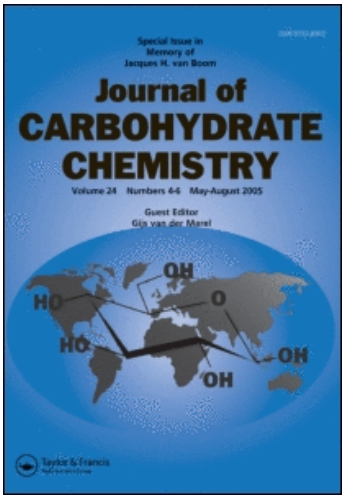

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Synthesis of a Precursor of β-D-GlcpNAc(1→2)-α-D-Manp-(1→3)-[β-D-Xylp-(1→2)]-β-D-Manp-(1→4)-β-D-Glcp

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SYNTHESIS OF A PRECURSOR OF β-D-GlcpNAc(1→2)-α-D-Manp-(1→3)-[β-D-Xylp-(1→2)]-β-D-Manp-(1→4)-β-D-Glcp[1]

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ABSTRACT

The glycosphingolipids isolated from spermatozoa of a fresh-water bivalve, Hyriopsis schlegelii, have a unique structure containing one or two mannosyl residues, novel linkages including an internal fucopyranosyl residue, as well as terminal xylosyl and 4-O-methyl-D-glucopyranosyl uronic acid groups. The pentasaccharide derivatives that constitute the partial structure of lipid IV were synthesized as follows. 4,6-Di-O-acetyl-2-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-3-O-benzyl-α-D-mannopyranosyl bromide was treated with 2,3-di-O-acetyl-1,6-anhydro-β-D-glucopyranose in the presence of silver zeolite to afford the corresponding trisaccharide. The formation of the β-glycoside took precedence as a major product in a ratio of 6.9:1. After debenzylation, the β-mannosyl trisaccharide derivative was condensed with 3,4,6-tri-O-acetyl-2-O-chloroacetyl- α -D-mannopyranosyl bromide in the presence of silver triflate, and the final pentasaccharide derivative was prepared by using a suitably protected tetrasaccharide as the glycosyl acceptor, 3-O-acetyl-6-O-benzyl-4-O-chloroacetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl bromide as the donor and silver triflate as the promoter, respectively.

INTRODUCTION

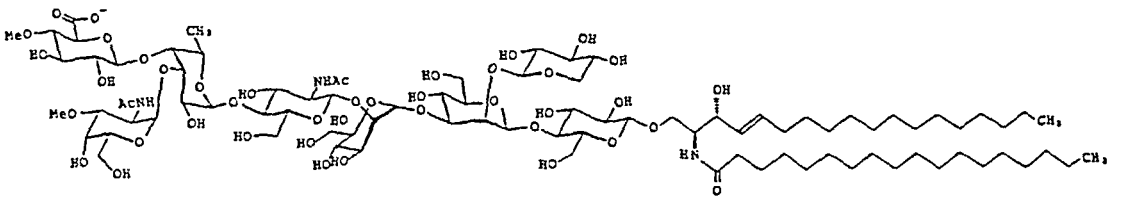
In the course of a systematic study on the spermatozoa glycosphingolipids classified as mollu series of the fresh-water biva-

lve, Hyriopsis schlegelii, T.Hori et al.[2] have isolated and characterized seven glycolipids. These neutral glycolipids differ from mammalian glycolipids in having mannosyl residues. They also have isolated a novel acidic glycolipid (Lipid IV) containing 4-O-methyl glucuronic acid, and elucidated the structure as 1.[3] In our previous paper,[4] we reported the synthesis of the non-reducing trisaccharide end of lipid IV, namely, 4-O-Me-β-D-Glc_pA-(1→4)-[3-O-Me-α-D-Gal_pNAc-(1→3)]-L-Fuc_p. The pentasaccharide reducing end of lipid IV was the target for the synthetic studies described here as part of our investigations on the synthesis of oligosaccharides of biological interest.

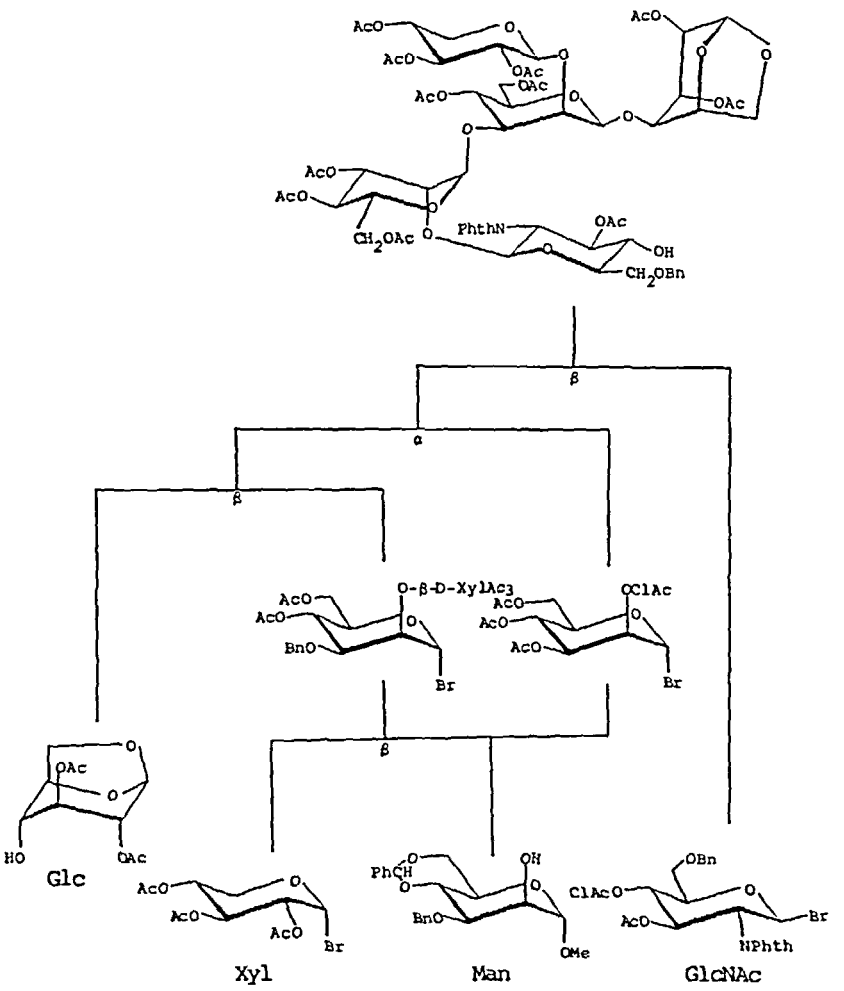
RESULTS AND DISCUSSION

In this work, the derivative 26, a precursor of O-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→2)-O-α-D-mannopyranosyl-(1→3)-O-[O-β-D-xylopyranosyl-(1→2)]-β-D-mannopyranosyl-(1→4)-O-β-D-glucopyranose, was synthesized, by stepwise condensation of suitably protected monosaccharide units. An 1,6-anhydro-D-glucopyranose derivative was used as the glycosyl acceptor, and bromide derivatives of D-xylose, D-mannose, and 2-acetamido-2-deoxy-D-glucopyranose as donors. A synthetic plan for the target compound 26 was designed as shown in Scheme 1.

