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Carbohydrate Research 279 (1995) 133–150

CARBOHYDRATE RESEARCH

Synthesis of the methyl α-glycosides of some isomalto-oligosaccharides specifically deoxygenated at position C-4

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Received 15 June 1995; accepted 25 July 1995

Abstract

Methyl α-isomaltoside and methyl α-isomaltotrioside specifically deoxygenated at position C-4 of various glucopyranosyl units were synthesized by condensation of either 1,6-di-*O*-acetyl-2,3-di-*O*-benzyl-4-deoxy-α,β-D-*xylo*-hexopyranose (**7**) or 1,6-di-*O*-acetyl-2,3,4-tri-*O*-benzyl-α,β-D-glucopyranose (**10**) [mediated by silver perchlorate and tin(IV) chloride] with suitably blocked derivatives of methyl α-D-glucopyranoside, its 4-deoxy analog **6**, or methyl 4′-deoxy α-isomaltoside (**13**), respectively.

Keywords: Synthesis; Methyl glycosides; α-Isomalto-oligosaccharides; Deoxyoligosaccharides

1. Introduction

In order to continue our probing for possible hydrogen-bonding interactions between ligands and anti-dextran antibodies [1], we are preparing isomalto di- and tri-saccharides that are deoxygenated at specific locations [2–4].

We here present a general procedure for preparing the methyl glycosides of α-isomalto-oligosaccharides specifically deoxygenated at C-4 of various glucopyranosyl units.

2. Results and discussion

Our target oligosaccharides mimic sequences in dextran antigens. Thus, high yields in the formation of α-(1 → 6) linkages are important. Because of the ease of preparation of

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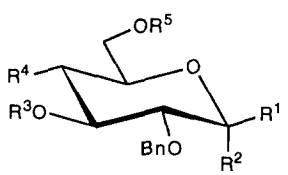
SSDI 0008-6215(95)00280-4

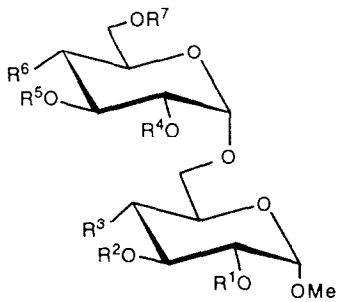
1-*O*-acyl saccharides, methods were developed using them as glycosyl donors in glycosidation reactions. Promoters such as tin(IV) chloride [5], iron(III) chloride [6,7], $BF_3 \cdot Et_2O$ [8], or TMSOTf [9] are suitable for the synthesis of 1,2-*trans* glycosides if a participating (acyl) group is present at position C-2 of the donor. Mukaiyama et al. [10] reported that 1,2-*cis* glycosides were obtained (using catalysis by trityl perchlorate) from a 1-*O*-acyl glycosyl donor if a non-participating (benzyl) group was present at C-2. They could improve the yields and the stereoselectivity of this reaction by using a combination of Lewis acids ($SnCl_4$, $GeCl_4$, $GaCl_3$, $InCl_3$, $HfCl_4$) and silver perchlorate when coupling with trimethylsilylated glycosyl acceptors [11,12]. We elected to employ their method.

For the syntheses of methyl α-isomalto-oligosaccharides deoxygenated at position C-4 of one or more glucopyranosyl units, we chose 1,6-di-*O*-acetyl-2,3-di-*O*-benzyl-4-deoxy-α,β-D-*xylo*-hexopyranose (**7**) as the glycosyl donor. Compound **7** was prepared from methyl 4,6-*O*-benzylidene-α-D-glucopyranoside, which was benzylated and then hydrolyzed with HCl (0.5%) in methanol to give methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside [13] (**1**) in quantitative yield. Monosaccharide **1** was blocked selectively at position O-6 using acetyl chloride and *sym*-collidine [14] (-40°C, 40 min), affording the monoacetyl derivative **2** [15] in 92% yield. This was converted to the phenylthiocarbonyl derivative **3** (90%) by phenylchlorothiocarbonate and *N*-hydroxysuccinimide. After reduction with tributyltin hydride, methyl 6-*O*-acetyl-2,3-di-*O*-benzyl-4-deoxy-α-D-*xylo*-hexopyranoside (**4**) was obtained in 95% yield. Intermediate **4** was quantitatively deacetylated (MeOH, NaOMe) and then silylated with chlorotrimethylsilane to afford compound **6** (91%) for future use as a glycosyl acceptor.



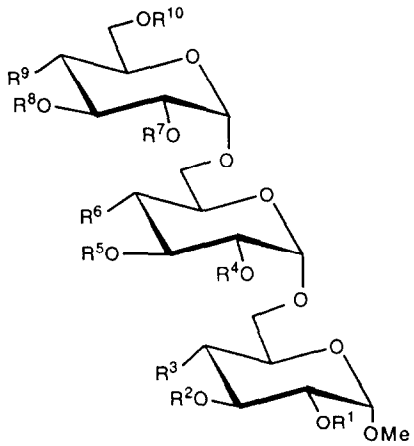
	R^1	R^2	R^3	R^4	R^5
1	H	OMe	Bn	OH	OH
2	H	OMe	Bn	OH	Ac
3	H	OMe	Bn	OPtc	Ac
4	H	OMe	Bn	H	Ac
5	H	OMe	Bn	H	H
6	H	OMe	Bn	H	TMS
7	OAc, H		Bn	H	Ac
8	OAc, H		Ac	H	Ac
9	H	OMe	Bn	OBn	TMS
10	OAc, H		Bn	OBn	Ac

Secondly, acetolysis (acetic anhydride–0.5% sulfuric acid, 5 min) of derivative **4** gave 1,6-di-*O*-acetyl-2,3-di-*O*-benzyl-4-deoxy-α,β-D-*xylo*-hexopyranose (**7**) in 90% yield. Prolonged acetolysis (8–24 h), using a higher concentration of sulfuric acid (1–2%) resulted in 1,3,6-tri-*O*-acetyl-2-*O*-benzyl-4-deoxy-α,β-D-*xylo*-hexopyranose (**8**). Both compounds **7** and **8** were used as a glycosyl donors. Methyl 2,3,4-tri-*O*-benzyl-6-*O*-trimethylsilyl-α-D-glucopyranoside (**9**) [16] was condensed (0°C, 24 h) with donor **7** in the presence of tin(IV) chloride and silver perchlorate to give disaccharide **11** (90%). Deacetylation of **11** with sodium methoxide in toluene and methanol (2 h, room temperature) afforded compound **12**, which after debenzylation gave disaccharide **17** in quantitative yield. Silylation of **12** with chlorotrimethylsilane (2.5 h, room temperature) yielded nucleophile **13** (88%).



	R^1	R^2	R^3	R^4	R^5	R^6	R^7
11	Bn	Bn	OBn	Bn	Bn	H	Ac
12	Bn	Bn	OBn	Bn	Bn	H	H
13	Bn	Bn	OBn	Bn	Bn	H	TMS
14	Bn	Bn	OBn	Bn	Ac	H	Ac
15	Bn	Bn	OBn	Bn	Ac	H	H
16	Bn	Bn	OBn	Bn	H	H	H
17	H	H	OH	H	H	H	H
18	Bn	Bn	H	Bn	Bn	OBn	Ac
19	Bn	Bn	H	Bn	Bn	OBn	H
20	Bn	Bn	H	Bn	Bn	OBn	TMS
21	H	H	H	H	H	OH	H
22	Bn	Bn	H	Bn	Bn	H	Ac
23	Bn	Bn	H	Bn	Bn	H	H
24	H	H	H	H	H	H	H
25	Bn	Bn	OBn	Bn	Bn	OBn	Ac
26	Bn	Bn	OBn	Bn	Bn	OBn	H
27	Bn	Bn	OBn	Bn	Bn	OBn	TMS

Condensation of derivative **9** [16] with glycosyl donor **8** in the presence of tin(IV) chloride and silver perchlorate (0°C, 24 h) afforded 87% of disaccharide **14**. Deacetylation of **14** with sodium methoxide in toluene and methanol at room temperature gave either **15** (88% after 5 min) or **16** (93% after 20 min). The selectively blocked disaccharide **15** could be used as an intermediate for the syntheses of higher oligosaccharides. Debenzylation of **16** yielded the target disaccharide **17** quantitatively. Condendensation [tin(IV) chloride, silver perchlorate, 0°C, 24 h] of acceptor **6** with 1,6-di-*O*-acetyl-2,3,4-tri-*O*-benzyl-α,β-D-glucopyranose (**10**) [17] gave disaccharide **18** (88%). Deacetylation resulted in compound **19**, which was debenzylated to give the fully deprotected disaccharide **21** (92%) [18]. Nucleophile **6** was condensed with donor **7** (0°C, 20 h) in the presence of tin(IV) chloride and silver perchlorate to provide **22** (92%). Deacetylation with sodium methoxide in toluene and methanol afforded **23** (90%), which after debenzylation gave methyl 4-deoxy-α-D-*xylo*-hexopyranosyl-(1 → 6)-4-deoxy-α-D-*xylo*-hexopyranoside (**24**) in quantitative yield. Partially deblocked disaccharide **19** was silylated with chlorotrimethylsilane (3 h) to afford reactive intermediate **20**. Nucleophile **20** was condensed with acetate **10** [17] [tin(IV) chloride, silver perchlorate, 0°C, 20 h] to yield trisaccharide **28** (87%). Deacetylation gave compound **29**, which was debenzylated to afford the deprotected methyl α-isomaltotrioside **30** [4]. When nucleophile **13** was condensed with derivative **10** [17] (0°C, 18 h) in the presence of tin(IV) chloride and silver perchlorate, trisaccharide **31** was obtained in 88% yield. After deacetylation compound **32** was isolated, which was debenzylated to give deblocked trisaccharide **33**. Methyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside [12] was deacetylated (MeOH, NaOMe) affording disaccharide **26** [19] and then silylated with chlorotrimethylsilane and imidazole yielding the versatile glycosyl acceptor **27** (85%). Condensation of compound **27** with donor **7** (0°C, 20 h) in the presence of tin(IV) chloride and silver perchlorate offered **34** in 88% yield. Deacetylation to give **35** (96%), followed by debenzylation, afforded the target methyl 4-deoxy-α-D-*xylo*-hexopyranosyl-(1 → 6)-α-D-glucopyranosyl-(1 → 6)-α-D-glucopyranoside (**39**) in quantitative yield. When derivative **27** was coupled with **8** (0°C, 20 h), compound **36** was obtained (86%). Deacetylation of trisaccharide **36** with sodium methoxide in toluene and methanol (room temperature, 21 min) gave the partially *O*-deacetylated compound **37**. When the reaction time was extended to 8 h, the fully *O*-deacetylated compound **38** (93%) was isolated. Our results of the deacetylation of both saccharides **14** and **36** demonstrate that Zemplén deacylation can be used to selectively remove the acetyl group from position 6 when there is another *O*-acetyl group in position 3, provided there is an *O*-benzyl group at position 2, while position 4 is deoxygenated. This observation can be added to the one already published [20] that an *O*-acyl group at position 3 of a carbohydrate moiety is also more stable to the conditions of Zemplén *O*-deacetylation than the one in position 6, when position 2 and 4 are, respectively, *O*-benzylated and deoxygenated. The structures of all compounds were confirmed by NMR spectroscopy.



