- and (1→3)-β-D-glucan structure, but with a slightly higher proportion of (1→4) to (1→3) linkages compared to lichenan, are also prominent constituents of the grains of oats[1,3] and barley[3]. The fine structures of lichenan and the cereal glucans were elucidated by studies of the D-gluco-oligosaccharides formed by partial acid hydrolysis[1] and by selective degradations with enzymes[2,3]. Partial acid hydrolysis of lichenan and oat β-D-glucan produced amorphous trisaccharides, *O*-β-D-glucopyranosyl-(1→3)-*O*-β-D-glucopyranosyl-(1→4)-D-glucose (**1**) and *O*-β-D-glucopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→3)-D-glucose (**2**), characterised as the crystalline β-undeca-acetates **10** and **13**, respectively[1]. The enzymic hydrolysis of lichenan yielded[2] crystalline **1** and **2** as the major products, and the crystalline tetrasaccharides *O*-β-D-glucopyranosyl-(1→3)-*O*-β-D-glucopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→

*To whom enquiries should be addressed.

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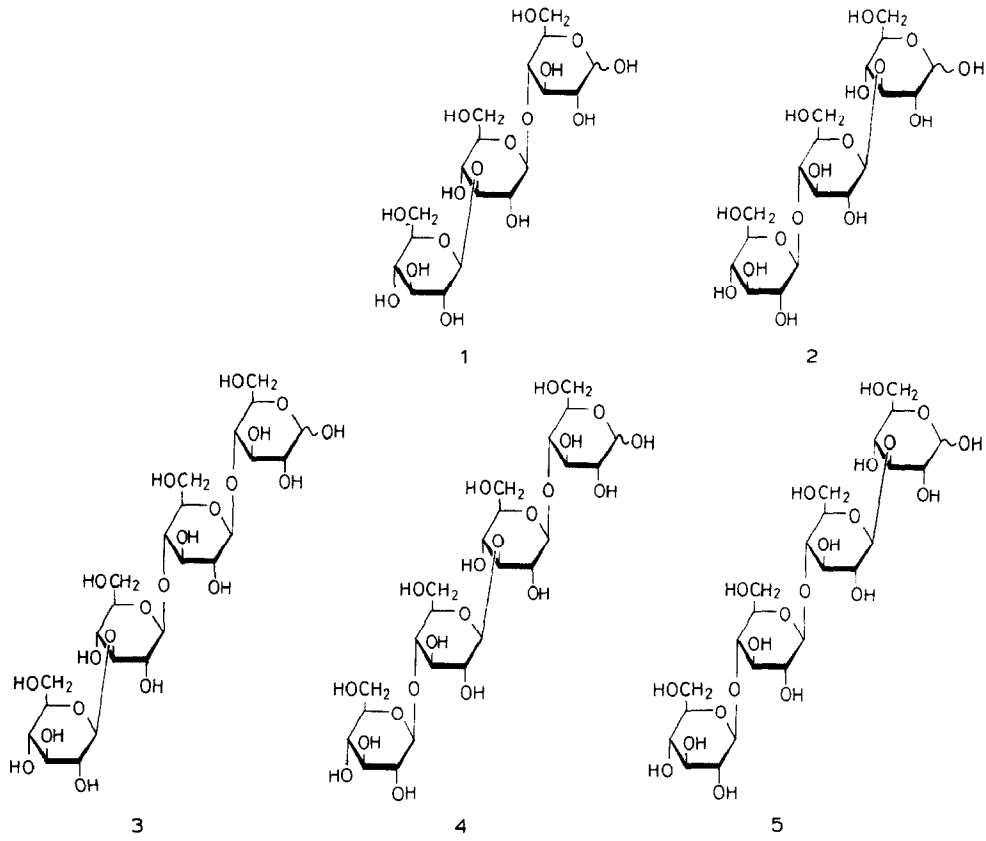