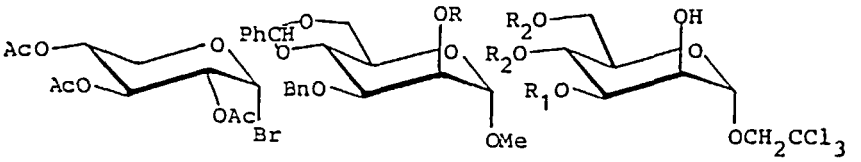
Methyl 3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (2), which was prepared from methyl α-D-mannopyranoside, according to Nashed,[5] was condensed with 2,3,4-tri-O-acetyl-α-D-xylopyranosyl bromide (1)[6] in dichloromethane for 12 h at 10 °C, in the presence of mercuric cyanide and molecular sieves. Purification of the crude product by column chromatography afforded in 28.5% yield the disaccharide derivative, methyl 2-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (15). In a parallel route, the disaccharide



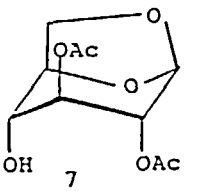
Lipid IV (1)



SCHEME 1 Retrosynthetic Analysis



1 2 R=H 3 R=ClAc 4 R_1=R_2=H 5 R_1=H, R_2=-CHPh- 6 R_1=Bn,R_2=-CHPh-



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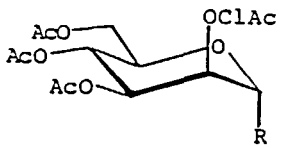
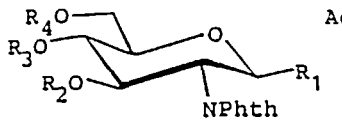
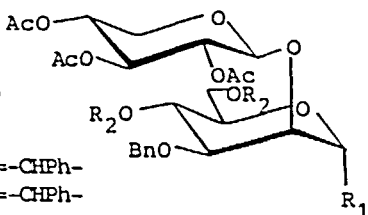


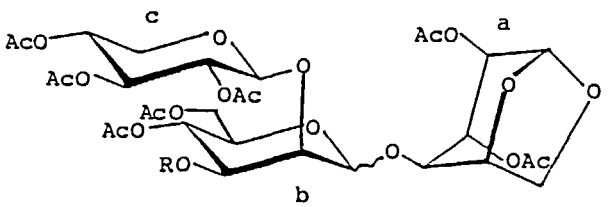
8 R=OAc 9 R=Br



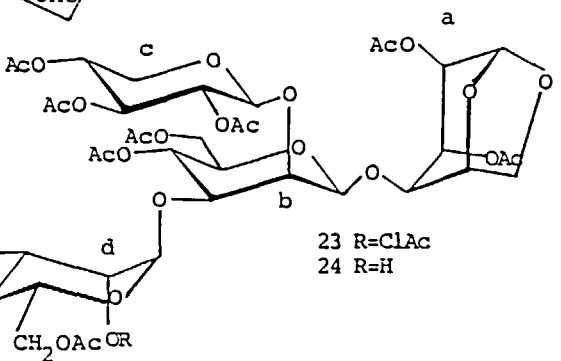
10 R_1=OH, R_2=H, R_3,R_4=-CHPh- 11 R_1=OAc,R_2=Ac,R_3,R_4=-CHPh- 12 R_1=OAc,R_2=Ac,R_3=H,R_4=Bn 13 R_1=OAc,R_2=Ac,R_3=ClAc,R_4=Bn 14 R_1=Br, R_2=Ac,R_3=ClAc,R_4=Bn



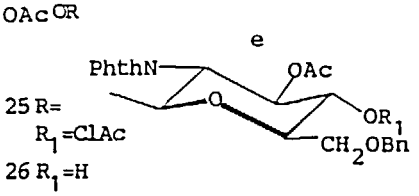
15 R_1=OMe, R_2=-CHPh- 16 R_1=OCH_2CCl_3,R_2=-CHPh- 17 R_1=OCH_2CCl_3,R_2=H 18 R_1=OH, R_2=H 19 R_1=OAc, R_2=Ac 20 R_1=Br, R_2=Ac



21α 21β R=Bn 22β R=H



23 R=ClAc 24 R=H



25 R= R_1=ClAc 26 R_1=H

derivative, 2,2,2-trichloroethyl 2-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (16) was obtained by condensation with 2,2,2-trichloroethyl 3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (6)[7] and compound 1 in 57.3% yield. 4,6-Di-O-acetyl-2-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-3-O-benzyl- α -D-mannopyranosyl bromide (20) was obtained in two and/or four steps from glycoside 15 and 16, respectively. Methyl glycoside derivative 15 was acetolyzed, and then brominated. Deprotection of the 2,2,2-trichloroethyl glycoside derivative (16) was effected in two consecutive steps: hydrolysis of the benzylidene group with 80% acetic acid to give 17, de-2,2,2-trichloroethylation with zinc-cupric sulfate in acetate buffer.[8] It led to 2-O-(2,3,4-tri-O-acetyl- β -D-xylopyranosyl)-3-O-benzyl-α-D-mannopyranose (18). After acetylation of 18, α-bromide (20) was readily prepared by replacement of the acetate group by treatment with titanium tetrabromide. β-Mannosidation reaction of 20 with the glycosyl acceptor, 2,3-di-O-acetyl-1,6-anhydro- β -D-glucopyranose (7)[9] in the presence of silver silicate according to Paulsen et al.,[10] followed by column chromatography, gave 63.3% yield of a mixture of the desired β-(1→4)-linked product (21β) and its α-anomer (21α) in a ratio of 2.67:1. Configuration at C-1b for 21α and 21β were assigned as α-D and β-D, respectively, from the ^{1}H NMR spectra,[11] which contained signals for H-1' at δ 5.044 with J=2.38 Hz for compound 21α and a singlet signal at 4.736 for compound 21β. When silver zeolite[12] was used as a promoter, the formation of the β-glycoside took precedence as a major product in a ratio of 6.9:1. The insoluble silver salt promotes the formation of the β-glycosidic linkage, when a non-participating group is present at C-2 of the glycon. Also the 4-O-acetyl function increases the β/α ratio of the glycosidic bond formation in accord with Boeckel et al..[13] Debenzylation of 21β with 5% Pd-C provided 3'-OH free trisaccharide (22β). 3,4,6-Tri-O-acetyl-2-O-chloroacetyl-α-D-mannopyranosyl bromide (9), obtain-