	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}
28	Bn	Bn	H	Bn	Bn	OBn	Bn	Bn	OBn	Ac
29	Bn	Bn	H	Bn	Bn	OBn	Bn	Bn	OBn	H
30	H	H	H	H	H	OH	H	H	OH	H
31	Bn	Bn	OBn	Bn	Bn	H	Bn	Bn	OBn	Ac
32	Bn	Bn	OBn	Bn	Bn	H	Bn	Bn	OBn	H
33	H	H	OH	H	H	H	H	H	OH	H
34	Bn	Bn	OBn	Bn	Bn	OBn	Bn	Bn	H	Ac
35	Bn	Bn	OBn	Bn	Bn	OBn	Bn	Bn	H	H
36	Bn	Bn	OBn	Bn	Bn	OBn	Bn	Ac	H	Ac
37	Bn	Bn	OBn	Bn	Bn	OBn	Bn	Ac	H	H
38	Bn	Bn	OBn	Bn	Bn	OBn	Bn	H	H	H
39	H	H	OH	H	H	OH	H	H	H	H

3. Experimental

General methods.—Melting points were determined on a Kofler hot stage. Optical rotations were measured at 25°C with a Perkin–Elmer automatic polarimeter, Model 241 MC. All reactions were monitored by thin-layer chromatography (TLC) on precoated slides of Silica Gel GF-254 (Analtech). Detection was effected by charring with 5% sulfuric acid in ethanol or, when applicable, with UV light. Preparative chromatography was performed by elution from columns of Silica Gel-60 (E. Merck, No. 9385). ^{1}H and

^{13}C NMR spectra were measured at ambient temperature using a Varian FX 300 or Varian Gemini spectrometer, operating at 300 MHz for protons and 75 MHz for ^{13}C. Chemical shifts recorded for solutions in $CDCl_3$ and D_2O were measured, respectively, from internal Me_4Si and methanol (δ_C 49.0). Proton signal assignments were done by COSY or homonuclear decoupling experiments. The non-equivalent geminal proton resonating at a lower field is denoted H-a and the one resonating at a higher field is denoted H-b. Accumulative runs of ^1H NMR spectra (minimally 128) failed to show any extraneous peaks, thus indicating purity. Carbon signal assignments were based on heteronuclear shift-correlated 2D experiments (HETCOR). Chemical-ionization mass spectra (CIMS), using ammonia as the reactive gas, were obtained with a Finnigan 1015D spectrometer. Reactions requiring anhydrous conditions were performed under dry nitrogen using common laboratory glassware, and reagents and solvents were handled with gas-tight syringes. Solutions in organic solvents were dried with anhyd sodium sulfate, and concentrated at 2 kPa and 40°C.

For the glycosidation reaction, a solution of tin(IV) chloride (1 M) in heptane was added to silver perchlorate suspended in ether, and the mixture was shielded from light and stirred at room temperature. After 1 h, the mixture was cooled to 0°C, and an ethereal solution of the appropriate 1-*O*-acetyl aldose, together with the primary *O*-trimethylsilyl derivative selected, were added. When starting material was no longer detected (TLC), the mixture was extracted with satd aq sodium bicarbonate and water, dried with sodium sulfate, concentrated, and purified on a column of silica gel.

For trimethylsilylation, suitably protected samples were dissolved in anhyd dichloromethane and imidazole was added. The reaction mixture was cooled to 0–5°C, and chlorotrimethylsilane was added dropwise. When starting material was no longer detected (TLC) the mixture was filtered, the filtrate was extracted with saturated aq sodium bicarbonate, water, dried, concentrated, and purified on a column of silica gel.

For deacylations, samples were dissolved in toluene and anhyd methanol. Sodium methoxide in methanol (1 M) was added, and the reaction mixture was stirred at room temperature. When starting material was no longer detected (TLC), the mixture was neutralized with Amberlite 120 (H^+), filtered, concentrated, and purified on a column of silica gel.

For debenzylations, samples were dissolved in 95% ethanol and Pd–C (5%) suspended in 95% ethanol was added. The reaction mixture was stirred under hydrogen at room temperature until starting material was no longer detected (TLC). The mixture was filtered through Celite (CAUTION Fire hazard), and the filtrate was concentrated and purified on a column of silica gel.

*Methyl 6-*O*-acetyl-2,3-di-*O*-benzyl-α-*D*-glucopyranoside* (**2**).—Methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside [13] (8.9 g, 23.8 mmol) was dissolved in *sym*-collidine (100 mL) and the mixture was cooled to −40°C. Acetyl chloride (1.8 mL, 25 mmol) was added dropwise, and after 40 min no starting material could be detected (TLC, 4:1 toluene–acetone). The reaction mixture was concentrated, diluted with CH_2Cl_2, extracted with aq satd $NaHCO_3$, water, dried, and purified on a column of silica gel affording compound **2** [15] (9 g, 92%).

*Methyl 6-*O*-acetyl-2,3-di-*O*-benzyl-4-*O*-phenoxythiocarbonyl-α-*D*-glucopyranoside* (**3**).—Methyl 6-*O*-acetyl-2,3-di-*O*-benzyl-α-D-glucopyranoside (4.3 g, 10.3 mmol) was

dissolved in toluene (250 mL) and *N*-hydroxysuccinimide (0.86 g), pyridine (4.3 mL), and phenylchlorothiocarbonate (4.16 mL, 30.6 mmol) were added. The reaction mixture was stirred at 80°C for 6 h and then left overnight at room temperature, after which time no starting material could be detected (TLC, 4:1 toluene–acetone). The mixture was extracted with 1 M aq citric acid, satd aq $NaHCO_3$, water, dried, concentrated, and purified on a column of silica gel (5:1 hexane–EtOAc). Compound **3** (5.1 g) was obtained in 90% yield: $[\alpha]_D$ +79.3° (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.43–7.02 (m, 10 H, 2 Ph), 5.53 (br dd, 1 H, H-4), 4.83 (d, 1 H, J_{gem} 11.3 Hz, 1/2 CH_2Ph), 4.68 (dd, 2 H, CH_2Ph), 4.53 (d, 1 H, 1/2 CH_2Ph), 4.51 (d, 1 H, H-1), 4.23 (dd, 1 H, $J_{5,6a}$ 9.3, $J_{6a,6b}$ 12.4 Hz, H-6a), 4.06–4.00 (m, 2 H, H-3, H-6b), 3.97–3.92 (m, 1 H, H-5), 3.54 (dd, 1 H, $J_{1,2}$ 3.4, $J_{2,3}$ 9.6 Hz, H-2), 3.28 (s, 3 H, OCH_3), 1.92 (s, 3 H, COCH_3); ^{13}C NMR ($CDCl_3$): δ 194.42 (*C*SOPh), 167.92 (*C*OCH$_3$), 97.99 (C-1), 79.58, 79.27, 79.04 (C-2, C-3, C-4), 75.46, 73.46 (*C*H$_2$Ph), 67.01 (C-5), 61.98 (C-6), 55.35 (OCH$_3$), 20.79 (CO*C*H$_3$); CIMS: *m/z* 570 $[M + NH_4]^+$. Anal. Calcd for $C_{30}H_{32}O_8S$: C, 65.20; H, 5.84; S, 5.80. Found: C, 65.24; H, 5.91; S, 5.88.

Methyl 6-O-acetyl-2,3-di-O-benzyl-4-deoxy-α-D-xylo-hexopyranoside (**4**).—Methyl 6-*O*-acetyl-2,3-di-*O*-benzyl-4-*O*-phenoxythiocarbonyl-α-D-glucopyranoside (**3**) (6 g, 10.8 mmol) was dissolved in toluene (250 mL), tributyltin hydride (4.3 mL) and AIBN (0.21 g) were added. The reaction mixture was stirred at 90°C for 2 h, at the end of which time no starting material could be detected. The reaction mixture was concentrated, and the residue was purified on a column of silica gel (5:1 toluene–ethyl acetate) giving 4.1 g (95%) of **4**: $[\alpha]_D$ +35.6° (*c* 1.201, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.47–7.20 (m, 10 H, 2 Ph), 4.92 (d, 1 H, J_{gem} 12.2 Hz, 1/2 CH_2Ph), 4.80 (d, 2 H, J_{gem} 11.7 Hz, CH_2Ph), 4.76 (d, 1 H, J_{gem} 11.6 Hz, 1/2 CH_2Ph), 4.76 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 4.23–4.12 (m, 2 H, H-6a, H-5), 4.11–3.99 (m, 2 H, H-3, H-6b), 3.56 (dd, 1 H, $J_{2,3}$ 9.4 Hz, H-2), 3.45 (s, 3 H, OCH_3), 2.14 (s, 3 H, COCH_3), 1.55 (br ddd, 1 H, H-4a), 1.32 (br dd, 1 H, H-4b); ^{13}C NMR ($CDCl_3$): δ 170.54 (*C*OCH$_3$), 98.85 (C-1), 80.16 (C-2), 74.84 (C-3), 73.20, 72.46 (*C*H$_2$Ph), 65.87 (C-6), 65.40 (C-5), 55.00 (OCH$_3$), 33.34 (C-4), 20.67 (CO*C*H$_3$); CIMS: *m/z* 418 $[M + NH_4]^+$. Anal. Calcd for $C_{23}H_{28}O_6$: C, 68.98; H, 7.05. Found: C, 69.04; H, 7.09.

