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SYNTHESIS OF BENZYL 2-AZIDO-2-DEOXY-4-*O*-β-D-GLUCOPYRANOSYL-α-D-GLUCOPYRANOSIDE AND 1,6-ANHYDRO-2-AZIDO-2-DEOXY-4-*O*-β-D-GLUCOPYRANOSYL-β-D-GLUCOPYRANOSE*

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ABSTRACT

The title compounds were prepared from cellobiose by means of two series of transformations. One series entailed the azidonitration of 3,6-di-*O*-acetyl-1,5-anhydro-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-D-*arabino*-hex-1-enitol to give 3,6-di-*O*-acetyl-2-azido-2-deoxy-4-*O*-(tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranosyl nitrate, which was then converted into the benzyl α-glycoside. Minor by-products of the azidonitration reaction were also identified. For the second synthesis, 1,6-anhydro-β-cellobiose was converted into 1,6-anhydro-4-*O*-(4,6-*O*-isopropylidene-β-D-glucopyranosyl)-β-D-glucopyranose (**15**). The azido function was then introduced at the C-2 position of the 1,6-anhydro residue, by a displacement reaction involving the 2,3-anhydro-D-*manno* analog of **15** as an intermediate compound.

INTRODUCTION

The ready availability of cellobiose (**1**) and various derivatives of it, renders compounds in this disaccharide series potentially suitable for the synthesis of oligosaccharides related structurally to some glycosaminoglycans. Hence, in order to transform **1** into a disaccharide sequence found in heparin (**2**) and heparan sulfate (**3**), the only major alteration required is the replacement of O-2 of **1** by an amino function, with retention of configuration. The present study deals with two procedures for the appropriate introduction of a 2-azido group which, in turn, may easily be reduced to an amino function as in **2** and **3**.

Synthesis of benzyl 2-azido-2-deoxy-4-O-β-D-glucopyranosyl-α-D-glucopyranoside (**13**). — In one procedure, 3,6-di-*O*-acetyl-1,5-anhydro-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-D-*arabino*-hex-1-enitol[1,2] (**4**) was converted into 3,6-di-*O*-acetyl-2-azido-2-deoxy-4-*O*-(tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranosyl nitrate (**5**), by reaction[3,4] with ceric ammonium nit-

*Dedicated to Professor Raymond U. Lemieux.

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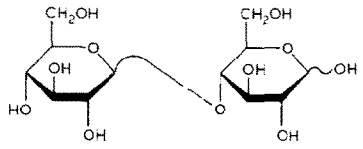

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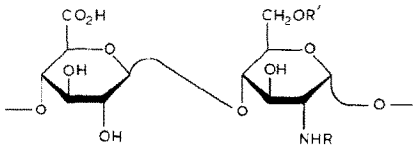

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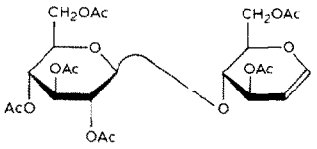
3 R = Ac, R′ = H



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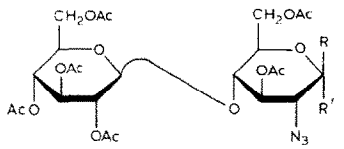
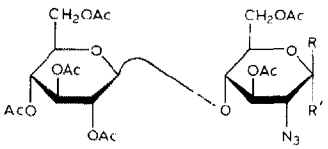
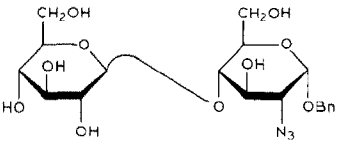


5 R = ONO_2, R′ = H
6 C-2 epimer of 5
7 R = H, R′ = ONO_2
8 R = H, R′ = Cl
9 R = H, R′ = OBn
10 R = OBn, R′ = H



11 R = H, R′ = NHAc
12 R = NHAc, R′ = H



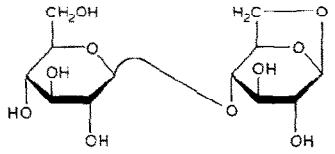
13

rate and sodium azide in acetonitrile. Several other products were formed in this reaction, by analogy with its application[4] to 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*lyxo*-hex-1-enitol, although the mixture was readily separated by a combination of column chromatography and fractional crystallization. Disaccharide **5**, which comprised about 35% of the mixture, was eluted together with 15% of (probably) the 2-azido-2-deoxy-D-*manno* epimer (**6**), followed by 15% of the α anomer of **5** (*i.e.*, **7**) and, finally, 35% of a 2:1 mixture of α- and β-glycosylamine derivatives **11** and **12**, which were separated subsequently on a second chromatographic column. Compounds **5**, **7**, **11**, and **12**, all of which were crystalline, were characterized principally by ^{1}H-n.m.r. spectroscopy.