ed from 2 by chloroacetylation followed by acetolysis and then treatment with hydrogen bromide in acetic acid, was condensed with 22β in the presence of silver triflate[14] to give the tetrasaccharide 23 in 70.7% yield. The ^{1}H NMR spectrum showed chloroacetyl methylene proton signals at δ 4.185 and 4.144 (each d, 2H, J=15.20 Hz) and ten acetyl group signals. Four signals for anomeric proton atoms at δ 5.415 (br. s, Glc-H_1), 4.786 (s, β-Man-H_1), 5.138 (d, J=4.95, Xyl-H_1) and 5.004 (d, J=1.83,α-Man-H_1). The α-D-configuration of the newly formed glycoside bond was indicated by the $J_{C,H}$ value of 170.5 Hz in the ^{13}C NMR spectrum and the coupling constant of 1.83 Hz for H-1_d in the ^{1}H NMR spectrum. De-chloroacetylation of tetrasaccharide derivative (23) with thiourea gave the corresponding tetrasaccharide derivative (24) as a syrup. The ^{13}C NMR data showed four signals for anomeric carbon atoms at 99.26 (Glc, $J_{C,H}$ 180.1 Hz), 99.37 (β-Man, 157.0 Hz), 101.49 (α-Man, 170.5 Hz) and 99.50 (Xyl, 173.5 Hz), respectively. 2-Deoxy-2-phthalimido-β-D-glucopyranose[15] was readily prepared according to Lemieux et al.,[16] from 1,3,4,6-tetra-O-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose, which was benzylidenated (10), acetylated(11), and then had its benzylidene acetal ring reductively opened using sodium cyanoborohydride-HCl(gas)-diethyl ether[17] to afford 1,3-di-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranose (12). Chloroacetylation of 12 and subsequent bromination by titanium tetrabromide gave 3-O-acetyl-6-O-benzyl-4-O-chloroacetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl bromide (14). Compound 24 was condensed with 14 in dichloromethane for 4 h at -15 °C in the presence of silver triflate-2,6-lutidine and molecular sieves, to give the pentasaccharide derivative 25 in 75.0% yield. $J_{C,H}$ value of 162.9 Hz in the ^{13}C NMR supported the configuration of the newly formed glycoside bond. De-chloroacetylation of 25 gave the corresponding pentasaccharide derivative (26) as a syrup. ^{13}C NMR spectral data of the synthesized compounds are given in Table 1.

TABLE 1 ^{13}C NMR Spectral data of 7, 13, 27, 15, 21β, 24, 25, and 26

		7	13	27	15	21β	24	25	26
Glc	C-1	99.03				99.12	99.26	99.24	99.23
	($J_{C,H}$)						(180.1)	(183.1)	
	2	68.92				69.63*	69.54*	69.51	69.55
	3	68.53				68.83	68.87	68.82	68.83
	4	71.74				70.74*	75.79	75.68	75.58
	5	76.08				68.25	73.09	73.01	73.34
	6	64.92				64.96	64.91	64.88	64.88
β Man	C-1					99.30	99.37	99.24	99.23
	($J_{C,H}$)						(157.0)	(158.7)	
	2					77.24	75.28	74.33	74.41
	3					72.72	77.49	76.89	77.30
	4					67.52	67.90	67.97	67.90
	5					72.85	72.60*	72.65*	72.63*
	6					62.80	62.61	62.52	62.57
α Man	C-1				99.77		101.49	99.20	99.16
	($J_{C,H}$)				(162.9)		(170.5)	(168.0)	
	2				74.09		69.39*	74.99*	75.00*
	3				70.18		71.15	69.04	69.12
	4				78.48		66.39*	65.88*	65.96*
	5				64.07		68.87*	69.27*	69.30*
	6				68.58		62.56	62.66	62.67
Xyl	C-1			101.02	99.52	99.12	99.50	99.24	99.40
	($J_{C,H}$)				(168.4)		(173.5)	(171.3)	
	2			70.22	70.67	68.74*	69.54*	69.51	69.48
	3			71.02	72.15	72.18*	69.04*	68.82*	68.98*
	4			68.31	68.79	68.40*	68.69	68.66*	68.66
	5			61.32	61.49	59.87	60.51	60.47	60.44
GlcNAc	1		89.87					97.13	97.04
	($J_{C,H}$)							(162.9)	
	2		53.51					54.44	54.40
	3		70.43					70.52	70.99
	4		70.91					71.40	69.91
	5		73.25					72.85*	72.98*
	6		67.84					68.51	68.79

* These assignments may be exchanged
Compound 27: methyl 2,3,4-tri-O-acetyl-β-D-xylopyranoside

In our synthetic work containing xylose, it was very difficult to decide the anomeric configuration because the coupling constants of xylose related compounds showed the range of $3.7 \leqq J_{1,2}(Hz) \leqq 6.6$ (Table 1) caused by $^4C_1 \rightleftarrows {}^1C_4$ equilibrium. Kovac and co-workers[18] have investigated the same ^1H NMR shifts of a series of acetylated methyl α-and β-D-xylopyranosides ($4.8 \leqq J_{1,2} \leqq 7.2$), and also Liptak et al.[19] have published the coupling constants range of $4.0 \leqq J_{1,2} \leqq 8.0$ in the case of the partial synthesis of xylose-containing carbohydrate chains from N-glycoproteins. de Bruyn[18] explained that H-5a appears at δ 3.69/3.80 in α-anomers, and at δ 4.04/4.14 in β-forms, while H-5b of α- and β-species are found at δ 3.34/3.46 and δ 3.35/3.36, respectively. These data are not in agreement with those provided in other publications.[19,20]. Even in the same $CDCl_3$ solution experiment, Mihashi's data[20] showed that H-5a appears at δ 3.49/3.79 in α-anomers, and at δ 3.74/3.91 in β-forms, while H-5b of α- and β-species are found at δ 3.40/3.54 and 2.95/3.07, respectively. These differences must occur as a function of solvent and signal resolution. We considered the problem of assigning anomeric configuration by using the following equation $\Delta|\delta H\text{-}5a - \delta H\text{-}5b|$ (Hz). As a rule,[18-22] the range of the equation values can be used to distinguish between α and β-anomers ; $0 \leqq \Delta(\alpha)\ |\delta H\text{-}5a - \delta H\text{-}5b| \leqq 60 \leqq \Delta(\beta)|\delta H\text{-}5a - \delta H\text{-}5b| \leq 110$. Our synthetic compounds containing xylose were assigned to have the β-D-configuration. The approximate percentage of the $^4C_1$ chair[6,23] is given in Table 2.