Methyl 2,3-di-O-benzyl-4-deoxy-α-D-xylo-hexopyranoside (**5**).—Derivative **4** was deacetylated as described under General methods, using toluene (10 mL), MeOH (30 mL), and NaOMe (0.01 mL) for 20 h. Purification on a column of silica gel (6:1 toluene–acetone) gave **5** (0.65 g, 91%): $[\alpha]_D$ +45.7° (*c* 0.542, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.28–7.05 (m, 10 H, Ph), 4.74 (d, 1 H, J_{gem} 12 Hz, 1/2 CH_2Ph), 4.65 (d, 1 H, 1/2 CH_2Ph), 4.61–4.54 (m, 3 H, CH_2Ph, H-1), 3.84 (br ddd, 1 H, $J_{3,4a}$ 5.1, $J_{2,3}$ 9.8, $J_{3,4b}$ 11.3 Hz, H-3), 3.70 (br dddd, 1 H, H-5), 3.50 (dd, 1 H, $J_{5,6a}$ 3.3, $J_{6a,6b}$ 11.6 Hz, H-6a), 3.40 (dd, 1 H, $J_{5,6b}$ 6.6 Hz, H-6b), 3.34 (dd, 1 H, $J_{1,2}$ 3.4 Hz, H-2), 3.26 (s, 3 H, OCH_3), 1.87 (br ddd, $J_{4a,5}$ 5.2 Hz, H-4a), 1.82 (br s, 1 H, O*H*), 1.36 (br ddd, 1 H, H-4b); ^{13}C NMR ($CDCl_3$): δ 98.99 (C-1), 80.41 (C-2), 75.07 (C-3), 73.30, 72.44 (*C*H$_2$Ph), 67.97 (C-5), 65.19 (C-6), 55.11 (OCH$_3$), 33.02 (C-4); CIMS: *m/z* 376 $[M + NH_4]^+$. Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.20; H, 7.31.

Methyl 2,3-di-O-benzyl-4-deoxy-6-O-trimethylsilyl-α-D-xylo-hexopyranoside (**6**).—Compound **5** (0.75 g) was silylated as described in the General methods, using CH_2Cl_2 (50 mL), imidazole (0.188 g, 2.8 mmol), and chlorotrimethylsilane (0.28 g, 0.32 mL,

2.53 mmol). The mixture was stirred for 1.5 h (TLC, 6:1 toluene–acetone). After workup and purification by silica gel column chromatography, 0.82 g of derivative **6** was obtained (91%): $[\alpha]_D$ +33.6° (*c* 1.007, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.28–7.14 (m, H, Ph), 4.74 (d, 1 H, J_{gem} 12.2 Hz, 1/2 CH_2Ph), 4.67 (d, 1 H, J_{gem} 11.6 Hz, 1/2 CH_2Ph), 4.62–4.57 (m, 3 H, CH_2Ph, H-1), 3.84 (br ddd, 1 H, $J_{3,4a}$ 5, $J_{3,4b}$ 11 Hz, H-3), 3.65 (m, 1 H, H-5), 3.47 (m, 2 H, H-6a, H-6b), 3.36 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 9.3 Hz, H-2), 3.26 (s, 3 H, OCH_3), 1.96 (br ddd, 1 H, $J_{4a,5}$ 2.2, $J_{4a,4b}$ 12.7 Hz, H-4a), 1.34 (br ddd, 1 H, H-4b), 0.01 [s, 9 H, Si(CH_3)$_3$]; ^{13}C NMR ($CDCl_3$): δ 98.96 (C-1), 80.58 (C-2), 75.44 (C-3), 73.27, 72.52 (*C*H_2Ph), 68.07 (C-5), 65.13 (C-6), 55.02 (O*C*H_3), 33.71 (C-4), −0.46 [Si(*C*H_3)$_3$]; CIMS: *m/z* 448 $[M + NH_4]^+$.

*1,6-Di-*O*-acetyl-2,3-di-*O*-benzyl-4-deoxy-α,β-*D*-xylo-hexopyranose* (**7**).—Methyl glycoside **4** (3 g, 7.5 mmol) was dissolved in Ac_2O (30 mL), and H_2SO_4 (0.5%) in Ac_2O (3.6 mL) was added. The mixture was stirred at room temperature for 5 min, when the reaction was complete (TLC, 4:1 toluene–ethyl acetate). Saturated aq $NaHCO_3$ was added, and the mixture was vigorously stirred for 30 min, then extracted with CH_2Cl_2 (3 times). The organic layer was washed with water, dried, and concentrated, and the residue was purified on a column of silica gel (7:1 toluene–ethyl acetate) giving compound **7** (2.87 g, 90%): $[\alpha]_D$ +47.5° (*c* 1.43, $CHCl_3$); ^1H NMR ($CDCl_3$): α anomer, δ 7.27–7.06 (m, 10 H, 2 Ph), 6.27 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.65–4.57 (m, 4 H, 2 CH_2Ph), 4.03–3.95 (m, 3 H, H-5, H-6a, H-6b), 3.82 (ddd, 1 H, $J_{3,4a}$ 5, $J_{3,4b}$ 14 Hz, H-3), 3.49 (dd, 1 H, $J_{2,3}$ 9.6 Hz, H-2), 2.08–1.95 (m, 1 H, H-4a), 2.04 (s, 3 H, COCH_3), 1.97 (s, 3 H, COCH_3), 1.52–1.42 (m, 1 H, H-4b); ^{13}C NMR ($CDCl_3$): α anomer, δ 170.78 (*C*OCH$_3$), 169.44 (*C*OCH$_3$), 90.73 (C-1), 79.14 (C-2), 74.48 (C-3), 73.14, 72.52 (*C*H_2Ph), 68.11 (C-5), 65.70 (C-6), 32.99 (C-4), 21.13 (CO*C*H_3), 20.82 (CO*C*H_3); β anomer, δ 94.05 (C-1), 81.29 (C-2), 78.27 (C-3), 75.08, 72.33 (*C*H_2Ph), 70.59 (C-5), 65.53 (C-6), 32.74 (C-4), 21.05 (CO*C*H_3); $\alpha:\beta = 4:1$; CIMS: *m/z* 446 $[M + NH_4]^+$. Anal. Calcd for $C_{24}H_{28}O_7$: C, 67.27; H, 6.59. Found: C, 67.35; H, 6.65.

*1,3,6-Tri-*O*-acetyl-2-*O*-benzyl-4-deoxy-α,β-*D*-xylo-hexopyranose* (**8**).—(a) Compound **4** (0.1 g, 0.25 mmol) was dissolved in Ac_2O (1 mL), and H_2SO_4 (1%) in Ac_2O (0.24 mL) was added. The reaction mixture was stirred for 24 h, when starting material could no longer be detected (TLC, 4:1 toluene–ethyl acetate). The mixture was worked-up as described for compound **7** and purified (silica gel, 6:1 toluene–acetone), giving syrupy compound **8** (0.085 g, 89.5%). (b) Monosaccharide **4** (3 g, 7.5 mmol) was acetolyzed for 8 h as described in case (a) using Ac_2O (30 mL) and H_2SO_4 (2%) in Ac_2O (3.6 mL). After purification on silica gel derivative **8** (3.0 g, 93.5%) was isolated: $[\alpha]_D$ +74.5° (*c* 1.226, $CHCl_3$); ^1H NMR ($CDCl_3$): α anomer, δ 7.30–7.11 (m, 5 H, Ph), 6.34 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.18 (br ddd, 1 H, H-3), 4.62 (d, 1 H, J_{gem} 12.3 Hz, 1/2 CH_2Ph), 4.51 (d, 1 H, 1/2 CH_2Ph), 4.13–3.96 (m, 3 H, H-5, H-6a, H-6b), 3.54 (dd, 1 H, $J_{2,3}$ 9.9 Hz, H-2), 2.10 (s, 3 H, COCH_3), 2.02 (s, 3 H, COCH_3), 2.00 (s, 3 H, COCH_3), 2.10–1.93 (m, 2 H, H-4a, H-4b); β anomer, δ 5.57 (d, $J_{1,2}$ 7.8 Hz, H-1), 4.96 (m, 1 H, H-3), 3.93–3.78 (m, 3 H, H-5, H-6a, H-6b); ^{13}C NMR ($CDCl_3$): α anomer, δ 170.65, 170.26, 169.35 (*C*OCH$_3$), 90.32 (C-1), 76.16 (C-2), 72.70 (*C*H_2Ph), 69.23 (C-3), 67.62 (C-5), 65.35 (C-6), 32.39 (C-4), 21.07 (2 C), 20.77 (CO*C*H_3); β anomer, δ 94.32 (C-1), 78.79 (C-2), 74.70 (*C*H_2Ph), 72.28 (C-3), 70.24 (C-5), 65.15

(C-6); $\alpha:\beta = 4.6:1$. CIMS: m/z 398 $[M + NH_4]^+$. Anal. Calcd for $C_{19}H_{24}O_8$: C, 59.97; H, 6.36. Found: C, 59.88; H, 6.32.

Methyl 6-O-acetyl-2,3-di-O-benzyl-4-deoxy-α-D-xylo-hexopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**11**).—Disaccharide **11** was prepared as described under General methods, using a solution of 1 M tin(IV) chloride in heptane (0.15 mL), silver perchlorate (0.03 g, 0.15 mmol), acetate **7** (1.28 g, 3.0 mmol), and methyl 2,3,4-tri-*O*-benzyl-6-*O*-trimethylsilyl-α-D-glucopyranoside (**9**) [16] (1.9 g, 3.5 mmol). After 24 h no starting material was detected in the reaction mixture (TLC, 3:1 heptane–ethyl acetate). Purification on a column of silica gel (4:1 heptane–ethyl acetate) gave **11** (2.6 g, 90%): $[\alpha]_D$ +61° (*c* 1.317, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.35–7.15 (m, 25 H, 5 Ph), 4.98 (br s, 1 H, H-1), 4.98–4.55 (m, 10 H, 5 CH_2Ph), 4.56 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.05–3.85 (m, 5 H, H-6a, H-6′a, H-3, H-3′, H-5′), 3.80–3.72 (m, H-5, H-6b, H-6′b), 3.65 (m, 1 H, H-4), 3.46–3.40 (m, 2 H, H-2, H-2′), 3.30 (s, 3 H, OCH_3), 1.96 (s, 3 H, COCH_3), 1.43 (br dd, 1 H, H-4′b); ^{13}C NMR ($CDCl_3$): δ 170.32 (*C*OCH$_3$), 97.63 (2 C, C-1, C-1′), 81.85 (C-3′), 80.25, 79.86 (C-2, C-2′), 77.69 (C-4), 75.43, 74.67, 73.01, 72.02 (2 C) (*C*H$_2$Ph), 73.84 (C-3′), 70.05 (C-5), 65.73 (2 C) (C-6, C-6′), 65.47 (C-5′), 54.79 (O*C*H$_3$), 33.08 (C-4′), 20.54 (CO*C*H$_3$); CIMS: m/z 850 $[M + NH_4]^+$. Anal. Calcd for $C_{50}H_{56}O_{11}$: C, 72.10; H, 6.78. Found: C, 71.85; H, 6.90.

