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Synthesis of methyl glycosides of some α-isomalto oligosaccharides specifically deoxygenated at position C-2

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Abstract

Methyl α-isomaltoside and methyl α-isomaltotrioside analogues specifically deoxygenated at position C-2 of various glucopyranosyl units were synthesized by condensation of either 6-*O*-acetyl-3-*O*-benzoyl-4-*O*-benzyl-1-*O*-*tert*-butyldimethylsilyl-2-deoxy-β-D-*arabino*-hexopyranose (trimethylsilyl triflate mediated) or 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl chloride (mediated by silver carbonate and silver triflate) with suitably blocked derivatives of methyl α-D-glucopyranoside, its 2-deoxy analogue, or methyl 2′-deoxy-α-isomaltoside.

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

1. Introduction

This laboratory is studying the binding of monoclonal, dextran-specific antibodies. We have developed a systematic method to map the H-bonding interaction between saccharide immunodeterminants and antibodies [1]. Presently we are studying IgG 35.8.2H, an anti-(1 → 6)-dextran capable of binding internal antigenic epitopes [2]. We have found (unpublished) that in IgG 35.8.2H there is a perturbable tryptophanyl residue in the general combining area [3], but that it is distant to the subsite possessing the highest affinity for its glucosyl residue. In order to probe possible H-bonding interactions we are preparing isomalto di- and tri-saccharides that are deoxygenated at specific locations [4,5]. We here present a general procedure for preparing the methyl glycosides

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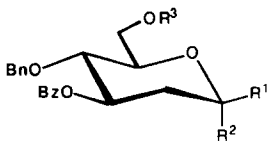
of α-isomalto oligosaccharides specifically deoxygenated at C-2 of various glucopyranosyl units.

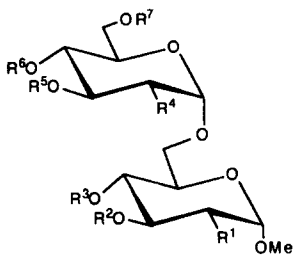
2. Results and discussion

It is known that 1-*O*-trimethylsilyl [6–14] and 1-*O*-*tert*-butyldimethylsilyl [14–18] glycosides are suitable as glycosyl donors. When these derivatives are employed in glycosylation reactions, it is usually in conjunction with trimethylsilyl triflate as the promoter [7–18]. Priebe et al. [14] and Kolar and co-workers [15–18] successfully used 1-*O*-*tert*-butyldimethylsilyl derivatives as donors in syntheses of 2-deoxy glycosides. Therefore, for the synthesis of α-isomalto oligosaccharides deoxygenated at C-2 of one or more glucopyranosyl units, we chose 6-*O*-acetyl-3-*O*-benzoyl-4-*O*-benzyl-1-*O*-*tert*-butyldimethylsilyl-2-deoxy-β-D-*arabino*-hexopyranose (**4**) as the glycosyl donor. This was prepared from methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α-D-*arabino*-hexopyranoside [4], which was central to other preparations, by treatment with borane–trimethylamine complex and aluminum chloride in toluene [19] to give **1** in 76% yield. Acetolysis (acetic anhydride–sulfuric acid) of **1** then gave 1,6-di-*O*-acetyl-3-*O*-benzoyl-4-*O*-benzyl-2-deoxy-α,β-D-*arabino*-hexopyranose (**2**) in quantitative yield. This was then treated for 16 h with tributyltin ethoxide [20], affording the monoacetyl derivative **3** in 85% yield. Finally, compound **3** was silylated with *tert*-butyldimethylsilyl chloride in dichloromethane in the presence of imidazole to give the target glycosyl donor **4** (89%). Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside [19] was condensed (−50°C, 48 h) with donor **4** in the presence of trimethylsilyl triflate. The product, methyl *O*-(6-*O*-acetyl-3-*O*-benzoyl-4-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-(1 → 6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**5**) was isolated in 81% yield. Treatment with 1 M HCl in methanol selectively removed the acetyl group and gave nucleophile **6** in 90% yield.

Nucleophile **1** was condensed with 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl chloride [21] in the presence of silver carbonate and silver triflate (−25°C, 20 h) to provide **7** in 83% yield. Deacylation of **7** with sodium methoxide in toluene and methanol (48 h, room temperature) then yielded compound **8** (93%), which after debenzylation gave **9** in quantitative yield. Condensation of nucleophile **1** with glycosyl donor **4** in the presence of trimethylsilyl triflate (−50°C, 14 h) afforded 88% of disaccharide **10** which after deacylation gave compound **11** (92%). Disaccharide **12** was obtained from derivative **11** (95%) by hydrogenolysis.

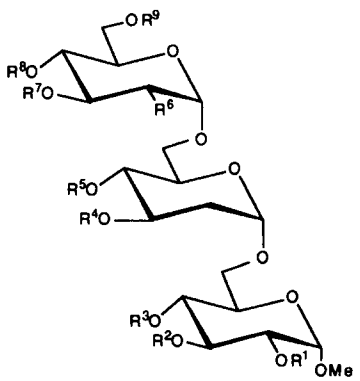


	R^1	R^2	R^3
1	H	OMe	H
2	OAc, H		Ac
3	OH, H		Ac
4	OTBS	H	Ac



	R^1	R^2	R^3	R^4	R^5	R^6	R^7
5	OBn	Bn	Bn	H	Bz	Bn	Ac
6	OBn	Bn	Bn	H	Bz	Bn	H
7	H	Bz	Bn	OBn	Bn	Bn	Ac
8	H	H	Bn	OBn	Bn	Bn	H
9	H	H	H	OH	H	H	H
10	H	Bz	Bn	H	Bz	Bn	Ac
11	H	H	Bn	H	H	Bn	H
12	H	H	H	H	H	H	H

Nucleophile **6** was condensed with silyl donor **4** (trimethylsilyl triflate, −50°C, 14 h) giving trisaccharide **13** in 80% yield. Deacylation resulted in compound **14**, which was debenzylated to afford trisaccharide **15**. When nucleophile **6** was condensed with 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl chloride [21] in the presence of silver carbonate and silver triflate (−25°C, 8 h), trisaccharide **16** was obtained in 85% yield. Deacylation to give **17** followed by debenzylation afforded methyl *O*-α-D-glucopyranosyl-(1 → 6)-*O*-(2-deoxy-α-D-*arabino*-hexopyranosyl)-(1 → 6)-α-D-glucopyranoside (**18**).



