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Note

Anomalous Zemplén deacylation of protected methyl 2-deoxy-α-D-*arabino*-hexopyranosides and related methyl α-isomaltosides and α-isomaltotriosides

Eva Petráková, Cornelis P.J. Glaudemans *

NIDDK, National Institutes of Health, Bethesda, MD 20892, USA

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Anomalous Zemplén deacylations of some protected (1 → 3)-linked disaccharides were reported by Lipták and co-workers [1]. They found that upon treatment with sodium methoxide in methanol, benzyl *O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-(1 → 3)-2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranoside retained its 2-*O*-benzoyl group. Later the same observation [2] was made on the corresponding 2-*O*-acetyl derivative as well. Similar findings of acyl group retention were reported [3,4] for methyl *O*-(2,4,6-tri-*O*-acetyl-3-*O*-methyl-β-D-glucopyranosyl)-(1 → 3)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside, methyl *O*-(2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-D-glucopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside, and benzyl *O*-(2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-D-glucopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-galactopyranoside.

Other instances of anomalous Zemplén deacylation have been described [5–7]. The common feature so far is that, following Zemplén deacylation of a protected saccharide, an acyl group at position 2 of that saccharidic unit was retained that bore a benzyl, allyl, or glycosyl group at position 3.

We here report our observation that methyl α-glycosides of isomalto oligosaccharides possessing a 3-*O*-benzoyl-4-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranosyl moiety underwent anomalous Zemplén deacylation. For compounds **9**, **11**, **13**, **15**, and **17**, which

* Corresponding author.

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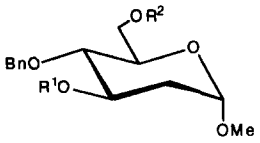
had been prepared as described [8,9], deacylation by sodium methoxide in toluene–methanol for from 15 min to 3 h was complete, except for the *O*-benzoyl group. Our conditions involved a range of concentrations of sodium methoxide (0.0017–0.016 M) typical of Zemplén deacylation [10]. Extension of the reaction time (24–96 h) resulted in the removal of the benzoyl group also. To evaluate this observation on monosaccharide precursors, we prepared derivatives **2–6**. Methyl 3-*O*-benzoyl-4-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranoside (**1**) [8] was acetylated with acetic anhydride in pyridine to yield **2** quantitatively. When compound **2** was deacylated using Zemplén's method (0.005 M sodium methoxide, methanol–toluene) [10] for 45 min, it reverted to the partially deblocked monosaccharide **1** in quantitative yield. Another 30 h were required to obtain **3** (98%). Compound **4** was obtained from **3** using conventional acetylation conditions (pyridine, acetic anhydride). On treatment with 0.024 M sodium methoxide (methanol–toluene) for 15 min, we were able to isolate **5** (84%), while the fully deacylated monosacharide **3** was obtained after an additional 20 min of reaction. Compound **3** was benzoylated (pyridine, benzoyl chloride) to give derivative **6** (97%) which was deacylated (0.0048 M sodium methoxide) to yield **1** (92%) after 1 h. For compound **7**, deacylation (0.016 M sodium methoxide, 45 min) gave **8** in quantitative yield, thus revealing yet another method [11–13] for the preparation of a derivative selectively deacylated at position 1.

Our results demonstrate that Zemplén deacylation can be used to selectively remove an *O*-acyl group from position 6 or 1 of a carbohydrate moiety possessing another *O*-acyl group at position 3, when position 2 is deoxygenated and position 4 is blocked by a benzyl group.

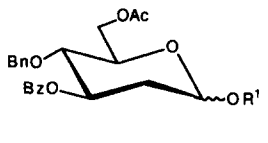
The structures of all compounds reported were confirmed by NMR spectroscopy.

