Carbohydrate Research, 209 (1991) 167–179
Elsevier Science Publishers B.V., Amsterdam

Synthesis of the oligosaccharides α-D-Glc*p*-(1→4)-D-Xyl*p*, α-D-Xyl*p*-(1→4)-D-Glc*p*, α-D-Glc*p*-(1→4)-α-D-Glc*p*-(1→4)-D-Xyl*p*, α-D-Glc*p*-(1→4)-α-D-Xyl*p*-(1→4)-D-Glc*p*, and α-D-Xyl*p*-(1→4)-α-D-Glc*p*-(1→4)-D-Glc*p*

Kenichi Takeo*, Yasuhiro Teramoto, Yumi Shimono
Department of Agricultural Chemistry, Kyoto Prefectural University, Shimogamo Kyoto 606 (Japan)
and Yasunori Nitta
Laboratory of Biophysical Chemistry, College of Agriculture, University of Osaka Prefecture, Sakai 591 (Japan)

(Received March 26th, 1990; accepted for publication in revised form July 23rd, 1990)

ABSTRACT

Syntheses are described of the disaccharides, α-D-Glc*p*-(1→4)-D-Xyl*p*, α-D-Xyl*p*-(1→4)-D-Glc*p*, and α-D-Xyl*p*-(1→4)-D-Xyl*p*, and the trisaccharides, α-D-Glc*p*-(1→4)-α-D-Glc*p*-(1→4)-D-Xyl*p*, α-D-Glc*p*-(1→4)-α-D-Xyl*p*-(1→4)-D-Glc*p*, and α-D-Xyl*p*-(1→4)-α-D-Glc*p*-(1→4)-D-Glc*p* as analogues of glucoamylase and soybean beta-amylases substrates.

INTRODUCTION

In the previous paper[1], we reported the synthesis of the tetrasaccharide *O*-α-D-Glc*p*-(1→4)-*O*-α-D-Xyl*p*-(1→4)-*O*-α-D-Xyl*p*-(1→4)-D-Glc*p*, which was found to be a competitive inhibitor useful for elucidating the binding mode of substrates to the active sites of Taka-amylase A (alpha amylase from *Aspergillus oryzae*) and porcine pancreatic alpha amylase[2]. In order to obtain further information on the binding of substrates to the catalytic sites of such *exo*-amylases as gluco-[3] [EC 3.2.1.3] and soybean beta-amylase[4] [EC 3.2.1.2], we required, as substrate analogues for these enzymes, synthetic di- and tri-saccharides in which one of the D-glucose units in maltose or maltotriose is replaced by a D-xylose residue, namely, *O*-α-D-glucopyranosyl-(1→4)-D-xylopyranose (**1**), *O*-α-D-xylopyranosyl-(1→4)-D-glucopyranose (**2**), *O*-α-D-glucopyranosyl-(1→4)-*O*-α-D-glucopyranosyl-(1→4)-D-xylopyranose (**4**), *O*-α-D-glucopyranosyl-(1→4)-*O*-α-D-xylopyranosyl-(1→4)-D-glucopyranose (**5**), and *O*-α-D-xylopyranosyl-(1→4)-*O*-α-D-(1→4)-D-glucopyranosyl-(1→4)-D-glucopyranose (**6**), and also *O*-α-D-xylopyranosyl-(1→4)-D-xylopyranose (**3**). The disaccharide **1** has previously been prepared from β-D-glucopyranosyl phosphate and D-xylose by the action of the enzyme from *Neisseria meningitidis*[5], and **3** has been synthesized chemically[6]. The trisaccharide **4** has been obtained enzymically as its methyl α-glycoside[7].

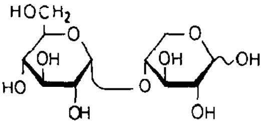
* Author for correspondence.

0008-6215/91/$03.50

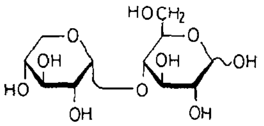
We now report the synthesis of di- (**1** and **2**) and tri-saccharides (**4**–**6**). The synthesis of **3** by a reaction sequence alternative to that reported[6] is also described.

RESULTS AND DISCUSSION

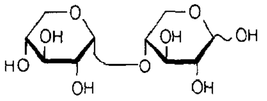
Glycosylation of benzyl 2,3-anhydro-β-D-ribopyranoside[8] (**8**) with 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride[1] (**7**) in ether in the presence of silver perchlorate[9] and 2,4,6-trimethylpyridine gave the α- (**9**, 69%) and β-(1→4)-linked disaccharide



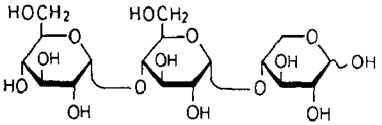
1



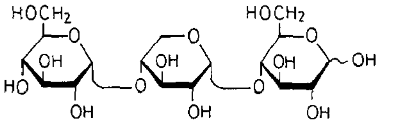
2



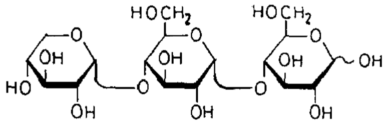
3



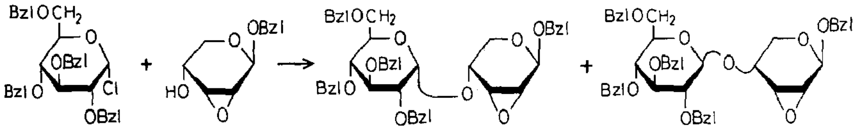
4



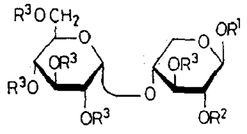
5



6



7 **8** **9** **10**



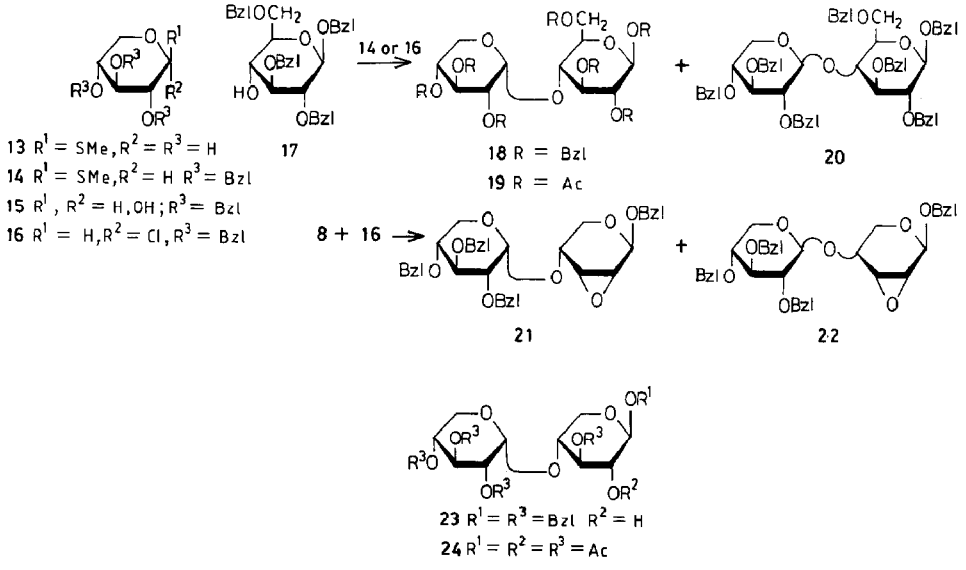
11 $R^1 = R^3 = Bzl, R^2 = H$
12 $R^1 = R^2 = R^3 = Ac$

derivative **10** (12%), after column chromatography. In the ^{13}C-n.m.r. spectra of **9** and **10**, the signals for C-1′ appeared at 95.4 and 103.4 p.p.m., indicating[10] the configurations at C-1′ in **9** and **10** to be α and β, respectively. Opening of the anhydro ring in **9** by treatment with benzyl alcoholate anion in benzyl alcohol[11] afforded 80% of **11**, which was hydrogenolyzed catalytically over Pd–C to give known **1**, further characterized by

conversion (acetic anhydride–sodium acetate[12]) into the crystalline β-heptaacetate **12**.

