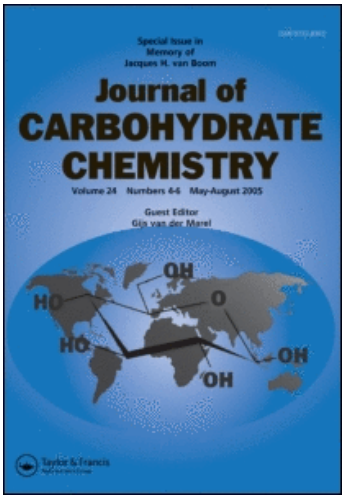

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SYNTHESIS OF FURANOSE GLYCOSIDES OF ABEQUOSE

(3,6-DIDEOXY-D-*XYLO*-HEXOSE)

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ABSTRACT

Hydrogenolysis of 2,3,5-tri-*O*-benzoyl-6-*O*-trityl-D-galactono-1,4-lactone (**2**) gave the corresponding 3-deoxy-D-*xylo*-hexono-1,4-lactone derivative (**3**), which on treatment with HBr in acetic acid afforded 2,5-di-*O*-benzoyl-6-bromo-3,6-dideoxy-D-*xylo*-hexono 1,4-lactone (**4**). Hydrogenation of **4** led to 3,6-dideoxy-D-*xylo*-hexono-1,4-lactone dibenzoate (**6**). The overall yield of **6** from D-galactono-1,4-lactone (**1**) was about 59%. Alternatively, compound **6** was prepared (67% overall yield from **1**) by hydrogenolysis of 6-bromo-6-deoxy-D-galactono-1,4-lactone tribenzoate (**5**), obtained by treatment of **2** with HBr in dry dichloromethane. Diisoamylborane reduction of **6** gave an anomeric mixture of 2,5-di-*O*-benzoyl-3,6-dideoxy-α,β-D-*xylo*-hexofuranose (**7**), which on *O*-debenzoylation afforded 3,6-dideoxy-D-*xylo*-hexose (abequose, **8**) whose tautomeric equilibrium was studied by ^{13}C NMR spectroscopy. Acetylation of **7** gave the 1-*O*-acetyl derivative (**9**) mainly in the β anomeric configuration. Tin (IV) chloride promoted glycosylation of **9** with methanol and ethanol afforded stereoselectively methyl (**10**) and ethyl 2,5-di-*O*-benzoyl-3,6-dideoxy-β-D-*xylo*-hexofuranoside (**11**), respectively.

INTRODUCTION

Abequose (3,6-dideoxy-D-*xylo*-hexose) is the immunodominant sugar of the lipopolysaccharide (LPS) *O*-specific chain of salmonella typhimurium and other species of salmonella.[1] Although 3,6-dideoxyhexoses have been identified in various Gram negative bacteria,[1] in most of the cases their anomeric configuration and