	R1	R2	R3	R4	R5	R6	R7	R8	R9
13	Bn	Bn	Bn	Bz	Bn	H	Bz	Bn	Ac
14	Bn	Bn	Bn	H	Bn	H	H	Bn	H
15	H	H	H	H	H	H	H	H	H
16	Bn	Bn	Bn	Bz	Bn	OBn	Bn	Bn	Ac
17	Bn	Bn	Bn	H	Bn	OBn	Bn	Bn	H
18	H	H	H	H	H	OH	H	H	H

The structures of all compounds were confirmed by NMR spectroscopy.

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 G F_{254} (Analtech). Detection was effected by charring with 5% H_2SO_4 in EtOH or, when applicable, with UV light. Preparative chromatography was performed by elution from columns of Silica Gel 60 (Merck, No. 9385). ^1H and ^{13}C NMR spectra were measured at ambient temperature using a Varian FX 300 or Varian Gemini spectrometer, operating at 300 MHz for ^1H 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 MeOH (δ_C 49.0). Proton-signal assignments were done by COSY or homonuclear decoupling experiments. The nonequivalent geminal proton resonating at a lower field is denoted Ha and the one resonating at a higher field is denoted Hb. Accumulative scans (minimally 128) of ^1H NMR spectra of purified samples (ca. 0.05 M) 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 1015 D spectrometer. Reactions requiring anhydrous conditions were

performed under dry N_2 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 deacylations, samples were dissolved in toluene and anhyd MeOH. Sodium methoxide in MeOH (1 M) was added and the mixture was stirred at room temperature. When starting material was no longer detected (TLC), the mixture was neutralized with Amberlite 120 (H^+) resin, filtered, concentrated, and purified on a column of silica gel.

For debenzylations, samples were dissolved in 95% EtOH and Pd–C (5%) suspended in 95% EtOH was added. The mixture was stirred under H_2 at atmospheric pressure and room temperature until no starting material was detected (TLC). The mixture was filtered through Celite, and the filtrate was concentrated and purified on a column of silica gel.

*Methyl 3-O-benzoyl-4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranoside* (**1**).—Methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-2-deoxy-α-D-*arabino*-hexopyranoside [4] (0.5 g, 1.35 mmol) was dissolved in toluene (50 mL) and borane–trimethylamine complex (0.6 g, 8.1 mmol), was added. After cooling the mixture to 0°C, aluminum chloride (0.75 g) was added gradually. No starting material could be detected after 30 min. The mixture was filtered through Celite, the filtrate was concentrated, the residue was dissolved in CH_2Cl_2, and this solution was extracted with water, dried, and concentrated. The crude product was purified on a column of silica gel (10:1 toluene–acetone) giving 0.38 g (76%) of **1**. Crystallization from 2-propanol gave **1**; mp 104–105°C; $[\alpha]_D$ +41° (*c* 0.83, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.07–7.17 (m, 10 H, Ph), 5.63 (m, 1 H, H-3), 4.85 (br d, 1 H, H-1), 4.73 (dd, 2 H, J_{gem} 11 Hz, CH_2Ph), 3.84 (m, 4 H, H-5, H-6a, H-6b, H-4), 3.56 (s, 3 H, OCH_3), 2.42 (ddd, 1 H, $J_{1,2a}$ 1.2, $J_{2a,3}$ 5.4, $J_{2a,2b}$ 12.9 Hz, H-2a), and 1.81 (ddd, 1 H, $J_{1,2b}$ 3.7, $J_{2b,3}$ 5.4, $J_{2a,2b}$ 12.9 Hz, H-2b); ^{13}C NMR ($CDCl_3$): δ 165.36 (*C*OPh), 97.89 (C-1), 76.12 (C-4), 74.47 (*C*H_2Ph), 72.31 (C-3), 71.02 (C-5), 61.81 (C-6), 54.46 (O*C*H_3), and 35.05 (C-2); CIMS: *m/z* 390 ($[M + NH_4]^+$) and 373 ($[M]^+$). Anal. Calcd for $C_{21}H_{24}O_6$: C, 67.73; H, 6.50. Found: C, 67.63; H, 6.51.

*1,6-Di-O-acetyl-3-O-benzoyl-4-O-benzyl-2-deoxy-α,β-*D-arabino-*hexopyranose* (**2**). —Methyl glycoside **1** (2.25 g, 6.04 mmol) was dissolved in Ac_2O (25 mL) and H_2SO_4 (1%) in Ac_2O (3 mL) was added. The mixture was stirred at room temperature for 20 min, when the reaction was complete (TLC, 6:1 toluene–acetone). 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 crystallized from 2-propanol giving compound **2** (2.54 g, 95%); mp 85.5–86.6°C; $[\alpha]_D$ +48° (*c* 0.90, $CHCl_3$); ^{1}H NMR ($CDCl_3$): α anomer, δ 8.07–7.17 (m, 10 H, Ph), 6.26 (br d, 1 H, H-1), 5.63 (ddd, 1 H, $J_{2a,3}$ 5.1, $J_{2b,3}$ 14, $J_{3,4}$ 8.8 Hz, H-3), 4.68 (dd, 2 H, J_{gem} 11 Hz, CH_2Ph), 4.34 (m, 2 H, H-6a, H-6b), 4.09 (m, 1 H, H-5), 3.79 (br d, $J_{4,5}$ 9.4 Hz, H-4), 2.43 (br dd, 1 H, H-2a), 2.14 (s, 3 H, COCH_3), 2.08 (s, 3 H, COCH_3), and 1.96 (br dd, 1 H, H-2b); ^{13}C NMR ($CDCl_3$): α anomer, d 170.39 (*C*OCH_3), 168.91 (*C*OCH_3), 165.32 (*C*OPh), 90.94 (C-1), 75.60 (C-4), 74.81 (*C*H_2Ph), 71.93 (C-3), 71.33 (C-5), 62.82 (C-6), 34.02 (C-2), 21.07 (CO*C*H_3), and 20.88 (CO*C*H_3); β anomer, δ 91.03 (C-1), 76.21 (C-4), 75.22 (*C*H_2Ph), 73.75 (C-3), 73.37 (C-5), 62.89 (C-6), and 34.90 (C-2); α:β = 10:1; CIMS: *m/z* 460 ($[M + NH_4]^+$). Anal. Calcd for $C_{24}H_{26}O_8$: C, 65.15; H, 5.92. Found: C, 64.99; H, 5.90.