Benzylation of methyl 1-thio-β-D-xylopyranoside[1] (**13**) with benzyl bromide and sodium hydride in *N*,*N*-dimethylformamide[13] afforded 92% of methyl 2,3,4-tri-*O*-benzyl-1-thio-β-D-xylopyranoside (**14**). Condensation of benzyl 2,3,6-tri-*O*-benzyl-β-D-glucopyranoside[14] (**17**) with **14** in ether in the presence of methyl trifluoromethanesulfonate[15] (methyl triflate) and molecular sieve afforded the α- (**18**, 20%) and β-(1→4)-linked disaccharide derivative **20** (51%) after column chromatography. The α and β configurations at C-1′ in **18** and **20** were apparent[10] from the ^{13}C-n.m.r. signals for C-1′ at 96.4 and 103.0 p.p.m., respectively. Reaction of **17** with **14** in 1,2-dichloroethane and *N*,*N*-dimethylfromamide in the presence of cupric bromide, tetrabutylammonium bromide, and molecular sieve[16] gave **18** (52%) and **20** (20%), after column chromatography. Catalytic hydrogenolysis of **18** provided **2**, characterized as the crystalline β-heptaacetate **19**.

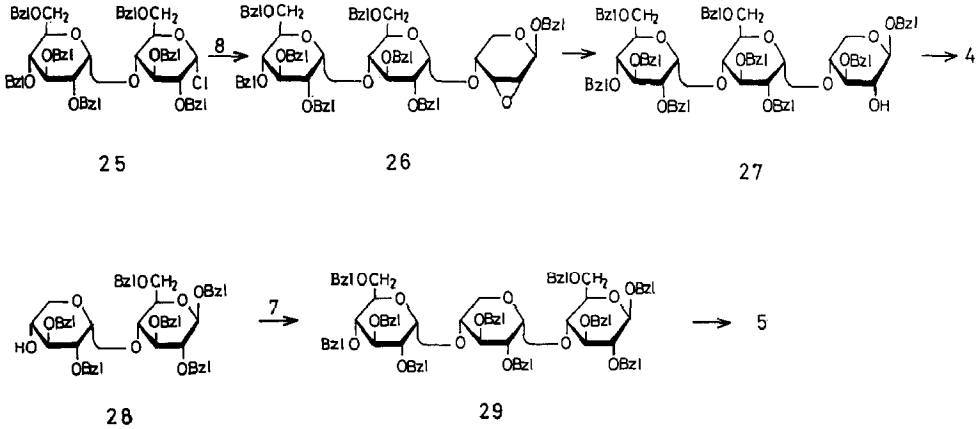
2,3,4-Tri-*O*-benzyl-D-xylopyranose[17] (**15**) was converted with oxalyl chloride and *N*,*N*-dimethylformamide in dichloromethane[18] into the corresponding α-chloride **16**, which was coupled with **8** in ether in the presence of silver perchlorate and 2,4,6-trimethylpyridine to give the α- (**21**, 41%) and β-(1→4)-linked disaccharide derivative **22** (40%), after column chromatography. The α and β configurations at C-1′ in **21** and **22** were clear from the ^{13}C-n.m.r. signals for C-1′ at 95.4 and 104.2 p.p.m., respectively. Treatment of **21** with benzyl alcoholate anion, as before, gave **23**, which was hydrogenolyzed to afford **3**, whose ^{13}C-n.m.r. spectrum was identical with that reported[19]. The disaccharide **3** was further characterized as the crystalline β-hexaacetate[6,20] **24**.



Reaction of **8** with hepta-*O*-benzyl-α-maltosyl chloride[21] (**25**), promoted by silver perchlorate as before, gave, after column chromatography, the trisaccharide derivative **26** (63%), the ^{13}C-n.m.r. spectrum of which contained the signal for C-1′ at 95.1 p.p.m.

Treatment of **26** with benzyl alcoholate anion gave **27**, hydrogenolysis of which provided **4**.

The synthesis of **5** was achieved by two routes. In the first, reaction of benzyl *O*-(2,3-di-*O*-benzyl-α-D-xylopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside[1] (**28**) with **7**, catalyzed by silver perchlorate as before, afforded the trisaccharide derivative **29** (73%), the ^{13}C-n.m.r. spectrum of which contained the signal for C-1″ at 98.8 p.p.m. Hydrogenolysis of **29** furnished **5**.

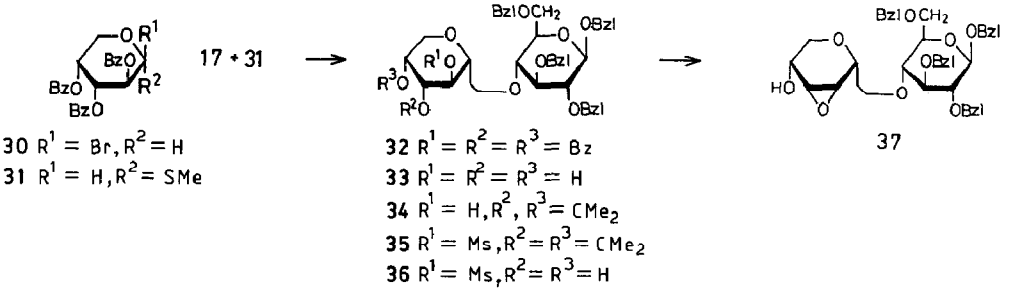


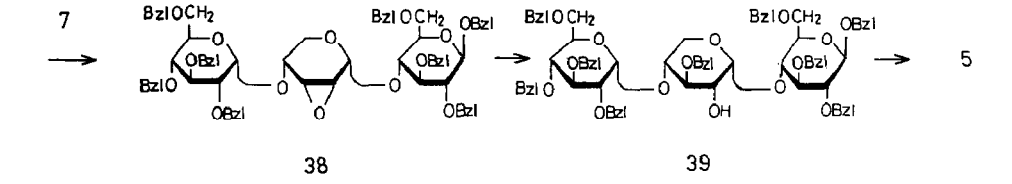
25 26 27

28 29

In a second route, 2,3,4-tri-*O*-benzoyl-β-D-arabinopyranosyl bromide[22] (**30**) was treated with sodium methanethiolate in aqueous acetone to afford 74% of methyl 2,3,4-tri-*O*-benzoyl-1-thio-α-D-arabinopyranoside (**31**), which was condensed with **17** in dichloromethane in the presence of dimethyl(methylthio)sulfonium triflate[23] (DMTST) and molecular sieve to give benzyl *O*-(2,3,4-tri-*O*-benzoyl-α-D-arabinopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**32**, 80%), after column chromatography. The disaccharide derivative **32** was transformed into benzyl *O*-(2,3-anhydro-α-D-ribopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**37**) by a reaction sequence involving *O*-debenzoylation (→**33**), treatment with 2,2-dimethoxypropane–*p*-toluenesulfonic acid in *N*,*N*-dimethylformamide (→**34**), methanesulfonylation (→**35**), *O*-deisopropylidenation (→**36**), and treatment with sodium methoxide[8]. Silver perchlorate-promoted glycosylation of **37** with **7**, as before, gave, after column chromatography, the trisaccharide derivative **38** (67%), the ^{13}C-n.m.r. spectrum of which showed the signal for C-1″ at 96.3 p.p.m. Opening of the epoxy ring in **38**, as before, afforded **39**, hydrogenolysis of which provided **5**.