EXPERIMENTAL

General Methods. Melting points were determined with a Yanagimoto micro melting-point apparatus and are uncorrected. Optical rotations were measured with a Jasco DIP-4 digital polarimeter. ^1H NMR and ^{13}C NMR spectra were recorded with JEOL FX-270 and JEOL GSX-400 MHz spectrometers. Thin-layer chromatography was

TABLE 2 ^{1}H NMR-Parameters of the Title Compounds in $CDCl_3$ at 400 MHz

	Coupling Constant(Hz)					δ (ppm)			Hz	Approx.
Comp.	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5a}$	$J_{4,5b}$	$J_{5a,5b}$	H-1	H-5a	H-5b	$\Delta\lvert\delta$H-5a-H-5b$\rvert$	% $^4C_1$
15	6.2	8.1		4.8	8.1	-11.9	4.59	4.30	3.35	95	75
16	6.0	7.7		4.8	7.9	-11.1	4.58	4.31	3.35	96	73
17	6.0	7.8		4.1	8.0	-12.1	4.53	4.26	3.36	90	73
18	5.5	7.2	7.0	4.2	7.0	-12.3	4.69	4.31	3.38	93	66
21α	4.6	7.1		3.7	5.7	-12.5	5.19	4.36	3.38	98	55
21β	3.7	5.5		3.3	4.2	-11.6	5.19	4.42	3.46	96	44
22	6.6	8.4		5.1	7.8	-11.9	4.92	4.18	3.43	75	80
23	5.0	6.8	6.2	4.0	6.2	-11.9	5.14	4.35	3.56	79	60
24	4.9	6.8		3.9	5.9	-12.1	5.14	4.36	3.60	76	59
25	5.0	6.7	6.0	3.8	6.0	-12.1	5.04	4.25	3.48	77	60

conducted on precoated silica gel plates (Merck GF-254), and the compounds were detected by quenching of UV fluorescence and by spraying with 10% H_2SO_4 solution. Column chromatography was carried out on silica gel (Merck Kieselgel 60).

Methyl 2-O-(2,3,4-Tri-O-acetyl-β-D-xylopyranosyl)-3-O-benzyl-4,6-O-benzylidene-α-D-mannopyranoside (15). To a solution of 2 (1.1 g, 2.95 mmol) in dichloromethane (10 mL) were added $Hg(CN)_2$ (1.12 g), molecular sieves 4A (1 g) and bromide 1 (1.5 g, 4.43 mmol), and the mixture was stirred for 12 h at 10 °C. The suspension was filtered and the filtrate extracted with chloroform. The extract was washed with water, dried, and concentrated to give a syrup which was chromatographed on silica gel with 40:1 benzene-acetone as eluent. The eluate containing the disaccharide fraction was concentrated to dryness to give pure 15 (530 mg,28.5 %), mp 195-196 °C, $[\alpha]_D^{20}$ -5.6°(c 1.6, chloroform); ^{1}H NMR ($CDCl_3$) δ7.495-7.244 (m, 10H, Ph), 5.591 (s, 1H, benzylidene H), 4.640 (d, 1H, $J_{1,2}$=1.46 Hz, H-1), 4.586 (d, 1H, $J_{1',2'}$=6.23 Hz, H-1'),4.299 (dd, 1H, $J_{5'a,5'b}$=11.91 Hz, H-5'a), 3.346 (dd, 1H, H-5'b), 3.341 (s, 3H, OMe), 2.065 (s, 3H, OAc), 2.053 (s, 6H, 2xOAc).

Anal. Calcd for $C_{32}H_{38}O_{13}$: C, 60.95; H, 6.07. Found: C, 60.99; H, 6.03.

2,2,2-Trichloroethyl α-D-mannopyranoside (4). Treatment of mannose pentaacetate (17.2 g), with 2,2,2-trichloroethanol (16 mL) in dichloromethane (100 mL) containing $BF_3 \cdot OEt_2$ (20 mL) and molecular sieves (AW 300, 8g, Union Showa K.K. Japan) for 12 h under reflux gave 2,2,2-trichloroethyl 2,3,4,6-tetra-O-acetyl-α-D-mannopyranoside, which was deacetylated with 0.5% sodium methoxide in methanol (40 mL) at room temperature to afford 4 (11.46 g, 83.8%), mp 162 °C; $[\alpha]_D^{20}$+65.2 ° (c 1.03, water); (lit. $[\alpha]_D$ +47.4 °(c 0.24, water), mp 160 °C), ^{1}H NMR($CDCl_3$) δ 5.061 (d, 1H, $J_{1,2}$=1.90 Hz, H-1), 4.362, 4.523 (each d, 2H, ^{2}J=11.8 Hz, Cl_3CCH_2-).

2,2,2-Trichloroethyl 4,6-O-Benzylidene- α-D-mannopyranoside (5). A mixture of 4 (10.0 g, 32.1 mmol), benzaldehyde (32 mL) in formic acid (32 mL) was shaken vigorously for 2 min. The mixture was poured into K_2CO_3 solution (88 g/ 250 mL) for neutralization, and then extracted with ethyl acetate (180 mL). The organic layer was washed with water, dried (Na_2SO_4), and concentrated in vacuo. The residual syrup was chromatographed on silica gel with 70:1 chloroform-methanol as eluent to give 5 (10.37 g, 80.8%), mp 152-153 °C.

Anal. Calcd for $C_{15}H_{17}Cl_3O_6$: C, 45.08; H, 4.29. Found: C, 45.04; H,4.22.

2,2,2-Trichloroethyl 3-O-Benzyl-4,6-O-benzylidene-α-D-mannopyranoside (6). A suspension of compound 5 (5.63 g, 14.09 mmol) and dibutyltin oxide (3.62 g, 14.09 mmol) in methanol (500 mL) was heated under reflux for 1 h, and then the solvent was evaporated. The resulting 2,3-O-dibutylstannylene derivative was dried under vacuum, and taken up in N,N-dimethylformamide (40 mL). Benzyl bromide (2.35 mL, 19.57 mmol) was added and the mixture was heated for 30 min at 100 °C, the solvent was evaporated in vacuo. The residue was chromatographed on silica gel using 4:1 hexane-ethyl acetate to give 6 (6.47 g, 93.8%), ^{1}H NMR ($CDCl_3$) δ 7.344 (m, 10H, Ph), 5.621 (s, 1H, benzylidene H), 5.111 (br.s, 1H, H-1), 2.911 (br.s, 1H, 2-OH).