*6-O-Acetyl-3-O-benzoyl-4-O-benzyl-2-deoxy-α,β-*D-arabino-*hexopyranose* (**3**).—Di-*O*-acetyl derivative **2** (1.2 g, 2.71 mmol) was dissolved in toluene (60 mL) and tributyltin ethoxide (0.75 mL, 3.93 mmol) was added. The mixture was heated under reflux for 16 h, during which time additional tributyltin ethoxide (0.15 mL) was added. As only traces of starting material remained, the mixture was concentrated and purified on a column of silica gel (2:1 hexane–EtOAc) giving **3** (0.92 g, 85%); mp 127–128°C (from 1:2 EtOAc–hexane); $[\alpha]_D$ +28° (*c* 0.84, $CHCl_3$); ^{1}H NMR ($CDCl_3$): α anomer, δ 8.07 (m, 2 H, Ph), 7.57 (m, 3 H, Ph), 7.27 (m, 5 H, Ph), 5.71 (ddd, 1 H, $J_{2a,3}$ 5.1, $J_{3,4}$ 9, $J_{2b,3}$ 14 Hz, H-3), 5.46 (br d, 1 H, H-1), 4.70 (dd, 2 H, J_{gem} 10.8 Hz, CH_2Ph), 4.35 (dd, 1 H, $J_{6a,6b}$ 11.8 Hz, H-6a), 4.33 (dd, 1 H, $J_{5,6b}$ 4.1 Hz, H-6b), 4.26 (ddd, 1 H, $J_{4,5}$ 6.6 Hz, H-5), 3.73 (br dd, 1 H, H-4), 2.99 (br s, 1 H, O*H*), 2.45 (ddd, 1 H, $J_{1,2a}$ 1.5, $J_{2a,2b}$ 12.9 Hz, H-2a), 2.12 (s, 3 H, COCH_3), and 1.87 (br dd, 1 H, $J_{1,2b}$ 3.4 Hz, H-2b); ^{13}C NMR ($CDCl_3$): α anomer, δ 170.90 (*C*OCH$_3$), 165.54 (*C*OPh), 91.66 (C-1), 76.44 (C-4), 74.59 (*C*H$_2$Ph), 72.23 (C-3), 69.15 (C-5), 63.41 (C-6), 35.38 (C-2), and 20.90 (CO*C*H$_3$); β anomer, δ 93.76 (C-1), 75.88 (C-4), 74.78 (*C*H$_2$Ph), 74.05 (C-3), 73.18 (C-5), 63.33 (C-6), 37.77 (C-2), and 20.90 (CO*C*H$_3$); α:β = 4.5:1 CIMS: *m/z* 418 ([M + NH$_4$]$^+$). Anal. Calcd for $C_{22}H_{24}O_7$: C, 65.99; H, 6.04. Found: C, 65.93; H, 6.08.

*6-O-Acetyl-3-O-benzoyl-4-O-benzyl-1-*O-tert-*butyldimethylsilyl-2-deoxy-β-*D-arabino-*hexopyranose* (**4**).—Compound **3** (0.5 g, 1.25 mmol) and imidazole (0.217 g, 3.34 mmol) were dissolved in CH_2Cl_2 (20 mL). *tert*-Butyldimethylsilyl chloride (0.254 g, 5.84 mmol) was added, and the mixture was heated at 40°C for 4 h and then left at room temperature overnight. No starting material remained in the mixture (TLC, 6:1 toluene–acetone), which was washed with phosphate buffer and water and dried. After concentration and purification on a column of silica gel (12:1 toluene–EtOAc) 0.57 g (89%) of **4** was isolated having $[\alpha]_D$ −30° (*c* 1.08, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.04–8.01 (m, 2 H, Ph), 7.99–7.55 (m, 1 H, Ph), 7.47–7.42 (m, 2 H, Ph), 7.24–7.15 (m, 5 H, Ph), 5.34 (ddd, 1 H, $J_{2a,3}$ 5.2, $J_{3,4}$ 8.3, $J_{2b,3}$ 13.5 Hz, H-3), 4.95 (dd, 1 H, $J_{1,2a}$ 2, $J_{1,2b}$ 9 Hz, H-1), 4.70 (d, 1 H, J_{gem} 11 Hz, 1/2 CH_2Ph), 4.56 (d, 1 H, 1/2 CH_2Ph), 4.42 (dd, 1 H, $J_{5,6a}$ 2.2, $J_{6a,6b}$ 11.8 Hz, H-6a), 4.30 (dd, 1 H, $J_{5,6b}$ 5.4 Hz, H-6b), 3.70 (dd, 1 H, $J_{4,5}$ 9.6 Hz, H-4), 3.63 (ddd, 1 H, H-5), 2.49 (ddd, 1 H, $J_{2a,2b}$ 12.5 Hz, H-2a), 2.05 (s, 3 H, COCH_3), 1.79 (br dd, 1 H, H-2b), 0.88 [s, 9 H, C(CH_3)$_3$], 0.11 (s, 3 H, SiCH_3), and 0.1 (s, 3 H, SiCH_3); ^{13}C NMR ($CDCl_3$): δ 170.56 (*C*OCH$_3$), 165.43 (*C*OPh), 94.41 (C-1), 76.31 (C-4), 74.68 (*C*H$_2$Ph), 74.39 (C-3), 73.07 (C-5), 63.53 (C-6), 39.23 (C-2), 25.77 [C(*C*H$_3$)$_3$], 20.95 (CO*C*H$_3$), −4.08 and −5.07 [Si(*C*H$_3$)$_2$]; CIMS: *m/z* 532 ([M + NH$_4$]$^+$). Anal. Calcd for $C_{28}H_{38}O_7Si$: C, 65.34; H, 7.44. Found: C, 65.30; H, 7.39.

Methyl O-*(6-O-acetyl-3-O-benzoyl-4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranosyl)-(1 → 6)-2,3,4-tri-O-benzyl-α-*D-*glucopyranoside* (**5**).—Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside [19] (0.393 g, 0.85 mmol) and the *tert*-butyldimethylsilyl derivative **4** (0.48 g, 0.93 mmol) were dissolved in dry CH_2Cl_2 (50 mL), and 4A molecular sieves (1.32 g) were added. After cooling to −50°C, trimethylsilyl triflate (0.18 mL, 0.9 mmol) was added gradually over a 2-day period. When no starting material remained (TLC, 6:1 toluene–acetone) triethylamine (1.6 mL) was added and the mixture was stirred for 30 min, then filtered through Celite. The filtrate was washed with citrate buffer (pH 4.5), phosphate buffer (pH 7.5), and water, dried, again filtered, and concentrated. The

