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Synthesis of Disaccharides Related to the *O*-Specific Polysaccharide of *Salmonella typhimurium*

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Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (*13*) has been glycosylated with 3,6-dideoxy-2,4-di-*O*-*p*-nitrobenzoyl-α-D-*xylo*-hexopyranosyl bromide (*4*) and its enantiomer (*5*) using mercury cyanide as catalyst and toluene and nitromethane as solvent. The anomeric ratio has been determined by ^{1}H NMR spectroscopy and is reversed going from the D to the L compound. Glycosylation of *13* with 2-*O*-benzyl-3,6-dideoxy-4-*O*-*p*-nitrobenzoyl-α-D-*xylo*-hexopyranosyl bromide (*9*) under similar reaction conditions gives exclusively the α-linked disaccharide while glycosylation using 2,4-di-*O*-benzyl-3,6-dideoxy-α-D-*xylo*-hexopyranosyl chloride (*12*) gives a 1:3 mixture of β- and α-linked disaccharides. Glycosylation of *13* with *12*, catalyzed by tetrabutylammonium bromide at elevated temperature, yields exclusively the α-linked disaccharide. The conformation of two of the deprotected disaccharides has been determined using hard sphere calculations and high field NMR data.

The disaccharide 3-*O*-(3,6-dideoxy-α-D-*xylo*-hexopyranosyl)-α-D-mannopyranose constitutes an important part of the determinant of the *O*-specific polysaccharide of *Salmonella typhimurium* and other species of the *Salmonella* serogroup B. The synthesis of glycosides of this disaccharide, and of larger oligosaccharide parts of the *O*-specific chain, has been previously published by Garegg *et al.*[1–5] As part of a programme to synthesize larger oligosaccharides containing α-linked 3,6-dideoxy-α-D- (or L)-hexopyranoses we have developed a novel route to crystalline derivatives of 3,6-dideoxy-α-D-*xylo*-hexopyranosyl halides, which have been subjected to reaction with methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside under varying conditions in order to optimize the glycosylation reaction. The conformation in aqueous solution of the disaccharides, possessing the β-D and α-L glycosidic configurations, has been deduced from NMR data and hard sphere calculations (HSEA).[6,7] Conformational data on the disaccharide with the α-D glycosidic configuration will be discussed in a forthcoming publication [8] together with other oligosaccharides related to the *O*-specific polysaccharide of a *Salmonella* strain.

RESULTS

Reduction of 3,6-dideoxy-D-*xylo*-hexono-1,4-lactone (*1*) (or the L form), obtained from D-(respectively-L)-galactono-1,4-lactone,[9] with diisoamyl borane in tetrahydrofuran afforded 3,6-dideoxy-D-*xylo*-hexose (*2*) in an overall yield from galactone-1,4-lactone of 62 %. Low temperature acylation with *p*-nitrobenzoyl chloride in pyridine, with 4-(dimethylamino)-pyridine as a catalyst, gave a 91 % yield of *3* as a mixture containing 80 % of the β-pyranose form. Treatment of the mixture with hydrogen bromide in acetic acid and dichloromethane gave, after chromatographic separation, the crystalline 3,6-dideoxy-2,4-di-*O*-*p*-nitrobenzoyl-α-D-*xylo*-hexopyranosyl bromide, (*4*) in 31 % yield. Analogous reactions were carried out within the L-series giving the crystalline bromide (*5*). When the crude bromide was reacted with methanol and silver carbonate in dichloromethane, crystalline

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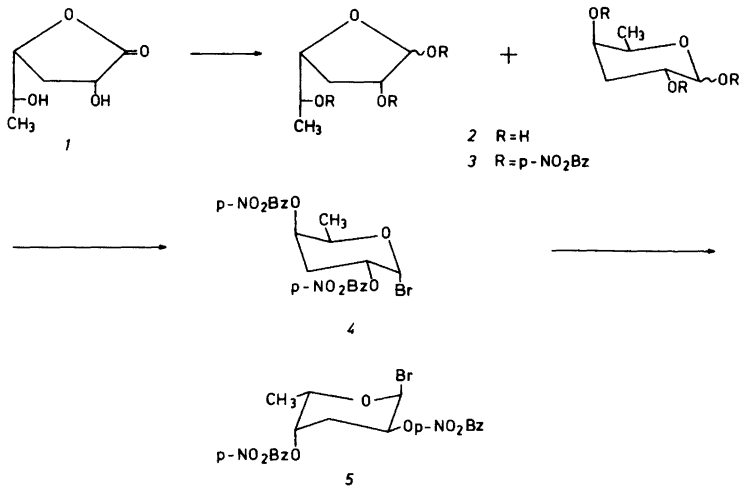


methyl 3,6-dideoxy-2,4-di-*O*-*p*-nitrobenzoyl-β-D-*xylo*-hexopyranoside (*6*) was obtained in a 55 % overall yield from *3*. Selective deacylation of *6* with potassium carbonate in methanol gave a 47 % yield of *7*, which was benzylated according to Klemer [10] to give *8* (88 % yield), and converted on treatment with hydrogen bromide in a dichloromethane, into the unstable bromide (*9*). Some decomposition was observed during the last step of this reaction.

Complete deacylation of *6* with sodium methoxide in methanol gave a 95 % yield of methyl 3,6-dideoxy-β-D-*xylo*-hexopyranoside (*10*), benzylation of which afforded the dibenzyl derivative (*11*) in 84 % yield. The glycoside (*11*) was reacted with hydrogen chloride in ether to give the chloride (*12*) in 95 % yield. The glycosyl halides (*4*), (*5*), (*9*) and (*12*) was individually reacted with excess of methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside (*13*), prepared according to Garegg *et al.*,[11] in order to compare the selectivity in the oligosaccharide synthesis. The results and conditions are presented in Table 1.

It is obvious that the highest selectivity in the preparation of 3,6-dideoxy-α-D-*xylo*-hexopyranosyl derivatives is achieved with tetrabutylammonium bromide as a catalyst and DMF–toluene (1:20) as the solvent. The reactions of halides (*4*) and (*5*) with *13* are not stereoselective and cannot be recommended for the synthesis of larger oligosaccharides. The glycosyl chloride (*12*), reacted under conditions A (Table 1), produces a high yield of disaccharide (70 %) with an acceptable stereoselectivity.