1. Experimental

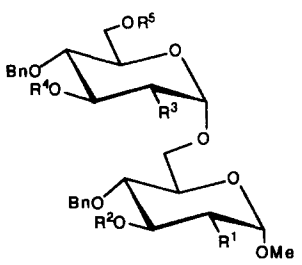
General methods.—Melting points were determined on a Kofler hot stage. Optical rotations were measured at 25°C with a Perkin–Elmer automatic polarimeter, Model 241 MC. All reactions were monitored by thin-layer chromatography (TLC) on precoated slides of Silica Gel G F_{254} (Analtech). Detection was effected by charring with 5% H_2SO_4 in EtOH and, 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 in the spectra recorded for solutions in $CDCl_3$ were measured from internal Me_4Si. Proton-signal assignments were made 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. Carbon-signal assignments were based on heteronuclear shift-correlated 2D experiments (HETCOR). Accumulative scans (minimally 128) of ^1H NMR spectra of purified samples (ca. 0.05 M) failed to show any extraneous peaks, thus indicating purity. Chemical ionization mass spectra (CIMS) using ammonia as the reactive gas were obtained with a Finigan 1015 D spectrometer. Reactions requiring anhydrous conditions were performed under dry nitrogen using



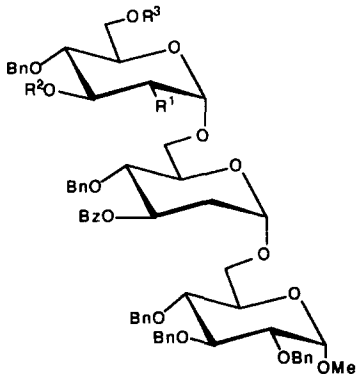
	R^1	R^2
1	Bz	H
2	Bz	Ac
3	H	H
4	Ac	Ac
5	Ac	H
6	Bz	Bz



	R^1
7	Ac
8	H



	R^1	R^2	R^3	R^4	R^5
9	OBn	Bn	H	Bz	Ac
10	OBn	Bn	H	Bz	H
11	H	Bz	OBn	Bn	Ac
12	H	Bz	OBn	Bn	H
13	H	Bz	H	Bz	Ac
14	H	Bz	H	Bz	H



	R^1	R^2	R^3
15	H	Bz	Ac
16	H	Bz	H
17	OBn	Bn	Ac
18	OBn	Bn	H

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. NaOMe (1 M) in MeOH 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^+) ion-exchange resin, filtered, and concentrated, and the residue was purified on a column of silica gel (for amounts of the reagents, and solvent systems, see individual cases).

*Methyl 6-O-acetyl-3-O-benzoyl-4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranoside* (**2**). —Methyl 3-*O*-benzoyl-4-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranoside (**1**) [8] (0.23 g, 0.61 mmol) was dissolved in pyridine (1.5 mL) and acetic anhydride (0.7 mL) was added. After 2 h, starting material was no longer detected (TLC, 6:1 toluene–acetone). MeOH and toluene were added to the mixture, which was concentrated and then purified on a column of silica gel (10:1 toluene–acetone) giving 0.28 g (98%) of **2**; $[\alpha]_D$ +49° (*c* 0.71, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.08 (m, 2 H, Ph), 7.62–7.18 (m, 8 H, Ph), 5.65 (ddd, 1 H, $J_{2a,3}$ 5.1, $J_{3,4}$ 8.8, $J_{2b,3}$ 14 Hz, H-3), 4.87 (br d, 1 H, $J_{1,2b}$ 3.2 Hz, H-1), 4.77 (d, 1 H, J_{gem} 11.2 Hz, 1/2 CH_2Ph), 4.63 (d, 1 H, 1/2 CH_2Ph), 4.39 (br d, 2 H, H-6a, H-6b), 3.99 (ddd, 1 H, $J_{5,6a}$ 3.4, $J_{5,6b}$ 6.8, $J_{4,5}$ 9.8 Hz, H-5), 3.74 (dd, 1 H, H-4), 3.38 (s, 3 H, OCH_3), 2.44 (br dd, 1 H, $J_{2a,2b}$ 12.4 Hz, H-2a), 2.11 (s, 3 H, COCH_3), and 1.87 (br dd, H-2b); ^{13}C NMR ($CDCl_3$): δ 170.52 (*C*OCH$_3$), 165.24 (*C*OPh), 97.87 (C-1), 76.19 (C-4), 74.43 (*C*H$_2$Ph), 72.48 (C-3), 68.77 (C-5), 63.21 (C-6), 54.60 (O*C*H$_3$), 35.02 (C-2), and 20.75 (CO*C*H$_3$); CIMS: *m/z* 432 ([M + NH_4]$^+$). Anal. Calcd for $C_{23}H_{26}O_7$: C, 66.65; H, 6.32. Found: C, 66.51; H, 6.29.

