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Synthesis of 2-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-5a-carba-α-D-mannopyranose, and 5a-carba-2-*O*- and 3,6-di-*O*-(α-D-mannopyranosyl)-α-D-mannopyranoses *

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ABSTRACT

Protected derivatives of the title carba-trisaccharide **1**, and carba-disaccharides **4** and **6** have been synthesised by conventional glycosylation of the precursors **8**, **9**, or **22** of 5a-carba-α-D-mannopyranose with sugar halides. These are carba-sugar analogues of the oligosaccharide chains frequently occurring as structural units in biologically important glycoconjugates, and could be utilised as the building blocks for construction of higher carba-oligosaccharides of biological interest.

INTRODUCTION

Recently, interest has been focused on the preparation of biologically important carba-oligosaccharides[2] related to cell-surface glycans[3]. We envisaged contributing to elucidation of the biological role of the oligosaccharide chain of common glycoconjugates, by providing several analogues of such oligosaccharides, composed partly of carba-sugars.

In previous papers[4] of this series, we described a synthesis of carba-disaccharides corresponding to such naturally occurring disaccharides as laminarabiose, cellobiose, maltose, and trehalose. These carba-sugar analogues have been utilized as model compounds for conformational analysis of true oligosaccharides or as substrate analogues for study of enzyme action.

We describe here the synthesis of the common branching trisaccharide **1**, α-D-mannopyranosyl (1 → 3) and (1 → 6)-linked 5a-carba-α-D-mannopyranose, and

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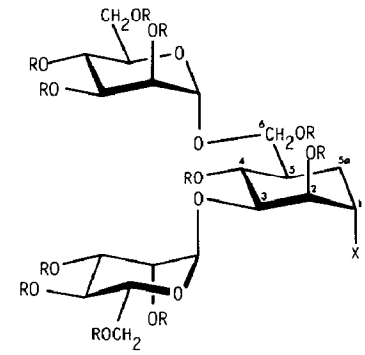
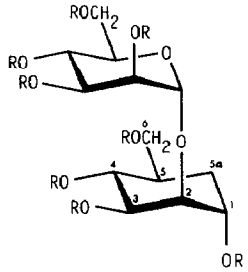
* Pseudo-Sugars, XXVIII. This paper also constitutes part II of the series Synthesis of Carba-oligosaccharides Related to Cell-surface Glycans. Part I, see ref. 1.



	R	X
1	H	OH
2	Ac	OAc
3	Ac	NHAc



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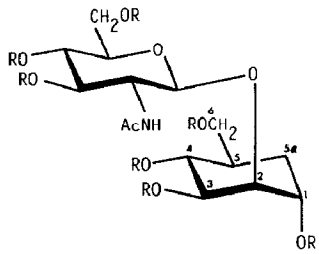
5 R = Ac



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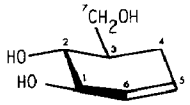
7 R = Ac



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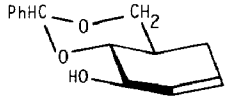

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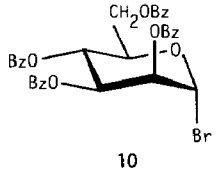

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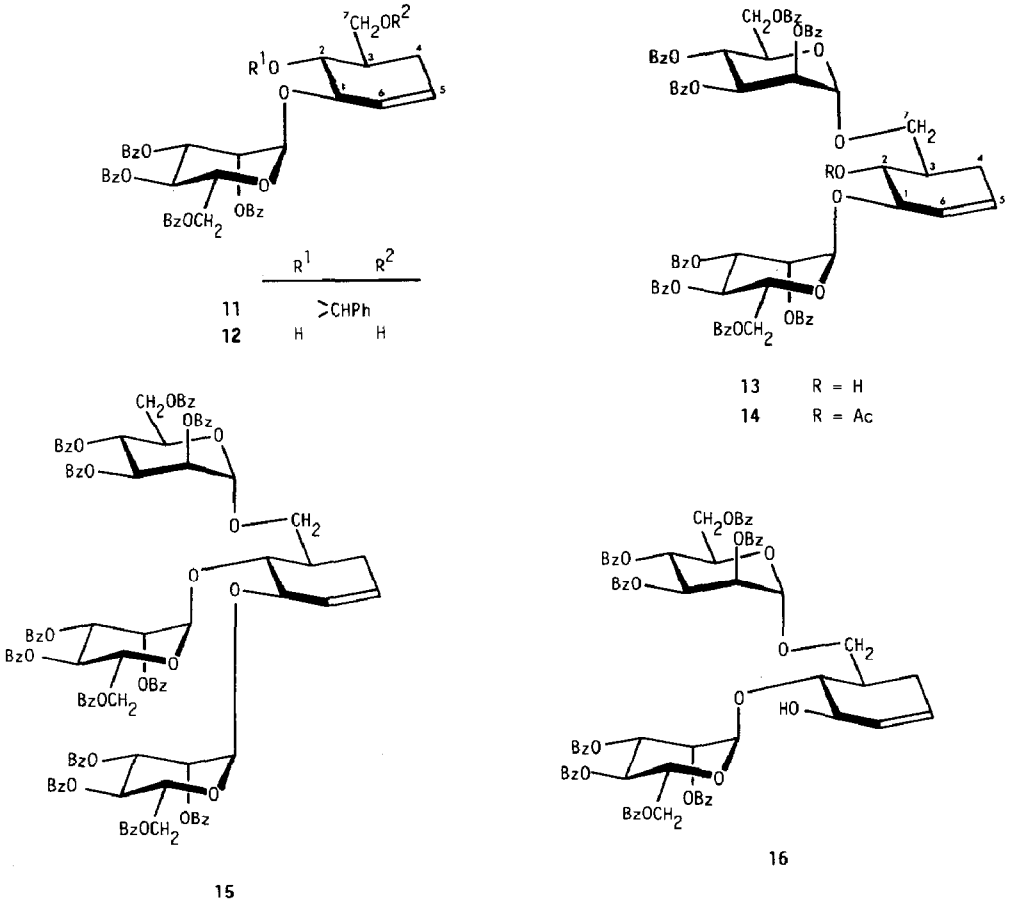
Scheme 1.

the disaccharide moieties **4** and **6**, composed of 5a-carba-α-D-mannopyranose and D-mannopyranose or 2-acetamido-2-deoxy-D-glucopyranose, linked at C-2 through glycosyl linkages, that frequently occur as structural units in glycoconjugates. These pseudo di- and tri-saccharides should also be useful for stereochemical studies, and, conceivably, these analogues might possess inhibitory activity against certain sugar transferases.