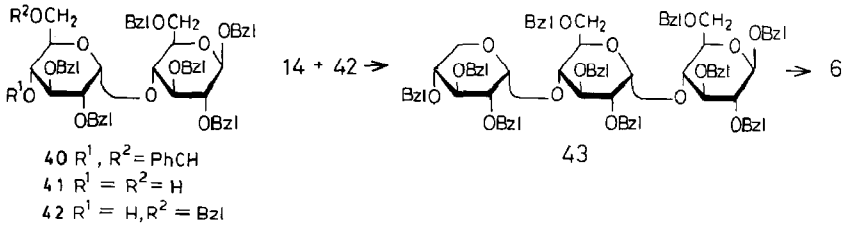
Removal of the benzylidene group from benzyl 2,3,6,2′,3′-penta-*O*-benzyl-4′,6′-*O*-benzylidene-β-maltoside[24] (**40**) with aqueous acetic acid gave 2,3,6,2′,3′-penta-*O*-benzyl-β-maltoside (**41**). Selective benzylation at HO-6′ in **41** *via* the stannylene derivative in benzene with benzyl bromide in the presence of tetrabutylammonium bromide[25] gave 86% of benzyl 2,3,6,2′,3′,6′-hexa-*O*-benzyl-β-maltoside (**42**). Glycosylation of **42** with **14**, assisted by cupric bromide–tetrabutylammonium bromide as before, afforded the trisaccharide derivative **43** (48%), the ^{13}C-n.m.r. spectrum of which contained the





signal for C-1″ at 96.5 p.p.m. Hydrogenolysis of **43** furnished **6**.

The di- (**1–3**) and tri-saccharides (**4–6**) were homogeneous by l.c., and gave ^{1}H-and ^{13}C-n.m.r. spectra, consistent with the structures assigned.



EXPERIMENTAL

General methods. — Unless stated otherwise, these were as described[1]. N.m.r. spectra (^{1}H, 90 MHz; ^{13}C, 22.6 MHz) were recorded with a Hitachi R-90H spectrometer for solutions in $CDCl_3$ and $(CD_3)_2SO$ (internal Me_4Si). N.m.r. spectra (^{1}H, 270 MHz; ^{13}C, 67.8 MHz) of **1–6** were recorded with a Jeol JNM GX-270 spectrometer for solutions in D_2O (^{1}H, external Me_4Si; ^{13}C, internal MeOH, δ_{Me_4Si} 49.8)

Benzyl O-(*2,3,4,6-tetra*-O-*benzyl*-α- *and* β-D-*glucopyranosyl*)-(*1→4*)-*2,3-anhydro*-β-D-*ribopyranoside* (**9** and **10**). — A solution of **7** (4.36 g, 7.8 mmol) in ether (50 mL) was added dropwise at 0° to a stirred mixture of **8** (1.35 g, 6.1 mmol), $AgClO_4$ (2.27 g, 10.9 mmol), and 2,4,6-trimethylpyridine (1.59 mL, 12.1 mmol) in ether (100 mL) with exclusion of moisture and light. The mixture was allowed to reach room temperature and stirred overnight at room temperature. Insoluble material was collected on a layer of Celite and washed with PhMe. The combined filtrate and washings were washed

successively with cold dil. HCl, aq. $NaHCO_3$, and water, dried, and evaporated. The residue was subjected to column chromatography (30:1→20:1 benzene–EtOAc, stepwise). Eluted first was **9** (3.12 g, 69%), m.p. 83–84° (from ether–hexane), $[\alpha]_D^{25}$ +48° (*c* 1.2, $CHCl_3$); R_F 0.51 (t.l.c. in 10:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 95.4 (C-1′), 94.4 (C-1), 68.0 (C-6′), 59.5 (C-5), 52.7 (C-3), and 49.45 (C-2).

Anal. Calc. for $C_{46}H_{48}O_9$: C, 74.17; H, 6.50. Found: C, 74.30; H, 6.57.

Eluted next was **10** (0.54 g, 12%), m.p. 127–128° (from EtOH), $[\alpha]_D^{25}$ +6° (*c* 1.0, $CHCl_3$); R_F 0.42 (t.l.c. in 10:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 103.4 (C-1′), 94.6 (C-1), 69.1 (C-6′), 59.0 (C-5), 53.1 (C-3), and 51.8 (C-2).

Found: C, 74.26; H, 6.54.

Benzyl O-(*2,3,4,6-tetra*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→4*)-*3*-O-*benzyl*-β-D-*xylopyranoside* (**11**). — Sodium hydride (0.74 g) was added portionwise and with stirring to benzyl alcohol (50 mL) and, when a clear solution had been formed, compound **9** (2.29 g) was added to the resulting solution of benzyl alcoholate anion in benzyl alcohol. The mixture was stirred for 5 h at 100°, and then cooled, diluted with MeOH, deionized with Amberlite IR-120 (H^+) resin, filtered, and the filtrate evaporated. Column chromatography (20:1 benzene–EtOAc) of the residue afforded **11** (2.11 g, 80%), m.p. 83–85° (from ether–hexane), $[\alpha]_D^{25}$ +12° (*c* 0.8, $CHCl_3$); ^{13}C-n.m.r. ($CDCl_3$): δ 101.3 (C-1) and 97.9 (C-1′).

Anal. Calc. for $C_{53}H_{56}O_{10}$: C, 74.63; H, 6.62. Found: C, 74.80; H, 6.53.

O-α-D-*Glucopyranosyl*-(1→4)-D-*xylopyranose* (**1**). — A solution of **11** (1.82 g) in 2-methoxyethanol (30 mL) was hydrogenated in the presence of 10% Pd–C (1 g) at normal pressure overnight at room temperature. The suspension was filtered through a Celite pad and washed with 50% MeOH, and the combined filtrate and washings were evaporated. The residue was purified by column chromatography (30:10:1 $CHCl_3$–MeOH–H_2O) to give amorphous **1** (0.59 g, 88%), $[\alpha]_D^{25}$ +93° (*c* 1.3, H_2O); lit.[5] +94.5° (*c* 1.88, H_2O); $R_{maltose}$ 0.93 (l.c.); n.m.r. (D_2O): ^{1}H, δ 5.15 (d, 0.4 H, $J_{1,2}$ 3.7 Hz, H-1α), 5.11 (d, 1 H, $J_{1',2'}$ 4.0 Hz, H-1′), and 4.53 (d, 0.6 H, $J_{1,2}$ 7.9 Hz, H-1β); ^{13}C, δ 100.9 (C-1′), 97.3 (C-1β), 92.85 (C-1α), 79.05 (C-4), 75.7, 74.7, 73.7, 73.2, 72.45, 72.05, 70.4, 65.1 (C-5β), 61.5 (C-6′), and 60.9 (C-5α).