For prospective use in the synthesis of blocks of such sequences as **2**, an α-chloride **8** was prepared (in 84% yield) by treament of **5** with tetraethylammonium chloride in acetonitrile. In a model glycoside synthesis, the reaction of **8** with benzyl alcohol, promoted by silver carbonate–silver triflate, afforded a 2:1 mixture of the benzyl α,β-glycosides **9** and **10**, which were fractionated by preparative t.l.c. Far higher selectivity in favor of the α anomer resulted when the nitrate **5** (or **7**) was treated with benzyl alcohol, in the presence of bromide ion and 2,4,6-trimethylpyridine, which afforded **9** almost exclusively. *O*-Deacetylation of **9** then

gave crystalline benzyl 2-azido-2-deoxy-4-*O*-β-D-glucopyranosyl-α-D-glucopyranoside (**13**).

Kinetic acetonation of 1,6-anhydro-β-cellobiose (**14**). — In the second reaction series, kinetically-controlled acetonation[5] of 1,6-anhydro-β-cellobiose[6] (**14**) with 2-methoxypropene was carried out, affording the 4′,6′-*O*-isopropylidene derivative (**15**) in 87% yield. This amorphous product was characterized further as the crystalline tetraacetate (**16**). Two minor acetonation products were shown to be, probably, the 2′,3′:4′,6′-di-*O*-isopropylidene derivative (**17**, yield, 5%) and the 2,2′:4′,6′-di-*O*-isopropylidene derivative (**19**, yield, 3%), both of which afforded crystalline diacetates (**18** and **20**, respectively).



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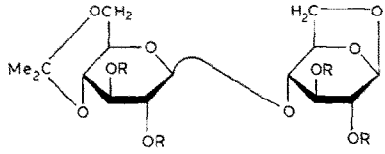

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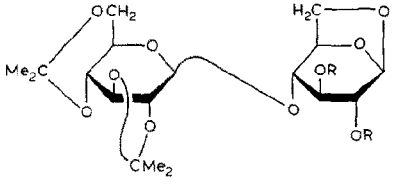

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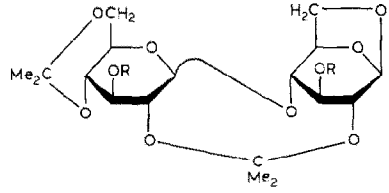

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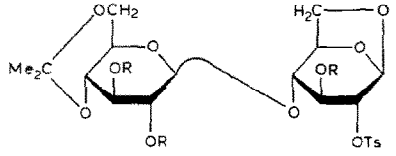

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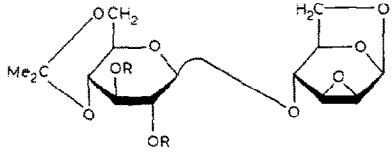

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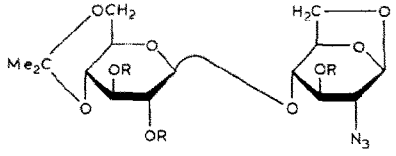

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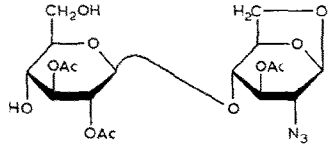

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Synthesis of 2,3-di-O-acetyl-1,6-anhydro-2-azido-2-deoxy-4-O-(2,3-di-O-acetyl-β-D-glucopyranosyl)-β-D-glucopyranose (**27**). — An azido function was introduced at the 2-position of *O*-isopropylidene derivative **15**, by analogy with the synthesis[7] of 1,6-anhydro-2-azido-2-deoxy-β-D-glucopyranose. In a reaction with 1.1 equiv. of *p*-toluenesulfonyl chloride, **15** gave a 60% yield of the 2-*O*-tosyl compound (**21**), purified further in the form of its triacetate (**22**). In subsequent steps, **21** was quantitatively converted by treatment with sodium methoxide into the 2,3-anhydro-D-mannose derivative **23** (characterized as a diacetate **24**) which, with sodium azide in aqueous ethanol, yielded the 2-azido product (**25**; yield, 77%), characterized as triacetate **26**.