*Methyl 4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranoside* (**3**).—Derivative **1** (0.2 g, 0.54 mmol), was deacylated as described under general methods, using toluene (3 mL), MeOH (3 mL), and NaOMe (0.1 mL). After 30 h, compound **3** (98%) was isolated by chromatography (6:1 toluene–acetone); $[\alpha]_D$ +106° (*c* 0.42, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.96–7.12 (m, 5 H, Ph), 4.67 (br s, 3 H, CH_2Ph, H-1), 3.96 (ddd, 1 H, $J_{2a,3}$ 5.1, $J_{3,4}$ 8.9, $J_{2b,3}$ 16.6 Hz, H-3), 3.75 (dd, 1 H, $J_{5,6a}$ 2.8, $J_{6a,6b}$ 11.9 Hz, H-6a), 3.69 (dd, 1 H, $J_{5,6b}$ 3.7 Hz, H-6b), 3.51 (m, 1 H, H-5), 3.20 (s, 3 H, OCH_3), 3.27 (dd, 1 H, H-4), 2.60 (br s, 2 H, O*H*), 2.02 (br dd, 1 H, $J_{2a,2b}$ 13.2 Hz, H-2a), and 1.56 (br dd, 1 H, H-2b); ^{13}C NMR ($CDCl_3$): δ 98.37 (C-1), 79.77 (C-4), 74.64 (*C*H$_2$Ph), 70.98 (C-5), 68.73 (C-3), 61.84 (C-6), 54.62 (O*C*H$_3$), and 37.45 (C-2); CIMS: *m/z* 286 ([M + NH_4]$^+$). Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.53; H, 7.41.

*Methyl 3,6-di-O-acetyl-4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranoside* (**4**).—Compound **3** was acetylated as described for monosaccharide **2**, to give **4** after purification by chromatography (10:1 toluene–acetone); $[\alpha]_D$ +103° (*c* 0.75, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.28–7.10 (m, 5 H, Ph), 5.26 (ddd, 1 H, $J_{2a,3}$ 5.2 Hz, H-3), 4.73 (br d, 1 H, $J_{1,2b}$ 3.1 Hz, H-1), 4.64 (d, 1 H, J_{gem} 11.2 Hz, 1/2 CH_2Ph), 4.54 (d, 1 H, 1/2 CH_2Ph), 4.25 (d, 2 H, H-6a, H-6b), 3.82 (m, 1 H, H-5), 3.47 (dd, 1 H, $J_{3,4}$ 9.3 Hz, H-4), 3.26 (s, 3 H, OCH_3), 2.22 (br dd, 1 H, $J_{2a,2b}$ 13.2 Hz, H-2a), 2.01 (s, 3 H, COCH_3), 1.94 (s, 3 H, COCH_3), and 1.63 (br dd, 1 H, H-2b); ^{13}C NMR ($CDCl_3$): δ 170.60 (*C*OCH$_3$), 169.77 (*C*OCH$_3$), 97.81 (C-1), 76.09 (C-4), 74.33 (*C*H$_2$Ph), 71.86 (C-3), 68.70 (C-5), 63.17 (C-6), 54.57 (O*C*H$_3$), 34.91 (C-2), 21.07 (CO*C*H$_3$), and 20.77 (CO*C*H$_3$); CIMS: *m/z* 370 ([M + NH_4]$^+$). Anal. Calcd for $C_{18}H_{24}O_7$: C, 61.35; H, 6.86. Found: C, 61.24; H, 6.84.