The disaccharides (*14*), (*15*), (*16*) and (*17*) were separated, purified and deacylated, followed by removal of the benzylidene groups

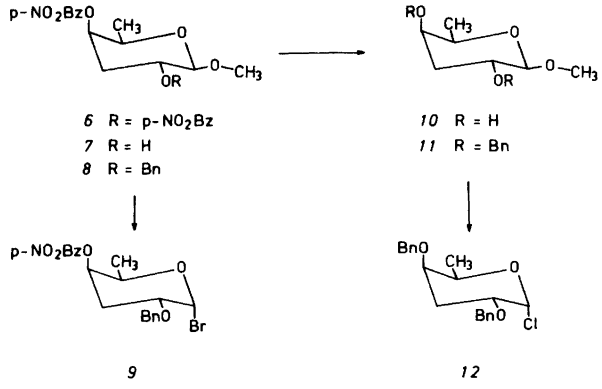


Table 1. Reactions and yields.

Compound	Reaction conditions [a]	Time/h	Temp./°C	Anomeric ratio (α/β) measured by NMR [b]	Anomeric ratio (α/β) of isolated products	Total yield of isolated disaccharides/%
4+13	A	40	20	0.56/0.44	0.77/0.23 [c]	43
5+13	A	96	−15	0.42/0.58	0.52/0.48 [d]	71
9+13	A	14	0	0.90/0.10 [e]	0.97/0.03	39
12+13	A	13	0	0.71/0.29	0.71/0.29	70
12+13	B	24	−50	decomposition	—	—
12+13	C	96	50	0.94/0.06	0.95/0.05	40

[a] A: $Hg(CN)_2$, toluene–nitromethane (1:1). B: AgTfl, CH_3CN. C: $(Bu)_4NBr$, DMF–toluene (1:20). [b] H6.1 and –OMe signals were integrated on the crude reaction mixtures. [c] Difficulties encountered in distinguishing the β-anomer from excess of aglycone. Minor by-products as reported.[1] [d] Difficulties in making β-anomer free from excess of aglycone. No by-products observed. [e] Several by-products obscured the interpretation of the ^1H NMR spectrum.

using aqueous acetic acid. Finally, the *O*-benzyl groups were removed by hydrogenolysis with palladium on charcoal and the free disaccharides (*18*), (*19*), (*20*) and (*21*) were isolated in yields of 57, 36, 57 and 19 %, respectively.

CONFORMATIONAL ANALYSIS

The disaccharides (*19*), (*20*) and (*21*) were subjected to conformational analysis using a combination of HSEA calculations and NMR data as published previously.[6,7] The resulting minimum energy conformations are given in Table 2 together with the ^1H NMR chemical shift changes. In Fig. 1 are shown the CPK models of the disaccharides (*19*) and (*20*) in their minimum energy conformations.

The results of nuclear Overhauser enhancement (n.O.e.) experiments are presented in Table 3; it is seen that both these and the chemical shift changes are in good agreement with the calculated minimum energy conformations of (*19*) and (*20*). Thus in (*19*) the observed

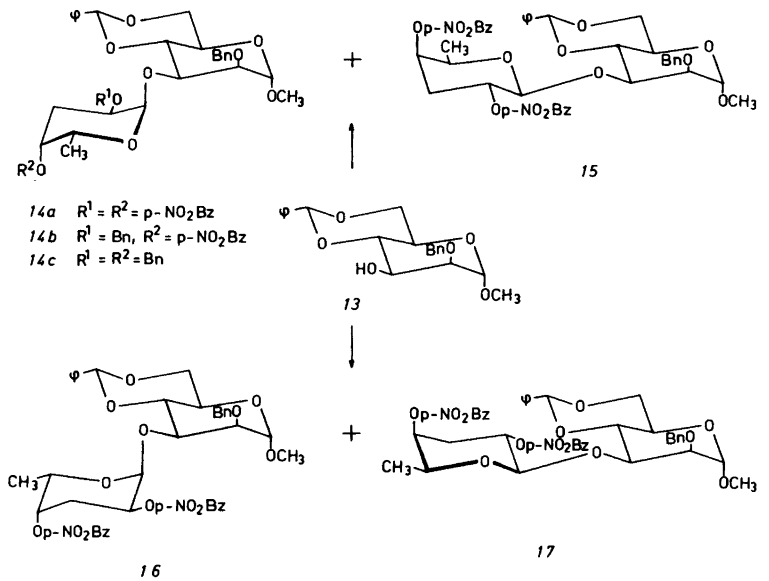


Table 2. Calculated minimum energy conformations [a] and observed ^{1}H NMR deshieldings [b] of methyl 3-*O*-(3,6-dideoxy-*xylo*-hexopyranosyl)-α-D-mannopyranosides.

Compound	ϕ_H°	ψ_H°	Interaction	Calculated Distance/Å	Deshielding ppm
19	54	14	H-3.2–O-5.1	2.52	0.18
20	45	30	H-5.1–O-3.2	2.49	
			H-5.1–O-4.2	2.60	0.30
			H-3.2–O-5.1	2.59	0.07
21	300	10	H-2.2–O-5.1	2.70	0.25
			H-3.2–O-5.1	2.57	0.13

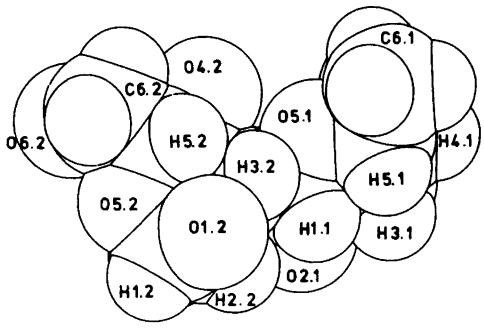
[a] The ϕ_H, ψ_H angles have been calculated in 2° steps and are considered significant within ±10°. [b] Comparison with model methyl glycosides.

relative n.O.e. from H-1.1 to H-2.2 and H-3.2 of 0.23 and 0.42, respectively, are in reasonable agreement with the calculated values of 0.27 and 0.38, respectively. Furthermore, H-3.2 is deshielded 0.18 ppm by *O*-5.1. In *20* both *O*-3.2 and *O*-4.2 are close to H-5.1 and H-5.1 is therefore deshielded 0.30 ppm. H-1.1 of *20* is relaxed by both H-2.2 and H-3.2 and the observed relative n.O.e.'s of 0.35 and 0.25, respectively, are in excellent agreement with the calculated values of 0.36 and 0.24, respectively. The expected deshielding of H-3.2 by the ring-oxygen in *19* and *20* is not considered significant,[12] this can best be explained by the reduced electronegativity of the ring-oxygen compared to that of a hydroxyl group.