residue was purified on a column of silica gel (8:1 toluene–acetone) giving compound **5** in 80% yield (0.58 g); mp 97–97.6°C (10:1 MeOH–EtOAc); $[\alpha]_D$ +53° (*c* 0.91, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.01–7.14 (m, 25 H, Ph), 5.64 (ddd, 1 H, H-3′), 5.03–4.56 (m, 8 H, 4 C*H*$_2$Ph), 5.03 (br d, 1 H, H-1′), 4.24 (br d, 2 H, H-6′a, H-6′b), 4.08–4.02 (m, 1 H, H-3), 3.98–3.92 (m, 1 H, H-5′), 3.89–3.80 (m, 3 H, H-5, H-6a, H-6b), 3.74–3.53 (m, 3 H, H-4′, H-4, H-2), 3.42 (s, 3 H, OC*H*$_3$), 2.48 (m, 1 H, H-2′a), and 1.85 (m, 1 H, H-2′b); ^{13}C NMR ($CDCl_3$): δ 170.39 (*C*OCH$_3$), 165.19 (*C*OPh), 97.84 (C-1), 97.15 (C-1′), 82.15 (C-3), 80.04 (C-2), 77.70 (C-4), 76.15 (C-4′), 75.60, 74.90, 74.47, 73.31 (*C*H$_2$Ph), 72.53 (C-3′), 69.73, 68.97 (C-5′, C-5), 65.88 (C-6), 63.10 (C-6′), 55.12 (O*C*H$_3$), 35.08 (C-2′), and 21.47 (CO*C*H$_3$); CIMS: *m/z* 865 ([M + NH_4]$^+$). Anal. Calcd for $C_{50}H_{54}O_{12}$: C, 70.91; H, 6.43. Found: C, 70.69; H, 6.47.

Methyl O-*(3*-O-*benzoyl-4*-O-*benzyl-2-deoxy-α*-D-arabino-*hexopyranosyl)-(1 → 6)-2,3,4-tri*-O-*benzyl-α*-D-*glucopyranoside* (**6**).—Compound **5** (0.37 g, 0.44 mmol) was dissolved in toluene (1 mL) and HCl in MeOH (1 M, 1.5 mL) was added. After 12 h at room temperature no starting material was present (TLC, 6:1 toluene–acetone). The mixture was neutralized with Amberlite IRA 400 (OH^-) resin, filtered, concentrated, and purified on a column of silica gel yielding **6** (0.315 g, 90%); $[\alpha]_D$ +24° (*c* 1.79, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.02–7.99 (m, 3 H, Ph), 7.58–7.15 (m, 22 H, Ph), 5.59 (m, 1 H, H-3′), 4.98 (m, 3 H, C*H*$_2$Ph, H-1′), 4.72 (m, 7 H, 3 C*H*$_2$Ph, H-1), 3.99 (m, 1 H, H-3), 3.74 (m, 6 H, H-4′, H-5, H-5′, H-6a, H-6′a, H-6b), 3.54 (m, 3 H, H-2, H-4, H-6′b), 3.38 (s, 3 H, OC*H*$_3$), 2.44 (m, 1 H, H-2′a), and 1.78 (m, 1 H, H-2′b); ^{13}C NMR: δ 165.39 (*C*OPh), 98.01 (C-1′), 97.36 (C-1), 82.27 (C-3), 80.16 (C-2), 77.81 (C-4), 76.26 (C-4′), 75.70, 75.00, 74.71, 73.48 (*C*H$_2$Ph), 72.56 (C-3′), 71.23, 69.87 (C-5, C-5′), 65.96 (C-6), 61.85 (C-6′), 55.27 (O*C*H$_3$), and 35.32 (C-2′); CIMS: *m/z* 823 ([M + NH_4]$^+$). Anal. Calcd for $C_{48}H_{52}O_{11}$: C, 71.62; H, 6.51. Found: C, 71.36; H, 6.58.

Methyl O-*(6*-O-*acetyl-2,3,4-tri*-O-*benzyl-α*-D-*glucopyranosyl)-(1 → 6)-3*-O-*benzoyl-4*-O-*benzyl-2-deoxy-α*-D-arabino-*hexopyranoside* (**7**).—Nucleophile **1** (0.41 g, 1.1 mmol) was dissolved in anhyd CH_2Cl_2 (60 mL), and silver carbonate (1.22 g, 4.43 mmol) and 4A molecular sieves (1 g) were added. The mixture was stirred at −25°C under N_2, and after 30 min silver triflate (0.12 g, 0.47 mmol) was added. 6-*O*-Acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl chloride [21] (0.69 g, 1.35 mmol) was dissolved in dry CH_2Cl_2 (10 mL) and added dropwise to this mixture over a period of 1 h. Only traces of starting material were detected after 20 h (TLC, 6:1 toluene–acetone). The mixture was filtered through Celite, washed with aq satd $NaHCO_3$ and water, then dried. Purification on silica gel (10:1 toluene–acetone) gave 0.77 g (83%) of **7**; mp 109–110°C (2-propanol); $[\alpha]_D$ +85° (*c* 0.71, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.89 (d, 2 H, Ph), 7.49–7.03 (m, 23 H, Ph), 5.51 (m, 1 H, H-3), 4.98 (br s, 1 H, H-1′), 4.83 (dd, 1 H, H-3), 4.74 (br s, 1 H, H-1), 4.21 (br d, 2 H, H-6′a, H-6′b), 4.04 (dd, 1 H, H-3′), 3.92–3.72 (m, 5 H, H-5, H-5′, H-4, H-6a, H-6b), 3.58–3.49 (m, 2 H, H-2′, H-3′), 3.26 (s, 3 H, OC*H*$_3$), 2.26 (br dd, 1 H, $J_{1,2a}$ 0.5, $J_{2a,3}$ 6.6, $J_{2a,2b}$ 12.8 Hz, H-2a), 1.95 (s, 3 H, COC*H*$_3$), and 1.57 (br dd, 1 H, $J_{1,2b}$ 3.7 Hz, H-2b); ^{13}C NMR ($CDCl_3$): δ 170.32 (*C*OCH$_3$), 165.17 (*C*OPh), 97.81 (C-1), 96.79 (C-1′), 81.54 (C-3′), 80.23 (C-2′), 77.11 (C-4′), 76.24 (C-4), 75.44, 74.83, 74.38 (*C*H$_2$Ph), 72.27 (2 C, *C*H$_2$Ph, C-3), 70.95 (C-5), 68.66 (C-5′), 65.58 (C-6),

62.92 (C-6′), 54.60 (OCH_3), 35.22 (C-2), and 20.79 ($COCH_3$); CIMS: *m/z* 864 ($[M + H_4]^+$). Anal. Calcd for $C_{50}H_{54}O_{12}$: C, 70.90; H, 6.43. Found: C, 70.75; H, 6.37.