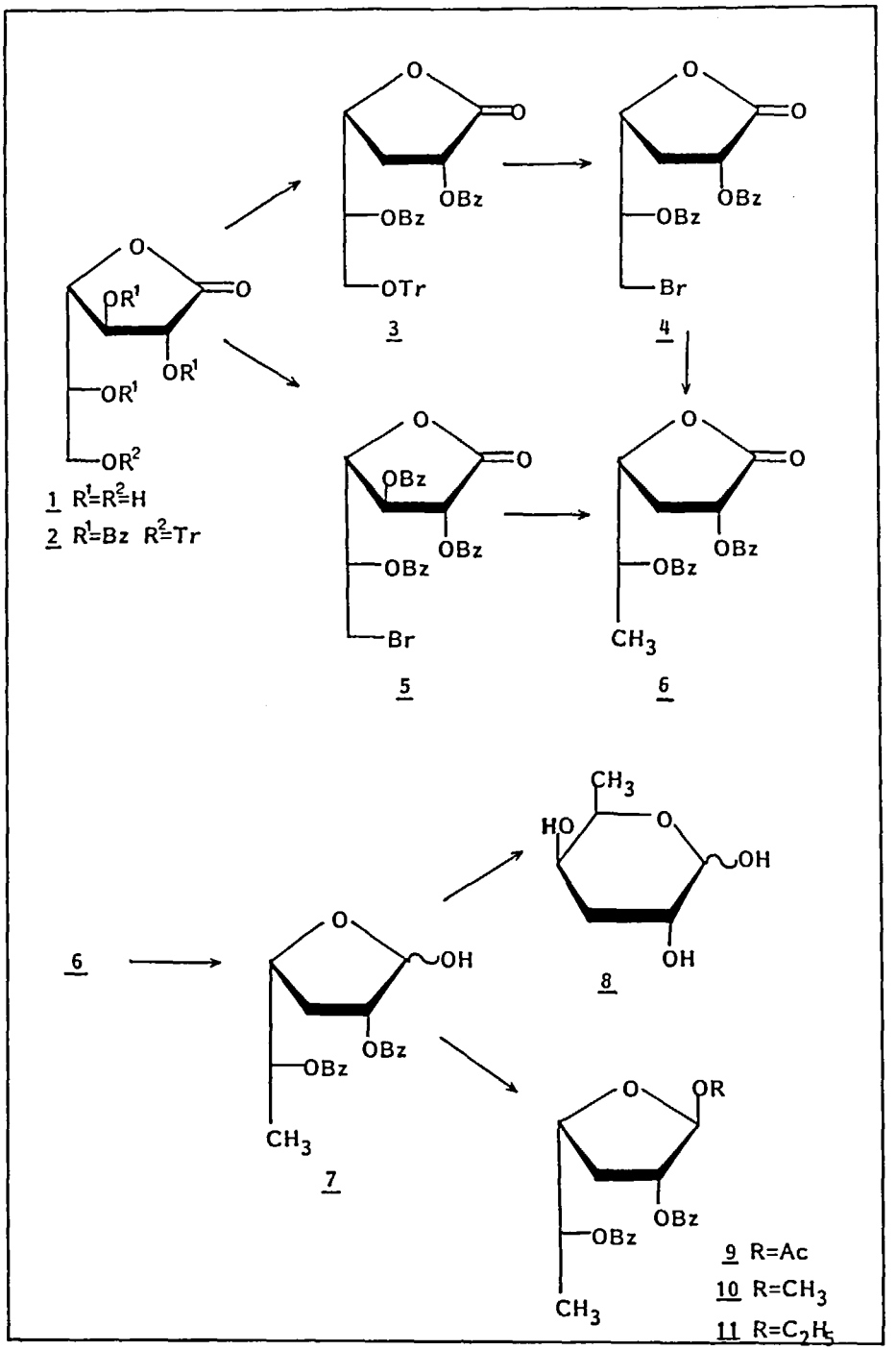
ring structure were not established. Therefore, the preparation of pyranoid and furanoid glycosides of 3,6-dideoxysugars would be useful for the spectroscopic determination of their ring structures. Also, glycosylation could be extended to the synthesis of oligosaccharides. Pyranoid glycosides and disaccharides of abequose have been prepared,[2] but furanoid glycosides have not been reported. The fact that furanose constituents (i.e., galactofuranose) in LPS have been frequently identified, and also that examples of LPS containing 3,6-dideoxyhexoses in the furanoid form have been found,[3] prompted us to synthesize glycosides of abequofuranose.

The key step in the present synthesis is the deoxygenation of C-3 and C-6 of a **D**-galactono-1,4-lactone derivative, which is further reduced by diisoamylborane to afford the furanose. We have employed a similar strategy for the synthesis of 3,6-dideoxy[4,5] and 3-deoxysugars.[6,7]

RESULTS AND DISCUSSION

Catalytic hydrogenation of 2,3,5-tri-*O*-benzoyl-6-*O*-trityl-**D**-galactono-1,4-lactone (**2**) in the presence of triethylamine afforded 2,5-di-*O*-benzoyl-3-deoxy-6-*O*-trityl-**D**-*xylo*-hexono-1,4-lactone (**3**), in 94% yield. Triethylamine promotes β-elimination of the C-3 benzoyloxy group, and the α,β-unsaturated intermediate is stereoselectively hydrogenated from the side opposite the lateral chain at C-4. A similar steroselectivity was observed for the hydrogenolysis of other lactones.[6,8]

Reaction of **3** with 30% HBr in acetic acid afforded the crystalline 6-bromodideoxylactone derivative (**4**) in 89% yield. The replacement of the trityl group by bromine was evidenced by the strong upfield shift of the C-6 signal (34 ppm) in the ^{13}C NMR spectrum of **3**, when compared to the same signal in **4**. The mass spectrum of **4** showed two peaks of approximately equal intensity for the molecular ion (M^+, m/z 432, 434) characteristic of bromine-containing compounds. Bromination of the lactone derivative **3** took aldonolactones which undergo substitution of the C-2 and primary Catalytic hydrogenation of **4** gave the crystalline 3,6-dideoxylactone derivative **6** in 78% yield. The first order ^1H NMR spectra obtained for **3**, **4**,and **6** enabled accurate measurement of vicinal proton coupling constants (Table 1), whose values were



almost identical to those observed for other, known 3-deoxylactones having a *cis* relationship for the C-2 and C-4 substituents of the ring.[4,6,8]