*Methyl 3-O-acetyl-4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranoside* (**5**).—Compound **4** (0.05 g, 0.14 mmol) was deacylated as described under general methods, using toluene (1 mL), anhyd MeOH (1 mL), and NaOMe (0.05 mL). After 15 min (TLC, 6:1 toluene–acetone), compound **5** was obtained following purification (0.037 g, 84%); $[\alpha]_D$ +96° (*c* 0.02, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.29 (ddd, 1 H, $J_{2a,3}$ 5.3, $J_{2b,3}$ 16.7 Hz, H-3), 4.77 (br d, 1 H, $J_{1,2b}$ 3.4 Hz, H-1), 4.71 (d, 1 H, J_{gem} 11.3 Hz, 1/2 CH_2Ph), 4.64 (d, 1 H, 1/2 CH_2Ph), 3.78 (m, 2 H, H-6a, H-6b), 3.69 (m, 1 H, H-5), 3.57 (dd, 1

H, $J_{3,4}$ 9.2 Hz, H-4), 3.30 (s, 3 H, OCH_3), 2.25 (br dd, $J_{2a,3}$ 5.1, $J_{2a,2b}$ 12.7 Hz, H-2a), 1.97 (s, 3 H, COCH_3), 1.64 (ddd, 1 H, H-2b), and 1.54 (s, 1 H, O*H*); ^{13}C NMR ($CDCl_3$): δ 169.92 (*C*OCH$_3$), 98.10 (C-1), 76.29 (C-4), 74.63 (*C*H$_2$Ph), 71.89 (C-3), 70.97 (C-5), 62.01 (C-6), 54.80 (O*C*H$_3$), 35.34 (C-2), and 21.37 (CO*C*H$_3$); CIMS: *m/z* 328 ([M + NH$_4$]$^+$). Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.14. Found: C, 62.34; H, 7.39.

*Methyl 3,6-di-*O*-benzoyl-4-*O*-benzyl-2-deoxy-α-*D-arabino-*hexopyranoside* (**6**).—Monosaccharide **1** (0.2 g, 0.54 mmol), was dissolved in pyridine (1 mL), and benzoyl chloride (0.18 mL, 1.5 mmol) was added. The mixture was stirred at room temperature for 30 min, after which no starting material could be detected (TLC, 6:1 toluene–acetone). After concentration of the solution the residue was dissolved in CH_2Cl_2, and this was extracted with aq satd $NaHCO_3$ and water. The dried solution was concentrated and the residue was purified on a column of silica gel (3.5:1 hexane–EtOAc) to give **6** (0.25 g, 97%); [α]$_D$ +76° (*c* 2.04, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.21–8.12 (m, 2 H, Ph), 7.67–7.23 (m, 13 H, Ph), 5.72 (ddd, 1 H, $J_{2a,3}$ 5.2, $J_{3,4}$ 11.2 Hz, H-3), 4.89 (bd, 1 H, H-1), 4.84 (d, 1 H, J_{gem} 10.8 Hz, 1/2 CH_2Ph), 4.70 (m, 3 H, 1/2 CH_2Ph, H-6a, H-6b), 4.17 (m, 1 H, H-5), 3.86 (dd, 1 H, $J_{4,5}$ 9.2 Hz, H-4), 3.45 (s, 3 H, OCH_3), 2.51 (br dd, $J_{2a,3}$ 4.5, $J_{2a,2b}$ 12.4 Hz, H-2a), and 1.95 (ddd, $J_{1,2b}$ 3.7 Hz, H-2b); ^{13}C NMR ($CDCl_3$): δ 166.47 (*C*OPh), 165.65 (*C*OPh), 98.03 (C-1), 76.66 (C-4), 74.66 (*C*H$_2$Ph), 72.61 (C-3), 69.13 (C-5), 63.80 (C-6), 54.71 (O*C*H$_3$), and 35.07 (C-2); CIMS: *m/z* 494 ([M + NH$_4$]$^+$). Anal. Calcd for $C_{28}H_{28}O_7$: C, 70.57; H, 5.92. Found: C, 70.69; H, 5.98.

*Methyl 3-*O*-benzoyl-4-*O*-benzyl-2-deoxy-α-*D-arabino-*hexopyranoside* (**1**).—Both derivatives **2** and **6** were deacylated as described under general methods. For compound **2** (0.07 g, 0.17 mmol), the amounts used were: toluene (1 mL), MeOH (1 mL), and NaOMe (0.01 mL). After 45 min, **1** (0.06 g, 95%) was isolated. For deacylation of **6** (0.05 g, 0.105 mmol), the amounts used were: toluene (1 mL), MeOH (1 mL), and NaOMe (0.01 mL). Starting material was no longer observed (TLC, 6:1 toluene–acetone) after 60 min, and **1** (0.036 g; 92%) was obtained in the usual way. NMR and CIMS data for compound **1** were identical with those published elsewhere [8].