Methyl 2,3-di-O-benzyl-4-deoxy-α-D-xylo-hexopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**12**).—Disaccharide **11** (1.3 g, 1.56 mmol) was deacetylated as described in the General methods, using toluene (30 mL), anhyd MeOH (30 mL), and NaOMe (1 M, 0.1 mL). The mixture was stirred for 2 h (TLC, 6:1 toluene–acetone). After workup and column chromatography on silica gel (5:1 toluene–acetone) 1.18 g of compound **12** was obtained (93.5%): $[\alpha]_D$ +72° (*c* 1.034, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.36–7.12 (m, 25 H, 5 Ph), 5.01–4.53 (m, 12 H, H-1, H-1′, 5 CH_2Ph), 4.03–3.42 (m, 11 H, H-3, H-3′, H-5, H-5′, H-6a, H-6′a, H-4, H-6b, H-6′b, H-2, H-2′), 3.31 (s, 3 H, OCH_3), 2.07 (s, 1 H, O*H*), 1.89 (m, 1 H, H-4′a), 1.44 (m, 1 H, H-4′b); ^{13}C NMR ($CDCl_3$): δ 97.71 (2 C, C-1, C-1′), 81.88 (C-3), 80.51, 79.97 (C-2, C-2′), 77.69 (C-4), 75.45, 74.73 (*C*H$_2$Ph), 74.07 (C-3′), 73.13, 72.09, 71.89 (*C*H$_2$Ph), 70.19 (C-5), 68.02 (C-5′), 65.75, 64.90 (C-6, C-6′), 54.87 (O*C*H$_3$), 32.82 (C-4). CIMS: m/z 808 $[M + NH_4]^+$. Anal. Calcd for $C_{48}H_{54}O_{10}$: C, 72.89; H, 6.88. Found: C, 72.84; H, 6.94.

Methyl 2,3-di-O-benzyl-4-deoxy-6-O-trimethylsilyl-α-D-xylo-hexopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**13**).—Disaccharide **12** (1.1 g, 1.4 mmol) was silylated as described under General methods using CH_2Cl_2 (40 mL), imidazole (0.22 g, mmol), chlorotrimethylsilane (0.22 mL, 1.7 mmol). After 3 h, no starting material could be detected (TLC, 6:1 toluene–acetone). Purification on a column of silica gel (7:1 toluene–acetone) gave **13** (1.1 g, 88%): $[\alpha]_D$ +57.8° (*c* 1.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.36–7.12 (m, 25 H, 5 Ph), 5.02 (d, 1 H, $J_{1',2'}$ 3.4 Hz, H-1′), 4.99–4.57 (m, 10 H, 5 CH_2Ph), 4.54 (d, 1 H, $J_{1,2}$ 4.1 Hz, H-1), 4.02–3.62 (m, 7 H, H-3, H-3′, H-5, H-5′, H-4, H-6a, H-6′a), 3.52–3.50 (m, 2 H, H-6b, H-6′b), 3.47–3.40 (m, 2 H, H-2, H-2′), 3.30 (s, 3 H, OCH_3), 2.01 (m, 1 H, H-4′a), 1.45 (m, 1 H, H-4′b), 0.08 [s, 9 H, Si(CH_3)$_3$]; ^{13}C NMR ($CDCl_3$): δ 97.86, 97.79 (C-1, C-1′), 81.97 (C-3), 80.66, 80.01 (C-2, C-2′), 77.81 (C-4), 75.52, 74.82 (*C*H$_2$Ph), 74.41 (C-3′), 73.20, 72.08, 72.00 (*C*H$_2$Ph), 70.27 (C-5), 68.08 (C-5′), 65.70, 64.97 (C-6, C-6′), 54.88 (O*C*H$_3$), 33.45 (C-4′), −0.54 [Si(*C*H$_3$)$_3$]. CIMS: m/z 880 $[M + NH_4]^+$.

*Methyl 3,6-di-O-acetyl-2-O-benzyl-4-deoxy-α-*D-xylo-*hexopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-*D-*glucopyranoside* (**14**).—Disaccharide **14** was prepared as described under General methods, using a heptane solution of tin(IV) chloride (1 M, 0.015 mL), silver perchlorate (0.003 g, 0.015 mmol), acetate **8** (0.128 g, 0.3 mmol), and derivative **9** [16] (0.193 g, 0.36 mmol). After 24 h no starting material could be detected in the reaction mixture (TLC, 6:1 toluene–acetone). Purification on a column of silica gel (10:1 toluene–acetone) gave **14** (0.245 g, 86.6%): $[\alpha]_D$ +87.7° (*c* 0.933, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.27–7.09 (m, 20 H, 4 Ph), 5.19 (br ddd, 1 H, $J_{3',4'a}$ 5.3, $J_{2',3'}$ 10.8 Hz, H-3′), 4.99 (d, 1 H, $J_{1',2'}$ 3.4 Hz, H-1′), 4.93 (d, 1 H, J_{gem} 11 Hz, 1/2 CH_2Ph), 4.89 (d, 1 H, J_{gem} 11.7 Hz, 1/2 CH_2Ph), 4.78 (d, 1 H, J_{gem} 10.9 Hz, 1/2 CH_2Ph), 4.68 (d, 1 H, J_{gem} 12.1 Hz, 1/2 CH_2Ph), 4.62 (d, 1 H, J_{gem} 11.2 Hz, 1/2 CH_2Ph), 4.54 (d, H, J_{gem} 12.5 Hz, CH_2Ph), 4.52 (br d, 1 H, H-1), 3.97–3.92 (m, 4 H, H-5′, H-3, H-6a, H-6′a), 3.77–3.55 (m, 4 H, H-5, H-6b, H-6′b, H-4), 3.42 (dd, 1 H, H-2′), 3.39 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 9.6, H-2), 3.33 (s, 3 H, OCH_3), 2.03 (m, 1 H, H-4′a), 1.98 (s, 3 H, COCH_3), 1.97 (s, 3 H, COCH_3), 1.37 (m, 1 H, H-4′b); ^{13}C NMR ($CDCl_3$): δ 170.53, 170.14 (*C*OCH$_3$), 97.86 (C-1), 97.59 (C-1′), 82.03 (C-3), 79.89 (C-2), 77.74 (C-4), 77.36 (C-2′), 75.56, 74.93, 73.25, 71.92 (*C*H$_2$Ph), 70.27 (C-5), 69.59 (C-3′), 65.94, 65.61 (C-6, C-6′), 65.06 (C-5′), 55.06 (O*C*H$_3$), 32.66 (C-4′), 21.12, 20.72 (CO*C*H$_3$). CIMS: *m/z* 802 $[M + NH_4]^+$. Anal. Calcd for $C_{45}H_{52}O_{12}$: C, 68.86; H, 6.68. Found: C, 68.77; H, 6.66.

*Methyl 3-O-acetyl-2-O-benzyl-4-deoxy-α-*D-xylo-*hexopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-*D-*glucopyranoside* (**15**).—Disaccharide **14** (0.06 g, 0.076 mmol) was deacetylated as decribed under General methods using toluene (3 mL), anhyd MeOH (3 mL), and NaOMe (1 M, 0.01 mL). The mixture was stirred for 5 min at room temperature (TLC, 6:1 toluene–acetone). After workup and column chromatography 0.05 g of compound **15** was obtained (87.7%): $[\alpha]_D$ +75.4° (*c* 0.658, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.30–7.17 (m, 20 H, 4 Ph), 5.21 (m, 1 H, H-3′), 4.99 (d, 1 H, $J_{1',2'}$ 3.4 Hz, H-1′), 4.96–4.53 (m, 9 H, H-1, 4 CH_2Ph), 3.96 (m, 1 H, H-3), 3.87–3.73 (m, 3 H, H-5, H-6a, H-6′a), 3.67–3.51 (m, 4 H, H-4, H-6b, H-6′b, H-5), 3.44–3.37 (m, 2 H, H-2, H-2′), 3.34 (s, 3 H, OCH_3), 2.02–1.98 (m, 4 H, H-4′a, COCH_3), 1.43 (br ddd, 1 H, H-4′b); ^{13}C NMR ($CDCl_3$): δ 170.47 (*C*OCH$_3$), 98.04 (C-1), 97.76 (C-1′), 82.12 (C-3), 80.03 (C-2), 77.84 (C-4), 77.67 (C-2′), 75.63, 75.00, 73.38, 72.01 (*C*H$_2$Ph), 70.37 (C-5), 69.89 (C-3′), 67.56 (C-5′), 66.02, 64.90 (C-6, C-6′), 55.12 (O*C*H$_3$), 32.13 (C-4′), 21.12 (CO*C*H$_3$). CIMS: *m/z* 760 $[M + NH_4]^+$.

*Methyl 2-O-benzyl-4-deoxy-α-*D-xylo-*hexopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-*D-*glucopyranoside* (**16**).—Disaccharide **14** (0.3 g, 0.382 mmol) was deacetylated as described under General methods, using toluene (2 mL), MeOH (2 mL), and NaOMe (1 M, 0.01 mL) for 20 min. Purification on a column of silica gel (4:1 toluene–acetone) gave **16** (0.25 g, 92.6%): $[\alpha]_D$ +94.0° (*c* 0.75, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.35–7.27 (m, 20 H, 4 Ph), 5.05–4.50 (m, 8 H, 4 CH_2Ph), 5.05 (d, 1 H, $J_{1'2'}$ 3.3 Hz, H-1′), 4.57 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.11–3.97 (m, 2 H, H-3′, H-3), 3.89–3.76 (m, 3 H, H-5′, H-5, H-6a), 3.68–3.49 (m, 4 H, H-4, H-6′a, H-6b, H-6′b), 3.45 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2), 3.38 (s, 3 H, OCH_3), 3.27 (dd, 1 H, $J_{2',3'}$ 9.1 Hz, H-2′), 1.89 (ddd, 1 H, $J_{3',4'a}$ 2, $J_{4'a,5'}$ 5, $J_{4'a,4'b}$ 12.7 Hz, H-4′a), 1.73 (br s, 1 H, O*H*), 1.60 (s, 1 H, O*H*), 1.48 (br ddd, 1 H, H-4′b); ^{13}C NMR ($CDCl_3$): δ 98.10 (C-1), 97.07 (C-1′), 82.09 (C-3),

81.52 (C-2'), 80.12 (C-2), 77.83 (C-4), 75.64, 75.01, 73.41, 71.56 (CH_2Ph), 70.31 (C-5), 68.27 (C-5'), 66.43 (C-3'), 66.17 (C-6), 65.22 (C-6'), 55.15 (OCH_3), 33.73 (C-4'). CIMS: m/z 718 $[M + NH_4]^+$. Anal. Calcd for $C_{41}H_{48}O_{10}$: C, 70.27; H, 6.90. Found: C, 70.05; H, 6.84.