O-(*2,3,4,6*-Tetra-O-*acetyl*-α-D-*glucopyranosyl*)-(*1→4*)-*1,2,3-tri*-O-*acetyl*-β-D-*xylopyranose* (**12**). — Compound **1** (0.15 g) was acetylated with Ac_2O (1.5 mL) and NaOAc (0.1 g) under reflux for 20 min. Crystallization of the product from MeOH gave **12** (0.24 g, 83%), m.p. 174–175°, $[\alpha]_D^{25}$ +62° (*c* 1.6, $CHCl_3$); n.m.r. ($CDCl_3$): ^{1}H, δ 5.71 (d, 1 H, $J_{1,2}$ 6.8 Hz, H-1) and 2.09–2.01 (4 s, 21 H, 7 OAc): ^{13}C, δ 170.2–168.6 (C=O), 96.4 (C-1′), 91.8 (C-1), 73.55 (C-4), 63.8 (C-5′), 62.0 (C-6), and 20.7 and 20.5 ($COCH_3$).

Anal. Calc. for $C_{25}H_{34}O_{17}$: C, 49.51; H, 5.65. Found: C, 49.46; H, 5.71.

Methyl 2,3,4-tri-O-*benzyl-1-thio*-β-D-*xylopyranoside* (**14**). — A solution of **13** (1.50 g) in *N,N*-dimethylformamide (25 mL) was treated with NaH (1.80 g; 50% mineral oil) for 1 h at room temperature and then cooled to 0°. Benzyl bromide (4 mL) was added dropwise and the mixture was stirred for 3 h at room temperature. Methanol was added to decompose the excess of hydride, most of the solvent was evaporated, and a solution of the residue in CH_2Cl_2 was washed with water, dried, and evaporated.

Column chromatography (4:1 hexane–EtOAc) of the residue afforded **14** (3.45 g, 92%), m.p. 66.5–68° (from hexane), $[\alpha]_D^{26}$ +1° (*c* 1.3, $CHCl_3$); ^{13}C-n.m.r. ($CDCl_3$); δ 138.4, 137.9, and 137.8 (aromatic C-1), 86.0 (C-1), 67.4 (C-5), and 12.8 (SMe).

Anal. Calc. for $C_{27}H_{30}O_4S$: C, 71.97; H, 6.71. Found: C, 72.11: H, 6.70.

Benzyl O-(*2,3,6-tri*-O-*benzyl*-α- *and* β-D-*xylopyranosyl*)-(*1→4*)-*2,3,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**18** and **20**). — (*a*) A mixture of **14** (0.38 g, 843 μmol), **17** (0.35 g, 647 μmol), and powdered molecular sieve 4A (3 g) in ether was stirred for 30 min at room temperature under Ar and cooled to 0°. Methyl triflate (0.48 mL, 4.2 mmol) was injected through a rubber septum and the mixture was stirred for 5 h at room temperature. Triethylamine (1.3 mL) was added, and the mixture was stirred for 30 min at room temperature, and filtered through a Celite pad which was washed with PhMe. The combined filtrate and washings were evaporated and the residue was subjected to column chromatography (50:1→30:1 benzene–EtOAc, stepwise) to give **18** (0.12 g, 20%) and **20** (0.31 g, 51%).

Compound **18**, syrup, had $[\alpha]_D^{25}$ +13° (*c* 1.5, $CHCl_3$); R_F 0.55 (t.l.c. in 15:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 102.1 (C-1), 96.4 (C-1′), 84.6 (C-4), 69.3 (C-6), and 60.9 (C-5′).

Anal. Calc. for $C_{60}H_{62}O_{10}$: C, 76.41; H, 6.63. Found: C, 76.58; H, 6.81.

Compound **20** had m.p. 109.5–110.5° (from ether–hexane), $[\alpha]_D^{25}$ +10° (*c* 1.0, $CHCl_3$); R_F 0.43 (t.l.c. in 15:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 103.0 (C-1′), 102.35 (C-1), 84,0 (C-4), 68.1 (C-6), and 63.5 (C-5′).

Found: C, 76.27; H, 6.70.

(*b*) A mixture of $CuBr_2$ (1.63 g, 7.3 mmol), Bu_4NBr (0.31 g, 961 μmol), and powdered molecular sieve 4A (5 g) in 1,2-dichloroethane (15 mL) and *N*,*N*-dimethylformamide (5 mL) was stirred for 1 h under Ar at room temperature. A solution of **14** (2.19 g, 4.9 mmol) and **17** (1.75 g, 3.2 mmol) in 1,2-dichloroethane (10 mL) was added and the mixture was stirred for 2 days at room temperature. Insoluble material was collected on a Celite pad and washed with CH_2Cl_2. The combined filtrate and washings washed successively with aq. $NaHCO_3$ and water, dried, and evaporated. Column chromatography of the product, as described in *a*, gave **18** (1.59 g, 52%) and **20** (0.61 g, 20%).

O-α-D-*Xylopyranosyl*-(*1→4*)-D-*glucopyranose* (**2**). — Hydrogenolysis of **18** (1.44 g) followed by column chromatography of the product, as described for the preparation of **1**, afforded amorphous **2** (0.41 g, 85%), $[\alpha]_D^{25}$ +123° (*c* 1.5, H_2O); $R_{maltose}$ 0.91 (l.c.); n.m.r. (D_2O): ^{1}H, δ 5.34 (d, 1 H, $J_{1',2'}$ 3.7 Hz, H-1′), 5.19 (d, 0.4 H, $J_{1,2}$ 4.0 Hz, H-1α), and 4.62 (d, 0.6 H, $J_{1,2}$ 7.9 Hz, H-1β); ^{13}C, δ 100.6 and 100.55 (C-1′), 96.7 (C-1β), 92.8 (C-1α), 77.7 and 77.5 (C-4), 77.15, 75.5, 74.9, 74.2, 73.9, 72.7, 72.2, 70.9, 70.05, 62.9 (C-5′), 61.6 (C-6β), and 61.5 (C-6α).

O-(*2,3,4-Tri*-O-*acetyl*-α-D-*xylopyranosyl*)-(*1→4*)-*1,2,3,6-tetra*-O-*acetyl*-β-D-*glucopyranose* (**19**). — Acetylation of **2** (0.13 g), as described for **1**, afforded **19** (0.21 g, 84%), m.p. 196–197° (from EtOH), $[\alpha]_D^{25}$ +40° (*c* 1.2, $CHCl_3$); n.m.r. ($CDCl_3$; ^{1}H, δ 5.75 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1) and 2.21–1.96 (4 s, 21 H, 7 OAc); ^{13}C, δ 170.25–168.5 (C=O), 95.9 (C-1′), 91.25 (C-1), 75.2 (C-4), 59.4 (C-5′), 62.5 (C-6), and 20.8 and 20.6 ($COCH_3$).

Anal. Calc. for $C_{25}H_{34}O_{17}$: C, 49.51; H, 5.65. Found: C, 49.47; H, 5.70.