The overall yield for the conversion of **1** into **6**, through the route described above, was about 59%. This yield could be even improved by conducting both the hydrogenolysis of the 3-benzoyloxy group and the bromine at C-6 in a single step, from 6-bromo-6-deoxy-2,3,5-tri-*O*-benzoyl-**D**-galactono-1,4-lactone (**5**). Compound **5** was prepared by reaction of **2** with a solution of HBr in acetic acid, and isolated as a syrup by column chromatography in a yield of 67%. A better yield of **5** was obtained when **2** was treated with a solution of HBr in dry dichloromethane. Although the ^{1}H NMR spectrum of **5** was very similar to that of **2**, except for the slight upfield shifting for H-6 in **5**, the ^{13}C NMR spectrum of **5** showed the C-6 signal strongly shifted upfield (35 ppm) with respect to the same signal in the spectrum of **2**. Hydrogenation of **5** in the presence of triethylamine resulted in the simultaneous hydrogenolysis of the C-3 substituent and of the bromine at C-6, to afford the dideoxylactone derivative **6**, in 67% overall yield from **1**. Although the yield of this shorter route was higher, the former synthesis of **6** (from **1**) has the advantage that the intermediate compounds (**3** and **4**) are crystalline and easier to purify.

Diisoamylborane reduction[5,6,11] of **6** afforded the anomeric mixture of 2,5-di-*O*-benzoyl-3,6-dideoxy-**D**-*xylo*-hexofuranose (**7**), in 81% yield. The ^{13}C NMR spectrum of **7** showed two signals in the anomeric region at 100.1 and 94.9 ppm attributed to the β and α anomers, respectively.[12] The β:α ratio (6:1) was estimated by averaging the integrated intensities of the C-1 and C-3 resonances for each anomer.

Sodium methoxide debenzoylation of **7** afforded 3,6-dideoxy-**D**-*xylo*-hexose (**8**, abequose) which showed the same optical rotation as the natural[13] and synthetic[13-15] products. The ^{13}C NMR spectrum of abequose (**8**) in D_2O-H_2O solution showed the signals for the pyranose and furanose forms, as already reported.[2] The resonances for the anomeric carbons appeared at δ 103.1 (β-furanose), 99.0 (β-pyranose), 96.0 (α-furanose), and 92.1 (α-pyranose), and, on the basis of their intensities, the relative abundance of these forms were estimated as 3:11:1:5, respectively. These values are in good agreement with those given for the equilibrium composition of 3-deoxy-**D**-*xylo*-hexose[16] (determined by ^{1}HNMR) and also of 3-deoxy-**D**-

Table 1. ^{1}H NMR data for Compounds 3-7, 9-11.

Compound	δ^a (ppm), J (Hz)						
	H-1 ($J_{1,2}$)	H-2 ($J_{2,3}$)	H-3 ($J_{3,3'}$)	H-3' ($J_{2,3'}$)	H-4 ($J_{3,4}$),($J_{3',4}$)	H-5 ($J_{4,5}$)	H-6 ($J_{5,6}$)
3	-	5.75(dd) (9.1)	2.83(ddd) (13.0)	2.12(ddd) (10.0)	5.05(m) (6.2),(9.4)	5.39(m) (4.6)	3.55(dd),3.42(dd) (5.2) (6.0)
4	-	5.76(dd) (9.3)	3.00(ddd) (13.2)	2.22(ddd) (9.4)	5.13(ddd) (6.7),(9.4)	5.42(m) (3.0)	3.78(dd),3.64(dd) (6.8) (5.9)
5	-	6.10(d) (6.0)	5.80(m)	-	5.20 (dd) (6.0)	5.80(m) (2.5)	3.73(m) -
6	-	5.77(dd) (9.3)	2.93(ddd) (13.2)	2.22(m) (9.7)	4.70(ddd) (6.4),(9.5)	5.36(m) (4.5)	1.48(d) (6.6)
7[b]	5.62(s) (< 0.5)	5.35(m) (6.7)	2.69(ddd) (14.3)	1.94(ddd) (2.1)	4.53(m) (8.0),(6.0)	5.35(m) (6.2)	1.40(d) (6.5)
9	6.43(s)	5.43(dd) (6.8)	2.68(ddd) (14.5)	2.06(m) (2.3)	4.52(ddd) (8.2),(6.0)	5.35(m) (6.0)	1.40(d) (6.5)
10	5.13(s) (< 1)	5.33(m) (6.8)	2.60(ddd) (14.2)	1.90(ddd) (2.2)	4.38(m) (8.1),(6.5)	5.33(m) (6.0)	1.42(d) (6.6)
11	5.24 (s) (< 1)	5.33(m) (6.9)	2.65(ddd) (14.3)	1.92(ddd) (2.2)	4.39(m) (8.0),(6.5)	5.33(m) (6.0)	1.42(d) (6.7)