RESULTS AND DISCUSSION

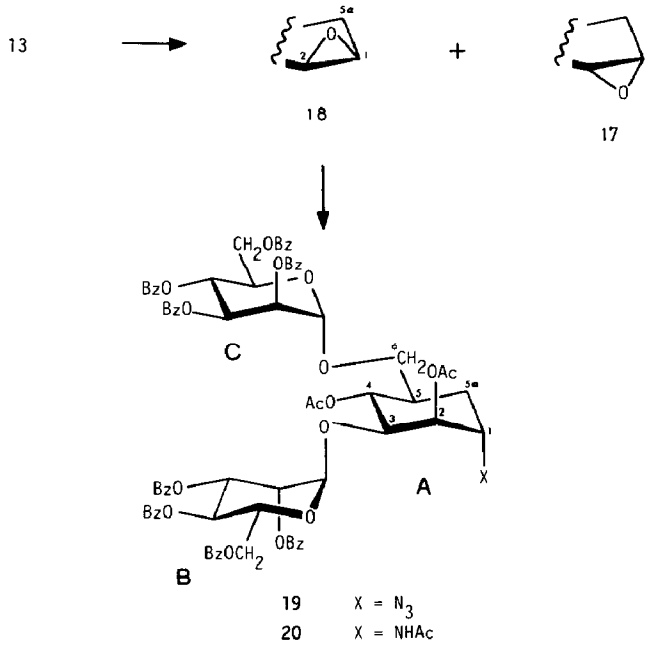
The precursor of 5a-carba-α-D-mannopyranose residue, (1*S*)-(1,3/2)-3-(hydroxymethyl)cyclohex-5-ene-1,2-diol (**8**) was first blocked by the 2,7-*O*-benzylidene function to transform it into the OH-1 unsubstituted derivative **9**. Glycosylation of **9** with 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl bromide[5] (**10**) in benzene in the presence of mercury(II) cyanide and Drierite for 21 h at 90° gave a single condensate **11** in 91% yield. The ^{1}H-NMR spectrum showed a doublet ($J_{1',2'}$ 1.8 Hz, δ 5.57) for the anomeric proton, indicative of the α-glycoside. Formation of the α-glycoside may also be expected by the nature of the glycosyl donor[6] **10** and the reaction conditions employed. *O*-Debenzylidenation of **11** with aqueous 80% acetic acid for 2 h at 60° afforded the diol **12** in 84% yield. Similar glycosylation of



Scheme 2.

12 with 2 molar equivalents of **10** in benzene–nitromethane (3:2, v/v) for 3 h at reflux temperature afforded, after chromatography on a column of silica gel, crystalline di-*O*- **13** (52%) and tri-*O*-(α-D-mannopyranosyl) derivatives **15** (19%). The ^{1}H-NMR spectra of **13** and **15** revealed signals due to the anomeric protons at δ 5.12 and 5.47 (*J* 1.8 Hz), and δ 5.26, 5.49, and 5.52 (*J* 1.5 Hz), respectively, indicating, in conjunction with the analytical data, the presence of two and three α-mannopyranosyl residues[7]. Compound **13** was converted into the acetate **14**, the ^{1}H-NMR spectrum of which showed a doublet of doublets (δ 5.31, $J_{1,2}$ 7.7, $J_{2,3}$ 10.6 Hz) attributable to H-2, confirming the C-1,7 positions to which α-D-mannopyranose residues were attached. Compound **11** was thus shown to be an important synthetic intermediate.

Attempts at selective glycosylation of the triol **8** were made under controlled conditions. When **8** was similarly treated with 3.5 molar equivalents of **10** in benzene–nitromethane (1:1, v/v) for one day at 0°, **13** (36%) and **15** (18%) were obtained, after chromatography, together with a minor component, the 2,7-di-*O*-



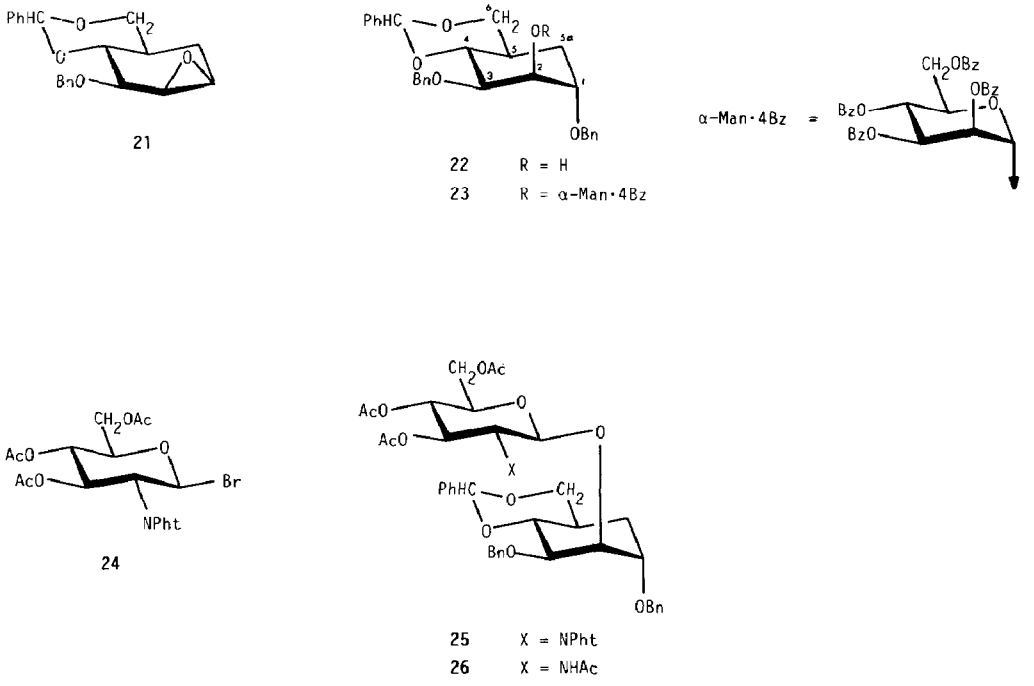
Scheme 3.

(α-D-mannopyranosyl) derivative **16** (2.7%). The structure of **16** was confirmed by the appearance of a triplet at δ 3.80 (*J* 8.8 Hz) due to the ring proton (C-2) attached to the carbon atom bearing the α-mannopyranose residue.

The protected precursor **13** of carba-trisaccharides should be a versatile synthetic intermediate for further transformations to various carba-oligosaccharides of biological interest.

First, epoxidation of **13** was carried out[8] by use of two molar equivalent of *m*-chloroperoxybenzoic acid in 1,2-dichloroethane in the presence of phosphate buffer at 50°. The two products were readily separable by chromatography on silica gel to afford the crystalline α- **17** (33%) and β-epoxides **18** (49%), the ^{1}H-NMR spectra of which (see Table I) revealed in each a pair of signals[8] due to epoxide protons at δ 3.62 (dd, *J* 4.2 and 1.3 Hz) and 3.17 (t, *J* 4.2 Hz), and δ 3.44 (d, *J* 3.3 Hz) and 3.27 (bs), respectively, supporting the proposed structures.