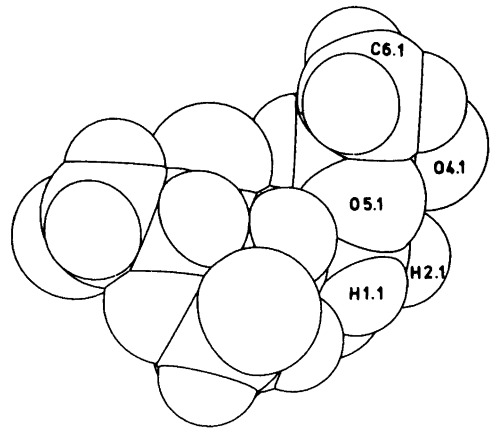
EXPERIMENTAL

Melting points are uncorrected. Optical rotations were measured on a Perkin Elmer 141 polarimeter. NMR spectra were obtained on Bruker WH-90 and HX 270 instruments. The spectra were measured in $CDCl_3$ or in D_2O solution with acetone as the internal reference (2.12 ppm). ^{13}C NMR spectra were measured in D_2O with dioxane as internal reference (67.4 ppm). Microanalyses were performed by Novo microanalytical laboratory.

3,6-Dideoxy-D-xylo-*hexose* (*2*). 2-Methyl-2-butene (34.0 ml, 321 mmol) was added dropwise over a period of 45 min to a stirred solution of

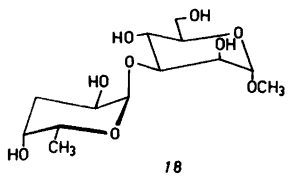


α-D-Man β-D-3,6-Dideoxy-*xylo*-hexose



α-D-Man α-L-3,6-Dideoxy-*xylo*-hexose

Fig. 1. CPK models of disaccharides (*19*) and (*20*) in the minimum energy conformation given in Table 1.



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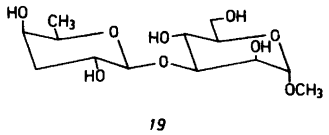

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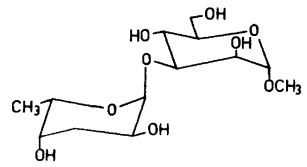

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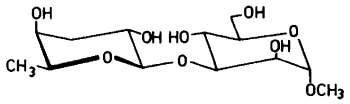

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borane dimethyl sulfide-complex (16.0 ml, 160 mmol BH_3) in freshly distilled THF (16 ml) at 5 °C in an atmosphere of argon. The mixture was stirred at 25 °C for 3 h and cooled to 5 °C. 3,6-Dideoxy-D-*xylo*-hexono-1,4-lactone [9] (4.09 g, 28.0 mmol) dissolved in THF (60 ml), was added dropwise at 5 °C over a period of 1 h. The mixture was stirred for 15 h at 20 °C. Water (20 ml) was added dropwise with stirring over a period of 45 min, whereupon the mixture was refluxed for 4 h, and concentrated *in vacuo*. The organic phase was extracted twice with water (50 ml). The combined aqueous phases were extracted twice with dichloromethane (100 and 50 ml) followed by diethyl ether (25 ml). Evaporation at 40 °C, 0.5 mm Hg gave 4.19 g (100 %) of glassy material (*2*). ^{13}C NMR: α-pyranose: 92.4 ppm (C-1); 63.9 (C-2); 33.0 (C-3); 66.8 (C-4); 69.2 (C-5); 16.4 (C-6), β-pyranose: 99.0 ppm (C-1); 67.2 (C-2); 37.9 (C-3); 69.2 (C-4); 74.9 (C-5) 16.7 (C-6), α-furanose: 95.9 ppm (C-1); 71.9 (C-2); 32.3 (C-3); 81.9 (C-4); 71.9 (C-5); 18.7 (C-6), β-furanose: 103.0 ppm (C-1); 76.2 (C-2); 34.5 (C-3); 83.0 (C-4); 70.4 (C-5); 19.1 (C-6).

3,6-Dideoxy-1,2,4-tri-O-p-*nitrobenzoyl*-β-D-xylo-*hexopyranose (3)*. The anomeric mixture of *2* (1.30 g, 8.8 mmol) was dissolved in pyridine (60 ml) and 4-dimethylamino-pyridine (100 mg) was added. The mixture was stirred and cooled to 0 °C. Finally, powdered *p*-nitrobenzoyl chloride (9.3 g, 50 mmol) was added in small portions over a period of 4 h at 0 °C. The mixture was stirred overnight at 20 °C. Water (20 ml) and dichloromethane (10 ml) were added and the stirring was continued for 2 h. The mixture was diluted with

Table 3. Observed [a] and calculated [b] nuclear Overhauser enhancements for disaccharides containing 3,6-dideoxy-*xylo*-hexopyranose.

Compound	Proton saturated	Relative and observed [a] NOE for protons			Calculated relative [b] NOE for protons		
19	H-1.1	H-5.1 0.36 (12.5 %)	H-2.2 0.23 (8.0 %)	H-3.2 0.42 (14.7 %)	H-5.1 0.35	H-2.2 0.27	H-3.2 0.38
20	H-1.1	H-2.1 0.41 (15.7 %)	H-2.2 0.35 (13.3 %)	H-3.2 0.25 (9.6 %)	H-2.1 0.41	H-2.2 0.36	H-3.2 0.24

[a] Performed in the difference mode. Accuracy considered to be of the order ±10 %. [b] Calculated for the minimum energy conformation as described in Ref. 6.

dichloromethane (75 ml) and extracted with water (250 ml). Successive washings with saturated aqueous sodium hydrogencarbonate, 2 M sulfuric acid, water, sodium hydrogencarbonate solution and water gave after drying and concentration *in vacuo* 4.76 g (91 %) of a mixture of *2* containing 80 % pyranose derivatives according to a proton NMR spectrum. ^{1}H NMR: *α*-pyranose: δ 6.73 (H-1); 5.62 (H-2); 2.56 (H-3a); 2.56 (H-3e); 5.46 (H-4); 4.42 (H-5); 1.30 (H-6). J_{12} 3.8 Hz, J_{45} 2.0, J_{56} 6.0. *β*-pyranose: δ 6.18 (H-1); 5.58 (H-2); 2.23 (H-3a); 2.77 (H-3e); 5.36 (H-4); 4.24 (H-5); 1.35 (H-6). J_{12} 8.1 Hz; J_{23a} 12.2; J_{23e} 5.6; J_{3a3e} 14.5; J_{3a4} 3.0; J_{3e4} 3.2; J_{45} 1.3; J_{56} 6.4.