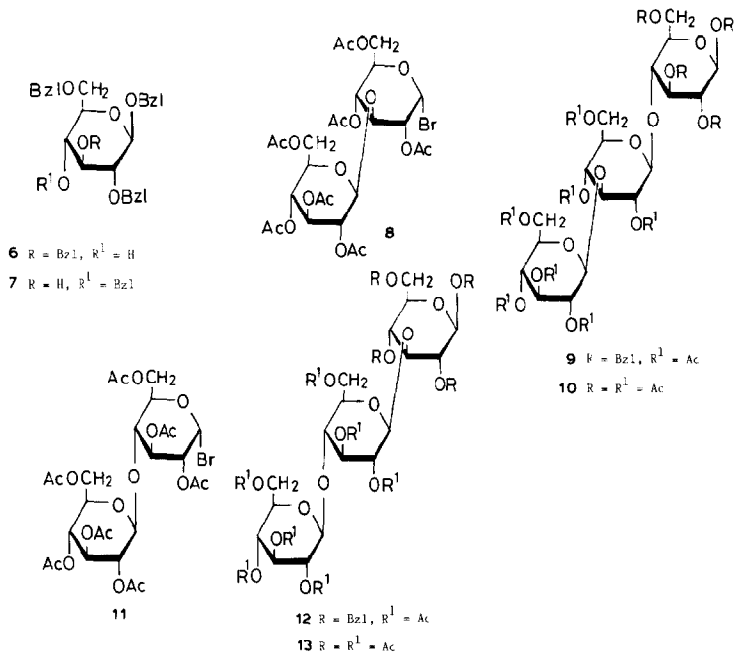
4)-D-glucose (**3**) and *O*-β-D-glucopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→3)-*O*-β-D-glucopyranosyl-(1→4)-D-glucose (**4**) as the minor products, whereas that of the cereal glucans released[3] the crystalline tetrasaccharide *O*-β-D-glucopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→3)-D-glucose (**5**), in addition to **1, 2, 3,** and **4**.

We now report the synthesis of the tri- and tetra-saccharides **1–5**.

RESULTS AND DISCUSSION

The syntheses of **1–5** were based on Koenigs–Knorr type condensations, whereby suitably benzylated mono-, di-, and tri-saccharides were coupled with an acetylated glycosyl α-bromide of mono-, di-, and tri-saccharides by using a combination of silver trifluoromethanesulfonate[4] (triflate) as catalyst and molecular sieve[5] as acid acceptor.

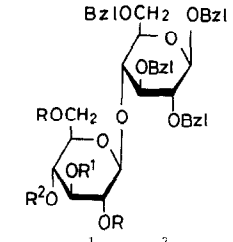
Glycosylation of benzyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside[6,7] (**6**) with hepta-*O*-acetyl-α-laminarabiosyl bromide[8] (**8**) gave a mixture, column chromatography of which on silica gel afforded 80% of the D-glucotrioside derivative **9**. *O*-



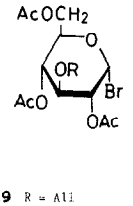
Deacetylation of **9** with methanolic sodium methoxide, followed by hydrogenolysis of the product in acetic acid over Pd/C, gave **1**, whose physical constants were in good agreement with those given in the literature[2]. The ^{13}C-n.m.r. spectrum of **1** in D_2O contained signals for C-1′, C-1″, C-1β, and C-1α at 105.3, 104.8, 98.4, and 94.4 p.p.m., respectively, and deshielded signals for C-3′, C-4α, and C-4β at 86.7, 81.4, and 81.3 p.p.m., respectively. The trisaccharide **1** was characterised as the β-undeca-acetate **10**[1].

Condensation of benzyl 2,4,6-tri-*O*-benzyl-β-D-glucopyranoside[9] (**7**) with hepta-*O*-acetyl-α-cellobiosyl bromide (**11**) afforded 82% of the D-glucotrioside derivative **12** after column chromatography. *O*-Deacetylation of **11**, followed by hydrogenolysis, gave **2**, having physical constants in good agreement with those reported[2]. The ^{13}C-n.m.r. spectrum of **2** in D_2O showed signals for C-1′ and C-1″ at 105.2 p.p.m., signals for C-1β and C-1α at 98.3 and 94.6 p.p.m., respectively, and deshielded signals for C-3β, C-3α, and C-4′ at 87.2, 85.0, and 81.3 p.p.m., respectively. Acetylation of **2** gave the β-undeca-acetate **13**[10]. Two sets of physical constants {m.p. 110°, $[\alpha]_D$ −8° (chloroform)[1]; m.p. 183°, $[\alpha]_D$ −22° (chloroform)[10]} have been reported for **13**; our data agreed with those of Ono and Dazai[10].