Methyl O-*(2,3,4-tri*-O-*benzyl-α*-D-*glucopyranosyl)-(1 → 6)-4*-O-*benzyl-2-deoxy-α*-D-arabino-*hexopyranoside* (**8**).—Disaccharide **7** (0.065 g, 0.077 mmol) was deacylated as described under general methods, using toluene (3 mL), MeOH (5 mL), and NaOMe (0.01 mL) for 48 h. Purification on silica gel (6:1 toluene–acetone) gave **8** (0.025 g, 93%); $[\alpha]_D$ +99° (*c* 0.77, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.33–7.12 (m, 20 H, Ph), 5.07 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1′), 4.70 (br d, 1 H, $J_{1,2}$ 2.8 Hz, H-1), 4.01 (dd, 1 H, $J_{2',3'}$ 9.1, $J_{3',4'}$ 9.3 Hz, H-3′), 3.92 (m, 1 H, H-3), 3.85 (dd, 1 H, $J_{5,6a}$ 4, $J_{6a,6b}$ 12.1 Hz, H-6a), 3.79 (br d, 1 H, H-6b), 3.75–3.61 (m, 4 H, H-5, H-5′, H-6′a, H-6′b), 3.53–3.42 (m, 3 H, H-4′, H-2′, H-4), 3.24 (s, 3 H, OCH_3), 2.01 (br dd, 1 H, $J_{2a,3}$ 5.3, $J_{2a,2b}$ 12.9 Hz, H-2a), and 1.45 (br dd, $J_{2b,3}$ 3.7 Hz, H-2b); ^{13}C NMR ($CDCl_3$): δ 98.35 (C-1), 97.07 (C-1), 81.66 (C-3′), 80.23 (C-2′), 79.77 (C-4′), 77.45 (C-4), 75.57, 75.01, 74.45, 72.51 (CH_2Ph), 71.02 (2 C, C-5, C-5′), 68.87 (C-3), 65.78 (C-6′), 61.96 (C-6′), 54.72 (OCH_3), and 37.38 (C-2); CIMS: *m/z* 718 ($[M + NH_4]^+$). Anal. Calcd for $C_{41}H_{48}O_{10}$: C, 70.26; H, 6.90. Found: C, 70.13 ; H, 6.86.

Methyl O-*α*-D-*glucopyranosyl-(1 → 6)-2-deoxy-α*-D-arabino-*hexopyranoside* (**9**).—Disaccharide **8** (0.025 g, 0.036 mmol) was debenzylated for 6 h as described under general methods (TLC, 15:1 CH_2Cl_2–MeOH). The crude product was purified on a silica gel column (2:1:1.75 2-propanol–H_2O–EtOAc) affording disaccharide **9** (0.012 g, 98%). Neither the ^{1}H nor the ^{13}C NMR spectrum revealed signals that would indicate the presence of aromatic residues. The compound had $[\alpha]_D$ +116° (*c* 1.0, H_2O); ^{1}H NMR (D_2O): δ 4.96 (d, 1 H, $J_{1',2'}$ 3.7 Hz, H-1′), 4.93 (br d, 1 H, $J_{1,2b}$ 3.2 Hz, H-1), 4.03 (dd, 1 H, $J_{5,6a}$ 4.2, $J_{6a,6b}$ 11 Hz, H-6a), 3.91–3.67 (m, 4 H, H-4, H-3, H-5, H-6b), 3.57 (dd, 1 H, $J_{1',2'}$ 3.5, $J_{2',3'}$ 9.9 Hz, H-2′), 3.49 (dd, 1 H, $J_{3',4'}$ 9.4 Hz, H-4′), 3.46 (dd, 1 H, $J_{5',6'a}$ 4.5, $J_{4',5'}$ 9.3 Hz, H-5′), 3.38 (s, 3 H, OCH_3), 2.17 (br dd, 1 H, $J_{2a,3}$ 5, $J_{2a,2b}$ 13.7 Hz, H-2a), and 1.74 (br dd, 1 H, H-2b); ^{13}C NMR (D_2O): δ 98.65 (C-1), 98.10 (C-1′), 73.34 (C-3′), 72.05 (C-3), 71.76 (C-2′), 71.09 (C-5′), 70.77 (C-5), 69.75 (C-4′), 68.74 (C-4), 65.84 (C-6), 60.75 (C-6′), 54.78 (OCH_3), 36.83 (C-2); CIMS: *m/z* 358 ($[M + NH_4]^+$).

Methyl O-*(6*-O-*acetyl-3*-O-*benzoyl-4*-O-D-arabino-*hexopyranosyl)-(1 → 6)-3*-O-*benzoyl-4*-O-*benzyl-2-deoxy-α*-D-arabino-*hexopyranoside* (**10**).—Compounds **1** (0.12 g, 0.32 mmol) and **4** (0.2 g, 0.39 mmol) were dissolved in dry CH_2Cl_2 (10 mL) and 4A molecular sieves (0.4 g) were added. The mixture was stirred for 30 min and cooled to −50°C, then trimethylsilyl triflate (0.062 mL, 0.324 mmol) was added gradually. No starting material could be detected after 14 h (TLC, 6:1 toluene–acetone). The mixture was worked-up as described for compound **5** and purified on silica gel (8:1 toluene–acetone), giving syrupy compound **10** (0.203 g, 88%); $[\alpha]_D$ +70° (*c* 0.73, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.12–8.08 (m, 4 H, Ph), 7.64–7.17 (m, 16 H, Ph), 5.75 (m, 1 H, H-3′), 5.64 (m, 1 H, H-3), 5.13 (br d, 1 H, H-1′), 4.86 (br d, 1 H, H-1), 4.24 (br d, 2 H, H-6′a, H-6′b), 4.04–3.86 (m, 3 H, H-5′, H-5, H-4), 3.78–3.67 (m, 2 H, H-4′, H-6), 3.38 (s, 3 H, OCH_3), 2.59 (m, 1 H, H-2a), 2.43 (m, 1 H, H-2′a), and 1.96–1.84 (m, 2 H, H-2b, H-2′b); ^{13}C NMR ($CDCl_3$): δ 170.46 ($COCH_3$), 165.42 (*C*OPh), 165.36 (*C*OPh), 97.98, 97.49 (C-1, C-1′), 76.45, 76.27 (C-4, C-4′), 74.69, 74.56 (CH_2Ph), 72.76 (2 C, C-3, C-3′), 70.18 (C-5), 69.07 (C-5′), 66.01 (C-6), 63.10 (C-6′), 54.74

(OCH_3), 35.36, 35.18 (C-2, C-2'), and 20.94 ($COCH_3$); CIMS: *m/z* 772 ($[M + NH_4]^+$). Anal. Calcd for $C_{43}H_{46}O_{12}$: C, 68.42; H, 6.14. Found: C, 68.52; H; 6.20.