Anal. Calcd for $C_{22}H_{23}Cl_3O_6$: C, 53.95; H, 4.73. Found: C, 54.22; H, 4.81.

2,2,2-Trichloroethyl 2-O-(2,3,4-Tri-O-acetyl-β-D-xylopyranosyl)-3-O-benzyl-4,6-benzylidene-α-D-mannopyranoside (16). To a solution of acceptor 6 (168 mg, 0.34 mmol), donor 1 (349 mg, 1.02 mmol) in dichloromethane (1 mL), molecular sieves (4A, 500 mg), and mercuric cyanide (519.2 mg) were added and stirred for 10 h at 0 °C. The suspension was filtered and the filtrate extracted with chloroform. The extract was washed with water, dried, and concentrated to give a syrup which was chromatographed on silica gel with 60:1 benzene-acetone as eluent. The eluate containing the disaccharide fraction was concentrated to dryness to give pure 16 (173 mg, 57.3%), $[\alpha]_D^{20}$ -5.2 °(c 1.5, chloroform); TLC (10:1 benzene-ethyl acetate), Rf 0.25; ^{1}H NMR($CDCl_3$) δ 7.492-7.274 (m, 10H, Ph), 5.600 (s, 1H, benzylidene H), 5.020 (d, 1H, $J_{1,2}$=1.47 Hz, H-1), 4.592 (d, 1H, $J_{1',2'}$=6.04 Hz, H-1'), 4.308 (dd, 1H, $J_{5'a,5'b}$= 11.09 Hz, H-5'a), 4.228 and 4.098 (each d, 2H, ^2J=11.55 Hz, CH_2CCl_3), 2.068, 2.061,2.046 (each s, 9H, 3xOAc).

Anal. Calcd for $C_{33}H_{37}Cl_3O_{13}$: C, 52.99; H, 4.99. Found: C, 53.24; H, 5.12.

2,2,2-Trichloroethyl 2-O-(2,3,4-Tri-O-acetyl-β-D-xylopyranosyl)-3-O-benzyl-α-D-mannopyranoside (17). Compound 16 (150 mg, 0.2 mmol) was treated with 80% acetic acid (3 mL) for 1 h at 40 °C. The syrup was chromatographed on a column of silica gel with 50:1 benzene-ethanol as eluent to afford 17 (73.4 mg, 56.4%); $[\alpha]_D^{22}$ -11.8 °(c 1.5, chloroform); TLC (8:1 benzene-ethanol) Rf 0.44; ^{1}H NMR ($CDCl_3$) δ 7.351 (m, 5H, Ph), 4.530 (d, 1H, $J_{1',2'}$=6.0 Hz, H-1'), 4.262 (dd, 1H, $J_{4',5'a}$=4.1, $J_{5'a,5'b}$=12.1 Hz, H-5'a), 3.362 (dd, 1H, $J_{4',5'b}$=8.0 Hz, H-5'b), 2.052 (s, 9H, 3xOAc).

Anal. Calcd for $C_{26}H_{33}Cl_3O_{13}$: C, 47.32; H, 5.02. Found: C, 47.21; H, 5.27.

2-O-(2,3,4-Tri-O-acetyl-β-D-xylopyranosyl)-3-O-benzyl-α-D-mannopyranose (18). A solution of compound 17 (407 mg, 0.62 mmol) in a mixture of acetic acid (1 mL) and acetic anhydride (0.05 mL) was added with stirring to a Zn-Cu reagent which was prepared by addition of zinc-dust (1.8 g) to acetate buffer (AcONa(3.3 g)/AcOH(3.3 mL)-H_2O(4.7 mL)) containing $CuSO_4$ (180 mg) solution (0.7 mL). The solution was stirred at room temperature for 10 h. The suspension was filtered and the filtrate extracted with chloroform. The extract was washed with water and concentrated to give a syrup, which was chromatographed on silica gel with 10:1 benzene-ethanol as eluent to give 18 (240.7 mg,73.8%).; $[\alpha]_D^{23}$ -50.3 °(c 0.9, 1:1 ethanol-H_2O); TLC (5:1 benzene-ethanol) Rf 0.33; ^{1}H NMR ($CDCl_3$) δ 7.421-7.213 (m, 5H, Ph); 2.021 (s, 9H, 3xOAc).

Anal. Calcd for $C_{24}H_{32}O_{13}$: C, 54.54; H, 6.00. Found: C, 54.33; H, 6.42.

1,4,6-Tri-O-acetyl-2-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-3-O-benzyl-α-D-mannopyranose (19). A) Compound 15 (530 mg, 0.84 mmol) was acetolyzed with concd H_2SO_4 (0.01 mL) in acetic anhydride(10 mL) for 3 h at 0 °C. The reaction solution was poured into ice-water, extracted with chloroform, washed with water, dried and then concentrated to a syrup which was chromatographed on silica gel. Compound 19 (298 mg, 54.2%) was eluted with 20:1 benzene-acetone. B) Compound 18 (240.7 mg, 0.455 mmol) was acetylated with 3:2 pyridine-acetic anhydride (10 mL) for 4 h at 40 °C. After the usual work-up, the material was chromatographed on silica gel to give pure compound 19 (295 mg): $[\alpha]_D^{23}$ -41.1°(c 1.0, chloroform); TLC (5:2 benzene-acetone) Rf 0.60; ^{1}H NMR ($CDCl_3$) δ 7.362-7.293 (m, 5H, Ph), 6.062 (d, 1H, $J_{1,2}$=2.19 Hz, H-1), 4.691 (d, 1H, $J_{1',2'}$=5.50 Hz, H-1'), 4.305 (dd, 1H, $J_{5'a,5'b}$=12.28 Hz, H-5'a), 3.375 (dd, 1H, H-5'b), 2.097, 2.033 (each s, 6H, 2xOAc), 2.083, 2.064 (each s, 12H, 4xOAc).

Anal. Calcd for $C_{30}H_{38}O_{16}$: C, 55.04; H, 5.85. Found: C, 55.39; H, 6.04.

4,6-Di-O-acetyl-2-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-3-O-benzyl-α-D-mannopyranosyl bromide (20). Compound 19 (70 mg, 0.11 mmol) was treated with 0.272 M titanium tetrabromide in 10:1 dichloromethane-ethyl acetate (2 mL) for 24 h at 40 °C. The solution was extracted with chloroform, washed with $NaHCO_3$ and water, dried, and concentrated to give 20 (54.4 mg); TLC (5:2 benzene-acetone) Rf 0.60.