The corresponding diol (**27**), prepared by hydrolytic removal of the *O*-isopropylidene group of **26**, is potentially suited for the preparation of multiple sequences of **2** or **3**, because it offers possibilities both for glycosidation at O-4′ and oxidation at C-6′.

EXPERIMENTAL

General methods. — Optical rotations were determined at room temperature. I.r. spectra were recorded with a Unicam SP-200 G grating spectrophotometer. N.m.r. spectra (^{1}H and ^{13}C) were recorded with a Bruker WH-90 or Varian XL-200 spectrometer; chemical shifts (δ) are reported with reference to tetramethylsilane. Solutions were usually evaporated at a bath temperature <40° under diminished pressure. Silica gel (230–400 mesh) was used for column chromatography. Microanalyses were performed by Guelph Analytical Laboratories, Guelph, Ont.

Azidonitration of 3,6-di-O-acetyl-1,5-anhydro-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-D-arabino-hex-1-enitol (**4**). — A solution of **4** (4.0 g, 7.14 mmol) in acetonitrile (36 mL) was added to a mixture of ceric ammonium nitrate (11.7 g, 3 eq.) and sodium azide (0.7 g, 1.5 eq.) at −15– −20°. The cooled mixture was stirred for 8 h, following which ice–water (100 mL) and chloroform (50 mL) were introduced. The organic layer was separated, the aqueous layer was extracted with chloroform, the combined organic layers were washed with ice–water (2 × 100 mL), dried, and evaporated, giving a white foam (5.4 g). Column chromatography using mixtures of ethyl acetate–benzene ranging from 1:3 to 1:1 yielded two fractions of material (2.7 g and 0.8 g, respectively), following which a third fraction (1.9 g) was eluted with 9:1 benzene–ethanol.

3,6-Di-O-acetyl-2-azido-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-β-D-glucopyranosyl nitrate (**5**). — The product eluted initially was crystallized from dichloromethane–hexane (yield, 1.2 g, 25.5%); m.p. 148°, $[\alpha]_D^{20}$ −9.85° (*c* 1.4, chloroform); ν_{max}^{KBr} 2110 (N_3), 1658 cm^{-1} (ONO_2); ^{1}H-n.m.r.: δ 5.56 (d, 1 H, H-1), 4.51 (d, 1 H , H-1′), 3.60 (dd, 1 H, H-2), 2.13 (s, 6 H, 2 OAc), 2.10, 2.03, 2.02, and 1.99 (4 s, 4 × 3 H, 4 OAc), $J_{1,2}$ 8.8, $J_{1,2}$ 7.9 Hz.

Anal. Calc. for $C_{24}H_{32}N_4O_{18}$: C, 43.38; H, 4.86; N, 8.43. Found: C, 43.30; H, 5.13; N, 8.32.

According to its ^{1}H-n.m.r. spectrum, the amorphous material consisted of a 2:3 mixture of **5** and the D-*manno* epimer (**6**) (δ 6.14; $J_{1,2}$ 3.1 Hz).

3,6-Di-O-acetyl-2-azido-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α-D-glucopyranosyl nitrate (**7**). — On recrystallization from dichloromethane–hexane, the material in the second eluate had m.p. 160–161°; $[\alpha]_D^{20}$ +26.7° (*c* 1.2, chloroform); ν_{max}^{KBr} 2100 (N_3), 1645 cm^{-1} (ONO_2); ^{1}H-n.m.r.: δ 5.86 (d, 1 H, H-1), 5.41 (d, 1 H, H-3), 4.42 (d, 1 H, H-1′), 3.62 (dd, 1 H, H-4), 3.10 (dd, 1 H, H-2′), 1.94, 1.85, 1.80, 1.79, 1.76, and 1.75 (6 s, 6 × 3 H, 6 OAc), $J_{1,2}$ 4.3, $J_{3,4}$ 9.3, $J_{1',2'}$ 7.8, $J_{4,3} = J_{4,5}$ = 9.3, and $J_{2,3}$ 10.7 Hz.