Treatment of **18** with an excess of sodium acetate in aqueous 90% 2-methoxyethanol for 2 days at reflux temperature resulted in the preferential diaxial cleavage of the epoxide ring accompanied by complete *O*-debenzoylation, and the product was successively acetylated in the usual manner to afford a single carba-trisaccharide undecaacetate **2** in 98% yield. Azidolysis of **18** with an excess of sodium azide in the presence of ammonium chloride for one day at 80°, followed by acetylation, afforded a single, crystalline azide **19** (97%). The structure of **19** was confirmed by its ^{1}H-NMR spectrum which indicated a narrow quartet (*J* 2.9 Hz) at δ 4.02, attributable to the proton (H-1) bonded to the carbon atom bearing



Scheme 4.

the azido function. Cleavage of the epoxide ring thus proceeded preferentially in a diaxial fashion, and the structure of **18** was assigned on the basis of these results. Hydrogenation of **19** in ethanol–ethyl acetate (1:1) in the presence of Raney nickel and acetic anhydride afforded the *N*-acetyl derivative **20** (68%), which was further converted into the undeca-*N*,*O*-acetate **3** (72%) by *O*-deacylation with methanolic sodium methoxide and successive acetylation.

The aglycon **22**, convertible into the 2-*O*-glycosylated 5a-carba-α-D-manno-pyranose moiety, was prepared from **9** by conventional epoxidation and benzylation (**9** → **21**, 88%)[1]. Reaction of **21** with 2% boron trifluoride–ether in benzyl alcohol at 0° proceeded selectively to afford the diaxially opened alcohol **22** (67%), the ^{1}H-NMR spectrum of which was fully interpreted on a first-order basis.

Condensation of **22** and **10** as in the preparation of **11** afforded a single compound **23** (90%). The signal due to the anomeric proton appeared as a doublet with a 1.5-Hz spacing at δ 5.61, supporting the assigned structure. Compound **23** was *O*-deacylated with methanolic sodium methoxide, *O*-debenzylidenated, and *O*-debenzylation by hydrogenolysis with 20% $Pd(OH)_2$–C, and then acetylated to give the octaacetate **5** (92%).

Likewise, condensation of **22** with 3,4,6-tri-*O*-acetyl-2-phthalimido-2-deoxy-β-D-glucopyranosyl bromide[9] (**24**) afforded the protected carba-disaccharide **25** (87%), the ^{1}H-NMR spectrum of which showed a signal due to the anomeric proton as a triplet (*J* 8.4 Hz) at δ 5.36, indicative of the β-glycoside. Hydrazinolysis of **25** followed by acetylation gave the *N*-acetyl derivative **26** (77%). Hy-

drogenolysis of **26** with 20% $Pd(OH)_2$–C and successive acetylation afforded **7** (93%).

Conformational analysis[10] by use of ^{13}C- and ^1H-NMR spectra of **2**, **5**, and **7**, and the corresponding free sugars **1**, **4**, and **6**, and biochemical assay thereof are under way.

EXPERIMENTAL

General methods.—Melting points were determined with a Mel–Temp capillary melting-point apparatus and uncorrected. Optical rotations were measured with a Jasco DIP-370 polarimeter. ^1H-NMR spectra were recorded for solutions in $CDCl_3$ (internal Me_4Si) with a Jeol JNM GSX-270 (270 MHz) instrument. TLC was performed on Silica Gel 60 GF (E. Merck, Darmstadt) with detection by charring with H_2SO_4. Column chromatography was conducted on Wakogel C-300 (300 Mesh). Organic solutions were dried over anhyd Na_2SO_4 and evaporated at $< 50°$ under diminished pressure.

(1R,3R,6R,10S)-3-Phenyl-10-O-(2,3,4,6-tetra-O-benzoyl-α-D-mannopyranosyl)-2,4-dioxabicyclo[4.4.0]dec-8-ene (**11**).—A stirred mixture of (1*R*,3*R*,6*R*,10*S*)-10-hydroxy-3-phenyl-2,4-dioxabicyclo[4.4.0]dec-8-ene[4] (**9**, 200 mg, 0.86 mmol), $Hg(CN)_2$ (400 mg, 1.58 mmol), powdered Drierite (400 mg), and dry benzene (40 mL) was refluxed to remove 12 mL of benzene. To the mixture was added 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl bromide[5] (**10**, 1.14 g, 1.72 mmol) and the mixture was refluxed for 21 h in the dark. The cooled mixture was neutralized with Et_3N and filtered through a Celite bed. The filtrate was evaporated and the residue was chromatographed on a column of silica gel (70 g) with 1:3 EtOAc–hexane, containing 0.5% Et_3N, as eluent. The main component was rechromatographed (silica gel, 25 g, 1:30 EtOAc–PhMe) to give **11** (633 mg, 91%) as a colorless syrup, $[\alpha]_D^{31}$ −83° (*c* 0.94, $CHCl_3$); ^1H-NMR (270 MHz, $CDCl_3$): δ 8.10–7.19 (m, 25 H, 5 Ph), 6.11 (t, 1 H, $J_{3',4'} = J_{4',5'} = 10.3$ Hz, H-4′), 5.96 (dd, 1 H, $J_{2',3'}$ 3.3 Hz, H-3′), 5.48 (m, 1 H, H-8), 5.80 (dd, 1 H, $J_{1',2'}$ 1.8 Hz, H-1′), 5.73 (m, 1 H, H-9), 5.69 (s, 1 H, H-3), 5.57 (d, 1 H, H-1′), 4.68 (dd, 1 H, $J_{5',6'a}$ 2.6, $J_{6',6'}$ 12.1 Hz, H-6′a), 4.64–4.56 (m, 2 H, H-10,5′), 4.42 (dd, 1 H, $J_{5',6'b}$ 4.2 Hz, H-6′b), 4.22 (dd, 1 H, $J_{5eq,6}$ 4.8, $J_{5,5}$ 11 Hz, H-5*eq*), 4.05 (dd, 1 H, $J_{5ax,6}$ 8.1 Hz, H-5*ax*), 3.71 (t, 1 H, $J_{1,6} = J_{1,10} = 11$ Hz, H-1), and 2.24–1.73 (m, 3 H, H-6,7a,7b).

Anal. Calcd for $C_{48}H_{42}O_{12}$: C, 71.10; H, 5.22. Found: C, 70.71; H, 5.31.

1L-(1,3/2)-3-Hydroxymethyl-1-O-(2,3,4,6-tetra-O-benzoyl-α-D-mannopyranosyl)-5-cyclohexene-1,2-diol (**12**).—A mixture of **11** (590 mg, 0.73 mmol) and 80% aq AcOH (15 mL) was stirred for 2 h at 60°, and then evaporated. The residue was chromatographed on a column of silica gel (30 g) with 1:7 Me_2CO–PhMe as eluent to give the diol **13** (440 mg, 84%) as a syrup, $[\alpha]_D^{25}$ −73° (*c* 0.79, $CHCl_3$); ^1H-NMR (270 MHz, $CDCl_3$): δ 8.11–7.25 (m, 20 H, 4 Ph), 6.08 (t, 1 H, $J_{3',4'} = J_{4',5'} = 9.9$ Hz, H-4′), 5.92 (dd, 1 H, $J_{2',3'}$ 2.9 Hz, H-3′), 5.80 (bd, 1 H, $J_{5,6}$ 1.8 Hz, H-6), 5.76 (dd, 1 H, $J_{1',2'}$ 1.8 Hz, H-2′), 5.69 (ddd, 1 H, $J_{4ax,5}$ 9.9, $J_{4eq,5}$ 4.4 Hz, H-5),

5.43 (d, 1 H, H-1'), 4.70 (dd, 1 H, $J_{5',6'a}$ 2.2, $J_{6',6'}$ 11.7 Hz, H-6'a), 4.63 (ddd, $J_{5',6'b}$ 5.1 Hz, H-5'), 4.51 (dd, 1 H, H-6'b), 4.37 (bd, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 3.93 (ddd, 1 H, $J_{2,3}$ 9.9, $J_{2,OH}$ 2.9 Hz, H-2), 3.84 (d, 1 H, 2-OH), 3.76 (2 t, 2 H, $J_{3,7} = J_{7,OH} = 5.5$ Hz, H-7), 3.11 (t, 1 H, 7-OH), and 2.18–1.85 (m, 3 H, H-3,4*ax*,4*eq*).