[a]Chemical shifts are relative to $(CH_3)_4Si$ (0 ppm). [b]Data for the β anomer.

Table 2. ^{13}C NMR Data for Compounds 3-7, 9-11.

Compound	δ^a (ppm)					
	C-1	C-2	C-3	C-4	C-5	C-6
3	171.5	68.3	30.8	75.2	73.4	62.1
4	170.1	68.0	30.4	74.6	72.3	28.3
5	168.8	74.1*	72.4*	79.1	71.7*	27.4
6	171.5	68.4*	30.9	77.4	70.5*	16.0
7[b]	100.9	78.8	32.0	79.7	71.7	16.4
9	100.1	77.6	31.9	81.1	70.9	16.1
10[c]	107.0	78.3	32.3	79.2	71.4	16.3
11[d]	105.8	78.3	32.3	79.2	71.4	16.3

[a]Chemical shifts are relative to $(CH_3)_4Si$ (0 ppm). [b]Data for the β anomer, [c]δ $\underline{C}H_3O$ 54.5, [d]δ $O\underline{C}H_2\underline{C}H_3$ 62.8 and 15.1, * signals may be interchanged.

gluco-heptofuranose,[6] which bear the same stereochemical relationship as **8** for C-2, C-4, and C-5. Acetylation of **7** at low temperature (0 °C) gave the 1-*O*-acetyl derivative **9** (90% yield), mainly in the β configuration (> 94%) as determined by NMR spectroscopy.

Glycosylation of **9** was performed using tin (IV) chloride as catalyst, which was previously employed to obtain *trans*-1,2-glycofuranosides from per-*O*-acyl sugar derivatives.[17,18] Thus, compound **9** was allowed to react with $SnCl_4$ in order to activate the anomeric center, presumably by formation of an acyloxonium ion by anchimeric participation of the C-2 acyl group. Nucleophilic attack of either methanol or ethanol on the acyloxonium ion gave the abequofuranoside derivatives **10** and **11** stereoselectively in isolated yields of 70-80%. The β anomeric configuration for these products was established on the basis of the $J_{1,2}$ value[19] (<1.0 Hz) and the chemical shift for C-1, which appeared strongly deshielded (> 5 ppm) in comparison with the 1-*O*-acetyl precursor **9**, as observed for related furanosides.[6,18]

EXPERIMENTAL

Melting points were determined with a Thomas-Hoover apparatus and are uncorrected. Optical rotations were recorded with a Perkin-Elmer 141 polarimeter. ^1H and ^{13}C NMR spectra were recorded with a Varian XL-100 spectrometer at 100.1 and 25.2 MHz, respectively, for solutions in $CDCl_3$. The apparent coupling constants reported are the line spacings directly observed. Mass spectra were recorded with a Varian MAT CH7 spectrometer coupled to a Varian MAT Data-system 166. Column chromatography was performed on silica gel 60 (Merck). TLC was carried out on precoated aluminum plates (0.2 mm) of silica gel 60F-254 (Merck). Detection was effected by exposure to UV light and by spraying the plates with 5% (v/v) H_2SO_4 in EtOH followed by heating.

2,3,5-Tri-O-benzoyl-6-O-trityl-D-galactono-1,4-lactone (2) - Compound **2** was prepared from D-galactono-1,4-lactone **(1)** as previously described.[20]

2,5-Di-O-benzoyl-3-deoxy-6-O-trityl-D-*xylo*-hexono-1,4-lactone (3). Compound **2** (1.46 g, 2.0 mmol) was dissolved in ethyl acetate (15 mL) containing triethylamine (1.5 mL) and hydrogenated at room temperature and 304 kPa over 10% Pd-charcoal (0.15 g). After 4 h, no starting material was detected by TLC and the reaction mixture was diluted with CH_2Cl_2 and the catalyst removed by filtration. The filtrate was washed with 5% HCl, water, saturated aqueous $NaHCO_3$, and water, dried ($MgSO_4$) and concentrated to give 1.15 g (94%) of compound **3** as a chromatographically homogeneous syrup (Rf 0.40, 9:1 toluene-EtOAc). The addition of ethanol to the syrup gave an amorphous solid; $[\alpha]_D$ -46° (c 0.8, $CHCl_3$).