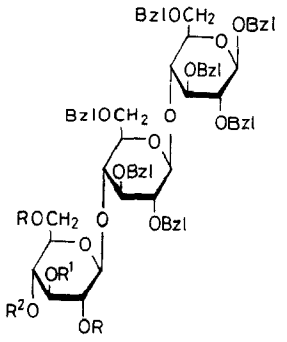
The synthesis of the tetrasaccharide **3** was achieved by two routes. In the first, benzyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,6-tri-*O*-benzyl-β-D-glucopyranosyl)-β-D-glucopyranoside[7] (**14**) was condensed with **8** to give 77% of the D-glucotetraoside derivative **25** after column chromatography. *O*-Deacetylation of **25**, followed by hydrogenolysis, afforded **3**, the physical constants of which agreed well with those



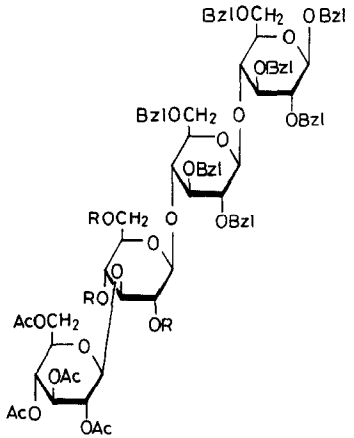
14 R = R^1 = Bzl, R^2 = H
15 R = R^2 = Ac, R^1 = All
16 R = R^2 = H, R^1 = All
17 R = R^2 = Bzl, R^1 = All
18 R = R^2 = Bzl, R^1 = H



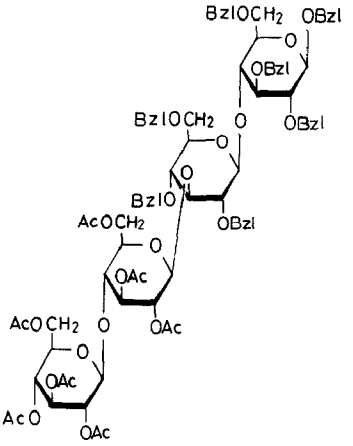
19 R = All
20 R = Ac



21 R = R^2 = Ac, R^1 = All
22 R = R^2 = H, R^1 = All
23 R = R^2 = Bzl, R^1 = All
24 R = R^2 = Bzl, R^1 = H



25 R = Ac
26 R = Bzl



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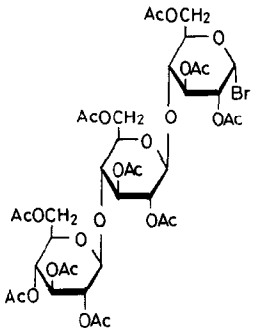
reported[3]. The ^{13}C-n.m.r. spectrum of **3** in D_2O contained* signals for C-1′, C-1″, and C-1‴ at 105.4 and 104.9 p.p.m., signals for C-1β and C-1α at 98.4 and 94.4 p.p.m. respectively, a deshielded signal for C-3‴ at 86.8 p.p.m., and deshielded signals for C-4′, C-4β, and C-4α at 81.3, 81.2, and 81.1, respectively.

In a second route to **3**, compound **14** was treated with 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-glucopyranosyl bromide[11] (**19**) to give 83% of benzyl *O*-(2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-D-glucopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**21**) after column chromatography. In the ^{13}C-n.m.r. spectrum of **21**, the signals for C-1″ appeared at

*The resonances observed in the ^{13}C-n.m.r. spectrum of **3** were all comparable with those in the spectrum kindly provided by Professor A. S. Perlin.