*Methyl 4-deoxy-α-*D-xylo-*hexopyranosyl-(1 → 6)-α-*D-*glucopyranoside* (**17**).—Disaccharide **16** (0.1 g, 0.13 mmol) was debenzylated as described under General methods for 20 h at room temperature (TLC, 2:1:1 2-propanol–water–ethyl acetate), filtered, and concentrated. The product was purified on a column of silica gel offering 0.04 g of **17**. Neither the ^1H nor ^{13}C NMR spectrum revealed signals that would indicate the presence of an aromatic residue. Compound **15** had $[\alpha]_D$ +170.7° (*c* 0.45, H_2O); ^1H NMR (D_2O): δ 4.95 (d, 1 H, $J_{1',2'}$ 3.7 Hz, H-1'), 4.79 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.01–3.90 (m, 3 H, H-5', H-3', H-6'a), 3.81–3.76 (m, 1 H, H-5), 3.72–3.43 (m, 7 H, H-6b, H-6'a, H-6'b, H-2, H-2', H-3, H-4), 3.40 (s, 3 H, OCH_3), 1.96 (m, 1 H, H-4a), 1.42 (br ddd, 1 H, $J_{4a,4b}$ 12 Hz, H-4b); ^{13}C NMR (D_2O): δ 99.53 (C-1), 98.69 (C-1'), 73.49 (2 C, C-3, C-2'), 71.34 (C-2), 70.31 (C-5), 69.61 (C-4), 69.03 (C-5'), 67.39 (C-3'), 65.61 (C-6), 63.77 (C-6'), 55.34 (OCH_3), 34.29 (C-4'). CIMS: m/z 358 $[M + NH_4]^+$.

*Methyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-*D*-glucopyranosyl-(1 → 6)-2,3-di-*O*-benzyl-4-deoxy-α-*D*-*xylo*-hexopyranoside* (**18**).—This disaccharide was prepared as described under General methods, using a heptane solution of tin(IV) chloride (1 M, 0.096 mL), silver perchlorate (0.019 g, 0.96 mmol), acetate **10** [17] (0.6 g, 1.0 mmol), and methyl 2,3-di-*O*-benzyl-4-deoxy-6-*O*-trimethylsilyl-α-D-*xylo*-hexopyranoside (**6**) (0.35 g, 0.81 mmol). After 24 h no starting material could be detected in the reaction mixture (TLC, 3:1 heptane–ethyl acetate). Purification on a column of silica gel (4:1 heptane–ethyl acetate) gave **18** (0.6 g, 88.2%): $[\alpha]_D$ +57.4° (*c* 0.317, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.28–7.09 (m, 20 H, 5 Ph), 4.93–4.47 (m, 10 H, 5 CH_2Ph), 4.70 (br d, 1 H, H-1'), 4.58 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 4.16 (br d, 2 H, H-6'a, H-6'b), 3.95–3.84 (m, 4 H, H-3, H-3', H-5, H-5'), 3.54 (dd, 1 H, $J_{5,6a}$ 6, $J_{6a,6b}$ 10.6 Hz, H-6a), 3.45 (dd, 1 H, $J_{2,3}$ 9.6 Hz, H-2), 3.39–3.32 (m, 3 H, H-4', H-6b, H-2'), 3.29 (s, 3 H, OCH_3), 2.02 (m, 1 H, H-4a), 1.92 (s, 3 H, $COCH_3$), 1.40 (br ddd, 1 H, H-4b); ^{13}C NMR ($CDCl_3$): δ 170.65 ($COCH_3$), 98.81, 96.92 (C-1, C-1'), 81.79 (C-3'), 80.44, 79.93 (C-2, C-2'), 77.18 (C-4'), 75.65, 74.87, 73.23, 72.96, 72.58 (CH_2Ph), 75.22 (C-3), 70.03 (C-6), 68.67 (C-5'), 66.46 (C-5), 63.00 (C-6'), 55.19 (OCH_3), 33.97 (C-4), 20.84 ($COCH_3$). CIMS: m/z 850 $[M + NH_4]^+$.

*Methyl 2,3,4-tri-*O*-benzyl-α-*D*-glucopyranosyl-(1 → 6)-2,3-di-*O*-benzyl-4-deoxy-α-*D*-xylo-hexopyranoside* (**19**).—Disaccharide **18** (0.3 g, 0.36 mmol) was deacetylated as described under General methods, using toluene (10 mL), anhyd MeOH (10 mL), and NaOMe (1 M, 0.1 mL). When no starting material was detected (4 h; TLC, 6:1 toluene–acetone), the mixture was purified on a column of silica gel (4:1 toluene–acetone) giving derivative **19** (0.26 g, 91.2%): $[\alpha]_D$ +59.4° (*c* 1.113, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.28–7.12 (m, 20 H, 4 Ph), 4.91–4.56 (m, 12 H, H-1, H-1', 5 CH_2Ph), 3.89–3.86 (m, 3 H, H-3, H-3', H-5), 3.67–3.36 (m, 7 H, H-6'a, H-6'b, H-6a, H-5', H-2, H-2', H-4'), 3.30 (s, 3 H, OCH_3), 2.05 (m, 1 H, H-4a), 1.43 (m, 1 H, H-4b); ^{13}C NMR ($CDCl_3$): δ 98.81, 97.11 (C-1, C-1'), 81.65 (C-3'), 80.44, 80.02 (C-2, C-2'), 77.33 (C-4'), 75.50, 74.88, 73.19, 72.91, 72.47 (CH_2Ph), 75.19 (C-3), 70.85 (C-5'), 70.05 (C-6), 66.50 (C-5), 61.76 (C-6'), 55.15 (OCH_3), 33.95 (C-4). CIMS: m/z 808

$[M + NH_4]^+$. Anal. Calcd for $C_{48}H_{54}O_{10}$: C, 72.89; H, 6.88. Found: C, 72.86; H, 6.90.

Methyl α-D-glucopyranosyl-(1 → 6)-4-deoxy-α-D-xylo-hexopyranoside (**21**).—Disaccharide **19** (0.05 g, 0.07 mmol), was debenzylated for 16 h as described under General methods (TLC, 2:1:1 2-propanol–H_2O–EtOAc). Purification (silica gel, 2:1:1.75 2-propanol–H_2O–EtOAc) gave disaccharide **21** (0.022 g, 91.7%). Neither the ^1H nor ^{13}C NMR spectrum revealed signals that would indicate the presence of an aromatic residue. Compound **21** had $[\alpha]_D$ +61.2° (*c* 0.983 H_2O) and NMR data identical with those published [18].

Methyl 6-O-acetyl-2,3-di-O-benzyl-4-deoxy-α-D-xylo-hexopyranosyl-(1 → 6)-2,3-di-O-benzyl-4-deoxy-α-D-xylo-hexopyranoside (**22**).—Disaccharide **22** was prepared as described under General methods, using a heptane solution of tin(IV) chloride (1 M, 0.04 mL), silver perchlorate (0.008 g, 0.04 mmol), acetate **7** (0.34 g, 0.081 mmol), and methyl 2,3-di-*O*-benzyl-4-deoxy-6-*O*-trimethylsilyl-α-D-*xylo*-hexopyranoside (**6**) (0.36 g, 0.84 mmol). After 24 h no starting material could be detected in the reaction mixture (TLC, 3:1 heptane–ethyl acetate). Purification on a column of silica gel (4:1 heptane–ethyl acetate) gave **22** (0.57 g, 92%): $[\alpha]_D$ +57.2° (*c* 1.075, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.26–7.10 (m, 20 H, 4 Ph), 4.75–4.55 (m, 10 H, H-1, H-1′, 4 CH_2Ph), 4.03–3.93 (m, 3 H, H-5′, H-6′a, H-6′b), 3.84–3.80 (m, 3 H, H-5, H-3, H-3′), 3.53 (dd, 1 H, $J_{5,6a}$ 6.4, $J_{6a,6b}$ 10.5 Hz, H-6a), 3.39–3.30 (m, 3 H, H-6b, H-2, H-2′), 3.22 (s, 3 H, OCH_3), 2.02–1.84 (m, 5 H, H-4a, H-4′a, COCH_3), 1.42–1.31 (m, 2 H, H-4b, H-4′b); ^{13}C NMR ($CDCl_3$): δ 170.75 (*C*OCH$_3$), 98.75, 97.81 (C-1, C-1′), 80.43, 80.29 (C-2, C-2′), 75.32 (C-3), 74.62 (C-3′), 73.24, 73.04, 72.61, 72.39 (*C*H$_2$Ph), 69.83 (C-6), 66.47 (C-5), 66.00 (C-6′), 65.76 (C-5′), 55.02 (O*C*H$_3$), 33.99, 33.32 (C-4, C-4′), 20.86 (CO*C*H$_3$). CIMS: *m/z* 744 $[M + NH_4]^+$. Anal. Calcd for $C_{43}H_{50}O_{10}$: C, 71.06; H, 6.93. Found: C, 70.94; H, 7.01.