Anal. Calcd for $C_{41}H_{38}O_{12}$: C, 68.14; H, 5.30. Found: C, 68.02; H, 5.20.

1L-(1,3 / 2)-1,7-Di- (**13**) *and 1,2,7-tri-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-*D*-mannopyranosyl)-3-(hydroxymethyl)cyclohex-5-ene-1,2-diol* (**15**).—A mixture of **12** (36 mg, 0.050 mmol), **10** (66 mg, 0.10 mmol), $Hg(CN)_2$ (50 mg, 0.20 mmol), powdered Drierite (50 mg), in 3:2 benzene–$MeNO_2$ (5 mL) was heated at reflux for 3 h in the dark. The mixture was filtered through a Celite bed and the filtrate was evaporated. The residue was chromatographed on a column of silica gel (20 g) with 1:15 butanone–PhMe containg 0.5% Et_3N as eluent to give, first, **15** (17.6 mg, 19%) as crystals, mp 130–132° (from EtOH), $[\alpha]_D^{23}$ −64° (*c* 1.4, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$): δ 8.11–7.08 (m, 60 H, 12 Ph), 6.22, 6.12, and 6.07 (3 t, each 1 H, *J* 9.9 Hz, H = 4',4'',4'''), 6.05–5.92 (m, 5 H, H-5,3',3'',3'''), 5.83–5.92 (m, 3 H, H-2',2'',2'''), 5.52, 5.49, and 5.26 (3 d, each 1 H, *J* 1.5 Hz, H-1',1'',1'''), 4.78–3.94 (m, 13 H, H = 1,2,7a,7a,5',6'a,6'b,5'',6''a,6''b,6'''a,6'''b), and 2.72–2.10 (m, 3 H, H-3,4*ax*,4*eq*).

Anal. Calcd for $C_{109}H_{90}O_{30}$: C, 69.64; H, 4.83. Found: C, 69.38; H, 4.83.

The second fraction gave **13** (33.6 mg, 52%) as crystals, mp 111–113° (from EtOH), $[\alpha]_D^{23}$ −60° (*c* 0.83, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$): δ 8.15–7.24 (m, 40 H, 8 Ph), 6.13 and 6.12 (2 t, each 1 H, *J* 10.3 Hz, H-4',4''), 5.98 and 5.92 (2 dd, each 1 H, $J_{2',3'(2'',3'')}$ 3.3, $J_{3',4'(3'',4'')}$ 10.3 Hz, H-3',3''), 5.86 and 5.78 (m, 2 H, H-5,6), 5.81 and 5.75 (2 dd, each 1 H, $J_{1',2'(1'',2'')}$ 1.8 Hz, H-2',2''), 4.77–4.52 (m, 6 H, H-5',6'a,6'b,5'',6''a,6''b), 4.37 (bd, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 4.15 (dd, 1 H, $J_{3,7a}$ 5.7, $J_{7,7}$ 9.5 Hz, H-7a), 3.97 (ddd, 1 H, $J_{2,3}$ 11.4, $J_{2,OH}$ 3.7 Hz, H-2), 3.70 (dd, 1 H, $J_{3,7b}$ 3.1 Hz, H-7b), 3.11 (d, 1 H, OH), and 2.43–2.07 (m, 3 H, H-3,4*ax*,4*eq*).

Anal. Calcd for $C_{75}H_{64}O_{21}$: C, 69.22; H, 4.96. Found: C, 69.36; H, 5.13.

Compound **13** (109 mg, 0.084 mmol) was treated with Ac_2O (3 mL) and pyridine (3 mL) overnight at room temperature. The mixture was evaporated and the residue was chromatographed on a column of silica gel (10 g) with 1:10 EtOAc–PhMe as eluent to give the acetate **14** (106 mg, 94%) as an amorphous powder, $[\alpha]_D^{23}$ −60.5° (*c* 1.17, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$): δ 8.13–7.22 (m, 40 H, 8 Ph), 6.12 and 6.11 (2 t, each 1 H, *J* 8.8 Hz, H-4',4''), 5.93 and 5.89 (2 dd, each 1 H, $J_{2',3'(2'',3'')}$ 3.1, $J_{3',4'(3'',4'')}$ 8.8 Hz, H-3',3''), 5.82 (m, 2 H, H-5,6), 5.72 and 5.57 (2 dd, 1 H, $J_{1',2'(1'',2'')}$ 1.8 Hz, H-2',2''), 5.35 and 5.10 (2 d, 1 H, H-1',1''), 5.31 (dd, 1 H, $J_{1,2}$ 7.7, $J_{2,3}$ 10.6 Hz, H-2), 4.73 and 4.69 (2 dd, each 1 H, $J_{5',6'a(5'',6''a)}$ 1.8, $J_{6',6'(6'',6'')}$ 11.7 Hz, H-6'a,6''a), 4.63–4.40 (m, 5 H, H-1,5',6'b,5'',6''b), 3.85 (dd, 1 H, $J_{3,7a}$ 6.6, $J_{7,7}$ 6.6 Hz, H-7a), 3.65 (dd, $J_{3,7b}$ 4.2 Hz, H-7b), 2.53–2.21 (m, 3 H, H-3,4*ax*,4*eq*), and 2.25 (s, 3 H, Ac).

Anal. Calcd for $C_{77}H_{66}O_{22}$: C, 68.85; H, 4.95. Found: C, 68.57; H, 5.10.

(1R,2R,3R)-3-(Hydroxymethyl)cyclohex-5-ene-1,2-diol (**8**).—(1*R*,2*R*,3*R*)-2,3-Diacetoxy-5-cyclohexene-1-carboxylic acid[11] was reduced with 3 molar equivalent

of $LiAlH_4$ in tetrahydrofuran to furnish, after conventional workup[1], the triol **8** quantitatively. Without further purification, this compound was thoroughly dried over P_2O_5 and used in the coupling reaction with the sugar halide.