Anal. Calc. for $C_{24}H_{32}N_4O_{18}$: C, 43.38; H, 4.86; N, 8.43. Found: C, 43.36; H, 4.92; N, 8.42.

1-N-Acetyl-3,6-di-O-acetyl-2-azido-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α- (**11**) *and -β-D-glucopyranosylamine* (**12**). — The third fraction isolated was re-chromatographed with 9:1 benzene–ethanol, to yield **11** (0.52 g, 11.0%); m.p. 126–127°, $[\alpha]_D^{20}$ +25.1° (*c* 2.7, chloroform); ν_{max}^{KBr} 3280 (NH), 2100 cm^{-1} (N_3); ^{1}H-n.m.r.: δ 7.19 [d, 1 H, NH (D_2O-exchanged)], 5.76 (dd, 1 H, H-1), $J_{NH,1}$ 7.6, and $J_{1,2}$ 5.4 Hz.

Anal. Calc. for $C_{26}H_{36}N_4O_{16}$: C, 47.27; H, 5.49; N, 8.48. Found: C, 47.13; H, 5.63; N, 8.64.

A mixture of **11** and **12** was then obtained, followed by **12** which, when recrystallized from methanol–diethyl ether–hexane, had m.p. 186–186.5° (yield, 0.25 g, 5.3%); $[\alpha]_D^{20}$ −8.1° (*c* 1.3, chloroform); ν_{max}^{KBr} 3270 (NH), 2100 cm^{-1} (N_3); ^{1}H-n.m.r. (3:1 benzene-d_6–$CDCl_3$): δ 6.17 [d, 1 H, NH (D_2O-exchanged)], $J_{NH,1}$ 9.3 Hz.

Anal. Calc. for $C_{26}H_{36}N_4O_{16}$: C, 47.27; H, 5.49; N, 8.48. Found: C, 47.15; H, 5.71; N, 8.41.

3,6-Di-O-acetyl-2-azido-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α-D-glucopyranosyl chloride (**8**). — To a solution of **5** (0.78 g, 1.17 mmol) in acetonitrile (18 mL) was added tetraethylammonium chloride (0.75 g, 4.56 mmol); 6 h later the solution was evaporated, and the residue dissolved in chloroform (25 mL). The chloroform solution was washed with water (2 ×), dried, evaporated to a solid that was recrystallized from dichloromethane–diethyl ether (yield, 0.63 g, 84%); m.p. 188–189° (dec.), $[\alpha]_D^{20}$ +64.3° (*c* 0.6, chloroform); ν_{max}^{KBr} 2090 cm^{-1} (N_3); ^{1}H-n.m.r.: δ 6.07 (d, 1 H, H-1), 5.48 (dd, 1 H, H-3), 4.53 (d, 1 H, H-1′), 3.80 (dd, 1 H, H-4), 3.73 (dd, 1 H, H-2), 2.12, 2.11, 2.09, 2.05, 2.03, and 1.99 (6 s, 6 × 3 H, 6 OAc), $J_{1,2}$ 3.8, $J_{3,4}$ 9.5, $J_{1',2'}$ 7.8, $J_{4,3} = J_{4,5}$ 9.5, and $J_{2,3}$ 10.3 Hz.

Anal. Calc. for $C_{24}H_{32}ClN_3O_{15}$: C, 45.18; H, 5.06; Cl, 5.56; N, 6.59. Found: C, 45.06; H, 5.35; Cl, 5.74; N, 7.01.

Benzyl 3,6-di-O-acetyl-2-azido-2-deoxy-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-α- (**9**) *and -β-D-glucopyranoside* (**10**). — A solution of the chloride **10** (168 mg, 0.26 mmol) in dichloromethane (3 mL) was added, at 0°, to a stirred suspension consisting of benzyl alcohol (142 mg, 5 eq.), silver triflate (15 mg, 0.06 mmol), silver carbonate (0.73 g, 10 eq.), Drierite (1.0 g), and di-

chloromethane (7 mL). After 18 h, additional dichloromethane was introduced, the suspension was filtered, and the filtrate was washed with water (3 ×), dried, and evaporated. Preparative liquid chromatography of the residual material (eluant, 1:1 ethyl acetate–hexane) afforded, initially, 52 mg (28%) of **10** (R_F 0.3), m.p. 168.5–169° (recrystallized from dichloromethane–diethyl ether), $[\alpha]_D^{20}$ −8.0° (*c* 0.4, chloroform); ^{1}H-n.m.r.: δ 7.35 (m, 5 H, Ar), 4.39 (d, 1 H, H-1), 3.44 (dd, 1 H, H-2), 2.14, 2.09, 2.08, 2.02, 2.00, and 1.97 (6 s, 6 × 3 H, 6 Ac), $J_{1,2}$ 8.3 and $J_{2,3}$ 10.3 Hz.