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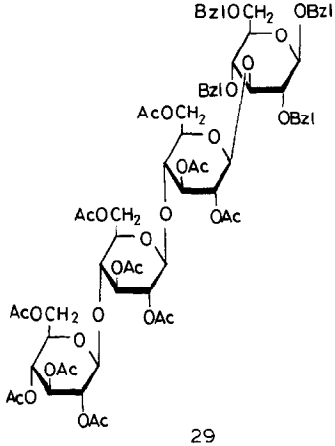

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100.1 p.p.m., indicating[12] the configuration at C-1″ to be β. *O*-Deacetylation of **21** with methanolic sodium methoxide in boiling methanol removed[9,11] the acetyl groups to give the 2″,4″,6″-triol **22** which, with benzyl bromide and sodium hydride in *N*,*N*-dimethylformamide[13], afforded **23**. Removal of the allyl group from **23** with palladium chloride[14] in aqueous acetic acid afforded **24** having HO-3″ unsubstituted. Glycosylation of **24** with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**20**) gave, after column chromatography, 83% of the D-glucotetraoside derivative **26** which, on successive *O*-deacetylation and hydrogenolysis, furnished **3**.

Reaction of **6** with **19** gave 84% of benzyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-D-glucopyranosyl)-β-D-glucopyranoside (**15**). The β configuration at C-1′ in **15** was clear[12] from the ^{13}C-n.m.r. signal at 100.1 p.p.m. *O*-Deacetylation of **15** in boiling methanolic sodium methoxide[9,11] (→ **16**), benzylation[13] (→ **17**), and *O*-deallylation[14] as above gave the 3′-ol **18**, which was coupled with **11** to afford 84% of the D-glucotetraoside derivative **27** after column chromatography. *O*-Deacetylation of **27**, followed by hydrogenolysis, gave **4**, whose physical constants agreed with those reported[2]. The ^{13}C resonances of **4** were consistent with those reported[15].

Glycosylation of **7** with deca-*O*-acetyl-α-cellotriosyl bromide[16] (**28**) gave 75% of the D-glucotetraoside derivative **29** after column chromatography. Removal of the protecting groups of **29**, as before, afforded **5**, the mutarotation value of which agreed well with that reported[2], as did the ^{13}C-n.m.r. spectrum[15]. However, the m.p. was higher than that reported[2], suggesting that **5** crystallises in two isomorphic forms.

EXPERIMENTAL

General methods. — Unless stated otherwise, these were as described[17]. ^{13}C-N.m.r. spectra were recorded at 22.6 MHz with a Hitachi R-90H spectrometer for

solutions in $CDCl_3$ and $(CD_3)_2SO$ (internal Me_4Si) or D_2O (internal sodium 4,4-dimethyl-4-silapentanoate-d_4). Column chromatography was performed on Silica Gel 9385 (Merck) with hexane–ethyl acetate mixtures (*1*, 1:1, *2*, 2:1; *3*, 3:2, *4*, 4:1; and *5*, 2:3).

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→4)-2,3,6-tri*-O-*benzyl-β*-D-*glucopyranoside* (**9**). — A solution of **8** (2.37 g, 3.4 mmol) in dry 1,2-dichloroethane (20 mL) was added dropwise during 30 min, with exclusion of moisture and light, to a stirred solution at −30° of **6** (1.22 g, 2.3 mmol) in anhydrous 1,2-dichloroethane (15 mL) containing silver triflate (1.04 g, 4 mmol) and powdered molecular sieve Type 4A (3 g). The mixture was allowed to attain 0° gradually, and then stirred at 0° for 1 h. Insoluble material was collected on a Celite pad and washed with dichloromethane, and the combined filtrate and washings were washed successively with aqueous sodium hydrogencarbonate and water, dried, and concentrated. Column chromatography (solvent *1*) of the syrupy residue gave amorphous **9** (2.09 g, 80%), $[\alpha]_D^{27}$ −25° (*c* 1.6, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 102.4, 100.7, and 99.8 (C-1,1′,1″).

Anal. Calc. for $C_{60}H_{70}O_{23}$: C, 62.17; H, 6.09. Found: C, 62.36; H, 5.91.

O-*β*-D-*Glucopyranosyl-(1→3)*-O-*β*-D-*glucopyranosyl-(1→4)-α*-D-*glucopyranose* (**1**). — A solution of **9** (1.65 g) in dry methanol (20 mL) was treated with methanolic M sodium methoxide (1 mL) at room temperature for 1 h, neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. A solution of the residue 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 layer of Celite and washed with methanol, and the combined filtrate and washings were concentrated. Toluene was evaporated from the residue, which crystallised from aqueous ethanol to give **1** (0.58 g, 81%), m.p. 227–230°, $[\alpha]_D^{26}$ +18 (2 min) → +13° (1 h, constant; *c* 2.5, water); lit.[2] m.p. 229–231°, $[\alpha]_D$ +19 → +13° (*c* 1.4, water).