Anal. Calcd for $C_{39}H_{32}O_7$: C, 76.45; H, 5.27. Found C, 76.24; H, 5.52.

2,5-Di-O-benzoyl-6-bromo-3,6-dideoxy-D-*xylo*-hexono-1,4-lactone (4). Compound **3** (1.0 g, 1.8 mmol) was dissolved in 32% HBr in acetic acid. The solution was stirred for 10 min at room temperature, and then diluted with CH_2Cl_2 (100 mL) and neutralized by extraction with saturated aqueous $NaHCO_3$. The organic extract was dried ($MgSO_4$) and the solvent evaporated. The residue was crystallized from ethanol to afford compound **4** (0.63 g, 89%). Recrystallization from ethanol gave material with mp 141-143 °C, $[\alpha]_D$-67.5° (c 0.5, $CHCl_3$). MS m/z (%) 434 (2.1), 432 (2.2), 353 (82), 231 (95), 205 (75), 109 (100), 105 (79), 77 (86), 51 (86).

Anal. Calcd for $C_{20}H_{17}BrO_6$: C, 55.44; H, 3.96; Br, 18.44. Found: C, 55.73; H, 4.25; Br, 18.25.

2,3,5-Tri-O-benzoyl-6-bromo-6-deoxy-D-galactono-1,4-lactone (5). Method (A): A solution of compound **2** (1.5 g, 2.05 mmol) in 32% HBr in acetic acid, was stirred for 10 min at room temperature and then treated as described for compound **4**. The reaction mixture showed two main spots by TLC (3:1 hexane-EtOAc) of Rf 0.55 and 0.94, the latter with identical mobility as triphenylmethanol. The compound of Rf 0.55 was isolated by column chromatography (3:1 hexane-EtOAc) as a homogeneous syrup (0.75 g, 67%), and it was identified as 2,3,5-tri-*O*-benzoyl-6-bromo-6-deoxy-**D**-galactono-1,4-lactone (**5**), $[\alpha]_D$ +22.5° (c 1, $CHCl_3$). MS m/z (%) 554 (1.5), 552 (1.7), 473 (75), 325 (70), 351 (89), 229 (92), 105 (100), 77 (61), 51 (32).

Anal. Calcd for $C_{27}H_{21}BrO_8$: C, 58.60; H, 3.82; Br, 14.44. Found: C, 58.88; H, 3.63; Br, 14.42.

Method (B): Dry HBr was bubbled through a stirred solution of **2** (3.0 g, 4.1 mmol) in CH_2Cl_2 (75 mL), cooled at 0 °C. After 1 h, the mixture was diluted with CH_2Cl_2 (100 mL) and treated as described for compound **4**. The 6-bromo-lactone derivative **5** was purified by column chromatography as indicated above (Method A), to yield 2.18 g (95%).

2,5-Di-O-benzoyl-3,6-dideoxy-D-*xylo*-hexono-1,4-lactone (6). (A) From 2,5-di-*O*-benzoyl-6-bromo-3,6-dideoxy-**D**-*xylo*-hexono-1,4-lactone (**4**.) - Compound **4** (0.5 g, 1.2 mmol) dissolved in ethyl acetate (10 mL) containing triethylamine (0.2 mL) was hydrogenated over 10% Pd-charcoal at atmospheric pressure. After 4 h the mixture was diluted with ethyl acetate (50 mL) and treated as described for the preparation of **3**. The residue obtained crystallized from ethanol to give compound **6** (0.32 g, 78%); mp 114-116° C; $[\alpha]_D$ -78° (c 1, $CHCl_3$).

Anal. Calcd for $C_{20}H_{18}O_6$: C, 67.42; H, 5.62. Found: C, 67.56; H, 5.48.

(B) From 2,3,5-tri-*O*-benzoyl-6-bromo-6-deoxy-**D**-galactono-1,4-lactone (**5**). A solution of compound **5** (0.38 g, 0.7 mmol) in ethyl acetate (10 mL)-triethylamine (0.5 mL) was hydrogenated for 4 h at room temperature at 304 kPa over 10% Pd-charcoal, and then treated as described for the preparation of **3**. The dideoxylactone **6** was obtained crystalline in 74% yield (0.18 g).