Glycosylation of **8**. *Preparation of* **13**, **15**, *and* 1L-*(1,3/2)-2,7-di-*O-*(2,3,4,6-tetra-O-benzoyl)-α-*D-*mannopyranosyl)-3-(hydroxymethyl)-cyclohex-5-ene-1,2-diol* (**16**).—A mixture of **8** (25 mg, 0.17 mmol). $Hg(CN)_2$ (100 mg, 0.40 mmol), Drierite (100 mg), and 1:1 benzene–$MeNO_2$ (10 mL) was refluxed to remove benzene (~2 mL), and, after being cooled to 0°, it was stirred with addition of **10** (396 mg, 0.60 mmol) for 25 h at 0° in the dark. The mixture was processed conventionally and the products were chromatographed on a column of silica gel (25 g) with 1:15 butanone–PhMe containing Et_3N (3%) as eluent to give **13** (81.5 mg, 36%), **15** (58.3 mg, 18%), and **16** (6.1 mg, 2.7%) as crystals, mp 119–121° (from EtOH); $[\alpha]_D^{23}$ −55° (*c* 1.2, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$): δ 8.12–7.19 (m, 40 H, 8 Ph), 6.11 and 6.10 (2 t, each 1 H, *J* 9.9 Hz, H-4′,4″), 6.01 and 5.90 (2 dd, each 1 H, $J_{2',3'(2'',3'')}$ 3.3, $J_{3',4'(3'',4'')}$ 9.9 Hz, H-3′,3″), 5.95–5.69 (m, 2 H, H-5,6), 5.75 and 5.73 (2 dd, each 1 H, $J_{1',2'(1'',2'')}$ 1.8 Hz, H-2′,2″), 5.36 and 5.10 (2 d, each 1 H, H-1′,1″), 4.86–4.42 (m, 6 H, H-5′,6′a,6′b,5″,6″a,6″b), 4.32 (bd, 1 H, $J_{1,2}$ 8.8 Hz, H-1), 4.11 (dd, 1 H, $J_{3,7a}$ 2.6, $J_{7,7}$ 9.5 Hz, H-7a), 3.88 (d, 1 H, $J_{1,OH}$ 2.9 Hz, OH), 3.80 (bt, 1 H, $J_{2,3}$ 8.8 Hz, H-2), 3.57 (dd, 1 H, $J_{3,7b}$ 6.6 Hz, H-7b), and 2.52–2.08 (m, 3 H, H-3,4*ax*,4*eq*).

Anal. Calcd for $C_{75}H_{64}O_{21}$: C, 69.22; H, 4.96. Found: C, 68.96; H, 4.95.

*1,2-Anhydro-3,6-di-*O-*(2,3,4,6-tetra-*O-*benzoyl-α-*D-*mannopyranosyl)-5a-carba-α-*D-*glucopyranose* (**17**) *and -β-*D-*mannopyranose* (**18**).—To a solution of **13** (200 mg, 0.154 mmol) in 1,2-dichloroethane (3 mL) were added aq M sodium phosphate(I) (1.5 mL), M sodium phosphate(II) (1.5 mL), and *m*-chloroperoxybenzoic acid (53 mg, 0.31 mmol), and the mixture was vigorously stirred for 20 h at 50°. After cooling, $CHCl_3$ (50 mL) was added and the mixture was successively washed with satd aq $Na_2S_2O_3$ and H_2O, dried, and evaporated. The residue was chromatographed on a column of silica gel (25 g) with 1:10 butanone–PhMe containing Et_3N (0.3%) as eluent to give **17** (66 mg, 33%) and **18** (99 mg, 49%).

Compound **17** had mp 128–129° (from EtOH), $[\alpha]_D^{22}$ −50° (*c* 0.76, $CHCl_3$); ^{1}H-NMR data are listed in Table I.

Anal. Calcd for $C_{75}H_{64}O_{22}$: C, 68.38; H, 4.90. Found; C, 68.37; H, 4.94.

Compound **18** had mp 128–130° (from EtOH), $[\alpha]_D^{22}$ −58° (*c* 1.2, $CHCl_3$); ^{1}H-NMR data are listed in Table I.

Anal. Found: C, 68.33; H, 4.97.

*5a-Carba-3,6-di-*O-*(α-*D-*mannopyranosyl)-α-*D-*mannopyranose undecaacetate* (**2**).—A mixture of **18** (24 mg, 0.018 mmol), anhyd NaOAc (8 mg, 0.09 mmol), and 90% aq 2-methoxyethanol (2 mL) was stirred for 2 days at 120°, and then evaporated. The residue was treated with Ac_2O (3 mL) and pyridine (3 mL) overnight at room temperature. After conventional processing, the product was chromatographed on a column of silica gel (1 g) with 1:4 acetone–PhMe as eluent to give **2** (17 mg, 98%) as an amorphous powder, $[\alpha]_D^{25}$ +49° (*c* 1, $CHCl_3$);

TABLE I

^{1}H-NMR data (270 MHz, $CDCl_3$) of compounds **17–20**

Proton		Chemical shifts (δ)			
		17	**18**	**19**	**20**
A	1	3.44d	3.17t	4.02d	4.37bdt
	2	~ 3.27	3.62dd	5.49t	5.61bt
	3	3.98d	3.94dd	4.02q	4.20dd
	4	3.78ddd	3.87bt	5.46t	5.35t
	5	2.32–1.75	2.02–1.85	2.40–2.01	2.34–1.91
	5a.*eq*		2.29dt		
	5a.*ax*		2.05dd		
	6a	4.26dd	3.93dd	3.89dd	3.90dd
	6b	3.49dd	3.69dd	3.56dd	3.79dd
	NH				6.04d
	OH	~ 3.27	3.02bs		
B,C	1	5.58d	5.46d	5.35d	5.30d
		5.10d	5.09d	5.10d	5.15d
	2	5.87dd	5.87dd	5.75dd	5.70dd
		5.76dd	5.73dd	5.52dd	5.55dd
	3	5.99dd	6.01dd	5.91dd	5.88dd
		5.91dd	5.89dd	5.81dd	5.80dd
	4	6.15t	6.14t	6.14t	6.22t
		6.14t	6.13t	6.14t	6.13t
	5	4.77–4.53	4.89–4.47	4.75–4.47	4.79–4.46
	6				
	OAc			2.36	2.27
				2.25	2.21
					2.05
		Coupling constants (Hz)			
A	$J_{1,2}$	3.3	4.2	2.9	3.3
	$J_{2,3}$		1.3	2.9	3.3
	$J_{3,4}$	8.1	9.3	9.5	8.4
	$J_{4,5}$	10.6	9.3	9.5	8.4
	$J_{5,5a.ax}$		11.4		
	$J_{5,5a.eq}$		5.5		
	$J_{5a,5a}$		15		
	$J_{5,6}$	4	7.7	5.5	7
	$J_{5,6'}$	2.9	1.8	4	4.4
	$J_{6,6}$	9.7	8.4	9.7	10.3
	$J_{1,5a.ax}$			2.9	3.3
	$J_{1,5a.eq}$		4.2	2.9	3.3
	$J_{1,NH}$				6.6
B,C	$J_{1,2}$	1.8	1.5	1.8	1.5
	$J_{2,3}$	3.1	3.3	3.3	3.3
	$J_{3,4}$	9.9	9.9	10.3	10.3
	$J_{4,5}$	9.9	9.9	10.3	10.3

^{1}H-NMR (270 MHz, $CDCl_3$): δ 5.33–5.03 (m, 9 H, H-1,2,4,2′,3′,4′,2″,3″,4″), 4.99 and 4.74 (2 d, each 1 H, $J_{1',2'}$ 1.5, $J_{1'',2''}$ 1.5 Hz, H-1′,1″), 4.31 and 4.26 (2 dd, each 1 H, $J_{5',6'a}$ 4.7, $J_{5'',6''a}$ 4.7 Hz, H-6′a,6″a), 4.13–3.98 (m, 5 H, H-3,5′,6′b,5″,6″b), 3.62

(dd, 1 H, $J_{5,6a}$ 5.7, $J_{6,6}$ 9.5 Hz, H-6a), 3.35 (dd, 1 H, $J_{5,6b}$ 4.4 Hz, H-6b), 2.21, 2.15, 2.14, 2.13, 2.11, 2.10, 2.07, 2.05, 1.984, and 1.981 (10 s, 3, 3, 6, 3, 3, 3, 3, 3, 3, and 3 H, 11 Ac), and 2.31–1.68 (m, 3 H, H-5,5a.*ax*,5a.*eq*).