3,6-Dideoxy-2,4 di-O-p-*nitrobenzoyl-α*-D-xylo-*hexopyranosyl bromide (4).* Crude *3* (4.5 g, 7.6 mmol) was dissolved in dichloromethane (15 ml) and cooled to 0 °C. Acetic acid saturated with hydrogen bromide (20 ml) was added and the mixture was stirred at 0 °C for 1 h. Filtration followed by dilution with dichloromethane (30 ml) and washing of the organic phase twice with ice water (50 ml), cold saturated sodium hydrogencarbonate (50 ml) and ice water, followed by drying (magnesium sulfate) and evaporation *in vacuo* gave a syrup which was purified on a silica gel column (400 g, ethyl acetate–pentane: 1:3). Concentration of the eluent at 30 °C and crystallization from diethyl ether (50 ml) gave 1.37 g bromide (*4*) (31 % from *2*), $[\alpha]_D^{20}$=+249° (c 0.2, $CHCl_3$), m.p.=91–95 °C, ^{1}H NMR: δ 6.83 (H-1); 5.28 (H-2); 2.59 (H-3a); 2.30 (H-3e); 5.39 (H-4); 4.44 (H-5); 1.31 (H-6). J_{12} 3.3 Hz; J_{23a} 11.6; J_{23e} 5,3; J_{3a3e} 12; J_{3a4} 3; J_{3e4} 3.2; J_{45} 1.3; J_{56} 6.8.

3,6 Dideoxy-2,4-di-O-p-*nitrobenzoyl-α*-L-xylo-*hexopyranosyl bromide (5).* This compound was prepared in the same way, starting from L-galactono-1,4-lactone, giving 30 % yield of bromide, *5*. $[\alpha]_D^{20}$=−255° (c 0.2, $CHCl_3$) m.p. 94–100 °C.

Methyl 3,6-dideoxy-2,4-di-O-p-*nitrobenzoyl-β*-D-xylo-*hexopyranoside (6).* The bromide *4* (prepared from *3* (4.50 g, 7.6 mmol)) was stirred with dry methanol (2.5 ml) in dry dichloromethane (15 ml) in the presence of silver carbonate (4.28 g, 14 mmol) for 16 h under a nitrogen atmosphere. The mixture was filtered through celite and evaporated *in vacuo* to give 3.3 g of syrup, which was dissolved in hot ethyl acetate (8 ml) and crystallized by slow addition of pentane (17 ml). Cooling to 0 °C and filtration afforded 1.43 g of *6*. Concentration of the mother liquor and chromatographic separation on silica gel (ethyl acetate–light petroleum 2:3) followed by crystallization gave another 0.49 g (total yield from *3*: 55 %). $[\alpha]_D^{20}$=+81° (c 0.3, $CHCl_3$), m.p. 177–178 °C, ^{1}H NMR: δ 4.59 (H-1); 5.23 (H-2); 2.02 (H-3a); 2.62 (H-3e); 5.26 (H-4); 3.98 (H-5); 1.33 (H-6). J_{12} 7.9; Hz; J_{23a} 10.8; J_{23e} 5.3; J_{3a3e} 14.1; J_{3a4} 3.0; J_{3e4} 3.3; J_{45} 1.3; J_{56} 6.5. Anal. $C_{21}H_{20}N_2O_{10}$: C, H, N.

Methyl 3,6-dideoxy-4-O-p-*nitrobenzoyl-β*-D-xylo-*hexopyranoside (7).* The methyl glycoside (*6*) (0.61 g, 1.3 mmol) was dissolved in hot methanol (50 ml) and cooled to 0 °C with stirring. Anhydrous potassium carbonate (60 mg, 0.43 mmol) was added and the stirring was continued for 75 min at 0 °C. The reaction was stopped by addition of concentrated hydrochloric acid (60 μl) followed by evaporation *in vacuo*. The residue was dissolved in dichloromethane (50 ml) and washed twice with water (10 ml). After drying (magnesium sulfate), filtration and evaporation *in vacuo* the product was purified by column chromatography (ethyl acetate–light petroleum: 7:5) giving 195 mg of *7* (47 %). $[\alpha]_D^{23}$ −65° (c 0.6, $CHCl_3$) m.p.: 129.5–131.0 °C ^{1}H NMR: δ 4.21 (H-1); 3.76 (H-2); 1.80 (H-3a); 2.41 (H-3e); 5.19 (H-4); 3.87 (H-5); 1.27 (H-6). J_{12} 7.5 Hz; J_{23a} 11.3; J_{23e} 5.6; J_{3a3e} 14.3; J_{3a4} 3.0; J_{3e4} 3.0; J_{45} 1.3; J_{56} 6.3. Anal. $C_{14}H_{17}NO_7$: C, H.

Methyl 2-O-*benzyl-3,6-dideoxy-4*-O-p-*nitrobenzoyl-β*-D-xylo-*hexopyranoside (8).* The glycoside *7* (177 mg, 0.57 mmol) was dissolved in dry toluene (5 ml), benzyl bromide (0.23 ml, 1.9 mmol) and silver oxide (350 mg 1.5 mmol) was added in the dark. The mixture was stirred for 24 h at 20 °C. Benzyl bromide (0.115 ml, 0.95 mmol) and silver oxide (150 mg, 0.65 mmol) were added and stirring continued in the dark for 24 h at 20 °C. After filtration and evaporation the material was purified on a silica gel column (ethyl acetate–light petroleum 3:7) giving 200 mg of *8* (88 %). $[\alpha]_D^{20}$ +47° (c 0.1, $CHCl_3$)(reported [1] +50° ($CHCl_3$)) ^{1}H NMR: δ 4.35 (H-1); 3.55 (H-2); 1.82 (H-3a); 2.36 (H-3e); 5.17 (H-4); 3.83 (H-5); 1.25 (H6). J_{12} 7.5 Hz; J_{23a} 11.0; J_{23e} 5.0; J_{3a3e} 14.3; J_{3a4} 3.0; J_{3e4} 3.0; J_{45} 1.3; J_{56} 6.6.

2-O-*Benzyl-3,6-dideoxy-4*-O-p-*nitrobenzoyl-β*-D-xylo-*hexopyranosyl bromide (9).* The methyl glycoside (*8*) (170 mg, 0.423 mmol) was dissolved in dry dichloromethane (10 ml) and cooled to −20 °C with stirring. Dry hydrogen bromide (5.7 mmol) in dichloromethane (10 ml) was added and the stirring was continued for 1 h and 45 min at −20 °C. The mixture was evaporated *in vacuo* at 0 °C and the evaporation was repeated with chloroform (5 ml) to give 195 mg (~100 %) of a light yellow syrup, which was used immediately for condensation. ^{1}H NMR: δ 6.65 (H-1); 3.73 (H-2); 2.28 (H-3a); 2.23 (H-3e); 5.26 (H-4); 4.32 (H-5); 1.23 (H-6). J_{12} 3.0 Hz; J_{23a} 10.5; J_{23e} 6.0; J_{3a4} 3.0; J_{3e4} 3.0; J_{45} 1.5; J_{56} 6.2.