2,5-Di-O-benzoyl-3,6-dideoxy-α,ß-D-*xylo*-hexofuranose (7). To a freshly prepared solution containing 12 mmol of bis(2-butyl-3-methyl)borane (diisoamylborane)[11] in tetra-hydrofuran (10 mL) was added compound **6** (1.0 g, 2.8 mmol) dissolved in tetrahydrofuran (4 mL). The mixture was stirred for 20 h at room temperature, under a static N_2 atmosphere, and then it was processed as described previously.[5,11] The product, which showed a single spot on TLC of Rf 0.12 (9:1 toluene-EtOAc) was purified by flash chromatography (4:1 toluene-EtOAc), to yield syrupy compound **7** (0.81 g, 81%), $[\alpha]_D$ -30° (c 1, $CHCl_3$).

Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.66. Found: C, 67.67; H, 5.79.

3,6-Dideoxy-D-*xylo*-hexose (abequose, 8). To a solution of compound **7** (0.15 g, 0.41 mmol) in CH_2Cl_2 (20 mL) at 0 °C, was added 0.5 M sodium methoxide in methanol (2 mL). The mixture was stirred for 2 h at 0 °C, after which no starting material was detected by TLC, and then neutralized with Dowex 50 W (H^+) ion-exchange resin, and filtered. The resin was washed with water, and the filtrate was extracted with water (4 x 25 mL). The aqueous solutions were combined, extracted with CH_2Cl_2, and concentrated to yield compound **8** (60 mg, 97%) as a syrup. The product was homogeneous by paper chromatography: R_{GLC}=2.2, $R_{rhamnose}$= 1.2 (6:4:3 BuOH-C_5H_5N-H_2O); $[\alpha]_D$ -4°(c 0.5, H_2O). Lit[13] -3.6° (H_2O).

1-O-Acetyl-2,5-di-O-benzoyl-3,6-dideoxy-ß-D-*xylo*-hexofuranose (9). Acetic anhydride (1.7 mL, 18 mmol) was added dropwise to a solution of compound **7** (0.5 g, 1.4 mmol) in dry pyridine (7 mL) chilled to 0 °C. The mixture was stirred for 2 h at 0 °C, and then allowed to reach room temperature, and stirred for an additional 0.5 h. Methanol was slowly added to the solution, which was concentrated after 0.5 h. Pyridine was removed by evaporation with toluene (3 x 20 mL). The residue was purified by column chromatography with 9:1 toluene-EtOAc. Compound **9** was isolated as a syrup (0.51 g, 91%); Rf 0.32 (toluene-EtOAc); $[\alpha]_D$ -66° (c 0.5, CH_3Cl).

Anal. Calcd for $C_{22}H_{22}O_7$: C, 66.32; H, 5.57. Found: C, 65.60; H, 5.49.

Methyl 2,5-Di-O-benzoyl-3,6-dideoxy-ß-D-*xylo*-hexofuranoside (10). Tin (IV) chloride (55 µl, 0.46 mmol) was added to a solution of **9** (0.1g, 0.25 mmol) in anhydrous CH_2Cl_2 (3mL), at 0 °C under N_2. After 15 min of stirring at 0°C, methanol (32 µL, 0.80 mmol) was

added, and the stirring was continued for 1 h. The solution was diluted with CH_2Cl_2 (30 mL) and extracted with saturated aqueous $NaHCO_3$ (2 x 30 mL) and water, dried (Na_2SO_4) and concentrated. The residue was purified by column chromatography on silica gel to yield compound **10** (68 mg, 73%), $[\alpha]_D$ -53° (c 0.4, $CHCl_3$).

Anal. Calcd for $C_{21}H_{22}O_6$: C, 68,09; H, 5.99. Found: C, 67.80; H, 6.02.

Ethyl 2,5-Di-O-benzoyl-3,6-dideoxy-ß-D-*xylo*-hexofuranoside (11). The procedure described above for the preparation of **10** was followed starting from **9** (0.1 g, 0.25 mmol) and ethanol (47 µL, 0.80 mmol). After the chromatographic purification, the ethyl glycoside **11** was obtained (77 mg, 80%), $[\alpha]_D$ -69.5° (c 1, $CHCl_3$).

Anal. Calcd for $C_{22}H_{24}O_6$: C, 68.74; H, 6.29.Found: C,68.53; H, 6.39.

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