Anal. Calcd for $C_{41}H_{56}O_{26}$: C, 51.04; H, 5.85. Found: C, 50.91; H, 5.72.

1D-(1,2,4 / 3,6)-1,3-Di-O-acetyl-6-azido-2,7-di-O-(2,3,4,6-tetra-O-benzoyl-α-D-mannopyranosyl)-4-(hydroxymethyl)cyclohexane-1,2,3-triol (**19**).—A mixture of **18** (155 mg, 0.12 mmol), NaN_3 (53 mg, 0.83 mmol), NH_4Cl (38 mg, 0.71 mmol), and 90% aq *N,N*-dimethylformamide (DMF, 4 mL) was stirred at 24 h at 80°, and then evaporated. After the usual processing, the product was chromatographed on a column of silica gel (17 g) with 1:15 EtOAc–PhMe as eluent to give **19** (164 mg, 97%) as crystals, mp 124–126° (from EtOH), $[\alpha]_D^{20}$ −25.5° (*c* 0.51, $CHCl_3$); ^{1}H-NMR data are listed in Table I.

Anal. Calcd for $C_{79}H_{69}N_{30}O_{24}$: C, 65.69; H, 4.82; N, 2.91. Found: C, 65.64; H, 4.84; N, 2.82.

N-*Acetyl-2,4-di-O-acetyl-5a-carba-3,6-di-O-(2,3,4,6-tetra-O-benzoyl-α-D-mannopyranosyl)-α-D-mannopyranosylamine* (**20**).—A solution of **19** (155 mg, 0.11 mmol) and AcOH (3 drops) in 1:1 EtOH–EtOAc (4 mL) was hydrogenated in the presence of Raney nickel (one spoonful) for 2 days at room temperature under atmospheric pressure. The catalyst was filtered and the filtrate was evaporated and the residue was chromatographed on a column of silica gel (4 g) with 1:4 butanone–PhMe as eluent to give **20** (106 mg, 68%) as crystals, mp 142–144° (from EtOH); $[\alpha]_D^{27}$ −30° (*c* 1, $CHCl_3$); ^{1}H-NMR data are listed in Table I.

Anal. Calcd for $C_{81}H_{73}O_{25}$: C, 66.61; H, 5.04; N, 0.96. Found: C, 66.32; H, 5.05; N, 0.95.

*5a-Carba-3,6-di-O-(α-D-mannopyranosyl)-α-D-mannopyranosylamine undeca-*N,O-*acetate* (**3**).—Compound **20** (105 mg, 0.072 mmol) was treated with methanolic M NaOMe (0.3 mL) in MeOH (3 mL) for 2 h at room temperature. After neutralization with Amberlite IR-120B (H^+) resin the mixture was evaporated and the residue was acetylated conventionally. The product was chromatographed on a column of silica gel with 1:8 EtOH–PhMe as eluent to give **3** (50 mg, 72%) as an amorphous solid, $[\alpha]_D^{25}$ +39° (*c* 1.57, $CHCl_3$); ^{1}H-NMR: δ 5.86 (d, 1 H, $J_{1,NH}$ 7 Hz, NH), 5.42–5.05 (m, 8 H, H-2,4,2′,3′,4′,2″,3″,4″), 5.01 and 4.80 (2 d, each 1 H, $J_{1',2'}$ 1.5, $J_{1'',2''}$ 1.5 Hz, H-1′,1″), 4.36–3.94 (m, 8 H, H-1,3,5′,6′a,6′b,5″,6″a,6″b), 3.64 (dd, 1 H, $J_{5,6a}$ 7, $J_{6,6}$, 9.9 Hz, H-6a), 3.55 (dd, 1 H, $J_{5,6b}$ 5.5 Hz, H-6b), 2.17, 2.16, 2.13, 2.12, 2.115, 2.11, 2.07, 2.02, 1.99, and 1.98 (10 s, 3, 3, 3, 3, 3, 3, 6, 3, 3, and 3 H, 11 Ac), and 2.21–1.73 (m, 3 H, H-5,5a.*ax*,5a.*eq*).

Anal. Calcd for $C_{41}H_{57}NO_{25}$: C, 51.09; H, 5.96; N, 1.45. Found: C, 50.90; H, 5.83; N, 1.43.

1,3-Di-O-benzyl-4,6-O-benzylidene-5a-carba-α-D-mannopyranose (**22**).—To a solution of 1,2-anhydro-3-*O*-benzyl-4,6-*O*-benzylidene-5a-carba-β-D-mannopyranose{(1*R*,2*R*,3*R*,5*R*,8*R*,10*R*)-2-benzyloxy-5-phenyl-4,6,11-trioxatricyclo[8.1.0.0^{3,8}]-undecane}[1] (**21**, 526 mg, 1.55 mmol) in benzyl alcohol (0.81 mL, 7.8 mmol) was added 2% $BF_3 \cdot OEt_2$ (10 mL), and the mixture was stirred for 50 min at 0° under

argon. The mixture was diluted with $CHCl_3$ (150 mL) and washed with satd aq $NaHCO_3$ and H_2O, dried, and evaporated. The product was chromatographed on a column of silica gel (20 g) with 1:15 butanone–PhMe as eluent to give **22** (478 mg, 67%) as a syrup, $[\alpha]_D^{25}$ +11° (*c* 1.2, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$): δ 7.50–7.25 (m, 15 H, 3 Ph), 5.63 (s, 1 H, C*H*Ph), 4.88, 4.68, 4.58 and 4.46 (4 d, each 1 H, *J* 11.7 Hz, 2 CH_2Ph), 4.17 (t, 1 H, $J_{1,2} = J_{2,3} = 2.9$ Hz, H-2), 4.12 (dd, 1 H, $J_{5,6e}$ 4.8, $J_{6,6}$ 11 Hz, H-6e), 3.99 (t, 1 H, $J_{3,4} = J_{4,5} = 9.6$ Hz, H-4), 3.87 (dd, 1 H, H-3), 3.81 (q, 1 H, $J_{1,5a.ax} = J_{1,5a.eq} = 2.9$ Hz, H-1), 3.66 (t, 1 H, $J_{5,6a}$ 11 Hz, H-6a), 2.59 (d, 1 H, $J_{2,OH}$ 0.7 Hz, OH), 2.29 (m, 1 H, H-5), 1.61 (dt, 1 H, $J_{5,5a.eq}$ 2.9, $J_{5a,5a}$ 13.9 Hz, H-5a.*eq*), and 1.48 (td, 1 H, $J_{5,5a.ax}$ 13.9 Hz, H-5a.*ax*).