Benzyl O-(*2,3,4-tri*-O-*benzyl*-α- *and* β-D-*xylopyranosyl*)-(*1→4*)-*2,3-anhydro*-β-D-*ribopyranoside* (**21** and **22**). — A solution of oxalyl chloride (1.7 mL) in CH_2Cl_2 (10 mL) was added dropwise at 0° to a solution of **15** (3.35 g) in CH_2Cl_2 (30 mL) containing *N,N*-dimethylformamide (0.2 mL). The mixture was kept for 30 min at room temperature and then evaporated. A solution of the residue in 1:1 hexane–EtOAc (20 mL) was filtered through a layer of silica gel (7 g) and the layer was washed with 1:1 hexane–EtOAc (20 mL). The combined filtrate and washings were evaporated to give 2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl chloride (**16**) as a syrup (3.22 g, 92%), $[\alpha]_D^{25}$ +90° (*c* 1.2, $CHCl_3$), which was used in the glycosylation step without purification. N.m.r. ($CDCl_3$): ^1H, δ 5.90 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1); ^{13}C, δ 93.6 (C-1).

A mixture of **8** (1.15 g, 5.2 mmol), $AgClO_4$ (1.95 g, 9.4 mmol), and 2,4,6-trimethylpyridine (1.36 mL, 10.3 mmol) in ether (100 mL) was treated with a solution of **16** (2.95 g, 6.7 mmol) in ether (30 mL) and processed as described for the reaction of **8** with **7**. Column chromatography (50:1→20:1 benzene–EtOAc, stepwise) of the product gave **21** (1.32 g, 41%) and **22** (1.30 g, 40%).

Compound **21**, syrup, had $[\alpha]_D^{25}$ +41° (*c* 0.9, $CHCl_3$), R_F 0.55 (t.l.c. in 10:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 95.4 (C-1′), 94.4 (C-1), 60.4 (C-5′), 59.5 (C-5), 52.6 (C-3), and 49.4 (C-2).

Anal. Calc. for $C_{38}H_{40}O_8$: C, 73.06; H, 6.45. Found: C, 73.50; H, 6.31.

Compound **22** had m.p. 110–111° (from EtOH), $[\alpha]_D^{25}$ +1° (*c* 1.1, $CHCl_3$); R_F 0.46 (t.l.c. in 10:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 104.2 (C-1′), 94.5 (C-1), 63.8 (C-5′), 59.1 (C-5), 52.8 (C-3), and 61.6 (C-2).

Found: C, 73.17; H, 6.53.

Benzyl-O-(*2,3,4-tri*-O-*benzyl*-α-D-*xylopyranosyl*)-(*1→4*)-*3*-O-*benzyl*-β-D-*xylopyranoside* (**23**). — Compound **21** (1.16 g) was treated with benzyl alcoholate anion in benzyl alcohol as described for **9**. Column chromatography (25:1 benzene–EtOAc) of the product gave **23** as a syrup (1.10 g, 81%), $[\alpha]_D^{25}$ +4° (*c* 1.1, $CHCl_3$); R_F 0.43 (t.l.c. in 10:1 benzene–EtOAc), ^{13}C-n.m.r. ($CDCl_3$): δ 101.3 (C-1) and 97.9 (C-1′).

Anal. Calc. for $C_{45}H_{48}O_9$: C, 73.75; H, 6.60. Found: C, 73.91; H, 6.49.

O-α-D-*Xylopyranosyl*-(*1→4*)-D-*xylopyranose* (**3**). — Hydrogenolysis of **23** (0.79 g) followed by column chromatography of the product, as described for the preparation of **1**, gave amorphous **3** (0.27 g, 90%), $[\alpha]_D^{25}$ +108° (*c* 1.5, H_2O); lit.[6] m.p. 170–178°, $[\alpha]_D$ +109.5°; ^1H-n.m.r. (D_2O): δ 5.15 (d, 0.4 H, $J_{1,2}$ 3.7 Hz, H-1α), 5.075 (d, 1 H, $J_{1',2'}$ 3.6 Hz, H-1′), and 4.53 (d, 0.6 H, $J_{1,2}$ 7.9 Hz, H-1β). The ^{13}C-n.m.r. spectrum was identical to that reported[19].

O-(*2,3,4-Tri*-O-*acetyl*-α-D-*xylopyranosyl*)-(*1→4*)-*1,2,3-tri*-O-*acetyl*-β-D-*xylopyranose* (**24**). — Acetylation of **23**, as described for **1**, afforded **24** (0.17 g, 85%), m.p. 136–137° (from MeOH), $[\alpha]_D^{25}$ +46° (*c* 1.1, $CHCl_3$); lit. m.p. 135.5–136.5°, $[\alpha]_D$ +45.7° (ref. 6); m.p. 135°, $[\alpha]_D^{20}$ +44.4° (ref. 20).

Benzyl O-(*2,3,4,6-tetra*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,3,6-tri*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→4*)-*2,3-anhydro*-β-D-*ribopyranoside* (**26**) — A mixture of **8** (0.81 g, 3.6 mmol), $AgClO_4$ (1.18 g, 5.7 mmol), and 2,4,6-trimethylpyridine (0.82 mL, 6.2 mmol) in ether (80 mL) was treated with a solution of **25** (4.70 g, 4.7 mmol) in

ether (40 mL). Processing of the mixture as described for the reaction of **8** with **7**, followed by column chromatography (30:1 benzene–EtOAc) of the product, afforded **26** as a syrup (2.70 g, 63%), $[\alpha]_D^{25}$ +52° (*c* 1.2, $CHCl_3$), R_F 0.53 (t.l.c. in 10:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 96.6 (C-1″), 95.1 (C-1′), and 94.45 (C-1), 68.3 and 68.1 (C-6,6′), 59.5 (C-5), 52.7 (C-3), and 49.2 (C-2).

Anal. Calc. for $C_{73}H_{76}O_{14}$: C, 74.47; H, 6.51. Found: C, 74.60; H, 6.66.

Benzyl O-(*2,3,4,6-tetra*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,3,6-tri*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→4*)-*3*-O-*benzyl*-β-D-*glucopyranoside* (**27**). — Treatment of **26** (2.50 g) with benzyl alcoholate anion in benzyl alcohol as described for **9**, followed by column chromatography (20:1 benzene–EtOAc) of the product, gave **27** as a syrup (2.21 g, 81%), $[\alpha]_D^{25}$ +33° (*c* 1.5, $CHCl_3$); R_F 0.43 (t.l.c. in 10:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 101.3 (C-1), 97.6 (C-1″), and 96.8 (C-1′).

Anal. Calc. for $C_{80}H_{84}O_{15}$: C, 74.75; H, 6.59. Found: C, 75.08; H, 6.67.

O-α-D-*Glucopyranosyl*-(*1→4*)-O-α-D-*glucopyranosyl*-(*1→4*)-D-*xylopyranose* (**4**). — Hydrogenolysis of **27** (2.06 g) as described for **11**, followed by column chromatography (15:10:1 → 5:5:1 $CHCl_3$–MeOH–H_2O, stepwise) of the product, afforded amorphous **4** (0.67 g, 88%), $[\alpha]_D^{23}$ +141.5° (*c* 1.1, H_2O); $R_{maltotriose}$ 0.90 (l.c.); n.m.r. (D_2O): ^{1}H, δ 5.36 (d, 1 H, $J_{1'',2''}$ 3.7 Hz, H-1″), 5.15 (d, 0.4 H, $J_{1,2}$ 7.9 Hz, H-1α), 5.12 (d, 1 H, $J_{1',2'}$ 3.7 Hz, H-1′), and 4.535 (d, 0.6 H, $J_{1,2}$ 7.9 Hz, H-1β); ^{13}C, δ 100.7 and 100.6 (C-1′,1″), 97.3 (C-1β), 92.85 (C-1α), 79.1 (C-4′), 77.8 and 77.4 (C-4), 75.7, 74.7, 74.1, 73.8, 73.6, 72.6, 72.3, 70.05, 71.7, 70.2, 65.1 (C-5β), 61.4 (C-6,6′), and 60.9 (C-5α).