Methyl O-*(4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranosyl)-(1 → 6)-4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranoside* (**11**).—Disaccharide **10** (0.035 g, 0.046 mmol) was deacylated by the general procedure, using toluene (1 mL), anhyd MeOH (1 mL), and NaOMe (1 M, 0.01 mL). The mixture was stirred overnight (TLC, 2:1 toluene–acetone). After workup and column chromatography 0.022 g of compound **11** was obtained (92%); $[\alpha]_D$ +112° (*c* 0.48, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.33–7.31 (m, 10 H, Ph), 5.00 (br d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.11–4.00 (m, 2 H, H-3, H-3'), 3.84 (dd, 1 H, $J_{5,6a}$ 4.5, $J_{6a,6b}$ 11.5 Hz, H-6a), 3.76–3.59 (m, 5 H, H-6'a, H-6b, H-6'b, H-5, H-5'), 3.33 (dd, 2 H, H-4, H-4'), 3.28 (s, 3 H, OCH_3), 2.34 (s, 1 H, O*H*), 2.20 (br dd, 1 H, $J_{2'a,3'}$ 5.4, $J_{2'a,2'b}$ 13.2 Hz, H-2'a), 2.09 (br dd, 1 H, $J_{2a,3}$ 4.9, $J_{2a,2b}$ 12.9 Hz, H-2a), 1.69–1.60 (m, 2 H, H-2b, H-2'b), and 1.24 (s, 1 H, O*H*); ^{13}C NMR ($CDCl_3$): δ 98.36, 97.84 (C-1, C-1'), 80.42, 79.95 (C-4, C-4'), 74.81, 74.56 (CH_2Ph), 71.36, 70.11 (C-5, C-5'), 69.18, 68.94 (C-3, C-3'), 66.07 (C-6), 61.90 (C-6'), 54.67 (OCH_3), 37.44, and 37.35 (C-2, C-2'); CIMS: *m/z* 522 ($[M + NH_4]^+$).

Methyl O-*(2-deoxy-α-*D-arabino-*hexopyranosyl)-(1 → 6)-2-deoxy-α-*D-arabino-*hexopyranoside* (**12**).—Disaccharide **11** (0.02 g, 0.040 mmol) was debenzylated by the general procedure. When no starting material remained (6 h; TLC, 15:1 CH_2Cl_2–MeOH) the mixture was purified on a column of silica gel (2:1:1.75 2-propanol–H_2O–EtOAc) affording disaccharide **9** (0.012 g, 92%). Neither the ^1H nor the ^{13}C NMR spectrum revealed signals that would indicate the presence of an aromatic residue. The compound had $[\alpha]_D$ +38° (*c* 0.78, H_2O); ^1H NMR (D_2O): δ 4.97 (br d, 1 H, H-1'), 4.84 (br d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 3.91–3.57 (m, 8 H, H-3, H-3', H-6a, H-6'a, H-5', H-5, H-6'b, H-6b), 4.41 (dd, 1 H, H-4'), 3.32 (dd, 1 H, H-4), 3.30 (s, 3 H, OCH_3), 2.10 (br dd, 2 H, H-2a, H-2'a), and 1.66 (br dd, 2 H, H-2b, H-2'b); ^{13}C NMR (D_2O): δ 98.81 (C-1), 97.37 (C-1'), 72.59, 71.29 (C-4, C-4'), 71.21, 70.69 (C-5, C-5'), 68.84, 68.63 (C-3, C-3'), 65.44 (C-6), 60.96 (C-6'), 54.81 (OCH_3), 36.91, and 36.85 (C-2, C-2'); CIMS: *m/z* 342 ($[M + NH_4]^+$).

Methyl O-*(6-O-acetyl-3-O-benzoyl-4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranosyl)-(1 → 6)-*O-*(3-O-benzoyl-4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranosyl)-(1 → 6)-2,3,4-tri-O-benzyl-α-*D-*glucopyranoside* (**13**).—Disaccharide **6** (0.19 g, 0.24 mmol) and donor **4** (0.15 g, 0.28 mmol) were dissolved in anhyd CH_2Cl_2 (10 mL), and 4A molecular sieves (0.4 g) were added. After cooling to −50°C, trimethylsilyl triflate (0.05 mL, 0.25 mmol) was added dropwise to the stirred mixture. No starting material remained after 14 h (TLC, 6:1 toluene–acetone), when triethylamine (0.035 mL, 0.25 mmol) was added. The mixture was worked-up as described for compound **5** and chromatographed on silica gel (3:1 hexane–EtOAc) yielding 0.23 g (80%) of **13**; $[\alpha]_D$ +69° (*c* 0.43, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.10–8.04 (m, 5 H, Ph), 7.90–7.15 (m, 30 H, Ph), 5.80–5.67 (m, 2 H, H-3', H-3''), 5.10–5.07 (m, 4 H, H-1', H-1'', CH_2Ph), 4.93–4.63 (m, 9 H, H-1, 4 CH_2Ph), 4.27 (m, 1 H, H-6''a), 4.12–4.07 (m, 1 H, H-3), 3.93–3.79 (m, 9 H, H-2, H-6''b, H-4, H-4', H-4'', H-6a, H-6b, H-6'a, H-6'b), 3.71–3.57 (m, 3 H, H-5, H-5', H-5''), 3.41 (s, 3 H, OCH_3), 2.61–2.51 (m, 1 H, H-2'a, H-2''a), 2.04 (s, 3 H, $COCH_3$), 1.95–1.87 (m, 1 H, H-2'b), and 1.01–0.89 (m, 1 H, H-2''b); ^{13}C NMR ($CDCl_3$): δ 170.70 ($COCH_3$), 165.61 (2 C, *C*OPh), 98.00, 97.59, 97.31 (C-1, C-1',

C-1″), 82.32 (C-3), 80.14 (C-2), 77.84 (C-4), 76.45, 76.28 (C-4′, C-4″), 75.67, 74.95, 74.79, 74.61, 73.44 (CH_2Ph), 72.85, 72.81 (C-3′, C-3″), 70.39, 69.90 (C-5, C-5′), 69.08 (C-5″), 65.86, 65.83 (C-6, C-6′), 63.08 (C-6″), 55.17 (OCH_3), 35.31, 35.16 (C-2′, C-2″), and 20.92 ($COCH_3$); CIMS: m/z 1204 ($[M + NH_4]^+$). Anal. Calcd for $C_{70}H_{74}O_{17}$: C, 70.81; H, 6.28. Found: C, 70.51; H, 6.37.