Anal. Calcd for $C_{28}H_{30}O_5$; C, 75.31; H, 6.77. Found: C, 74.97; H, 6.84.

1,3-Di-O-benzyl-4,6-O-benzylidene-5a-carba-2-O-(2,3,4,6-tetra-O-benzoyl-α-D-mannopyranosyl)-α-D-mannopyranose (**23**).—A mixture of **22** (250 mg, 0.56 mmol), $Hg(CN)_2$ (500 mg, 2.0 mmol), Drierite (500 mg), and benzene (30 mL) was refluxed to remove 10 mL of benzene, and the mixture was heated at reflux after addition of **10** (740 mg, 1.1 mmol) for 48 h, and then processed conventionally. The product was chromatographed on a column of silica gel (40 g) with 1:30 EtOAc–PhMe as eluent to give **23** (515 mg, 90%) as crystals, mp 80–82° (from EtOH); $[\alpha]_D^{27}$ −39° (*c* 1.44, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$): δ 8.10–7.60 (m, 35 H, 7 Ph), 6.03 (t, 1 H, $J_{3',4'} = J_{4',5'} = 10.3$ Hz, H-4′), 5.92 (dd, 1 H, $J_{1',2'}$ 1.5, $J_{2',3'}$ 3.3 Hz, H-2′), 5.86 (dd, 1 H, H-3′), 5.75 (s, 1 H, C*H*Ph), 5.61 (d, 1 H, H-1′), 4.90 and 4.62 (2 d, each 1 H, *J* 12.5 Hz, CH_2Ph), 4.63 (dd, 1 H, $J_{5',6'a}$ 2.6, $J_{6',6'}$ 12.1 Hz, H-6′a), 4.45 and 4.33 (2 d, each 1 H, *J* 11.7 Hz, CH_2Ph), 4.44 (dd, 1 H, $J_{5',6'b}$ 5.3 Hz, H-6′b), 4.32 (bdd, 1 H, $J_{1,2}$ 3.3, $J_{2,3}$ 2.9 Hz, H-2), 4.33–4.26 (m, 1 H, H-5′), 4.17 (t, 1 H, $J_{3,4} = J_{4,5} = 9.8$ Hz, H-4), 4.16 (dd, 1 H, $J_{5,6eq}$ 4, $J_{6,6}$ 11 Hz, H-6*eq*), 3.94 (dd, 1 H, H-3), 3.81 (t, 1 H, $J_{5,6ax}$ 11 Hz, H-6*ax*), 3.79 (q, 1 H, $J_{1,5a.ax} = J_{1,5a.eq} = 3.3$ Hz, H-1), 2.35–2.25 (m, 1 H, H-5), 1.68 (dt, 1 H, $J_{5,5a.eq}$ 3.3, $J_{5a,5a}$ 12.8 Hz, H-5a.*eq*), and 1.58 (td, 1 H, $J_{5,5a.ax}$ 12.8 Hz, H-5a.*ax*).

Anal. Calcd for $C_{62}H_{56}O_{14}$: C, 72.64; H, 5.51. Found: C, 72.43; H, 5.57.

5a-Carba-2-O-(α-D-mannopyranosyl)-α-D-mannopyranose octaacetate (**5**).—Compound **23** (51 mg, 0.05 mmol) was *O*-deacylated by treatment with methanolic M NaOMe as in the preparation of **3**. The product was then dissolved in EtOH (2 mL) and hydrogenolyzed in the presence of 20% $Pd(OH)_2$–C (30 mg) under atmospheric pressure for 68 h at room temperature. The catalyst was filtered and the filtrate was evaporated to give an amorphous solid, TLC (1:2 EtOH–EtOAc) of which showed a single spot (R_F 0.14). The free carba-disaccaharide was acetylated in the usual way and chromatographed on a column of silica gel (2 g) with 1:4 butanone–PhMe as eluent to give **5** (31 mg, 92%) as a syrup, $[\alpha]_D^{27}$ +34° (*c* 1.5, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$): δ 5.33 and 5.32 (2 t, each 1 H, $J_{3,4} = J_{4,5} = 9.9$, $J_{3',4'} = J_{4',5'} = 9.9$ Hz, H-4,4′), 5.27 (dd, 1 H, $J_{1',2'}$ 1.5, $J_{2',3'}$ 2.9 Hz, H-2′), 5.26 (dd, 1 H, $J_{2,3}$ 5.9 Hz, H-3), 5.18 (dd, 1 H, H-3′), 5.07 (q, 1 H, $J_{1,2} = J_{1,5a.ax} = J_{1,5a.eq} = 2.9$ Hz, H-1), 5.05 (d, 1 H, H-1′), 4.27 (dd, 1 H, $J_{5',6'a}$ 5.9, $J_{6',6'}$ 12.4 Hz, H-6′a), 4.15 (dd, 1 H, $J_{2,3}$ 5.9 Hz, H-2), 4.14 (dd, 1 H, $J_{5',6'b}$ 2.2 Hz,

H-6′b), 4.13 (dd, 1 H, $J_{5,6a}$ 5.1, $J_{6,6}$ 11.7 Hz, H-6a), 4.02 (ddd, 1 H, H-5′), 3.97 (dd, 1 H, $J_{5,6b}$ 3.7 Hz, H-6b), 2.15, 2.11, 2.10, 2.07, 2.04, and 2.02 (7 s, 3 , 3, 6, 3, 3, 3, and 3 H, 8 Ac).

Anal. Calcd for $C_{29}H_{40}O_{18}$: C, 51.48; H, 5.96. Found: C, 51.70; H, 5.83.