Methyl 3,6-dideoxy-β-D-xylo-*hexopyranoside*

(10). Methyl 3,6-dideoxy-2,4-di-*O*-*p*-nitrobenzoyl-β-D-*xylo*-hexopyranoside (*6*) (1.23 g 2.68 mmol) was suspended in methanol (5 ml) and sodium methoxide (0.1 M, 20 ml) was added. The mixture was stirred for 2.5 h at 20 °C, cooled to 0 °C and filtered. The filtrate was neutralized by stirring with ion exchange resin (Amberlite IRC 50) for 1 h. Concentration to 10 ml followed by addition of water (20 ml), filtration and evaporation gave 530 mg of a syrup which was purified by preparative TLC (methanol–ethyl acetate: 3:17) to give 413 mg (95 %) of *10* as a syrup. $[\alpha]_D^{23}$ −66° (c 0.9, MeOH), (Reported [13] −69 °) ^{1}H NMR: δ 4.17 (H-1); 3.54 (H-2); 1.61 (H-3a): 2.04 (H-3e); 3.68 (H-4); 3.70 (H-5); 1.10 (H-6). J_{12} 8.0 Hz; J_{23a} 12.4; J_{23e} 4.4; J_{3a3e} 14.2; J_{3a4} 3.2; J_{3e4} 3.2; J_{45} 1.2; J_{56} 6.2.

*Methyl 2,4-di-*O*-benzyl-3,6-dideoxy-β-*D*-xylo-hexopyranoside (11)*. The glycoside (*10*) (413 mg, 2.56 mmol) was dissolved n dry *N,N*-dimethylformamide (DMF) (8 ml) and added dropwise to a stirred suspension of sodium hydride (500 mg, 11.5 mmol) in DMF. The mixture was stirred for 30 min and benzyl bromide (1.22 ml, 10.3 mmol) was added dropwise. After 3 h of stirring at 20 °C TLC (ethyl acetate–light petroleum 3:17) showed the reaction to be complete. The mixture was left overnight and methanol (2 ml) was added by stirring, which was continued for 2 h.

The mixture was poured into water (50 ml) and extracted 3 times with ethyl acetate (30 ml). The extract was washed twice with water (30 ml) dried (magnesium sulfate),filtered and evaporated *in vacuo* to give 1.18 g. Separation on a silica gel column (ethyl acetate–light petroleum 3:17) gave 730 mg (84 %) of *11*. $[\alpha]_D^{20}$ −55° (c 0.3, $CHCl_3$). ^{1}H NMR: δ 4.26 (H-1); 3.54 (H-2); 1.46 (H-3a); 2.31 (H-3e); 3.34 (H-4); 3.59 (H-5); 1.25 (H-6). J_{12} 7.5 Hz; J_{23a} 10.5; J_{23e} 5.3; J_{3a3e} 14.2; J_{3a4} 2.9; J_{3e4} 3.4; J_{45} 1.4; J_{56} 6.0. Anal. $C_{21}H_{26}O_4$: C, H.

*2,4-Di-*O*-benzyl-3,6-dideoxy-α-*D*-xylo-hexopyranosyl chloride (12)*. The glycoside (*11*) (200 mg, 0.58 mmol) was dissolved by stirring in dry diethyl ether (15 ml) and the solution was saturated with dry hydrogen chloride. After stirring at 20 °C for 35 min the solution was again saturated with HCl and the stirring was continued for 1 h and 10 min. Toluene (3 ml) was added and the mixture was evaporated *in vacuo*. Evaporation was repeated with toluene (5 ml) giving 190 mg (95 %) of *12*. ^{1}H NMR: δ 6.23 (H-1); 4.00 (H-2); 1.95 (H-3a); 2.18 (H-3e); 3.46 (H-4); 4.13 (H-5); 1.22 (H-6). J_{12} 3.4 Hz; J_{23a} 11.2; J_{23e} 4.7; J_{3a3e} 12.5; J_{3a4} 2.3; J_{3e4} 1.2; J_{45} 1.7; J_{56} 6.5. The chloride was used immediately in the next step due to instability.

*Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(3,6-dideoxy-2,4-di-*O*-p-nitrobenzoyl-α-*D*-xylo-hexopyranosyl)-α-*D*-mannopyranoside (14a) and β-isomer (15)*. Methyl 2-*O*-benzyl-4,6-*O*-benzyliden-α-D-mannopyranoside (*13*) [11] (558 mg, 1.5 mmol) was dissolved in dry toluene (20 ml) and toluene (15 ml) was distilled off at atmospheric pressure. Dry nitromethane (20 ml), mercury cyanide (2.53 g, 10 mmol) and molecular sieves (4Å, 5g) were added and the mixture was stirred under a nitrogen atmosphere for 16 h at 20 °C. A solution of *4* (559 mg, 1.1 mmol) in toluene (12 ml) was dried over molecular sieves for 1 h and added dropwise during 6 h. The mixture was stirred for 40 h at 20 °C. It was filtered through celite and the filter was washed with dichloromethane (50 ml). The filtrate was washed with water (100 ml), saturated sodium hydrogencarbonate solution (100 ml) and water (100 ml). Drying (magnesium sulfate), filtration and evaporation gave 1.00 g of a glassy syrup. ^{1}H NMR (270 MHz) showed that the glycosylation was almost quantitative with the anomeric ratio of α/β=0.56/0.44. The disaccharides were separated on a silica gel column (ethyl acetate–toluene: 1:4) and the first fraction gave 283 mg (32 %) of α anomer (*14a*) which was crystallized from ether–pentane (1:2), yield 232 mg $[\alpha]_D^{23}$ +95° (c 0.1, $CHCl_3$) (reported [1] +90°) m.p. 104.5–109.0 °C (reported: 105–108 °C).[1] ^{1}H NMR: δ 5.40 (H-1.1); 5.37 (H-2.1); 2.40 (H-3.1a); 2.19 (H-3.1e); 5.17 (H-4.1); 3.39 (H-5.1); 1.09 (H-6.1); 4.83 (H-1.2); 3.82 (H-2.2); 4.28 (H-3.2); 4.05 (H-4.2); 3.72 (H-5.2); 4.14 (H-6.2); 3.77 (H-6.2′). $J_{12.1}$ 3.5 Hz; $J_{23a.1}$ 12.0; $J_{23e.1}$ 4.5; $J_{3a3e.1}$ 13.5; $J_{3a4.1}$ 2.0; $J_{3e4.1}$ 1.0; $J_{45.1}$ 2.0; $J_{56.1}$ 7.0; $J_{12.2}$ 2.0; $J_{23.2}$ 3.2; $J_{34.2}$ 10.0.