2,3-Di-O-acetyl-1,6-anhydro-4-O-(4,6-di-O-acetyl-3-O-benzyl-2-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-α- and β-D-mannopyranosyl)-β-D-glucopyranose (21α and 21β). A stirred mixture of compound 7 (101 mg, 0.41 mmol), compound 20 (304 mg, 0.44 mmol) and molecular sieves 4A (300 mg) in dichloromethane (3 mL) was kept for 1 h at room temperature, and to this mixture was added silver zeolite (530 mg). The mixture was stirred for 40 h at room temperature, and filtered through Celite. The filtrate was concentrated in vacuo. The residue was chromatographed on silica gel in 10:1 benzene-acetone to give 21α (35.1 mg,10.2%), and 21β (241.3 mg, 70.0%). The use of silver silicate as the promoter for the condensation reaction instead of silver zeolite afforded 21α and 21β in 17.2 and 46.1% yield, respectively.

21β: $[\alpha]_D^{20}$ -93.2 (c 0.96, chloroform); TLC (5:2 benzene-acetone) Rf 0.49; ^{1}H NMR ($CDCl_3$) δ 7.364-7.282 (m, 5H, Ph), 5.418 (br.s,1H, H-1), 5.187 (d, 1H, $J_{1",2"}$=3.67 Hz, H-1"), 4.736 (s, 1H, H-1'), 4.421 (dd, 1H, $J_{4",5"a}$=3.30, $J_{5'a,5'b}$=11.64 Hz, H-5"a), 3.455 (dd, 1H, $J_{4",5"b}$=4.21 Hz, H-5"b), 2.146, 2.132, 2.098, 2.093, 2.073, 2.047, 2.037 (each s, 21H, 7xOAc).

21α: $[\alpha]_D^{20}$ -45.1 °(c 0.84, chloroform); TLC (5:2 benzene-acetone) Rf 0.57; ^{1}H NMR ($CDCl_3$) δ 7.334-7.289 (m, 5H, Ph), 5.435 (br.s, 1H, H-1), 5.044 (d, 1H, $J_{1',2'}$=2.38 Hz, H-1'), 5.187 (d, 1H, H-1"), 4.357 (dd, 1H, $J_{4",5"a}$=3.67, $J_{5"a,5"b}$=12.46 Hz, H-5"a), 3.381 (dd, 1H, $J_{4",5"b}$=5.67 Hz, H-5"b), 2.136, 2.126, 2.076, 2.070, 2.048, 2.042, 2.021 (each s, 21H, 7xOAc).

Anal. Calcd for $C_{38}H_{48}O_{21}$: C, 54.29; H, 5.75. Found: 21β ; C, 54.34; H, 5.82. Found: 21α; C, 54.45; H, 5.71.

2,3-Di-O-acetyl-1,6-anhydro-4-O-(4,6-di-O-acetyl-2-O-(2,3,4-tri-O-acetyl-β -D-xylopyranosyl)-β-D-mannopyranosyl)- β-D-glucopyranose (22). A mixture of compound 21 (350 mg, 0.42 mmol) and 5% Pd-C(80 mg) in methanol (5 mL) was stirred at room temperature in a hydrogen atmosphere until the reaction was complete. The product was isolated in the usual manner, and crystallized from benzene-dichloromethane to give 22 (298.5 mg, 95.5%); $[\alpha]_D^{26}$ -75.1 ° (c 1.7, chloroform); mp 188-189 °C; TLC (20:1 chloroform-methanol) Rf 0.48; ^{1}H NMR ($CDCl_3$) δ 5.433 (br.s, 1H, H-1), 4.919 (d,1H, $J_{1'',2''}$=6,60 Hz, H-1"), 4.775 (s, 1H, H-1'), 4.183 (dd, 1H, $J_{5''a,5''b}$=11.91 Hz, H-5"a), 3.431 (dd, 1H, H-5"b), 2.985 (br.s, 1H, 3'-OH), 2.141, 2.137, 2.110, 2.093, 2.048 (each s, 15H, 5xOAc), 2.067 (s, 6H, 2xOAc).

Anal. Calcd for $C_{31}H_{42}O_{21}$: C, 49.60; H, 5.64. Found: C, 49.22; H, 5.94.

Methyl 3-O-Benzyl-4,6-O-benzylidene-2-O-chloroacetyl-α -D-mannopyranoside (3). To a solution of compound 2 (1.84 g, 4.03 mmol) in pyridine-CH_2Cl_2(1 mL-15 mL) was added chloroacetyl chloride (0.65 mL, 8.1 mmol), portionwise at 0 °C. After the mixture was stirred for 3 h at room temperature, water was added, stirring was continued for 30 min, and the mixture was diluted with chloroform. The chloroform solution was washed with water, aqueous HCl, water, dried, and concentrated in vacuo. The residue was chromatographed on silica gel using hexane-ethyl acetate to give 3 (1.95 g, 89.4%);$[\alpha]_D^{21}$+4.8 °(c 1.3, chloroform); TLC (2:1 hexane-ethyl acetate) Rf 0.67.

Anal. Calcd for $C_{23}H_{25}ClO_7$: C, 51.10; H, 4.66. Found: C, 49.86; H, 4.77.

1,3,4,6-Tetra-O-acetyl-2-O-chloroacetyl-α-D-mannopyranose (8) Compound 3 (802.2 mg, 1.48 mmol) was treated with acetolysis reagent (Ac_2O-H_2SO_4, 90 mL-8 mL) for 3 h at room

temperature. The mixture was poured into ice-water, extracted with chloroform, the extract washed with water, dried (Na_2SO_4), concentrated *in vacuo* and then chromatographed on silica gel using 3:1 hexane-ethyl acetate to give compound 8 (648 mg, 85.4%), $[\alpha]_D^{21}$+129.0 °(*c* 0.07, chloroform), TLC (2:1 hexane-ethyl acetate) Rf 0.3; ^1H NMR ($CDCl_3$) δ 6.100 (d, 1H, $J_{1,2}$=1.6 Hz, H-1), 2.182, 2.091, 2.052, 2.023 (each s, 12H, 4xOAc).

Anal. Calcd for $C_{16}H_{21}ClO_{11}$: C, 45.24; H, 4.98. Found: C, 44.86; H, 5.12.