Methyl O-*(4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranosyl)-(1 → 6)*-O-*(4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranosyl)-(1 → 6)-2,3,4-tri-*O-*benzyl-α-*D-*glucopyranoside* (**14**).—Trisaccharide **13** (0.07 g, 0.059 mmol) was deacylated for 24 h using toluene (0.5 mL), anhyd MeOH (0.5 mL), and NaOMe (0.01 mL) (TLC, 3:1 toluene–acetone). After purification on silica gel (2:1 toluene–acetone) compound **14** was obtained (0.045 g, 92%); $[\alpha]_D$ +73° (*c* 1.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.31–7.14 (m, 25 H, Ph), 4.96 (br dd, 2 H, H-1′, H-1″), 4.57 (br d, 1 H, H-1), 4.99–4.55 (m, 10 H, 5 CH_2Ph), 4.01 (m, 3 H, H-3, H-3′, H-3″), 3.81–3.45 (m, 9 H, H-6a, H-6′a, H-6″a, H-6″b, H-6b, H-6′b, H-5, H-5′, H-5″), 3.34–3.28 (m, 3 H, H-4, H-4′, H-4″), 3.33 (s, 3 H, OCH_3), 2.10 (m, 2 H, H-2a, H-2′a), and 1.61 (m, 2 H, H-2b, H-2′b); ^{13}C NMR ($CDCl_3$): δ 97.98 (C-1), 97.73, 97.59 (C-1′, C-1″), 82.16 (C-3), 80.26 (C-2), 80.09, 79.94 (C-4′, C-4″), 77.81 (C-4), 75.68, 74.77 (2 C), 74.51, 73.28 (CH_2Ph), 71.30, 70.39, 69.75 (C-5, C-5′, C-5″), 69.22, 68.92 (C-3′, C-3″), 65.81 (2 C, C-6, C-6′), 61.89 (C-6″), 55.10 (OCH_3), and 37.40 (2 C, C-2′, C-2″); CIMS: m/z 955 ($[M + NH_4]^+$).

Methyl O-*(2-deoxy-α-*D-arabino-*hexopyranosyl)-(1 → 6)*-O-*(2-deoxy-α-*D-arabino-*hexopyranosyl)-(1 → 6)-α-*D-*glucopyranoside* (**15**).—Trisaccharide **14** (0.04 g, 0.043 mmol), was debenzylated for 12 h by the general procedure (TLC, 2:1:1 2-propanol–H_2O–EtOAc). Purification on silica gel (2:1:1.75 2-propanol–H_2O–EtOAc) gave trisaccharide **15** (0.020 g, 95%). Neither the ^{1}H nor the ^{13}C NMR spectrum revealed signals that would indicate the presence of an aromatic residue. The compound had $[\alpha]_D$ +142° (*c* 1.12, H_2O); ^{1}H NMR (D_2O): δ 4.94–4.92 (m, 2 H, H-1′, H-1″), 4.70 (br d, 1 H, H-1), 3.85–3.75 (m, 2 H, H-3′, H-3″), 3.74–3.52 (m, 9 H, H-6a, H-6′a, H-6″a, H-6″b, H-5′, H-5″, H-3, H-6b, H-6′b), 3.45 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 9.7 Hz, H-2), 3.38 (dd, 1 H, $J_{3,4}$ 9.1, $J_{4,5}$ 9.7 Hz, H-4), 3.36–3.24 (m, 3 H, H-4′, H-5, H-4″), 3.31 (s, 3 H, OCH_3), 2.12–2.04 (m, 2 H, H-2′a, H-2″a), and 1.68–1.56 (m, 2 H, H-2′b, H-2″b); ^{13}C NMR (D_2O): δ 99.62 (C-1), 97.16, 97.01 (C-1′, C-1″), 73.64 (C-2), 72.51 (C-3), 71.45 (C-4), 71.24 (2 C, C-4′, C-4″), 70.63, 70.07, 69.75 (C-5, C-5′, C-5″), 68.79, 68.54 (C-3, C-3″), 65.41, 65.25 (C-6, C-6′), 60.93 (C-6″), 55.37 (OCH_3), 36.89, and 36.80 (C-2′, C-2″); CIMS: m/z 504 ($[M + NH_4]^+$).

Methyl O-*(6-O-acetyl-2,3,4-tri-*O-*benzyl-α-*D-*glucopyranosyl)-(1 → 6)*-O-*(3-O-benzoyl-4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranosyl)-(1 → 6)-2,3,4-tri-*O-*benzyl-α-*D-*glucopyranoside* (**16**).—Disaccharide **6** (0.27 g, 0.335 mmol) was dissolved in dry CH_2Cl_2 (20 mL), and Ag_2CO_3 (0.37 g, 1.34 mmol) and 4A molecular sieves (0.35 g) were added. The mixture was cooled to −25°C and stirred for 30 min under N_2, then AgOTf (0.037 g, 0.144 mmol) and 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α,β-D-glucopyranosyl chloride [21] (0.21 g, 0.411 mmol) were added. Another portion of the chloride (0.05 g) was added after 6 h. After a further 2 h (TLC, 2:1 hexane–EtOAc), the mixture was worked-up as for compound **7**. The crude product was subjected to column chromatography on silica gel and 0.365 g (85%) of **16** was obtained; $[\alpha]_D$ +82° (*c* 0.98, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.92 (br d, 2 H, Ph), 7.55–7.16 (m, 38 H, Ph), 5.53 (ddd, 1 H,