1,3-Di-O-benzyl-4,6-O-benzylidene-5a-carba-2-O-(3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-α-D-mannopyranose (**25**).—A mixture of **22** (96 mg, 0.21 mmol), $Hg(CN)_2$ (300 mg, 1.2 mmol), Drierite (300 mg), and benzene (15 mL) was refluxed to remove 5 mL of benzene, and then, after cooling, 3,4,6-tri-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl bromide[8] (**24**, 210 mg, 0.42 mmol) was added and the mixture was was refluxed for 3 days in the dark. After treatment with Et_3N, the mixture was filtered through a Celite bed and the filtrate was evaporated and the residue was chromatographed on a column of silica gel (40 g) with 1 : 10 butanone–PhMe containing 0.5% Et_3N as eluent to give recovered **22** (12.5 mg) and **25** (112 mg, 62%) as a syrup, $[\alpha]_D^{28}$ +20° (*c* 0.9, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$): δ 7.89–7.15 (m, 19 H, 4 Ph), 5.78 (dd, 1 H, $J_{2',3'}$ 10.6, $J_{3',4'}$ 9.5 Hz, H-3′), 5.53 (s, 1 H, C*H*Ph), 5.36 (d, 1 H, $J_{1',2'}$ 8.4 Hz, H-1′), 5.17 (t, 1 H, $J_{4',5'}$ 9.5 Hz, H-4′), 4.73 and 4.67 (2 d, each 1 H, *J* 12.5 Hz, CH_2Ph), 4.45 (dd, 1 H, H-2′), 4.37 and 4.23 (2 d, each 1 H, *J* 11.4 Hz, CH_2Ph), 4.33 (dd, 1 H, $J_{5',6'a}$ 4.8, $J_{6',6'}$ 12.1 Hz, H-6′a), 4.15 (dd, 1 H, $J_{5',6'b}$ 2.4 Hz, H-6′b), 4.04 (t, 1 H, $J_{1,2} = J_{2,3}$ = 2.5 Hz, H-2), 3.88–3.75 (m, 4 H, H-3,6a,6b,5′), 3.38 (q, 1H, $J_{1,5a.ax} = J_{1,5a.eq}$ = 2.5 Hz, H-1), 3.32 (t, 1 H, $J_{3,4} = J_{4,5}$ 11 Hz, H-4), 2.05 (m, 1 H, H-5), 2.04 and 1.87 (2 s, 6 and 3 H, 3 Ac), 1.10 (dt, 1 H, $J_{5,5a.eq}$ 2.5, $J_{5a,5a}$ 13.6 Hz, H-5a.*eq*), and 0.72 (td, 1 H, $J_{5,5a.ax}$ 13.6 Hz, H-5a.*ax*).

Anal. Calcd for $C_{48}H_{49}NO_{14}$: C, 66.73; H, 5.72; N, 1.62. Found: C, 66.85; H, 5.96; N, 1.60.

2-O-(2-Acetamido-3,4,6-tri-O-acetyl-2-deoxy-β-D-glucopyranosyl)-1,3-di-O-benzyl-4,6-O-benzylidene-5a-carba-α-D-mannopyranose (**26**).—A mixture of **25** (90 mg, 0.10 mmol) and hydrazine hydrate (2 mL, 80%) was heated for 1.5 h at 100° and then evaporated to dryness. The residue was acetylated conventionally and the product was chromatographed on a column of silica gel (4 g) with 1 : 3 acetone–PhMe as eluent to give **26** (62 mg, 77%) as crystals, mp 191–192° (from EtOH); $[\alpha]_D^{27}$ −0.9° (*c* 1.2, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$): δ 7.52–7.25 (m, 15 H, 3 Ph), 5.63 (s, 1 H, C*H*Ph), 5.61 (dd, 1 H, $J_{2',3'}$ 10.4, $J_{3',4'}$ 9.2 Hz, H-3′), 5.59 (d, 1 H, $J_{2',NH}$ 8.1 Hz, NH), 5.02 (d, 1 H, $J_{1',2'}$ 8.1 Hz, H-1′), 5.01 (t, 1 H, $J_{4',5'}$ 9.2 Hz, H-4′), 4.84 and 4.63 (2 d, each 1 H, *J* 11.4 Hz, CH_2Ph), 4.57 and 4.42 (2 d, each 1 H, *J* 11.7 Hz, CH_2Ph), 4.27 (dd, 1 H, $J_{5',6'a}$ 4.6, $J_{6',6'}$ 12.4 Hz, H-6′a), 4.15 (bt, $J_{1,2} = J_{2,3}$ = 2.6 Hz, H-2), 4.13 (dd, 1 H, $J_{5',6'b}$ 2.2 Hz, H-6′b), 4.15–4.07 (m, 1 H, H-5′), 3.98 (t, 1 H, $J_{5,6ax} = J_{6,6}$ = 9.9 Hz, H-6*ax*), 3.89 (dd, 1 H, $J_{5,6eq}$ 2.7 Hz, H-6*eq*), 3.71 (dd, 1 H, $J_{3,4}$ 11.2 Hz, H-3), 3.69 (q, 1 H, $J_{1,5a.ax} = J_{1,5a.eq}$ = 2.6 Hz, H-1), 3.64 (t, 1 H, $J_{4,5}$ 11.2 Hz, H-4), 3.46 (dt, 1 H, H-2′), 2.32–2.14 (m, 1 H, H-5), 2.03, 2.02, and 1.74 (3 s, 3, 6, and 3 H, 4 Ac), 1.57 (dt, 1 H, $J_{5,5a.eq}$ 2.6 Hz, $J_{5a,5a}$ 13.9 Hz, H-5a.*eq*), and 1.34 (td, $J_{5,5a.ax}$ 13.9 Hz, H-5a.*ax*).

Anal. Calcd for $C_{42}H_{49}NO_{13}$: C, 65.02; H, 6.37; N, 1.81. Found: C, 65.19; H, 6.41; N, 1.83.

*2-O-(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-5a-carba-α-D-mannopyranose octa-*N,O*-acetate* (**7**).—Compound **26** (83 mg, 0.11 mmol) was hydrogenolyzed in EtOH as described in the preparation of **5**, and the product was acetylated in the usual manner and chromatographed on a column of silica gel (7 g) with 1:2 acetone–PhMe as eluent to give **7** (67 mg, 93%) as crystals, mp 206–207° (from EtOH); $[\alpha]_D^{28}$ −23° (*c* 1, $CHCl_3$); ^{1}H-NMR (270 MHz, $CDCl_3$): δ 5.72 (d, 1 H, $J_{2',NH}$ 8.8 Hz, NH), 5.26 (t, 1 H, $J_{3,4} = J_{4,5} = 10.3$ Hz, H-4), 5.20 (t, 1 H, $J_{2',3'} = J_{3',4'} = 9.9$ Hz, H-3′), 5.05 (t, 1 H, $J_{4',5'}$ 9.9 Hz, H-4′), 4.94 (q, 1 H, $J_{1,2} = J_{1,5a.ax} = J_{1,5a.eq} = 3.3$ Hz, H-1), 4.89 (dd, 1 H, $J_{2,3}$ 3.3 Hz, H-3), 4.61 (d, 1 H, $J_{1',2'}$ 8.4 Hz, H-1′), 4.23 (dd, 1 H, $J_{5',6'a}$ 4.8, $J_{6',6'}$ 12.9 Hz, H-6′a), 4.19 (t, 1 H, H-2), 4.06 (dd, 1 H, $J_{5,6a}$ 5.5, $J_{6,6}$ 11 Hz, H-6a), 4.03 (dd, 1 H, $J_{5',6'b}$ 1.8 Hz, H-6′b), 3.97 (ddd, 1 H, H-2′), 3.93 (dd, 1 H, $J_{5,6b}$ 2.3 Hz, H-6b), 3.65 (ddd, 1 H, $J_{4',5'}$ 9.9 Hz, H-5′), 2.12, 2.10, 2.08, 2.04, 2.03, 2.02, 2.01, and 1.94 (8 s, each 3 H, 8 Ac).

Anal. Calcd for $C_{29}H_{41}NO_{17}$: C, 51.55; H, 6.12; N, 2.07. Found: C, 51.24; H, 5.85; N, 2.06.

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