3,4,6-Tri-O-acetyl-2-O-chloroacetyl-α-D-mannopyranosyl Bromide (9). Compound 8 (44.7 mg, 0.1 mmol) was treated with 25% HBr-AcOH (2 mL) in dichloromethane (2 mL) for 3 h at room temperature. The solution was poured into ice-water, extracted with chloroform, and the extract washed with $NaHCO_3$ and water. The dried solution was concentrated to give 9 (39.8 mg, 89.3%); TLC (2:1 hexane-ethyl acetate) Rf 0.36.

2,3-Di-O-acetyl-1,6-anhydro-4-O-(4,6-di-O-acetyl-3-O-(3,4,6-tri-O-acetyl-2-O-chloroacetyl- α -D-mannopyranosyl)-2-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)- β -D-mannopyranosyl)- β -D-glucopyranose (23). A solution of the bromide 9 (24.2 mg, 0.0543 mmol) in dichloromethane (1 mL) was added to a cooled (-20 °C) solution of compound 22β (20 mg, 0.0272 mmol), silver triflate (23.3 mg), molecular sieves 4A (30 mg), and 2,6-lutidine (8.2 μL) in dichloromethane (1 mL). After stirring at -20 °C for 3 h and at room temperature for 7 h, the mixture was diluted with chloroform. The solid was removed by filtration and washed with chloroform. The combined filtrates were washed with cold water, 3% hydrochloric acid and water, dried (Na_2SO_4) and concentrated. The syrup was chromatographed on silica gel with 30:1 benzene-ethanol to give a syrupy compound 23 (21.0 mg, 70.7%); $[\alpha]_D^{20}$-61.0° (*c* 0.9, chloroform), TLC (8:1 benzene-ethanol) Rf 0.47; ^1H NMR ($CDCl_3$) δ 5.415 (br.s, 1H, H-1 of Glc unit), 4.786 (s ,1H, H-1 of β-Man unit), 5.138 (d, 1H, $J_{1,2}$=4.95 Hz, H-1 of Xyl unit), 4.376-

4.323 (m, 1H, H-5a, overlapping with H-5(α-Man)), 3.569-3.548 (m, 1H, H-5b, overlapping with H-5 (β-Man)), 5.004 (d, 1H, $J_{1,2}$=1.83 Hz, H-1 of α-Man unit), 2.165, 2.128, 2.112, 2.104, 2.100, 2.094, 2.060, 2.057, 2.050, 2.011 (each s, 30H, 10xOAc).

Anal. Calcd for $C_{45}H_{59}ClO_{30}$: C, 48.45; H, 5.33. Found: C, 48.22; H, 5.01.

2,3-Di-O-acetyl-1,6-anhydro-4-O-(4,6-di-O-acetyl-3-O-(3,4,6-tri-O-acetyl- α-D-mannopyranosyl)-2-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-β-D-mannopyranosyl)-1,6-anhydro-β-D-glucopyranose (24). Thiourea (20 mg) was added to the solution of compound 23 (21.0 mg, 0.019 mmol) in pyridine-ethanol (6:1,1 mL). After stirring for 1.5 h at 80 °C, the solution was extracted with chloroform. The organic layer was washed with saturated sodium hydrogen carbonate and then water, then dried. Evaporation of the solvent gave a syrup that was chromatographed on silica gel. Elution with 30:1 chloroform-ethanol provided compound 24 (14.1 mg, 71.7%).; $[\alpha]_D^{20}$-55.9 °(c 0.7, chloroform); TLC (8:1 benzene-ethanol) Rf 0.33; ^{1}H NMR ($CDCl_3$) δ5.415 (br.s, 1H, H-1, of Glc unit), 4.806 (s, 1H, H-1 of β-Man unit), 5.140 (d, 1H, $J_{1,2}$=4.94 Hz, H-1 of Xyl unit), 4.359 (dd, 1H, $J_{5a,5b}$=12.09 Hz, H-5a), 3.599 (dd, 1H, H-5b, overlapping with H-5 (β-Man), 4.986 (d, 1H, $J_{1,2}$=1.85 Hz, H-1 of α-Man unit), 2.163, 2.106, 2.104, 2.096, 2.094, 2.073, 2.062, 2.035 (each s, 24H, 8xOAc), 2.060(s, 6H, 2xOAc).

Anal. Calcd for $C_{43}H_{58}O_{29}$: C, 49.71; H, 5.63. Found : C, 50.03; H, 5.29.

4,6-O-Benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranose (10). 2-Deoxy-2-phthalimido- β -D-glucopyranose (390 mg, 1.26 mmol) was benzylidenated with benzaldehyde (5.1 mL) and zinc chloride (900 mg) for 12 h at room temperature. The mixture was extracted with chloroform. The organic layer was washed with $NaHCO_3$ solution and water, dried (Na_2SO_4) and concentrated . The syrup was chromatographed on silica gel in 50:1 chloroform-

methanol to give compound 10, which was crystallized from chloroform-benzene: $[\alpha]_D^{25}$ -25.3°(c 0.47,methanol-water 1:1) mp 198 - 201 °C; TLC (15:1 chloroform-methanol) Rf 0.33; ^{1}H NMR (CD_3OD) δ 7.881-7.729 (m, 4H, Ph), 5.581 (s, 1H, benzylidene H), 5.480 (br.d, 1H, $J_{1,2}$=8.61 Hz, H-1), 3.200, 2.484 (br.s, 1H, each OH).

Anal. Calcd for $C_{21}H_{19}NO_7$: C, 63.47; H, 4.82; N, 3.52. Found: C, 63.59; H, 5.11; N, 3.76.

1,3-Di-O-acetyl-4,6-O-benzylidene-2-deoxy-2-phthalimido-β-D-glucopyranose (11). Compound 10 (155 mg) was acetylated with 5:8 pyridine-acetic anhydride (13 mL) for 4 h at 40 °C. After the usual work-up, compound 11 was crystallized from ethanol (177 mg): mp 273 - 278 °C, $[\alpha]_D^{22}$ -7.5 °(c 0.1, chloroform); TLC (3:2 hexane-ethyl acetate) Rf 0.43; ^{1}H NMR (CD_3OD) δ 7.898-7.738 (m, 4H, Ph), 6.577 (d, 1H, $J_{1,2}$=8.80 Hz, H-1), 2.001, 1.901 (each s, 6H, 2xOAc).

Anal. Calcd for $C_{25}H_{23}NO_9$: C, 62.37; H, 4.82; N, 2.91. Found: C, 62.10; H, 4.67; N, 2.70.