The second fraction was acetylated with acetic anhydride in pyridine in order to change the polarity of the aglycone. Purification by preparative TLC (toluen–ethyl acetate: 4:1) gave 100 mg (11 %) crystalline (*15*), which was recrystallized from ether–pentane, $[\alpha]_D^{22}$ +51° (c 0.2 $CHCl_3$), m.p. 108–113 °C. ^{1}H NMR: δ 4.93 (H-1.1); 5.29 (H-2.1); 1.97 (H-3.1a); 2.66 (H-3.1e); 5.24 (H-4.1); 3.87 (H-5.1); 1.21 (H-6.1); 4.61 (H-1.2); 3.66 (H-2.2); 4.28 (H-3.2); 4.22 (H-4.2); 3.87 (H-5.2); 4.26 (H-6.2); 3.87 (H-6.2′). $J_{12.1}$ 8.0 Hz; $J_{23a.1}$ 11.5; $J_{23e.1}$ 5.0; $J_{3a3e.1}$ 14.0; $J_{3a4.1}$ 3.5; $J_{3e4.1}$ 3.0; $J_{45.1}$ 1.5; $J_{56.1}$ 6.5; $J_{12.2}$ 1.5; $J_{23.2}$ 2.5; $J_{34.2}$ 10.0. Anal. $C_{41}H_{40}N_2O_{15}$: C, H.

*Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(3,6-dideoxy-2,4-di-*O*-p-nitrobenzoyl-α-*L*-xylo-hexopyranosyl)-α-*D*-mannopyranoside (16) and β-isomer (17)*. The glycoside *13* (612 mg, 1.65 mmol) and *5* (670 mg, 1.32 mmol) were reacted in the presence of mercury cyanide (1.66 g, 6.6 mmol) essentially as described above though keeping the temperature at −15 °C for 72 h and then at 20 °C for 24 h. The same work-up

procedure gave 1.07 g of a glassy syrup. ^{1}H NMR showed the glycosylation to be quantitative with a ratio α/β=0.42/0.58. Separation on a silica gel column (toluene–ethyl acetate: 8:13) gave 387 mg (37 %) of *16* and 358 mg (34 %) of *17*.

The disaccharide *16* was crystallized from ethyl acetate–light petroleum at −78 °C. $[\alpha]_D^{22}$ −149° (c 0.3, $CHCl_3$) m.p. 115−122 °C. ^{1}H NMR: δ 5.39 (H-1.1); 5.36 (H-2.1); 2.55 (H-3.1a); 2.26 (H-3.1e); 5.26 (H-4.1); 4.46 (H-5.1); 0.87 (H-6.1); 4.64 (H-1.2); 3.76 (H-2.2); 4.32 (H-3.2); 4.24 (H-4.2); 3.84 (H-5.2); 4.25 (H-6.2); 3.87 (H-6.2′). $J_{12.1}$ 4.0 Hz; $J_{23a.1}$ 12.0; $J_{23e.1}$ 3.5; $J_{3a3e.1}$ 14.5; $J_{3a4.1}$ 3.0; $J_{3e4.1}$ 3.5; $J_{45.1}$ 1.5; $J_{56.1}$ 8.0; $J_{12.2}$ 1.7; $J_{23.2}$ 3.0; $J_{34.2}$ 8.0; $J_{56.2}$ 5.5; $J_{66'.2}$ 11.5. Anal. $C_{41}H_{40}N_2O_{15}$: C, H.

Crystallization of *17* was performed under similar conditions. $[\alpha]_D^{23}$ −2.1° (c 0.1, $CHCl_3$) m.p. 158−165 °C. ^{1}H NMR: δ 5.06 (H-1.1); 5.31 (H-2.1); 2.00 (H-3.1a); 2.62 (H-3.1e); 5.29 (H-4.1); 4.00 (H-5.1); 1.41 (H-6.1); 4.65 (H-1.2); 4.04 (H-2.2); 4.27 (H-3.2); 4.08 (H-4.2); 3.78 (H-5.2); 4.19 (H-6.2); 3.81 (H-6.2′); $J_{12.1}$ 8.0 Hz; $J_{23a.1}$ 12.0; $J_{23e.1}$ 5.0; $J_{3a3e.1}$ 13.5; $J_{3a4.1}$ 3.0; $J_{3e4.1}$ 3.0; $J_{45.1}$ 1.2; $J_{56.1}$ 6.5; $J_{12.2}$ 1.5; $J_{23.2}$ 3.2; $J_{34.2}$ 10.0; $J_{45.2}$ 8.0. Anal. $C_{41}H_{40}N_2O_{15}$: C, H.

Methyl 2-O-benzyl-3-O-(2-O-benzyl-3,6-dideoxy-4-O-p-nitrobenzoyl-α-D-xylo-hexopyranosyl)-4,6-O-benzylidene-α-D-mannopyranoside (14b). The glycoside *13* (150 mg, 0.40 mmol) was dissolved in dry toluene (10 ml) and 8 ml was removed by distillation at atmospheric pressure. Mercury cyanide (500 mg, 2.0 mmol), dry nitromethane (5 ml) and molecular sieves (4Å, 2 g) were added and the mixture was stirred under nitrogen at 20 °C for 6 h followed by cooling to 0 °C. The bromide (*9*) (prepared from *8* 170 mg, 0.423 mmol) and dried in toluene (3 ml over molecular sieves for 1 h) was added dropwise during 45 min at 0 °C. Stirring was continued for 4 h at 0 °C and 10 h at 20 °C. The mixture was filtered through celite and the filter was washed 3 times with toluene (10 ml). The filtrate was washed twice with water (15 ml), dried (magnesium sulfate) and filtered. Evaporation and separation on a silica gel column (ethyl acetate−toluene 1:10) gave 116 mg (39 %) of *14b*. $[\alpha]_D^{20}$ +130° (c 0.6, $CHCl_3$)(reported 129° ($CHCl_3$)). ^{1}H NMR: δ 5.42 (H-1.1); 3.72 (H-2.1); 2.18 (H-3.1a); 2.03 (H-3.1e); 5.08 (H-4.1); 4.32 (H-5.1); 1.04 (H-6.1); 4.82 (H-1.2); 3.79 (H-2.2); 4.24 (H-3.2); 3.74 (H-4.2); 4.34 (H-5.2); 3.82 (H-6.2); 3.88 (H-6.2′). $J_{12.1}$ 3.6 Hz; $J_{23a.1}$ 12.0; $J_{23e.1}$ 4.0; $J_{3a3e.1}$ 14.4; $J_{3a4.1}$ 3.2; $J_{3e4.1}$ 3.2; $J_{45.1}$ 1.5; $J_{56.1}$ 6.0; $J_{12.2}$ 1.5; $J_{34.2}$ 5.2; $J_{45.2}$ 2.0; $J_{56.2}$ 0; $J_{56'.2}$ 0; $J_{66'.2}$ 9.2.