O-*(2,3,4,6-Tetra*-O-*acetyl-β*-D-*glucopyranosyl)-(1→3)*-O-*(2,4,6-tri*-O-*acetyl-β*-D-*glucopyranosyl)-(1→4)-1,2,3,6-tetra*-O-*acetyl-β*-D-*glucopyranose* (**10**). — Compound **1** (0.34 g) was acetylated[18] with acetic anhydride (8 mL) and sodium acetate (0.4 g) under reflux for 30 min. Crystallisation of the product from ethanol gave **10** (0.51 g, 78%), m.p. 121–123°, $[\alpha]_D^{26}$ −20° (*c* 2.3, chloroform); lit.[1] m.p. 121–123°, $[\alpha]_D$ −22° (chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 100.7 and 100.4 (C-1′,1″), and 91.5 (C-1).

Benzyl O-*(2,3,4,6-tetra*-O-*acetyl-β*-D-*glucopyranosyl-(1→4)*-O-*(2,3,6-tri*-O-*acetyl-β*-D-*glucopyranosyl)-(1→3)-2,4,6-tri*-O-*benzyl-β*-D-*glucopyranoside* (**12**). — A mixture of **7** (1.44 g, 2.7 mmol), silver triflate (1.73 g, 6.7 mmol), and powdered molecular sieve Type 4A (9 g) in 1,2-dichloroethane (20 mL) was treated with a solution of **11** (2.79 g, 4 mmol) in 1,2-dichloroethane (25 mL), as described for the preparation of **9**. Column chromatography (solvent *1*) of the product gave amorphous **12** (2.53 g, 82%), $[\alpha]_D^{27}$ −23° (*c* 1.6, chloroform). ^{13}C-N.m.r. data

($CDCl_3$): δ 101.9, 100.6, and 99.8 (C-1,1′,1″).

Anal. Calc. for $C_{60}H_{70}O_{23}$: C, 62.17; H, 6.09. Found: C, 62.40; H, 6.21.

O-β-D-*Glucopyranosyl-(1→4)*-O-β-D-*glucopyranosyl-(1→3)*-α-D-*glucopyranose* (**2**). — *O*-Deacetylation of **12** (1.99 g), followed by hydrogenolysis, as described for **9**, afforded **2** (0.70 g, 80%), m.p. 234–237° (dec.) (from aqueous ethanol), $[\alpha]_D^{26}$ +17 (2 min) → +12° (1 h, constant; *c* 2, water); lit.[2] m.p. 236–239°, $[\alpha]_D$ +16.5 → +12° (*c* 1.5, water).

O-*(2,3,4,6-Tetra*-O-*acetyl*-β-D-*glucopyranosyl)-(1→4)*-O-*(2,3,6-tri*-O-*acetyl*-β-D-*glucopyranosyl)-(1→3)-1,2,4,6-tetra*-O-*acetyl*-β-D-*glucopyranose* (**13**). — Acetylation of **2** (0.41 g), as described for **1**, gave **13** (0.63 g, 80%), m.p. 184–186° (from ethanol), $[\alpha]_D^{26}$ −22.5° (*c* 1.2, chloroform); lit. m.p. 108–110°, $[\alpha]_D$ −8° (chloroform)[1]; m.p. 182.5–183°, $[\alpha]_D$ −22° (*c* 3, chloroform)[10]. ^{13}C-N.m.r. data ($CDCl_3$): δ 100.8 and 100.7 (C-1′,1″), and 91.6 (C-1).

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→4)*-O-*(2,3,6-tri*-O-*benzyl*-β-D-*glucopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**25**). — A mixture of **14** (2.0 g, 2.1 mmol), silver triflate (1.01 g, 3.9 mmol), and powdered molecular sieve Type 4A (5 g) in 1,2-dichloroethane (20 mL) was treated with **8** (2.3 g, 3.3 mmol) in 1,2-dichloroethane (20 mL), as described for the preparation of **9**. Column chromatography (solvent *1*) of the product afforded amorphous **25** (2.52 g, 77%), $[\alpha]_D^{26}$ −21° (*c* 1.6, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 102.3, 100.7, and 99.9 (C-1,1′,1″,1‴).