Methyl 2,3-di-O-benzyl-4-deoxy-α-D-xylo-hexopyranosyl-(1 → 6)-2,3-di-O-benzyl-4-deoxy-α-D-xylo-hexopyranoside (**23**).—Disaccharide **22** (0.3 g, 0.41 mmol) was deacetylated for 4 h using toluene (20 mL), MeOH (20 mL), and NaOMe (1 M, 0.1 mL) (TLC, 6:1 toluene–acetone). After purification (silica gel, 2.5:1 toluene–acetone) compound **23** was obtained (0.25 g, 89.9%): $[\alpha]_D$ +77.7° (*c* 0.525, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.28–7.15 (m, 20 H, 4 Ph), 4.75–4.56 (m, 10 H, H-1, H-1′, 4 CH_2Ph), 3.84–3.80 (m, 4 H, H-3, H-3′, H-5, H-5′), 3.57–3.30 (m, 6 H, H-6a, H-6′a, H-2, H-2′, H-6b, H-6′b), 3.23 (s, 3 H, OCH_3), 2.03–1.83 (m, 2 H, H-4a, H-4′a), 1.38 (m, 2 H, H-4b, H-4′b); ^{13}C NMR ($CDCl_3$): δ 98.76, 97.91 (C-1, C-1′), 80.41 (2 C, C-2, C-2′), 75.22 (C-3), 74.72 (C-3′), 73.20, 72.90, 72.46, 72.13 (*C*H$_2$Ph), 69.87 (C-6), 68.16 (C-5′), 66.50 (C-5), 65.18 (C-6′), 55.02 (O*C*H$_3$), 33.90, 32.92 (C-4, C-4′). CIMS: *m/z* 702 $[M + NH_4]^+$. Anal. Calcd for $C_{41}H_{48}O_9$: C, 71.91; H, 7.06. Found: C, 71.78; H, 7.13.

Methyl 4-deoxy-α-D-xylo-hexopyranosyl-(1 → 6)-4-deoxy-α-D-xylo-hexopyranoside (**24**).—Disaccharide **23** (0.2 g, 0.29 mmol) was debenzylated for 16 h as described under General methods. When no starting material remained (12 h, TLC, 2:1:1.5 2-propanol–H_2O–EtOAc) the mixture was purified (silica gel, 2:1:1.75 2-propanol–H_2O–EtOAc) giving **24** (0.09 g, 94.7%). Neither the ^1H nor ^{13}C NMR spectrum revealed signals that would indicate the presence of an aromatic residue: $[\alpha]_D$ +166.7° (*c* 1.05, H_2O); ^1H NMR (D_2O): δ 4.88 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1′), 4.76 (d, 1 H, $J_{1,2}$

3.5 Hz, H-1), 4.02 (m, 1 H, H-5), 3.92–3.79 (m, 3 H, H-3′, H-3, H-5′), 3.68 (dd, 1 H, $J_{5,6a}$ 5, $J_{6a,6b}$ 11 Hz, H-6a), 3.61–3.33 (m, 5 H, H-6′a, H-6′b, H-6b, H-2, H-2′), 3.33 (s, 3 H, OCH_3), 1.96–1.88 (m, 2 H, H-4a, H-4′a), 1.50 (br ddd, 1 H, $J_{4a,4b}$ 11.9 Hz, H-4b), 1.36 (br ddd, 1 H, $J_{4'a,4'b}$ 11.9 Hz, H-4′b); ^{13}C NMR (D_2O): δ 100.21 (C-1), 98.73 (C-1′), 73.46, 73.10 (C-2, C-2′), 69.15 (C-5′), 68.97 (C-6), 67.47 (C-3′), 67.39 (C-3), 67.32 (C-5), 63.81 (C-6′), 55.29 (OCH_3), 34.45, 34.31 (C-4, C-4′). CIMS: *m/z* 342 $[M + NH_4]^+$.

Methyl 6-O-acetyl-2,3,4-tri-O-benzyl-α-D-glucopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-D-glucopyranosyl-(1 → 6)-2,3,-di-O-benzyl-4-deoxy-α-D-xylo-hexopyranoside (**28**).—Disaccharide **19** (0.4 g, 0.5 mmol) was silylated using CH_2Cl_2 (30 mL), imidazole (0.046 g, 0.67 mmol), and chlorotrimethylsilane (0.065 g, 0.6 mmol) for 3 h. After purification (silica gel, 8:1 toluene–acetone) 0.41 g of **20** (93.8%) was obtained; ^{1}H NMR ($CDCl_3$): δ 7.32–7.13 (m, 20 H, 5 Ph), 4.95–4.58 (m, 12 H, H-1, H-1′, 5 CH_2Ph), 3.96–3.88 (m, 3 H, H-3, H-3′, H-5), 3.75–3.38 (m, 8 H, H-6′a, H-5′, H-6′b, H-6a, H-4′, H-2′, H-2, H-6b), 3.33 (s, 3 H, OCH_3), 2.10 (m, 1 H, H-4a), 1.45 (m, 1 H, H-4b), 0.07 [s, 9 H, $Si(CH_3)_3$]; ^{13}C NMR ($CDCl_3$): δ 98.83, 97.02 (C-1, C-1′), 81.89 (C-3′), 80.51, 80.12 (C-2, C-2′), 77.29 (C-4′), 75.56, 74.73, 73.24, 72.84, 72.49 (CH_2Ph), 75.28 (C-3), 71.41 (C-5′), 69.84 (C-6), 66.41 (C-5), 61.48 (C-6′), 55.11 (OCH_3), 34.14 (C-4), −0.36 [$Si(CH_3)_3$]. Compound **28** was prepared as described under General methods, using a heptane solution of tin(IV) chloride (1 M, 0.02 mL), silver perchlorate (0.004 g, 0.02 mmol), derivative **20** (0.3 g, 0.35 mmol), and acetate **10** [17] (0.24 g, 0.4 mmol). The mixture was stirred for 20 h (TLC, 2:1 hexane–EtOAc). After purification on a column of silica gel (3:1 hexane–EtOAc) 0.39 g of **28** was obtained (88.6%): $[\alpha]_D$ +64.2° (*c* 0.45, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.30–7.17 (m, 40 H, 8 Ph), 4.97–4.51 (m, 19 H, H-1, H-1′, H-1″, 8 CH_2Ph), 4.08 (m, 2 H, H-6″a, H-6″b), 3.96–3.77 (m, 6 H, H-3, H-3′, H-3″, H-5, H-5′, H-5″), 3.71–3.22 (m, 9 H, H-6′a, H-4′, H-6a, H-4″, H-2, H-2′, H-2″, H-6′b, H-6b), 3.32 (s, 3 H, OCH_3), 2.09 (m, 1 H, H-4a), 1.95 (s, 3 H, $COCH_3$), 1.48 (m, 1 H, H-4b); ^{13}C NMR ($CDCl_3$): δ 170.67 ($COCH_3$), 98.84 (C-1), 98.99, 96.99 (C-1′, C-1″), 81.88, 81.66 (C-3′, C-3″), 80.57, 80.23, 80.02 (C-2, C-2′, C-2″), 77.63, 77.16 (C-4′, C-4″), 75.59, 74.95, 74.89, 73.26, 72.88, 72.50, 72.27 (CH_2Ph), 75.29 (C-3), 70.58, 68.72 (C-5′, C-5″), 69.80 (C-6′), 66.50 (C-5), 65.85 (C-6), 63.01 (C-6″), 55.17 (OCH_3), 34.01 (C-4), 20.86 ($COCH_3$). CIMS: *m/z* 1283 $[M + NH_4]^+$. Anal. Calcd for $C_{77}H_{84}O_{16}$: C, 73.08; H, 6.69. Found: C, 72.80; H, 6.82.

Methyl 2,3,4-tri-O-benzyl-α-D-glucopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-D-glucopyranosyl-(1 → 6)-2,3-di-O-benzyl-4-deoxy-α-D-xylo-hexopyranoside (**29**).—Compound **28** (0.3 g, 0.24 mmol) was deacetylated as described under General methods using toluene (5 mL), MeOH (5 mL), and NaOMe (1 M, 0.1 mL). After 10 h no starting material was detected (TLC, 6:1 toluene–acetone). The reaction mixture was neutralized with Amberlite 120 (H^+), filtered, concentrated, and purified on a column of silica gel (6:1 toluene–acetone) giving 0.28 g (96.5%) of **29**: $[\alpha]_D$ +80.2° (*c* 0.783, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.28–7.13 (m, 40 H, 8 Ph), 4.94–4.50 (m, 19 H, H-1, H-1′, H-1″, 8 CH_2Ph), 3.98–3.60 (m, 11 H, H-3, H-3′, H-3″, H-5, H-6a, H-5′, H-5, H-6′a, H-4″, H-6b, H-6″a), 3.50–3.35 (m, 6 H, H-4′, H-2, H-2′, H-2″, H-6′b, H-6″b), 3.31 (s, 3 H, OCH_3), 2.07 (m, 1 H, H-4a), 1.62 (br s, 1 H, *OH*), 1.46 (m, 1 H, H-4b); ^{13}C NMR

($CDCl_3$): δ 97.80, 97.06, 96.95 (C-1, C-1′, C-1″), 81.81, 81.50 (C-3′, C-3″), 80.51, 80.21, 80.13 (C-2, C-2′, C-2″), 77.59, 77.52 (C-4′, C-4″), 77.35 (2 C, CH_2Ph), 75.49 (C-3), 75.24, 74.89, 73.21, 72.86, 72.46, 72.28 (CH_2Ph), 70.84, 70.58 (C-5, C-5′), 69.82 (C-6′), 66.47 (C-5), 65.84 (C-6), 61.86 (C-6″), 55.12 (OCH_3), 33.98 (C-4). CIMS: m/z 1241 $[M + NH_4]^+$.

Methyl α-D-glucopyranosyl-(1 → 6)-α-D-glucopyranosyl-(1 → 6)-4-deoxy-α-D-xylo-hexopyranoside (**30**).—Trisaccharide **29** (0.14 g, 0.11 mmol) was debenzylated for 20 h as described under General methods. After purification (silica gel, 2:1:1.75 2-propanol–EtOAc–H_2O) compound **30** (0.057 g, 94.7%) was isolated: $[\alpha]_D$ +169.9° (*c* 1.027, H_2O) [3].