Benzyl O-(*2,3,4,6-tetra*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→4*)-O-(*2,3-di*-O-*benzyl*-α-D-*glucopyranosyl*)-(*1→4*)-*2,3,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**29**). — The product obtained by treatment of a mixture of **28** (0.49 g, 574 μmol), $AgClO_4$ (0.24 g, 1.2 mmol), and 2,4,6-trimethylpyridine (0.17 mL, 1.3 mmol) in ether (10 mL) with a solution of **7** (0.42 g, 751 μmol) in ether (5 mL), as described previously, was subjected to column chromatography (30:1 benzene–EtOAc) to give **29** as a syrup (0.58 g, 73%), $[\alpha]_D^{26}$ +28° (*c* 1.1, $CHCl_3$); R_F 0.43 (t.l.c. in benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 102.1 (C-1), 98.8 (C-1″), 96.3 (C-1′), 69.2 and 68.3 (C-6,6″), and 61.4 (C-5′).

Anal. Calc. for $C_{87}H_{90}O_{15}$: C, 75.96; H, 6.59. Found: C, 76.15; H, 6.80.

Methyl 2,3,4-tri-O-*benzoyl*-*1*-*thio*-α-D-*arabinopyranoside* (**31**). — A solution of **30** (19.5 g) in acetone (75 mL) was added dropwise at 0° to a mixture of 15% aq. NaSMe (24 mL) and acetone (150 mL). The mixture was stirred for 40 min at room temperature and the acetone was evaporated. The residue was extracted with $CHCl_3$ and the extract was washed with water, dried, and evaporated. The residue was crystallized from EtOH and recrystallized from EtOH–acetone to give **31** (13.5 g, 74%), m.p. 119–120°, $[\alpha]_D^{20}$ −180° (*c* 1.1, $CHCl_3$); n.m.r. ($CDCl_3$): ^{1}H, δ 8.22–7.22 (m, 15 H, 3 Ph), 4.79 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), and 2.29 (s, 3 H, SMe); ^{13}C, δ 165.3, 165.25, and 165.1 (C=O), 83.75 (C-1), 71.3, 68.8, and 68.5 (C-2,3,4), 65.8 (C-5), and 12.2 (SMe).

Anal. Calc. for $C_{27}H_{24}O_7S$: C, 65.84; H, 4.91. Found: C, 65.92; H, 5.06.

Benzyl O-(*2,3,4-tri*-O-*benzoyl*-α-D-*arabinopyranosyl*)-(*1→4*)-*2,3,6*-tri-O-*benzyl*-β-D-*glucopyranoside* (**32**). — A solution of **31** (6.68 g, 13.6 mmol) in CH_2Cl_2 (50 mL) was added dropwise at 0° under Ar to a stirred mixture of **17** (5.64 g, 10.4 mmol), DMTST

(10.5 g, 40.6 mmol), and powdered molecular sieve 4A (60 g) in CH_2Cl_2 (200 mL). The mixture was stirred for 2 h at room temperature, filtered through a Celite pad, and the solids were washed with CH_2Cl_2. The combined filtrate and washings were washed successively with aq. $NaHCO_3$ and water, dried, and evaporated. Column chromatography (20:1 benzene–EtOAc) of the product gave amorphous **32** (10.28 g, 80%), $[\alpha]_D^{20}$ −105° (*c* 1.1, $CHCl_3$); R_F 0.55 (t.l.c. in 10:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 165.4, 165.3, and 165.0 (C=O), 102.0 (C-1), 100.5 (C-1′), 68.9 (C-6), and 63.3 (C-5′).

Benzyl O-α-D-*arabinopyranosyl*-(*1*→*4*)-*2,3,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**33**). — A solution of **32** (8.95 g) in MeOH (60 mL) and CH_2Cl_2 (20 mL) was treated with methanolic M NaOMe (0.1 mL) and kept for 2 h at room temperature. The solution was made neutral with Amberlite IR-120 (H^+) resin, the mixture filtered, and the filtrate evaporated. Crystallization of the residue from EtOH afforded **33** (5.62 g, 92%), m.p. 171–173°, $[\alpha]_D^{26}$ +10° (*c* 0.2, $CHCl_3$); ^{13}C-n.m.r. [$(CD_3)_2SO$]: δ 103.3 (C-1), 101.6 (C-1′), 69.4 (C-6), and 65.8 (C-5′).

Anal. Calc. for $C_{39}H_{44}O_{10}$: C, 69.63; H, 6.59. Found: C, 69.75; H, 6.64.

Benzyl O-(*3,4*-O-*isopropylidene*-α-D-*arabinopyranosyl*)-(*1*→*4*)-*2,3,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**34**). — A mixture of **33** (5.14 g), 2,2-dimethoxypropane (10 mL), and $TsOH \cdot H_2O$ (0.1 g) in *N,N*-dimethylformamide (20 mL) was stirred for 3 h at room temperature. The mixture was diluted with CH_2Cl_2, washed successively with aq. $NaHCO_3$ and water, dried, and evaporated. Crystallization of the residue from MeOH gave **34** (4.68 g, 86%), m.p. 136–137°. $[\alpha]_D^{26}$ −9° (*c* 0.6, $CHCl_3$); n.m.r. ($CDCl_3$): ^{1}H, δ 7.39–7.20 (m, 20 H, 4 Ph), and 1.51 and 1.32 (2 s, each 3 H, CMe_2); ^{13}C, δ 138.4, 138.1, 137.8, and 137.2 (aromatic C-1). 109.85 (CMe_2), 102.65 and 102.2 (C-1,1′), 69.4 (C-6), 63.2 (C-5′), and 27.9 and 25.9 (CMe_2).

Anal. Calc. for $C_{42}H_{48}O_{10}$: C, 70.77; H, 6.79. Found: C, 70.71; H, 6.85.

Benzyl O-(*3,4*-O-*isopropylidene*-*2*-O-*methylsulfonyl*-α-D-*arabinopyranosyl*)-(*1*→*4*)-*2,3,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**35**). — A solution of **34** (4.44 g) in pyridine (20 mL) was cooled to 0°, treated with CH_3SO_2Cl (1.46 mL), and kept for 3 h at room temperature. The mixture was poured into ice–water and extracted with $CHCl_3$. The extract was washed successively with cold dil. HCl, aq. $NaHCO_3$, and water, dried, and evaporated. Column chromatography (15:1 benzene–EtOAc) of the product gave amorphous **35** (4.18 g, 84%), $[\alpha]_D^{26}$ −15° (*c* 1.2, $CHCl_3$); R_F 0.37 (t.l.c. in 10:1 benzene–EtOAc); n.m.r. ($CDCl_3$): ^{1}H, δ 7.39–7.19 (m, 20 H, 4 Ph), 3.05 (s, 3 H, OMs), and 1.56 and 1.32 (2 s, each 3 H, CMe_2); ^{13}C, δ 138.8, 138.6, 138.2, and 137.1 (aromatic C-1), 110.6 (CMe_2), 102.0 (C-1), 99.0 (C-1′), 69.5 (C-6), 62.9 (C-5′), 39.2 (CH_3SO_2), and 27.6 and 26.0 (CMe_2).