Anal. Calc. for $C_{87}H_{98}O_{28}$: C, 65.65; H, 6.21. Found: C, 65.79; H, 6.34.

O-β-D-*Glucopyranosyl-(1→3)*-O-β-D-*glucopyranosyl-(1→4)*-O-β-D-*glucopyranosyl-(1→4)*-α-D-*glucopyranose* (**3**). — *O*-Deacetylation of **25** (2.15 g), followed by hydrogenolysis, as described for **9**, gave **3** (0.69 g, 77%), m.p. 220–223° (dec.) (from aqueous methanol), $[\alpha]_D^{26}$ +13 (2 min) → +10° (1 h, constant; *c* 1.4, water); lit.[3] m.p. 221–223° (dec.), $[\alpha]_D$ +13 (2 min) → +11° (1 h, constant; *c* 3.5, water).

Benzyl O-*(2,4,6-tri*-O-*acetyl-3*-O-*allyl*-β-D-*glucopyranosyl)-(1→4)*-O-*(2,3,6-tri*-O-*benzyl*-β-D-*glucopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**21**). — A mixture of **14** (3.0 g, 3.1 mmol), silver triflate (1.90 g, 7.4 mmol), and powdered molecular sieve Type 4A (10 g) in 1,2-dichloroethane (40 mL) was treated with **19** (2.52 g, 6.2 mmol) in 1,2-dichloroethane (20 mL), as described for the preparation of **9**. Column chromatography (solvent *2*) of the product gave amorphous **21** (3.33 g, 83%), $[\alpha]_D^{27}$ −15° (*c* 1.4, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 170.4, 168.9, and 168.5 (3 C=O), 134.1 and 116.1 (CH_2=CH), 102.3 (C-1,1′), 100.1 (C-1″), and 20.9, 20.7, and 20.6 (3 $COCH_3$).

Anal. Calc. for $C_{76}H_{84}O_{19}$: C, 70.14; H, 6.51. Found: C, 70.32; H, 6.62.

Benzyl O-*(3*-O-*allyl*-β-D-*glucopyranosyl)-(1→4)*-O-*(2,3,6-tri*-O-*benzyl*-β-D-*glucopyranosyl)-(1→4)-2,3,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**22**). — A solution of **21** (3.06 g) in methanol (50 mL) containing methanolic M sodium methoxide (3 mL) was boiled under reflux for 30 min. Processing of the mixture, as described for

the preparation of **1**, gave **22** (2.57 g, 93%), $[\alpha]_D^{26}$ +1.5° (*c* 1.4, chloroform).

Anal. Calc. for $C_{70}H_{78}O_{16}$: C, 71.53; H, 6.69. Found: C, 71.24; H, 6.53.

Benzyl O-(3-O-allyl-2,4,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**23**). — A solution of **22** (2.48 g) in *N,N*-dimethylformamide (20 mL) was stirred with sodium hydride (0.8 g, 50% mineral oil) at room temperature for 1 h, and then cooled to 0°. Benzyl bromide (1.2 mL) was added, and the mixture was stirred at room temperature for 2 h. 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. Column chromatography (solvent *3*) of the residue gave amorphous **23** (2.53 g, 83%), $[\alpha]_D^{26}$ +7° (*c* 2.2, chloroform).

Anal. Calc. for $C_{91}H_{96}O_{16}$: C, 75.60; H, 6.69. Found: C, 75.34; H, 6.80.

Benzyl O-(2,4,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**24**). — A mixture of **23** (2.22 g), palladium chloride (0.3 g), and sodium acetate (1.38 g) in acetic acid–water (20:1, 15 mL) was stirred at room temperature for 8 h. 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 *4*) of the product gave amorphous **24** (1.73 g, 80%), $[\alpha]_D^{26}$ +11° (*c* 1.2, chloroform).

Anal. Calc. for $C_{88}H_{92}O_{16}$: C, 75.19; H, 6.60. found: C, 75.33; H, 6.74.