Methyl 6-O-acetyl-2,3,4-tri-O-benzyl-α-D-glucopyranosyl-(1 → 6)-2,3-di-O-benzyl-4-deoxy-α-D-xylo-hexopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**31**).—Trisaccharide **31** was prepared as described under General methods using tin(IV) chloride in heptane (1 M, 0.03 mL), silver perchlorate in ether (0.006 g, 0.03 mmol), and ethereal solutions of disaccharide **13** (0.56 g, 0.65 mmol), and 1,6-di-*O*-acetyl-2,3,4-tri-*O*-benzyl-α,β-D-glucopyranose (**10**) [17] (0.45 g, 0.75 mmol). After 18 h no starting material could be detected (TLC, 2:1 hexane–ethyl acetate), and the mixture was extracted with aq satd $NaHCO_3$, water, then dried, filtered, concentrated, and purified on column of silica gel (4:1 hexane–EtOAc) giving **31** (0.72 g, 88%): $[\alpha]_D$ +72.3° (*c* 1.29, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.31–7.13 (m, 40 H, 8 Ph), 5.00–4.51 (m, 19 H, H-1, H-1′, H-1″, 8 CH_2Ph), 4.22–3.35 (m, 17 H, H-6″a, H-6″b, H-3, H-3″, H-3′, H-5″, H-5′, H-6a, H-5, H-6b, H-6′a, H-4″, H-4, H-2, H-2′, H-2″, H-6′b), 3.26 (s, 3 H, OCH_3), 2.04 (m, 1 H, H-4′a), 1.97 (s, 3 H, $COCH_3$), 1.51 (m, 1 H, H-4′b); ^{13}C NMR ($CDCl_3$): δ 170.60 ($COCH_3$), 97.86 (2 C), 96.86 (C-1, C-1′, C-1″), 82.00, 81.79 (C-3, C-3″), 80.65, 80.09, 79.95 (C-2, C-2′, C-2″), 77.82, 77.02 (C-4, C-4″), 75.57 (2 C), 74.93, 74.88, 73.26, 72.69, 72.14 (2 C) (CH_2Ph), 74.30 (C-3′), 70.49 (C-5), 69.84 (C-6′), 68.59 (C-5″), 66.66 (C-5′), 65.72 (C-6), 62.91 (C-6″), 54.94 (OCH_3), 33.74 (C-4′), 20.75 ($COCH_3$). CIMS: m/z 1282 $[M + NH_4]^+$. Anal. Calcd for $C_{77}H_{84}O_6$: C, 73.08; H, 6.69. Found: C, 72.82; H, 6.75.

Methyl 2,3,4-tri-O-benzyl-α-D-glucopyranosyl-(1 → 6)-2,3-di-O-benzyl-4-deoxy-α-D-xylo-hexopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**32**).—Trisaccharide **31** (0.3 g, 0.24 mmol) was deacetylated for 3 h using toluene (20 mL), anhyd MeOH (20 mL), and NaOMe (0.01 mL) (TLC, 6:1 toluene–acetone). After purification (silica gel, 2:1 hexane–EtOAc) compound **32** (0.26 g, 89.7%) was obtained: $[\alpha]_D$ +64.6° (*c* 0.775, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.33–7.16 (m, 40 H, 8 Ph), 5.00–4.53 (m, 19 H, 8 CH_2Ph, H-1, H-1′, H-1″), 4.01–3.92 (m, 3 H, H-3, H-3′, H-3″), 3.89–3.80 (m, 1 H, H-5′), 3.76–3.61 (m, 8 H, H-6a, H-6′a, H-6″a, H-5, H-5″, H-6b, H-6′b, H-6″b), 3.59–3.53 (m, 2 H, H-4, H-4″), 3.49–3.39 (m, 3 H, H-2, H-2′, H-2″), 3.28 (s, 3 H, OCH_3), 2.10 (br ddd, 1 H, H-4′a), 1.67 (br ddd, 1 H, H-4′b); ^{13}C NMR ($CDCl_3$): δ 97.98, 97.90, 97.23 (C-1, C-1′, C-1″), 82.05, 81.76 (C-3, C-3″), 80.70, 80.12 (2 C) (C-2, C-2′, C-2″), 77.88, 77.44 (C-4, C-4″), 75.60 (2 C), 74.98 (2 C) (CH_2Ph), 74.37 (C-3′), 73.32, 72.79, 72.17 (2 C) (CH_2Ph), 70.88, 70.49 (C-5, C-5″), 70.15, 65.90 (C-6, C-6′), 66.75 (C-5′), 61.86 (C-6″), 54.99 (OCH_3), 33.91 (C-4′). CIMS: m/z 1282 $[M + NH_4]^+$. Anal. Calcd for $C_{75}H_{82}O_{15}$: C, 73.63; H, 6.76. Found: C, 73.85; H, 6.89.

Methyl α-D-*glucopyranosyl-(1 → 6)-4-deoxy-*α-D-xylo-*hexopyranosyl-(1 → 6)-*α-D-*glucopyranoside* (**33**).—Trisaccharide **32** (0.15 g, 0.12 mmol) was debenzylated for 20 h at room temperature (TLC, 2:1:1 2-propanol–H_2O–EtOAc). After filtration and concentration of the filtrate, the product was purified (silica gel, 2:1:1.75 2-propanol–H_2O–EtOAc) offering 0.058 g of **33** (94%). Neither the ^1H nor ^{13}C NMR spectrum revealed signals that would indicate the presence of an aromatic residue. Compound **33** had $[\alpha]_D$ +83.2° (*c* 1.143, H_2O); ^1H NMR (D_2O): δ 4.99 (d, 1 H, $J_{1',2'}$ 3.7 Hz, H-1'), 4.95 (d, 1 H, $J_{1'',2''}$ 3.7 Hz, H-1''), 4.83 (d, 1 H, *J* 3.7 Hz, H-1), 4.20 (m, 1 H, H-5'), 4.01 (dd, 1 H, $J_{5,6a}$ 4.6, $J_{6a,6b}$ 11 Hz, H-6a), 3.88–3.39 (m, 15 H, H-3', H-3'', H-3, H-6''a, H-6'a, H-6b, H-6''b, H-4, H-2, H-6'b, H-2', H-2'', H-4'', H-5, H-5''), 3.44 (s, 3 H, OCH_3), 2.05 (m, 1 H, H-4'a), 1.59 (m, 1 H, H-4'b); ^{13}C NMR (D_2O): δ 99.56 (C-1), 98.63 (C-1'), 97.91 (C-1''), 73.58, 73.41, 73.27 (C-3, C-2', C-3''), 72.14 (C-5''), 71.66 (C-2''), 71.37 (C-2), 70.25 (C-5), 69.75, 69.66 (C-4, C-4'), 69.00 (C-6'), 67.48 (C-3'), 67.34 (C-5'), 65.63 (C-6), 60.71 (C-6''), 55.36 (OCH_3), 34.49 (C-4'). CIMS: *m/z* 520 $[M + NH_4]^+$.

Methyl 6-O-*acetyl-2,3-di-*O-*benzyl-4-deoxy-*α-D-xylo-*hexopyranosyl-(1 → 6)-2,3,4-tri-*O-*benzyl-*α-D-*glucopyranosyl-(1 → 6)-2,3,4-tri-*O-*benzyl-*α-D-*glucopyranoside* (**34**). —Methyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl-(1 → 6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**25**) [12] was deacetylated as described under General methods, giving compound **26** [19]. Derivative **26** (0.5 g, 0.56 mmol) was silylated using imidazole (0.04 g, 0.75 mmol) and chlorotrimethylsilane (0.08 mL) affording derivative **27** (0.46 g) in 85% yield: $[\alpha]_D$ +48.9° (*c* 1.345, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.31–7.11 (m, 30 H, 6 Ph), 4.97–4.52 (m, 14 H, H-1, H-1', 6 CH_2Ph), 4.01–3.95 (m, 2 H, H-3, H-3'), 3.79–3.57 (m, 8 H, H-6a, H-5, H-5', H-6b, H-6'a, H-4, H-4', H-6'b), 3.49 (dd, 1 H, $J_{1',2'}$ 3.6, $J_{2',3'}$ 9.4 Hz, H-2'), 3.43 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 9.6 Hz, H-2), 3.33 (s, 3 H, OCH_3), 0.03 [s, 9 H, $Si(CH_3)_3$]; ^{13}C NMR ($CDCl_3$): δ 97.89 (C-1), 97.06 (C-1'), 82.06 (C-3), 81.62 (C-3'), 80.09 (2 C, C-2, C-2'), 77.68, 77.18 (C-4, C-4'), 75.61, 75.41, 74.89, 74.62, 73.28, 72.19, (CH_2Ph), 71.34, 70.34 (C-5, C-5'), 65.75 (C-6), 61.41 (C-6'), 55.03 (OCH_3), −0.40 [3 C, $Si(CH_3)_3$].

Compound **34** was prepared as described under General methods, using a heptane solution of tin(IV) chloride (1 M, 0.03 mL), silver perchlorate (0.006 g, 0.03 mmol), and ethereal solutions of acetate **7** and with derivative **27** (0.53 g, 0.55 mmol). The mixture was stirred overnight (TLC, 2:1, hexane–EtOAc). After workup and column chromatography on silica gel (4:1 hexane–EtOAc) 0.61 g of trisaccharide **34** (88.4%) was obtained: $[\alpha]_D$ +72.4° (*c* 0.915, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.30–7.16 (m, 40 H, 8 Ph), 5.00 (m, 1 H, $J_{1'',2''}$ 3.4 Hz, H-1''), 4.95–4.50 (m, 18 H, H-1', H-1'', 8 CH_2Ph), 3.98–3.60 (m, 14 H, H-3, H-3', H-6a, H-6'a, H-6''a, H-3'', H-5'', H-6b, H-6'b, H-6''b, H-4, H-4', H-5, H-5'), 3.41–3.34 (m, 3 H, H-2, H-2', H-2''), 3.32 (s, 3 H, OCH_3), 1.98 (s, 3 H, $COCH_3$), 1.90 (m, 1 H, H-4''a), 1.41 (m, 1 H, H-4''b); ^{13}C NMR ($CDCl_3$): δ 170.73 ($COCH_3$), 97.99 (C-1), 97.91, 97.01 (C-1', C-1''), 82.09, 81.58 (C-3, C-3'), 80.53, 80.26, 80.12 (C-2, C-2', C-2''), 77.66 (2 C, C-4, C-4'), 75.69, 75.42, 74.99, 74.84, 73.38, 72.43, 72.32, 72.08 (CH_2Ph), 74.18 (C-3''), 70.62, 70.49 (C-5, C-5'), 65.98, 65.67 (3 C) (C-6, C-6', C-6'', C-5''), 55.17 (OCH_3), 33.35 (C-4''), 20.82 ($COCH_3$). CIMS: *m/z* 1283 $[M + NH_4]^+$. Anal. Calcd for $C_{77}H_{84}O_{16}$: C, 73.08; H, 6.69. Found: C, 73.01; H, 6.72.