Benzyl O-(*2*-O-*methylsulfonyl*-α-D-*arabinopyranosyl*)-(*1*→*4*)-*2,3,6-tri*-O-*benzyl*-β-D-*glucopyranoside* (**36**). — To a solution of **35** (3.98 g) in AcOH (50 mL) at 90° was added water (20 mL) in small portions. The mixture was stirred for 20 min, and then cooled, and concentrated. The last traces of solvents were removed by repeated evaporation of PhMe from the residue, column chromatography of which then gave amorphous **36** (3.39 g, 90%), $[\alpha]_D^{26}$ +1° (*c* 1.4, $CHCl_3$); R_F 0.47 (t.l.c. in 9:1 benzene–EtOH); n.m.r. ($CDCl_3$): ^{1}H, δ 7.38–7.11 (m, 20 H, 4 Ph) and 3.01 (s, 3 H, OMs); ^{13}C, δ 101.9 (C-1),

99.6 (C-1′), 68.75 (C-6), 65.8 (C-5′), and 38.6 (CH_3SO_2).

Benzyl O-(*2,3-anhydro-α-*D-*ribopyranosyl*)-(*1→4*)-*2,3,6-tri*-O-*benzyl-β-*D-*glucopyranoside* (**37**). — Compound **36** (3.15 g) was dissolved in MeOH (60 mL) containing Na (0.3 g). The solution was kept overnight at room temperature, and then cooled, and made neutral with dil. H_2SO_4. The mixture was concentrated and the residue was extracted with $CHCl_3$. The extract was washed with water, dried, and evaporated. Crystallization of the residue from EtOH gave **37** (2.28 g, 83%), m.p. 129–130°, $[\alpha]_D^{26}$ +18° (*c* 1.0, $CHCl_3$); ^{13}C-n.m.r. ($CDCl_3$): δ 102.4 (C-1), 94.8 (C-1′), 69.4 (C-6), 61.1 (C-5′), 54.7 (C-3′), and 53.3 (C-2′).

Anal. Calc. for $C_{39}H_{42}O_9$: C, 71.54; H, 6.47. Found: C, 71.50; H, 6.45.

Benzyl (2,3,4,6-tetra-O-*benzyl-α-*D-*glucopyranosyl*)-(*1→4*)-O-(*2,3-anhydro-α-*D-*ribopyranosyl*)-(*1→4*)-*2,3,6-tri*-O-*benzyl-β-*D-*glucopyranoside* (**38**). — The product obtained by treatment of a mixture of **37** (1.65 g, 2.5 mmol), $AgClO_4$ (1.02 g, 4.9 mmol), and 2,4,6-trimethylpyridine (0.71 mL, 5.4 mmol) in ether (40 mL) and 1,2-dimethoxyethane (15 mL) with a solution of **7** (1.83 g, 3.3 mmol) in ether (20 mL), as described previously, was subjected to column chromatography (30:1 → 20:1 benzene–EtOAc, stepwise) to give **38** (1.80 g, 67%), m.p. 136–140° (from EtOH–CH_2Cl_2), $[\alpha]_D^{25}$ +53.5° (*c* 1.0, $CHCl_3$); ^{13}C-n.m.r. ($CDCl_3$): δ 102.4 (C-1), 96.3 (C-1″), 94.2 (C-1′), 69.4 (C-6), 68.3 (C-6″), 58.25 (C-5′), 54.0 (C-3), and 50.4 (C-2).

Anal. Calc. for $C_{73}H_{76}O_{14}$: C, 74.47; H, 6.51. Found: C, 74.32; H, 6.44.

Benzyl (2,3,4,6-tetra-O-*benzyl-α-*D-*glucopyranosyl*)-(*1→4*)-O-(*3-*O-*benzyl-α-*D-*xylopyranosyl*)-(*1→4*)-*2,3,6-tri*-O-*benzyl-β-*D-*glucopyranoside* (**39**). — The product obtained by treatment of **38** (1.61 g) with benzyl alcoholate anion in benzyl alcohol, as described for **9**, was subjected to column chromatography (20:1 benzene–EtOAc) to give **39** as a syrup (1.34 g, 76%), $[\alpha]_D^{25}$ +21° (*c* 1.4, $CHCl_3$); R_F 0.33 (t.l.c. in 10:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 102.4 (C-1), 100.7 (C-1″), 97.9 (C-1′), 69.1 and 68.0 (C-6,6″), and 61.5 (C-5′).

Anal. Calc. for $C_{80}H_{84}O_{15}$: C, 74.75; H, 6.59. Found: C, 74.95; H, 6.69.

O-α-D-*Glucopyranosyl-(1→4)*-O-α-D-*xylopyranosyl-(1→4)*-D-*glucopyranose* (**5**). — Hydrogenolysis of **29** (0.37 g) followed by column chromatography of the product, as described for the preparation of **4**, gave amorphous **5** (0.12 g, 85%), $[\alpha]_D^{25}$ +142° (*c* 1.4, H_2O); $R_{maltotriose}$ 0.94 (l.c.); n.m.r. (D_2O): ^{1}H, δ 5.31 (d, 1 H, $J_{1'',2''}$ 3.7 Hz, H-1″), 5.18 (d, 0.4 H, $J_{1,2}$ 4.0 Hz, H-1α), 5.10 (d, 1 H, $J_{1',2'}$ 4.0 Hz, H-1′), and 4.61 (d, 0.6 Hz, $J_{1,2}$ 7.9 Hz, H-1β); ^{13}C, δ 100.85 (C-1″), 100.4 and 100.3 (C-1′), 96.7 (C-1β), 92.8 (C-1α), 78.8 (C-4′), 78.0 and 77.75 (C-4), 77.1, 75.4, 74.9, 74.1, 73.7, 73.3, 72.7, 72.45, 72.3, 72.2, 70.8, 70.4, 62.0 (C-6″), 61.6 (C-6β), and 61.5 (C-5′, 6α).

Compound **5** (0.41 g, 85%) was also obtainable from **39** (1.12 g) by an analogous procedure.

Benzyl O-(*2,3-di*-O-*benzyl-α-*D-*glucopyranosyl*)-(*1→4*)-*2,3,6-tri*-O-*benzyl-β-*D-*glucopyranoside* (**41**). — A solution of **40** (4.13 g) in AcOH (50 mL) and acetone (25 mL) was boiled under reflux, water (25 mL) was added dropwise, and the mixture was stirred for 40 min under reflux. Processing of the mixture, as described for **35**, and crystallization of the residue from EtOH gave **41** (3.31 g, 88%), m.p. 113–114°, $[\alpha]_D^{25}$ +13° (*c* 1.1,

$CHCl_3$); ^{13}C-n.m.r. ($CDCl_3$): δ 102.1 (C-1), 96.3 (C-1′), 68.8 (C-6), and 62.1 (C-6′).

Anal. Calc. for $C_{54}H_{58}O_{11}$: C, 73.45; H, 6.62. Found: C, 73.52; H, 6.70.