Anal. Calc. for $C_{31}H_{39}N_3O_{16}$: C, 52.46; H, 5.54; N, 5.92. Found: C, 52.63; H, 5.68; N, 6.51.

The second product isolated (R_F 0.25) was **9** (79 mg, 42%), m.p. 181–182° (recrystallized from dichloromethane–diethyl ether), $[\alpha]_D^{20}$ +77.7° (*c* 1.0, chloroform); ^{1}H-n.m.r.: δ 5.48 (dd, 1 H, H-3), 4.99 (d, 1 H, H-1), 4.74 (d, 1 H, PhCH), 4.51 (d, 1 H, H-1′), 3.72 (dd, 1 H, H-4), 2.16, 2.12, 2.10, 2.02, 2.00, and 1.98 (6 s, 6 × 3 H, 6 Ac), $J_{1,2}$ 3.8 and $J_{1',2'}$ 7.5 Hz.

Anal. Calc. for $C_{31}H_{39}N_3O_{16}$: C, 52.46; H, 5.54; N, 5.92. Found: C, 52.59; H, 5.73; N, 6.44.

Conversion of **5** *or* **7** *into glycoside* **9**. — A solution of admixed **5** and **7** (0.42 g, 0.64 mmol), tetrabutylammonium bromide (0.62 g, 3 eq.), 2,4,6-trimethylpyridine (0.5 mL), and benzyl alcohol (0.35 g, 5 eq.), was prepared in dichloromethane (10 mL). After 48 h, additional dichloromethane was introduced, the solution was then washed successively with dilute hydrochloric acid, water-saturated sodium hydrogencarbonate, and water, dried, and evaporated. The residue, purified by "flash" chromatography[8], afforded α-glycoside **9** (0.3 g, 66%), m.p. 181–182°.

*Benzyl 2-azido-2-deoxy-4-*O*-β-*D*-glucopyranosyl-α-*D*-glucopyranoside* (**13**). — A solution of sodium methoxide in methanol (0.47M, 0.2 mL) was added to a stirred suspension of **9** (10 mL). After 2 h, the clear solution was neutralized with Dowex 50W-X8 ion-exchange resin (H^+), and evaporated. The residue was dissolved in hot water and, on cooling, 0.49 g (83%) of **13** separated out, m.p. 179°, $[\alpha]_D^{20}$ +110.9° (*c* 0.9, methanol); ν_{max}^{KBr} 2100 cm^{-1} (N_3); ^{1}H-n.m.r. [$(CD_3)_2SO$–D_2O]: 4.94 (d, 1 H, H-1), 4.68 (d, 1 H, PhCH), 4.47 (d, 1 H, PhCH′), 4.24 (d, 1 H, H-1′), $J_{1,2}$ 3.8, and $J_{1',2'}$ 7.8 Hz.

Anal. Calc. for $C_{19}H_{27}N_3O_{10}$: C, 49.89; H, 5.95; N, 9.19. Found: C, 49.77; H, 6.02; N, 8.93.

*1,6-Anhydro-4-*O*-(4,6-*O*-isopropylidene-β-*D*-glucopyranosyl)-β-*D*-glucopyranose* (**15**). — 2-Methoxypropene (1.5 mL, 15.6 mmol) was added dropwise at 0° to a stirred suspension of 1,6-anhydro-β-cellobiose[6] (**14**) 4.52 g, 13.9 mmol) in acetone (45 mL) containing *p*-toluenesulfonic acid (30 mg). After 1 h, additional 2-methoxypropene (1.5 mL) was introduced, and 3 h later the solution was brought to pH 8 with ammonia, and evaporated. Column chromatography afforded amorphous **15** (4.44 g, 87%), $[\alpha]_D^{20}$ −91.9° (*c* 3.5, methanol); ^{13}C-n.m.r. (D_2O): δ 103.5 (C-1), 102.9 (CMe_2), 102.4 (C-1′), 29.4 (Me,*e*), 19.9 (Me,*a*).