Benzyl O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-(1→3)-O-(2,4,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-benzyl-β-D-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**26**). — The product obtained by treatment of a mixture of **24** (1.50 g, 1.1 mmol), silver triflate (0.66 g, 2.6 mmol), and powdered molecular sieve Type 4A (3 g) in 1,2-dichloroethane (15 mL) with a solution of **20** (0.88 g, 2.1 mmol) in 1,2-dichloroethane (10 mL), as described previously, was subjected to column chromatography (solvent *2*) to give amorphous **26** (1.54 g, 83%), $[\alpha]_D^{27}$ −1° (*c* 2, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 102.4, 101.9, and 100.0 (C-1,1′,1″,1‴).

Anal. Calc. for $C_{102}H_{110}O_{25}$: C, 70.57; H, 6.39. Found: C, 70.72; H, 6.25.

O-Deacetylation of **26** (1.30 g), followed by hydrogenolysis, as described previously, gave **3** (0.36 g, 72%), m.p. and mixture m.p. 220–223° (dec.), $[\alpha]_D^{26}$ +13 (2 min) → +10° (1 h, constant; *c* 1.1, water). The ^{13}C-n.m.r. spectrum was identical to that of the compound previously obtained.

Benzyl 2,3,6-tri-O-benzyl-4-O-(2,4,6-tri-O-acetyl-3-O-allyl-β-D-glucopyranosyl)-β-D-glucopyranoside (**15**). — The product obtained by treatment of a mixture of **6** (3.0 g, 5.5 mmol), silver triflate (3.14 g, 12.2 mmol), and powdered molecular sieve Type 4A (15 g) in 1,2-dichloroethane (30 mL) with a solution of **19** (4.54 g, 11.1 mmol) in 1,2-dichloroethane (30 mL), as described previously, was subjected to column chromatography (solvent *2*) to give **15** (4.05 g, 84%), m.p. 104–105°

(from light petroleum), $[\alpha]_D^{26}$ −15° (*c* 1.2, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 170.3, 168.9, and 168.5 (3 C=O), 134.0 and 116.5 (CH_2=CH), 102.3 (C-1), 100.1 (C-1′), and 20.8, 20.7, and 20.5 (3 CO*C*H$_3$).

Anal. Calc. for $C_{49}H_{56}O_{14}$: C, 67.73; H, 6.50. Found: C, 67.76; H, 6.57.

*Benzyl 4-O-(3-O-allyl-β-*D*-glucopyranosyl)-2,3,6-tri-O-benzyl-β-*D*-glucopyranoside* (**16**). — *O*-Deacetylation of **15** (3.35 g), as described for the preparation of **22**, gave **16** (2.79 g, 92%), m.p. 76–77° (from ether–light petroleum), $[\alpha]_D^{26}$ +6.5° (*c* 2.3, chloroform).

Anal. Calc. for $C_{43}H_{50}O_{11}$: C, 69.52; H, 6.78. Found: C, 69.60; H, 6.72.

*Benzyl 4-O-(3-O-allyl-2,4,6-tri-O-benzyl-β-*D*-glucopyranosyl)-2,3,6-tri-O-benzyl-β-*D*-glucopyranoside* (**17**). — Compound **16** (2.51 g) was treated in *N,N*-dimethylformamide (20 mL) with sodium hydride (1.2 g; 50% mineral oil), followed by benzyl bromide (2.8 mL), as described for the preparation of **23**, to give **17** (3.04 g, 89%), m.p. 97–98° (from light petroleum–ether), $[\alpha]_D^{26}$ +9° (*c* 1.3, chloroform).

Anal. Calc. for $C_{64}H_{68}O_{11}$: C, 75.87; H, 6.76. Found: C, 75.75; H, 6.83.

*Benzyl 2,3,6-tri-O-benzyl-4-O-(2,4,6-tri-O-benzyl-β-*D*-glucopyranosyl)-β-*D*-glucopyranoside* (**18**). — A mixture of **17** (2.55 g), palladium chloride (0.49 g), and sodium acetate (2.3 g) in acetic acid–water (20:1, 20 mL) was stirred at room temperature for 7 h, and then processed as described for the preparation of **24**. Column chromatography (solvent *4*) of the product afforded amorphous **18** (2.01 g, 82%), $[\alpha]_D^{26}$ +10° (*c* 1.8, chloroform).