Methyl 2-O-benzyl-4,6-O-benzylidene-3-O-(2,4-di-O-benzyl-3,6-dideoxy-α-D-xylo-hexopyranosyl)-α-D-mannopyranoside (14c). The glycoside *13* (220 mg, 0.59 mmol) was dissolved in toluene (5 ml) and toluene (4 ml) was distilled off. *N,N*-Dimethylformamide (0.4 ml), toluene (8 ml), molecular sieves (1 g, 4Å) and tetrabutylammonium bromide (200 mg, 0.65 mmol) were added and the mixture stirred for 6 h. The chloride (*12*) (190 mg, 0.55 mmol) dissolved in toluene (2 ml) was added and the mixture was stirred at 50 °C for 4 d. The mixture was filtered, diluted with toluene (10 ml), washed with saturated sodium hydrogencarbonate solution (10 ml), water (10 ml) and dried (magnesium sulfate). Filtration and evaporation gave 460 mg of a syrup. Separation on a silica gel column (toluene–ethyl acetate 7:1) gave 143 mg (38 %) of *19* as the main fraction. $[\alpha]_D^{22}$ +28° (c 2.5, $CHCl_3$). ^{1}H NMR: δ 5.38 (H-1.1); 3.74 (H-2.1); 1.85 (H-3.1a); 2.09 (H-3.1e); 3.30 (H-4.1); 3.67 (H-5.1); 1.12 (H-6.1); 4.73 (H-1.2); 3.74 (H-2.2); 4.33 (H-3.2); 4.24 (H-4.2); 3.79 (H-5.2); 4.03 (H-6.2); 3.83 (H-6.2′). $J_{12.1}$ 3.1 Hz; $J_{23a.1}$ 12.0; $J_{23e.1}$ 4.5; $J_{3a3e.1}$ 13.0; $J_{3a4.1}$ 2.2; $J_{3e4.1}$ 3.0; $J_{45.1}$ 1.0; $J_{56.1}$ 6.7; $J_{12.2}$ 1.1; $J_{23.2}$ 3.0; $J_{34.2}$ 9.0; $J_{45.2}$ 9.0.

A small fraction (7 mg, 2 %), which according to ^{1}H NMR was the β-linked disaccharide, was eluted after *14c*.

Methyl 2-O-benzyl-3-O-(2,4-di-O-benzyl-3,6-dideoxy-α-D-xylo-hexopyranosyl)-α-D-mannopyranoside (22). The aglycone (*13*) (223 mg, 0.60 mmol) was dissolved in toluene (6 ml) and 5 ml was distilled off. Mercury cyanide (200 mg, 0.8 mmol), nitromethane (5 ml), and molecular sieves (4Å, 1 g) were added and the mixture stirred for 6 h at 20 °C under nitrogen atmosphere. The chloride (*12*) (180 mg, 0.52 mmol), dissolved in toluene (3 ml) and dried for 2 h over molecular sieves (4Å, 0.3 g), was added dropwise with stirring at 0 °C. The mixture was stirred for 4 h at 0 °C and 9 h at 20 °C. The reaction mixture was filtered through celite, diluted with dichloromethane (40 ml), washed with sodium hydrogencarbonate solution, potassium iodide solution (30 ml), water (30 ml) and dried (magnesium sulfate). Filtration and evaporation gave 368 mg of syrup which was separated on a silica gel column (toluene–ethyl acetate 5:1) to give a disaccharide fraction of 245 mg (70 %, with an anomeric ratio β/α=2/5 seen from a ^{1}H NMR spectrum) and an aglyconic fraction of 80 mg. The disaccharides could not be separated chromatographically and the benzylidene group was therefore removed by stirring with 80 % acetic acid (10 ml) for 2 h at 60 °C. The mixture was evaporated and the resulting syrup was separated on a silica gel column (ethyl acetate–light petroleum: 7:5). The first fraction was evaporated giving 110 mg of *22* (36 % overall from *12* $[\alpha]_D^{25}$

+30° (c 1.1, $CHCl_3$). ^1H NMR: δ 4.96 (H-1.1); 3.83 (H-2.1); 1.82 (H-3.1a) 2.11 (H-3.1e); 3.33 (H-4.1); 3.85 (H-5.1); 1.06 (H-6.1); 4.67 (H-1.2); 3.76 (H-2.2); 3.85 (H-3.2); 3.97 (H-4.2); 3.60 (H-5.2); 3.80 (H-6.2); 3.75 (H-6.2'). $J_{12.1}$ 3.1 Hz; $J_{23a.1}$ 12.0; $J_{23e.1}$ 4.5; $J_{3a3e.1}$ 13.0; $J_{3a4.1}$ 2.3; $J_{3e4.1}$ 3.0; $J_{45.1}$ 1.0; $J_{56.1}$ 6.6; $J_{12.2}$ 1.2; $J_{23.2}$ 3.0; $J_{34.2}$ 9.5; $J_{45.2}$ 9.5; $J_{56.2}$ 3.8; $J_{56'.2}$ 5.0; $J_{66'.2}$ 11.5.

Evaporation of the second fraction gave 45 mg (15 % overall from *12*) of the β-isomer. $[\alpha]_D^{25}$ +5° (c 0.8, $CHCl_3$). ^1H NMR: δ 4.41 (H-1.1); 3.65 (H-2.1); 1.44 (H-3.1a); 2.34 (H-3.1e); 3.34 (H-4.1); 3.68 (H-5.1); 1.25 (H-6.1); 4.52 (H-1.2); 3.77 (H-2.2); 3.80 (H-3.2); 3.91 (H-4.2); 3.56 (H-5.2); 3.90 (H-6.2); 3.79 (H-6.2'). $J_{12.1}$ 7.5 Hz; $J_{23a.1}$ 12.0; $J_{23e.1}$ 4.7; $J_{3a3e.1}$ 13.9; $J_{3a4.1}$ 2.5; $J_{3e3.1}$ 3.2; $J_{45.1}$ 1.0; $J_{56.1}$ 6.5; $J_{12.2}$ 1.1; $J_{23.2}$ 3.0; $J_{34.2}$ 9.5; $J_{45.2}$ 9.5; $J_{56.2}$ 3.8; $J_{56'.2}$ 5.0; $J_{66'.2}$ 11.5.