Anal. Calc. for $C_{15}H_{24}O_{10}$: C, 49.45; H, 6.64. Found: C, 49.29; H, 6.76.

The 2,3,2′,3′-tetra-*O*-acetyl derivative (**16**) had m.p. 149–150° (recrystallized from dichloromethane–diethyl ether–hexane), $[\alpha]_D^{20}$ −85.8° (*c* 2.1, chloroform); ^{1}H-n.m.r.: δ 5.42 (s, 1 H, H-1), 5.12 (dd, 1 H, H-3′), 5.02 (s, 1 H, H-3), 4.83 (d, 1 H, H-1′), 4.58 (d, 1 H, H-5), 2.11, 2.10, 2.03 (× 2) (3 s, 4 Ac), 1.46, and 1.38 (2 s, 2 Me), $J_{3,2} = J_{3,4}$ 9.3, $J_{1,2}$ 7.8, and $J_{5,6}$ 5.8 Hz.

Anal. Calc. for $C_{23}H_{32}O_{14}$: C, 51.88; H, 6.06. Found: C, 52.31; H, 6.42.

*1,6-Anhydro-4-*O*-(2,3:4,6-di-*O*-isopropylidene-β-*D*-glucopyranosyl)-β-*D*-glucopyranose* (**17**) *and 1,6-anhydro-4-*O*-(4,6-*O*-isopropylidene-β-*D*-glucopyranosyl)-2,2′-*O*-isopropylidene-β-*D*-glucopyranose* (**19**). — Material having greater mobility on the column than **15** was recovered, and rechromatographed (eluant, 3:1 ethyl acetate–hexane). The first product eluted was syrupy **19** (0.17 g, 3%), which afforded a diacetate (**20**), m.p. 258–260° (dec.) (recrystallized from dichloromethane–ether–hexane); $[\alpha]_D^{20}$ −49.5° (*c* 0.9, chloroform); ^{1}H-n.m.r.: δ 5.27 (s, 1 H, H-1′), 5.03 (dd, 1 H, H-3), 4.68 (d, 1 H, H-3′), 4.56 (d, 1 H, H-5), 4.51 (d, 1 H, H-1), 2.11, 2.07 (2 s, 2 Ac), 1.46, 1.38, 1.36, and 1.28 (4 s, 4 Me), $J_{3,2} = J_{3,4}$ 9.5, $J_{5',6'}$ 4.9, and $J_{1,2}$ 7.8 Hz.

Anal. Calc. for $C_{22}H_{32}O_{12}$: C, 54.09; H, 6.60. Found: C, 54.49; H, 6.73.

On continued elution of the column, 0.28 g (5%) of **17** was obtained, m.p. 187–188° (recrystallized from ethyl acetate–diethyl ether); $[\alpha]_D^{20}$ −71.8° (*c* 0.9, chloroform). The diacetate (**18**) had m.p. 179–180° (recrystallized from dichloromethane–diethyl ether–hexane); ^{1}H-n.m.r.: δ 4.98 (d, 1 H, H-1′), 4.76 (d, 1 H, H-5), 4.53 (s, 1 H, H-2), 3.51 (dd, 1 H, H-2′), 2.11, 2.12 (2 s, 2 Ac), 1.52, 1.45 (× 2), and 1.42 (3 s, 4 Me).

*1,6-Anhydro-4-*O*-(4,6-*O*-isopropylidene-β-*D*-glucopyranosyl)-2-*O*-p-tolylsulfonyl-β-*D*-glucopyranose* (**21**), *and 3,2′,3′-tri-*O*-acetyl derivative* (**22**). — A solution of *p*-toluenesulfonyl chloride (1.32 g, 1.1 eq.) in pyridine (5 mL) was added to a solution of **15** (2.28 g, 6.27 mmol) in pyridine (22 mL) at 0°. After 3 days, ice–water was introduced, the mixture was extracted (2 ×) with chloroform, the extract was washed with water (2 ×), dried, evaporated, and the residual solvent codistilled with toluene (3 ×). Column chromatography of the residue (eluant, 19:1 chloroform–methanol) afforded **21** (1.96 g, 60%), m.p. 107–111° (recrystallized from acetone–chloroform), $[\alpha]_D^{20}$ −52.7° (*c* 2.4, methanol). The derived triacetate (**22**) had m.p. 165–166° (recrystallized from diethyl ether–hexane), $[\alpha]_D^{20}$ −74.9° (*c* 2.4, chloroform); ^{1}H-n.mr.: δ 7.80, 7.34 (m, 4 H, Ar), 5.10 (dd, 1 H, H-3′), 4.99 (s, 1 H, H-3), 4.78 (d, 1 H, H-1′), 2.44 (s, 3 H, $CH_3C_6H_4$), 2.03, 2.02, 2.00 (3 s, 3 Ac), 1.45, and 1.36 (2 s, 2 Me).