$J_{2'a,3'}$ 5.2, $J_{2'b,3'}$ 14.2, $J_{3',4'}$ 9 Hz, H-3'), 5.17 (br d, 1 H, $J_{1'',2''}$ 3.4 Hz, H-1''), 5.00 (dd, 2 H, J_{gem} 10.6 Hz, CH_2Ph), 4.97 (br d, 1 H, $J_{1',2'}$ 2.8 Hz, H-1'), 4.58 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 5.04–4.55 (m, 12 H, 6 CH_2Ph), 4.16 (br dd, 2 H, H-6''a, H-6''b), 4.03 (dd, 1 H, $J_{2,3}$ 11, $J_{3,4}$ 9.1 Hz, H-3), 3.98 (dd, 1 H, $J_{4',5'}$ 9.4 Hz, H-4'), 3.94–3.66 (m, 6 H, H-3'', H-6'a, H-6a, H-6b, H-5, H-5''), 3.58–3.39 (m, 5 H, H-2, H-2', H-4, H-4'', H-6'b), 3.37 (s, 3 H, OCH_3), 2.34 (br dd, 1 H, $J_{1',2'a}$ 0.5, $J_{2'a,2'b}$ 12.5, $J_{2'a,3'}$ 5.1 Hz, H-2'a), 1.98 (s, 3 H, COCH_3), and 1.58 (ddd, 1 H, $J_{1',2'b}$ 3.6, H-2'b); ^{13}C NMR ($CDCl_3$): δ 170.53 (*C*OCH$_3$), 165.36 (*C*OPh), 97.94 (C-1), 97.26 (C-1'), 96.79 (C-1''), 82.22, 81.66 (C-3, C-3''), 80.36, 80.09 (C-2, C-2''), 77.79, 77.16 (C-4, C-4''), 76.08 (C-4'), 75.05 (2 C), 74.95 (2 C), 74.49, 73.42, 72.25 (7 C, *C*H$_2$Ph), 72.37 (C-3'), 71.40 (C-5), 69.86 (C-5'), 68.74 (C-5''), 65.79, 65.01 (C-6, C-6'), 63.00 (C-6''), 55.19 (O*C*H$_3$), 35.29 (C-2'), and 20.94 (CO*C*H$_3$); CIMS: *m/z* 1298 ([M + NH$_4$]$^+$). Anal. Calcd for $C_{77}H_{82}O_{17}$: C, 72.28; H, 6.46. Found: C, 72.12 ; H, 6.47.

Methyl O-*(2,3,4-tri*-O-*benzyl*-α-D-*glucopyranosyl)-(1 → 6)*-O-*(4*-O-*benzyl-2-deoxy*-α-D-arabino-*hexopyranosyl)-(1 → 6)-2,3,4-tri*-O-*benzyl*-α-D-*glucopyranoside* (**17**).—Trisaccharide **16** (0.2 g, 0.16 mmol) was deacylated for 96 h as described above using toluene (3 mL), anhyd MeOH (3 mL), and NaOMe (0.01 mL) (TLC, 4:1 toluene–acetone). After purification on silica gel compound **17** (0.17 g, 95%) was isolated; $[\alpha]_D$ +75° (*c* 0.66, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.33–7.13 (m, 35 H, Ph), 5.10 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.97–4.51 (m, 14 H, 7 CH_2Ph), 4.83 (br d, 1 H, H-1'), 4.54 (d, 1 H, $J_{1'',2''}$ 3.4 Hz, H-1''), 4.02–3.90 (m, 3 H, H-3, H-3', H-3''), 3.79–3.69 (m, 6 H, H-6a, H-6b, H-6'a, H-6'b, H-6''a, H-6''b), 3.86–3.43 (m, 8 H, H-5, H-5', H-5'', H-4, H-4'', H-4', H-2, H-2''), 3.30 (s, 3 H, OCH_3), 2.05 (br dd, 1 H, $J_{2'a,3'}$ 5.4, $J_{2'a,2'b}$ 13.2 Hz, H-2'a), 1.72 (br s, 1 H, O*H*), 1.59 (br s, 1 H, O*H*), and 1.32 (ddd, 1 H, H-2'b); ^{13}C NMR ($CDCl_3$): δ 97.97 (C-1), 97.65 (C-1'), 96.96 (C-1''), 82.16, 81.62 (C-3, C-3''), 80.26, 80.08 (C-2, C-2''), 79.41, 77.86 (C-4, C-4''), 75.67, 75.53, 75.05, 74.83, 74.34, 73.33, 72.29 (*C*H$_2$Ph), 71.46, 70.93, 69.81 (C-5, C-5', C-5''), 68.81 (C-3'), 65.81, 65.12 (C-6, C-6'), 61.96 (C-6''), 55.08 (O*C*H$_3$), and 37.28 (C-2'); CIMS: *m/z* 1151 ([M + NH$_4$]$^+$). Anal. Calcd for $C_{68}H_{76}O_{15}$: C, 72.06; H, 6.76. Found: C, 71.87 ; H, 6.80.

Methyl O-α-D-*glucopyranosyl-(1 → 6)*-O-*(2-deoxy*-α-D-arabino-hexopyranosyl)-(1 → 6)-α-D-*glucopyranoside* (**18**).—Trisaccharide **17** (0.1 g, 0.09 mmol) was debenzylated for 5 h at room temperature (TLC, 2:1:1 2-propanol–H_2O–EtOAc). After filtration and concentration of the filtrate, the product was purified on silica gel yielding 93% of **18** (0.041 g). Neither the ^{1}H nor the ^{13}C NMR spectrum revealed signals that would indicate the presence of an aromatic residue. The compound had $[\alpha]_D$ +142° (*c* 0.79, H_2O); ^{1}H NMR (D_2O): δ 4.94 (br d, 1 H, $J_{1',2'}$ 3 Hz, H-1'), 4.85 (d, 1 H, $J_{1'',2''}$ 3.6 Hz, H-1''), 4.60 (br d, 1 H, H-1), 3.92–3.30 (m, 17 H, H-3', H-6a, H-6b, H-6''a, H-4, H-4'', H-6''b, H-3, H-3'', H-5, H-5', H-5'', H-6'a, H-6'b, H-2, H-2'', H-4'), 3.30 (s, 3 H, OCH_3), 2.09 (br dd, 1 H, $J_{2'a,3'}$ 5.3, $J_{2'a,2'b}$ 13.5 Hz, H-2'a), and 1.63 (br dd, 1 H, $J_{1',2'b}$ 3.3 Hz, H-2'b); ^{13}C NMR (D_2O): δ 99.39 (C-1), 97.77, 97.00 (C-1', C-1''), 73.42, 73.16 (C-3, C-3''), 71.86, 71.57 (C-2, C-2''), 71.19, 70.95, 70.70 (C-4, C-4', C-4''), 69.83, 69.56, 69.48 (C-5, C-5', C-5''), 68.61 (C-3'), 65.70, 65.07 (C-6, C-6'), 60.52 (C-6''), 55.18 (O*C*H$_3$), and 36.66 (C-2'); CIMS: *m/z* 520 ([M + NH$_4$]$^+$).

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