Anal. Calc. for $C_{61}H_{64}O_{11}$: C, 75.29; H, 6.63. Found: C, 75.41; H, 6.50.

*Benzyl O-(2,3,4,6-tetra-O-acetyl-β-*D*-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-acetyl-β-*D*-glucopyranosyl)-(1→3)-O-(2,4,6-tri-O-benzyl-β-*D*-glucopyranosyl)-(1→4)-2,3,6-tri-O-benzyl-β-*D*-glucopyranoside* (**27**). — The product obtained by treatment of a mixture of **18** (1.88 g, 1.9 mmol), silver triflate (1.09 g, 4.2 mmol), and powdered molecular sieve Type 4A (9 g) in 1,2-dichloroethane (20 mL) with a solution of **11** (2.70 g, 3.9 mmol) in 1,2-dichloroethane (30 mL) was subjected to column chromatography (solvent *1*) to give amorphous **27** (2.58 g, 84%), $[\alpha]_D^{26}$ −10° (*c* 1.4, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 102.4, 101.7, 100.7, and 99.9 (C-1,1′,1″,1‴).

Anal. Calc. for $C_{87}H_{98}O_{28}$: C, 65.65; H, 6.21. Found: C, 65.47; H, 6.38.

*O-β-*D*-Glucopyranosyl-(1→4)-O-β-*D*-glucopyranosyl-(1→3)-O-β-*D*-glucopyranosyl-(1→4)-*D*-glucopyranose* (**4**). — *O*-Deacetylation of **27** (2.41 g), followed by hydrogenolysis, as described previously, gave **4** (0.82 g, 81%), m.p. 224–227° (dec.) (from aqueous methanol), $[\alpha]_D^{26}$ +21° (*c* 1.4, dimethyl sulfoxide); lit.[2] m.p. 223–226°, $[\alpha]_D$ +20° (*c* 1.6, aqueous 90% acetic acid). ^{13}C-N.m.r. data [$(CD_3)_2SO$]: δ 103.4, 102.9, and 102.4 (C-1′,1″,1‴), 96.5 (C-1β), 91.8 (C-1α), and 87.1 (C-3′).

*Benzyl O-(2,3,4,6-tetra-O-acetyl-β-*D*-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-acetyl-β-*D*-glucopyranosyl)-(1→4)-O-(2,3,6-tri-O-acetyl-β-*D*-glucopyranosyl)-(1→3)-2,4,6-tri-O-benzyl-β-*D*-glucopyranoside* (**29**). — The product obtained by treatment of a mixture of **7** (0.87 g, 1.6 mmol), silver triflate (0.74 g, 2.9 mmol), and powdered molecular sieve Type 4A (4 g) in 1,2-dichloroethane (10 mL) with a

solution of **28** (2.38 g, 2.4 mmol) in 1,2-dichloroethane (20 mL) was subjected to column chromatography (solvent 5) to give amorphous **29** (1.74 g, 75%), $[\alpha]_D^{26}$ −14.5° (*c* 1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 101.9, 101.8, 101.5, and 100.6 (C-1,1′,1″,1‴).

Anal. Calc. for $C_{72}H_{86}O_{31}$: C, 59.75; H, 5.99. Found: C, 59.93; H, 6.11.

O-β-D-*Glucopyranosyl-(1→4)*-O-β-D-*glucopyranosyl-(1→4)*-O-β-D-*glucopyranosyl-(1→3)*-α-D-*glucopyranose* (**5**). — *O*-Deacetylation of **29** (1.60 g), followed by hydrogenolysis, as described previously, gave **5** (0.58 g, 78%), m.p. 257–260° (dec.) (from aqueous ethanol), $[\alpha]_D^{26}$ +12 (2 min) → +9° (3 h, constant; *c* 2, water); lit.[3] m.p. 241–245° (dec.), $[\alpha]_D$ +11 (5 min) → +8° (3 h, constant; *c* 2.7, water). ^{13}C-N.m.r. data (D_2O): δ 105.1 and 104.9 (C-1′,1″,1‴), 98.2 (C-1), 94.5 (C-1), 87.1 (C-3), and 84.9 (C-3).

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