*Methyl 3-O-(3,6-dideoxy-α-*D*-xylo-hexopyranosyl)-α-*D*-mannopyranoside (18).* The disaccharide (*14a*) (215 mg, 0.264 mmol) was stirred for 20 h at 20 °C with sodium methoxide in methanol (0.1 M, 10 ml). The mixture was neutralized with ion exchange resin (Amberlite) IRC 50) and filtered. After concentration *in vacuo* the residue was treated with charcoal in ethyl acetate for 1 h. Filtration through celite and evaporation left 130 mg of material. This was dissolved in 80 % acetic acid (5 ml) and left for 3.5 d. Water (10 ml) was added and the solution was concentrated at 40 °C and 10 mm Hg. The coevaporation with water was repeated twice to give 90 mg material, which was dissolved in methanol (40 ml) and hydrogenated at 110 atm. pressure of hydrogen over palladium on charcoal (50 mg, 5 %) for 20 h. Filtration through celite and evaporation left a residue which was separated on a silica gel plate (ethyl acetate–methanol 2:1) giving 50 mg (57 %) of *18*. $[\alpha]_D^{23}$ +117° (c 0.2, H_2O) [reported ^{1}+113° (H_2O)] ^1H NMR: δ 4.99 (H-1.1); 3.91 (H-2.1); 1.95 (H-3.1a); 1.87 (H-3.1e) 3.73 (H-4.1); 4.00 (H-5.1); 1.05 (H-6.1); 4.66 (H-1.2); 3.94 (H-2.2); 3.73 (H-3.2); 3.73 (H-4.2); 3.56 (H-5.2); 3.81 (H-6.2); 3.68 (H-6.2'). $J_{12.1}$ 3.9 Hz; $J_{23a.1}$ 12.5; $J_{23e.1}$ 5.6; $J_{3a3e.1}$ 14.1; $J_{3a4.1}$ 3.0; $J_{3e4.1}$ 3.4; $J_{45.1}$ 1.4; $J_{56.1}$ 6.4; $J_{12.2}$ 1.8; $J_{23.2}$ 2.8; $J_{34.2}$ 8.2; $J_{45.2}$ 8.3; $J_{56.2}$ 2.3; $J_{56'.2}$ 5.6; $J_{66'.2}$ 11.9. ^{13}C NMR: 101.4 ppm (C-1.1); 64.7 (C-2.1); 34.1 (C-3.1); 69.5 (C-4.1); 68.0 (C-5.1); 16.5 (C-6.1); 101.9 (C-1.2); 71.2 (C-2.2); 79.6 (C-3.2) 67.2 (C-4.2); 73.8 (C-5.2); 62.8 (C-6.2); 55.9 (OMe) $J_{ClHl.1}$ 170 Hz; $J_{ClHl.2}$ 171.

*Methyl 3-O-(3,6-dideoxy-β-*D*-xylo-hexopyranosyl)-α-*D*-mannopyranoside (19).* The disaccharide (*15*) was deprotected in essentially the same way to give *19* in 40 % yield. $[\alpha]_D^{22}$ −1.3° (c 0.3, H_2O), ^1H NMR: δ 4.39 (H-1.1); 3.67 (H-2.1); 1.63 (H-3.1a); 2.13 (H-3.1e); 3.74 (H-4.1); 3.76 (H-5.1); 1.11 (H-6.1); 4.73 (H-1.2); 4.03 (H-2.2); 3.84 (H-3.2); 3.70 (H-4.2); 3.57 (H-5.2); 3.84 (H-6.2); 3.70 (H-6.2'). $J_{12.1}$ 8.0 Hz; $J_{23a.1}$ 12.0; $J_{23e.1}$ 5.3; $J_{3a3e.1}$ 13.4; $J_{3a4.1}$ 2.9; $J_{3e4.1}$ 2.9; $J_{45.1}$ 0.8; $J_{56.1}$ 6.9; $J_{12.2}$ 1.9; $J_{23.2}$ 3.2; $J_{34.2}$ 9.5; $J_{45.2}$ 9.7; $J_{56.2}$ 2.1; $J_{56'.2}$ 5.6; $J_{66'.2}$ 12.0. ^{13}C NMR: 103.7 ppm (C-1.1); 66.1 (C-2.1); 37.6 (C-3.1); 73.2 (C-4.1); 68.9 (C-5.1); 16.4 (C-6.1); 101.4 (C-1.2); 68.6 (C-2.2); 79.3 (C-3.2); 66.1 (C-4.2); 75.2 (C-5.2); 61.7 (C-6.2); 55.9 (OMe). $J_{ClHl.1}$ 159 Hz; $J_{ClHl.2}$ 170.

*Methyl 3-O-(3,6-dideoxy-α-*L*-xylo-hexopyranosyl)-α-*D*-mannopyranoside (20).* The disaccharide (*16*) was deprotected essentially as described above to give *20* in 57 % yield. $[\alpha]_D^{23}$ −26.2° (c 0.5, H_2O). ^1H NMR: δ 4.86 (H-1.1); 3.94 (H-2.1); 1.97 (H-3.1a); 1.89 (H-3.1e); 3.77 (H-4.1); 4.14 (H-5.1); 1.04 (H-6.1); 4.72 (H-1.2); 4.02 (H-2.2); 3.73 (H-3.2); 3.69 (H-4.2); 3.56 (H-5.2); 3.83 (H-6.2); 3.70 (H-6.2'). $J_{12.1}$ 3.7 Hz; $J_{23a.1}$ 11.9; $J_{23e.1}$ 5.6; $J_{3a3e.1}$ 13.3; $J_{3a4.1}$ 3.2; $J_{3e4.1}$ 3.5; $J_{45.1}$ 1.5; $J_{56.1}$ 6.0; $J_{12.2}$ 2.1; $J_{23.2}$ 2.4; $J_{34.2}$ 9.1; $J_{45.2}$ 9.1; $J_{56.2}$ 2.2; $J_{56'.2}$ 5.6; $J_{66'.2}$ 11.9. ^{13}C NMR: 96.5 ppm (C-1.1); 64.3 (C-2.1); 34.1 (C-3.1); 69.6 (C-4.1); 67.8 (C-5.1); 16.5 (C-6.1); 101.8 (C-1.2); 68.0 (C-2.2); 77.2 (C-3.2); 66.4 (C-4.2); 73.8 (C-5.2); 62.2 (C-6.2); 56.0 (OMe) $J_{ClHl.1}$ 168 Hz; $J_{ClHl.2}$ 172.

*Methyl 3-O-(3,6-dideoxy-β-*L*-xylo-hexopyranosyl)-α-*D*-mannopyranoside (21).* Deprotection of *17* as described above gave *21* (8 mg) in 19 % yield. ^1H NMR: δ 4.51 (H-1.1); 3.64 (H-2.1); 1.63 (H-3.1a); 2.11 (H-3.1e); 3.71 (H-4.1); 3.71 (H-5.1); 1.10 (H-6.1); 4.67 (H-1.2); 4.08 (H-2.2); 3.79 (H-3.2); 3.72 (H-4.2); 3.56 (H-5.2); 3.80 (H-6.2); 3.68 (H-6.2'). $J_{12.1}$ 7.8 Hz; $J_{23a.1}$ 12.0; $J_{56.1}$ 5.8; $J_{12.2}$ 1.8; $J_{23.2}$ 3.0; $J_{34.2}$ 9.4; $J_{45.2}$ 9.3; $J_{56.2}$ 2.6; $J_{56'.2}$ 6.0; $J_{66'.2}$ 12.0.

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