Benzyl O-*(2,3,6-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside* (**42**). — A mixture of **41** (3.15 g) and Bu_2SnO (0.98 g) in benzene (60 mL) was boiled for 2 h under reflux with azeotropic removal of water. Tetrabutylammonium bromide (1.31 g) and $PhCH_2Br$ (0.92 mL) were added and the mixture was stirred overnight under reflux. The mixture was evaporated and a solution of the residue in CH_2Cl_2 was washed with water, dried, and evaporated. Column chromatography (20:1 benzene–EtOAc) of the product gave **42** as a syrup (2.98 g, 86%), $[\alpha]_D^{25}$ +12° (*c* 1.3, $CHCl_3$); R_F 0.43 (t.l.c. in 10:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 102.2 (C-1), 96.5 (C-1′), and 69.7 and 69.2 (C-6,6′).

Anal. Calc. for $C_{61}H_{64}O_{11}$: C, 75.29; H, 6.63. Found: C, 75.51; H, 6.79.

Benzyl O-*(2,3,4-tri-*O*-benzyl-α-*D*-xylopyranosyl)-(1→4)-*O*-(2,3,6-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1→4)-2,3,6-tri-*O*-benzyl-β-*D*-glucopyranoside* (**43**). — The product obtained by treatment of a mixture of **42** (2.18 g, 2.2 mmol), $CuBr_2$ (1.12 g, 5 mmol), Bu_4NBr (0.28 g, 840 μmol), and powdered molecular sieve 4A (5 g) in 1,2-dichloroethane (25 mL) and *N*,*N*-dimethylformamide (5 mL) with **14** (1.51 g, 3.4 mmol), as described previously, was subjected to column chromatography (30:1 benzene–EtOAc) to give **43** as a syrup (1.47 g, 48%), $[\alpha]_D^{25}$ +35° (*c* 1.5, $CHCl_3$); R_F 0.45 (t.l.c. in 15:1 benzene–EtOAc); ^{13}C-n.m.r. ($CDCl_3$): δ 102.2 (C-1), 96.5 (C-1″), 96.2 (C-1′), 69.0 (C-6,6′), and 60.8 (C-5′).

Anal. Calc. for $C_{87}H_{90}O_{15}$: C, 75.96; H, 6.59. Found: C, 76.27; H, 6.67.

O-α-*D*-*Xylopyranosyl-(1→4)*-O-α-*D*-*glucopyranosyl-(1→4)*-*D*-*glucopyranose* (**6**). — Hydrogenolysis of **43** (1.29 g), followed by column chromatography of the product as described for the preparation of **4**, gave amorphous **6** (0.37 g, 84%), $[\alpha]_D^{23}$ +152° (*c*1.05, H_2O); $R_{maltotriose}$ 0.84 (l.c.); n.m.r. (D_2O): ^{1}H, δ 5.38 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1 or 1″), 5.345 (d, 1 H, $J_{1,2}$ 3.05 Hz, H-1′ or 1″), 5.20 (d, 0.4 H, $J_{1,2}$ 4.0 Hz, H-1α), and 4.63 (d, 0.6 H, $J_{1,2}$ 7.9 Hz, H-1β); ^{13}C, δ 100.8 (C-1″), 100.5 and 100.4 (C-1′), 96.7 (C-1β), 92.8 (C-1α), 78.0, 77.8, and 77.5 (C-4,4′), 77.1, 75.5, 74.9, 74.3, 74.1, 73.9, 72.65, 72.5, 72.4, 72.2, 72.1, 70.85, 70.0, and 63.0, 61.6, and 61.4 (C-6,6′,5″).

REFERENCES

1 K. Takeo, M. Nakagen, Y. Teramoto, and Y. Nitta, *Carbohydr. Res.*, 201 (1990) 261–275.
2 A. Suzuki, K. Takeo, and Y. Nitta, *Nippon Nōgeikagaku Kaishi*, 64 (1990) 420.
3 K. Hiromi, Y. Nitta, C. Numata, and S. Ono, *Biochem. Biophys. Acta*, 302 (1973) 362–375; K. Hiromi, M. Ohnishi, and A. Tanaka, *Mol. Cell. Biochem.*, 51 (1983) 79–95.
4 T. Suganuma, M. Ohnishi, K. Hiromi, and Y. Morita, *Agric. Biol Chem.*, 44 (1980) 1111–1117; Y. Isoda and Y. Nitta, *J. Biochem. (Tokyo)*, 99 (1968) 1631–1637.
5 E. W. Putman, C. F. Litt, and W. Z. Hassid., *J. Am. Chem. Soc.*, 77 (1955) 4351–4353.
6 J. Hirsch, P. Kováč, and E. Pétraková, *Carbohydr. Res.*, 106 (1982) 203–216.
7 C. E. Weill and R. Rebhann, *Carbohydr. Res.*, 3 (1966) 242–245.
8 P. J. Garegg, *Acta. Chem. Scand.*, 14 (1960) 957–958.
9 K. Igarashi, J. Irisawa, and T. Homma, *Carbohydr. Res.*, 39 (1975) 213–225; 39 (1975) 341–345.
10 K. Bock and C. Petersen, *Adv. Carbohydr. Chem. Biochem.*, 41 (1983) 27–66; K. Bock, C. Petersen, and H. Petersen, *ibid.*, 42 (1984) 193–225.
11 P. Kováč, J. Hirsch, V. Kovácik, and P. Kočiš, *Carbohydr. Res.*, 85 (1980) 41–49.

12 M. L. Wolfrom and A. Thompson, *Methods Carbohydr. Chem.*, 2 (1963) 211–215.
13 J. S. Brimacombe, *Methods Carbohydr. Chem.*, 6 (1972) 376–378.
14 J.-M. Petit and P. Sinaÿ, *Carbohydr. Res.*, 64 (1978) 9–16; K. Takeo, K. Okushio, K. Fukuyama, and T. Kuge, *ibid.*, 121 (1983) 167–173.
15 H. Löhn, *J. Carbohydr. Chem.*, 6 (1987) 301–306.
16 S. Sato, M. Mori, Y. Ito, and T. Ogawa, *Carbohydr. Res.*, 155 (1986) c6–c10.
17 S. Tejima, R. K. Ness, R. L. Kaufman, and H. G. Fletcher, Jr., *Carbohydr. Res.*, 7 (1968) 485–490.
18 T. Iversen and D. R. Bundle, *Carbohydr. Res.*, 103 (1982) 29–40.
19 E. Pétraková and P. Kováč, *Chem. Zvesti*, 35 (1981) 551–556.
20 J.-P. Utille and P. J. A. Vottero, *Carbohydr. Res.*, 53 (1977) 259–262.
21 K. Takeo and T. Imai, *Carbohydr. Res.*, 165 (1987) 123–128.
22 H. G. Fletcher, Jr., and C. S. Hudson, *J. Am. Chem. Soc.*, 72 (1950) 4173–4177.
23 P. Fügedi and P. J. Garegg, *Carbohydr. Res.*, 149 (1986) c9–c12.
24 A. Lipták, I. Jodál, and P. Nánási, *Carbohydr. Res.*, 52 (1976) 17–22.
25 S. David, A. Thieffry, and A. Veyrières, *J. Chem. Soc., Perkin Trans. 1*, (1981) 1796–1801.