Anal. Calc. for $C_{25}H_{36}O_{15}$: C, 52.17; H, 5.63; S, 4.97. Found: C, 52.29; H, 5.65; S, 5.00.

*1,6:2,3-Dianhydro-4-*O*-(2,3-di-*O*-acetyl-4,6-*O*-isopropylidene-β-*D*-glucopyranosyl)-β-*D*-mannose* (**24**). — Sodium methoxide in methanol (0.47M, 7.6 mL, 1 eq.) was added to a stirred solution of **20** (1.84 g, 3.55 mmol) in chloroform (30 mL). After 1 h, solid sodium *p*-toluenesulfonate was removed by filtration, the filtrate was evaporated, and the residue (**23**) was acetylated to give **24** (1.29 g,

84%); m.p. 243–245° (crystallized from diethyl–ether–hexane), $[\alpha]_D^{20}$ −72.9° (*c* 1.4, chloroform); ^{1}H-n.m.r.: δ 5.64 (d, 1 H, H-1), 5.13 (dd, 1 H, H-3′), 4.94 (dd, 1 H, H-2′), 4.71 (d, 1 H, H-1′), 3.41 (dd, 1 H, H-2), 3.22 (d, 1 H, H-3), 2.03 (s, 6 H, 2 Ac), 1.44, and 1.35 (2 s, 2 Me).

Anal. Calc for $C_{19}H_{26}O_{11}$: C, 53.02; H, 6.09. Found: C, 53.16; H, 5.90.

3-O-Acetyl-1,6-anhydro-2-azido-2-deoxy-4-O-(2,3-di-O-acetyl-4,6-O-isopropylidene-β-D-glucopyranosyl)-β-D-glucopyranose (**26**). — A solution of amorphous **23** (0.14 g) and sodium azide (0.17 g) in 60% ethanol (4 mL) was heated under reflux for 38 h, and then evaporated. Acetylation of the residue afforded **26** (0.15 g, 77%), m.p. 139–140° (recrystallized from dichloromethane–diethyl ether–hexane); $[\alpha]_D^{20}$ −46.4° (*c* 2.0, chloroform); ν_{max}^{KBr} 2105 cm^{-1} (N_3); ^{1}H-n.m.r.: δ 5.44 (s, 1 H, H-1), 4.99 (dd, 1 H, H-2′), 4.82 (d, 1 H, H-1′), 3.18 (m, 1 H, H-2), 2.10, 2.03 (× 2) (2 s, 3 Ac), 1.48, and 1.39 (2 s, 2 Me).

Anal. Calc. for $C_{21}H_{29}N_3O_{12}$: C, 48.93; H, 5.67; N, 8.15. Found: C, 49.33; H, 5.63; N, 7.85.

3-O-Acetyl-1,6-anhydro-2-azido-2-deoxy-4-O-(2,3-di-O-acetyl-β-D-glucopyranosyl)-β-D-glucopyranose (**27**). — A solution of **26** (0.16 g) in 80% acetic acid (2 mL) was kept at room temp. for 6 h, evaporated, the residue dissolved in chloroform (5 mL), and the solution washed successively with water, sodium hydrogencarbonate, water, dried, and evaporated to give a solid (yield, 0.14 g), $[\alpha]_D^{20}$ −8.5° (*c* 1.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$ exchanged with D_2O): δ 5.98 (s, 1 H, H-1), 5.22 (s, 1 H, H-3), 5.04 (dd, 1 H, H-3′), 4.92 (dd, 1 H, H-2′), 4.76 (d, 1 H, H-1′), 3.68 (dd, 1 H, H-4′), 3.58 (s, 1 H, H-4), 2.11, 2.07, and 2.03 (3 s, 3 Ac), $J_{1',2'}$ 7.6, $J_{2',3'}$ 9.5, and $J_{3',4'}$ 9.5 Hz.

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