Methyl 2,3-di-O-benzyl-4-deoxy-α-D-xylo-hexopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-D-glucopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**35**).—Trisaccharide **34** (0.25 g, 0.2 mmol) was deacetylated overnight using toluene (15 mL), anhyd MeOH (15 mL), and NaOMe (0.1 mL) (TLC, 6:1 toluene–acetone). After purification (silica gel, 7:1 toluene–acetone) compound **35** (0.23 g, 96%) was obtained: $[\alpha]_D$ +84.3° (*c* 1.207, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.32–7.11 (m, 40 H, 8 Ph), 4.98 (d, 1 H, $J_{1,2}$ 3.3 Hz, H-1), 4.95–4.50 (m, 18 H, H-1′, H-1″, 8 CH_2Ph), 3.98–3.61 (m, 8 H, H-3, H-3′, H-3″, H-6a, H-6′a, H-5, H-5′, H-5″), 3.46–3.35 (m, 7 H, H-4, H-4′, H-6″a, H-2, H-2′, H-2″, H-6″b), 3.31 (s, 3 H, OCH_3), 1.84 (m, 1 H, H-4″a), 1.41 (m, 1 H, H-4″b); ^{13}C NMR ($CDCl_3$): δ 97.95, 97.80, 97.00 (C-1, C-1′, C-1″), 82.04, 81.52 (C-3, C-3′), 80.69, 80.24, 80.07 (C-2, C-2′, C-2″), 77.67 (2 C, C-4, C-4′), 75.63, 75.34, 74.93, 74.78 (*C*H_2Ph), 74.28 (C-3″), 73.32, 72.32, 72.17, 72.07 (*C*H_2Ph), 70.56, 70.41 (C-5, C-5′), 68.09 (C-5″), 65.74 (2 C, C-6, C-6′), 65.16 (C-6″), 55.11 (O*C*H_3), 32.96 (C-4″). CIMS: *m/z* 1241 $[M + NH_4]^+$. Anal. Calcd for $C_{75}H_{82}O_{15}$: C, 73.63; H, 6.76. Found: C, 73.79; H, 6.80.

Methyl 3,6-di-O-acetyl-2-O-benzyl-4-deoxy-α-D-xylo-hexopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-D-glucopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**36**).—Trisaccharide **36** was prepared as described in General methods, using a heptane solution of tin(IV) chloride (1 M, 0.0165 mL), silver perchlorate (0.0033 g, 0.0165 mmol), acetate **8** (0.13 g, 0.34 mmol), and with silyl derivative **27** (0.39 g, 0.4 mmol). The mixture was stirred overnight (TLC, 6:1 toluene–acetone). After purification (silica gel, 8:1 toluene–acetone) 0.42 g of compound **36** was obtained (85.7%): $[\alpha]_D$ +88.2° (*c* 1.08, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.26–7.09 (m, 35 H, 7 Ph), 5.19 (m, 1 H, H-3″), 5.03 (d, 1 H, $J_{1'',2''}$ 3.3 Hz, H-1″), 4.95–4.47 (m, 16 H, H-1, H-1′, 7 CH_2Ph), 3.99–3.90 (m, 4 H, H-6a, H-6′a, H-5″, H-6″a), 3.80–3.61 (m, 7 H, H-5, H-5′, H-4, H-4′, H-6b, H-6′b, H-6″b), 3.41–3.36 (m, 3 H, H-2, H-2′, H-2″), 3.23 (s, 3 H, OCH_3), 2.31 (s, 3 H, COCH_3), 2.27–1.96 (m, 4 H, H-4″a, COCH_3), 1.42–1.30 (m, 1 H, H-4″b); ^{13}C NMR ($CDCl_3$): δ 170.52, 170.08 (*C*OCH$_3$), 97.92, 97.61, 96.97 (C-1, C-1′, C-1″), 82.05, 81.50 (C-3, C-3′), 80.09 (2 C, C-2, C-2′), 77.70, 77.52, 77.42 (C-2″, C-4, C-4″), 75.61, 75.25, 74.91, 74.87, 73.28, 72.29, 71.73 (*C*H_2Ph), 70.66, 70.44 (C-5, C-5′), 69.69 (C-3″), 65.71, 65.62 (2 C) (C-6, C-6′, C-6″), 65.04 (C-5″), 55.09 (O*C*H_3), 32.69 (C-4″), 21.11, 20.71 (CO*C*H_3). CIMS low resolution: *m/z* 1234.5 $[M + NH_4]^+$. Anal. Calcd for $C_{72}H_{80}O_{17}$: C, 71.03; H, 6.62. Found: C, 71.05; H, 6.58.

Methyl 3-O-acetyl-2-O-benzyl-4-deoxy-α-D-xylo-hexopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-D-glucopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-D-glucopyranoside (**37**).—Derivative **36** (0.2 g, 0.16 mmol) was deacetylated for 20 min as described under General methods using toluene (5 mL), anhyd MeOH (5 mL), and NaOMe (1 M, 0.1 mL). Purification (silica gel, 6:1 toluene–acetone) gave **37** (0.18 g, 93.3%): $[\alpha]_D$ +91.9° (*c* 0.283, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.33–7.19 (m, 35 H, 7 Ph), 5.22 (m, 1 H, H-3″), 5.06–4.53 (m, 17 H, H-1, H-1′, H-1″, 7 CH_2Ph), 4.02–3.42 (m, 16 H, H-3, H-3′, H-6a, H-6′a, H-5, H-5′, H-5″, H-4, H-4′, H-6b, H-6′b, H-6″a, H-6″b, H-2, H-2′, H-2″), 3.36 (s, 3 H, OCH_3), 1.56 (m, 4 H, H-4″a, COCH_3), 1.45 (m, 1 H, H-4″b); ^{13}C NMR ($CDCl_3$): δ 170.27 (*C*OCH$_3$), 97.99, 97.66, 97.09 (C-1, C-1′, C-1″), 82.13, 81.58 (C-3, C-3′), 80.14 (2 C), 77.77 (C-2, C-2′, C-2″), 77.65 (2 C) (C-4, C-4′), 75.71, 75.32, 74.93 (2 C), 73.38, 72.42, 71.82 (*C*H_2Ph), 70.70, 70.44 (C-5, C-5′), 69.87 (C-3″), 67.55

(C-5″), 65.87, 65.73 (C-6, C-6′), 64.91 (C-6″), 55.17 (OCH_3), 32.19 (C-4″), 21.21 ($COCH_3$). CIMS: m/z 1193 $[M + NH_4]^+$.

*Methyl 2-O-benzyl-4-deoxy-α-*D*-xylo-hexopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-*D*-glucopyranosyl-(1 → 6)-2,3,4-tri-O-benzyl-α-*D*-glucopyranoside* (**38**).—Trisaccharide **37** (0.15 g, 0.13 mmol) was deacetylated for 8 h using toluene (10 mL), anhyd MeOH (10 mL), and NaOMe (0.01 mL) (TLC, 6:1 toluene–acetone). After purification (silica gel, 2:1 hexane–EtOAc) compound **38** (0.135 g, 93%) was obtained: $[\alpha]_D$ +93.8° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.27–7.13 (m, 35 H, 7 Ph), 4.99 (d, 1 H, $J_{1'',2''}$ 3 Hz, H-1″), 4.93–4.37 (m, 16 H, H-1, H-1′, 7 CH_2Ph), 3.96–3.89 (m, 3 H, H-3, H-3′, H-3″), 3.78–3.32 (m, 13 H, H-6a, H-6′a, H-5, H-5′, H-5″, H-6b, H-6′b, H-4, H-4′, H-6″a, H-2, H-2′, H-6″b), 3.30 (s, 3 H, OCH_3), 3.17 (dd, 1 H, $J_{2'',3''}$ 9.2 Hz, H-2″), 1.78 (m, 1 H, H-4″a), 1.39 (m, 1 H, H-4″b); ^{13}C NMR ($CDCl_3$): δ 97.99, 97.10, 96.93 (C-1, C-1′, C-1″), 82.11, 81.56 (C-3, C-3′), 81.48 (C-2″), 80.24, 80.11 (C-2, C-2′), 77.74, 77.67 (C-4, C-4′), 75.73, 75.36, 74.97, 74.90, 73.37, 72.42, 71.35 (CH_2Ph), 70.52, 70.39 (C-5, C-5′), 68.24 (C-3″), 66.40 (C-5″), 65.94 (2 C, C-6, C-6′), 65.20 (C-6″), 55.19 (OCH_3), 33.71 (C-4″). CIMS: m/z 1150 $[M + NH_4]^+$. Anal. Calcd for $C_{68}H_{76}O_{15}$: C, 72.07; H, 6.76. Found: C, 71.86; H, 6.73.

*Methyl 4-deoxy-α-*D*-xylo-hexopyranosyl-(1 → 6)-α-*D*-glucopyranosyl-(1 → 6)-α-*D*-glucopyranoside* (**39**).—Trisaccharide **35** (0.35 g, 0.29 mmol) was debenzylated as described under General methods. When no starting material remained (20 h, TLC, 2:1:1.5 2-propanol–H_2O–EtOAc), the mixture was purified on a column of silica gel (2:1:1.75 2-propanol–H_2O–EtOAc) affording compound **39** (0.135 g, 93.8%): $[\alpha]_D$ +168.7° (*c* 0.825, H_2O); ^{1}H NMR (D_2O): δ 4.91–4.88 (m, 2 H, H-1′, H-1″), 4.75 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1), 3.95–3.25 (m, 17 H, H-3″, H-5″, H-4, H-4′, H-6a, H-6′a, H-6b, H-6′b, H-2, H-2′, H-3, H-3′, H-5, H-5′, H-2″, H-6″a, H-6″b), 3.35 (s, 3 H, OCH_3), 1.91 (m, 1 H, H-4″a), 1.37 (br ddd, 1 H, H-4″b); ^{13}C NMR (D_2O): δ 99.90 (C-1), 98.94, 98.32 (C-1′, C-1″), 73.91, 73.83 (2 C) (C-3, C-3′, C-2″), 71.92, 71.69 (C-2, C-2′), 70.86 (C-5′), 70.49 (C-5), 70.06, 69.98 (C-4, C-4′), 69.37 (C-5″), 67.76 (C-3″), 66.03 (2 C, C-6, C-6′), 64.11 (C-6″), 55.68 (OCH_3), 34.61 (C-4″). CIMS: m/z 520 $[M + NH_4]^+$.

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