1,3-Di-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranose (12). A solution of the compound 11 (500 mg, 1.04 mmol) and sodium cyanoborohydride (565 mg) in dry tetrahydrofuran (15 mL) containing powdered 3A molecular sieves (1.6 g) was cooled to 0 °C. Hydrogen chloride in diethyl ether was added until the solution was acidic (pH paper, gas evolution). After 20 min. at 0 °C, the mixture was poured into ice-water, and the product was extracted with chloroform, the organic layer was washed with water, dried and then concentrated. The products were purified by chromatography on silica gel using 1:1 hexane-ethyl acetate as an eluent. The compound 12 (425 mg,84.7%) was obtained.; $[\alpha]_D^{21}$ +30.1°(c 1.72, chloroform); TLC (5:1 benzene-acetone) Rf 0.55.

Anal. Calcd for $C_{25}H_{25}NO_9$: C, 62.11; H, 5.21; N, 2.90. Found: C, 61.91; H, 5.33; N, 2.87.

1,3-Di-O-acetyl-6-O-benzyl-4-O-chloroacetyl-2-deoxy-2-phthalimido-β-D-glucopyranose (13). To a solution of

compound 12 (440 mg, 0.91 mmol) in pyridine-dichloromethane (0.2 mL-3.6 mL) was added chloroacetyl chloride (0.12 mL), portionwise at 0 °C. After the mixture was stirred for 4 h at room temperature, water was added, stirring was continued for 30 min, and the mixture was diluted with chloroform. The chloroform solution was washed with water, aqueous HCl, water, dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel in 3:1 hexane-ethyl acetate to give 13 (353 mg, 69.3%) : $[\alpha]_D^{18}$ +67.2 ° (*c* 1.02, chloroform); TLC (3:2 hexane-ethyl acetate) Rf 0.37; ^{1}H NMR ($CDCl_3$) δ 7.880-7.740, 7.381-7.297 (each m, 4H and 5H, Ph), 6.503 (d, 1H, $J_{1,2}$=8.98 Hz, H-1), 1.986, 1.863 (each s, 6H, 2xOAc).

Anal. Calcd for $C_{27}H_{26}ClNO_{10}$: C, 57.91; H, 4.68; N, 2.50. Found: C, 57.68; H, 4.95; N, 2.61.

3-O-Acetyl-6-O-benzyl-4-O-chloroacetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl Bromide (14). After treatment of 13 (315 mg, 0.563 mmol) with 0.272M titanium tetrabromide in 10:1 dichloromethane-ethyl acetate (15.4 mL) for 1 h at 0 °C, the solution was extracted with chloroform, washed with $NaHCO_3$, and water, dried, and concentrated to give 14 quantitatively.; TLC (2:1 hexane-ethyl acetate) Rf 0.71.

2,3-Di-O-acetyl-1,6-anhydro-4-O-[4,6-di-O-acetyl-3-O-(3,4,-6-tri-O-acetyl-2-O-(3-O-acetyl-6-O-benzyl-4-O-chloroacetyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-α-D-mannopyranosyl)-2-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-β-D-mannopyranosyl]-β-D-glucopyranose(25). A solution of the phthalimido derivative β-bromide 14 (290 mg, 0.499 mmol) in dichloromethane (10 mL) was added to a cooled (-15 °C) solution of compound 24 (105 mg, 0.101 mmol), silver triflate (160 mg), molecular sieves 4A (300 mg), and 2,6-lutidine (50 μL) in dichloromethane (10 mL). After stirring at -15 °C for 4 h and at room temperature for 12 h, the mixture was diluted with chloroform. The solid was removed by filtration and washed with chloroform. The combined filtrates

were washed with cold water, 3% hydrochloric acid and water. Concentration left a syrup which was chromatographed on silica gel using 100:1 chloroform-methanol. Solvent removal gave compound 25 (116.6 mg, 75.0%); $[\alpha]_D^{25}$-76.2 °(c 0.31,chloroform); TLC (8:1 benzene-ethanol) Rf 0.54, ^{1}H NMR ($CDCl_3$) δ 5.394 (br.s, 1H, H-1 of Glc unit), 4.706 (s, 1H, H-1 of β-Man unit), 5.042 (d, 1H, $J_{1,2}$=4.95 Hz, H-1 of Xyl unit), 4.251 (dd, 1H, $J_{5a,5b}$=12.09 Hz, H-5a of Xyl unit), 3.480 (dd, 1H, H-5b of Xyl unit), 4.608 (d, 1H, $J_{1,2}$=1.57 Hz, H-1 of α-Man unit), 5.304 (d, 1H, $J_{1,2}$=8.33 Hz, H-1 of GlcNAc unit), 7.959-7.742 (m, 4H, Ph), 7.384-7.295 (m, 5H, Ph), 2.199, 2.134, 2.071, 2.067, 2.032, 2.010, 1.984, 1.966, 1.860 (each s, 27H, 9xOAc), 2.100 (s, 6H, 2xOAc).

Anal. Calcd for $C_{68}H_{80}ClNO_{37}$ H_2O: C, 52.46; H, 5.18; N, 0.90. Found: C, 52.20; H, 4.94; N, 0.83.

2,3-Di-O-acetyl-1,6-anhydro-4-O-[4,6-di-O-acetyl-3-O-(3,4,-6-tri-O-acetyl-2-O-(3-O-acetyl-6-O-benzyl-2-deoxy-2-phthalimido-β-D-glucopyranosyl)-α-D-mannopyranosyl)-2-O-(2,3,4-tri-O-acetyl-β-D-xylopyranosyl)-β-D-mannopyranosyl]-β-D-glucopyranose (26). Thiourea (140 mg) was added to the solution of compound 25 (151 mg, 0.098 mmol) in pyridine-ethanol (6:1, 7 mL), stirred for 1.5 h at 80 °C. After the usual work-up, the material was chromatographed on a column of silica gel with 30:1 chloroform-ethanol as eluent to give 26 (131 mg,91.3%); mp 123 - 125 °C, $[\alpha]_D^{25}$ -75.9 °(c 1.94, chloroform), TLC(8:1 benzene-ethanol) Rf 0.35, ^{1}H NMR ($CDCl_3$) δ 5.393 (br.s, 1H, H-1 of Glc unit), 4.708 (s, 1H, H-1 of β-Man unit), 5.049 (d, 1H, $J_{1,2}$=4.76 Hz, H-1 of Xyl unit), 4.634 (d, 1H,$J_{1,2}$=1.65 Hz, H-1 of α-Man unit), 5.292 (d, 1H, $J_{1,2}$=8.43 Hz, H-1 of GlcNAc unit), 2.195, 2.134, 2.099, 2.096, 2.069, 2.064, 2.027, 1.984, 1.974, 1.956, 1.925 (each s, 33H, 11xOAc).

Anal. Calcd for $C_{66}H_{79}NO_{36}$: C, 54.23; H, 5.45; N, 0.96. Found: C, 54.59; H, 5.74; N, 0.82.

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