*6-*O*-acetyl-3-*O*-benzoyl-4-*O*-benzyl-2-deoxy-α,β-*D-arabino-*hexopyranose* (**8**).—Protected monosaccharide **7** [8] (0.1 g, 0.23 mmol) was deacylated as described under general methods, using toluene (3 mL), MeOH (3 mL), and NaOMe (0.1 mL). After 45 min derivative **8** was isolated (0.085 g, 94%). Its analytical data were identical with those described [8].

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* (**10**).—Compound **9** [8] (0.1 g, 0.12 mmol) was deacylated as described under general methods, using toluene (3 mL), MeOH (3 mL), and NaOMe (0.01 mL). After 3.5 h, disaccharide **10** (0.09 g, 95%) was isolated. Its NMR and CIMS data were identical with those reported [8].

Methyl O*-(2,3,4-tri-*O*-benzyl-α-*D-glucopyranosyl)-(1 → 6)-3-*O*-benzoyl-4-*O*-benzyl-2-deoxy-α-*D-arabino-*hexopyranoside* (**12**).—Disaccharide **11** [8] (0.09 g, 0.11 mmol) was deacylated as described under general methods, using toluene (3 mL), MeOH (5 mL), and NaOMe (0.05 mL). After 2 h (TLC, 6:1 toluene–acetone) the material was worked-up, and compound **12** was crystallized from 2-propanol yielding 0.082 g (96%);

mp 85.5–86°C; $[\alpha]_D$ +74° (*c* 0.42, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.90 (d, 2 H, Ph), 7.53–7.05 (m, 15 H, Ph), 5.49 (m, 1 H, H-3), 5.08 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1'), 4.73 (br d, 1 H, H-1), 4.99–4.59 (m, 8 H, 4 CH_2Ph), 4.03 (br d, $J_{2',3'}$ 9.3, $J_{3',4'}$ 9.0 Hz, H-3'), 3.89 (br d, 1 H, $J_{6'a,6'b}$ 11.8 Hz, H-6'a), 3.82–3.63 (m, 6 H, H-6'b, H-6a, H-6b, H-4, H-5, H-5'), 3.54–3.50 (m, 2 H, H-2', H-4'), 3.27 (s, 3 H, OCH_3), 2.23 (br dd, 1 H, H-2a), and 1.61 (br dd, 1 H, H-2b); ^{13}C NMR ($CDCl_3$): δ 165.40 (*C*OPh), 98.00 (C-1), 97.06 (C-1'), 81.60 (C-3'), 80.46 (C-2'), 77.45 (C-4'), 76.39 (C-4), 75.51, 75.02, 74.51 (*C*H_2Ph), 72.46 (2 C, *C*H_2Ph, C-3), 71.06, 70.99 (C-5, C-5'), 65.71 (C-6), 61.90 (C-6'), 54.73 (O*C*H_3), and 35.25 (C-2); CIMS: *m/z* 822 ($[M + NH_4]^+$). Anal. Calcd for $C_{48}H_{52}O_{11}$: C, 71.62; H, 6.51. Found: C, 70.93 ; H, 6.50.

Methyl O-*(3-O-benzoyl-4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranosyl)-(1 → 6)-3-O-benzoyl-4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranoside* (**14**).—Disaccharide **13** [8] (0.077 g, 0.1 mmol) was deacylated as described under general methods, using toluene (5 mL), anhyd MeOH (5 mL), and NaOMe (0.01 mL). After 1 h no starting material could be detected (TLC, 6:1 toluene–acetone). Purification gave compound **14** (0.065 g, 90%); $[\alpha]_D$ +73° (*c* 0.72, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.10–8.06 (m, 4 H, Ph), 7.60–7.57 (m, 2 H, Ph), 7.50–7.45 (m, 4 H, Ph), 7.30–7.15 (m, 10 H, Ph), 5.71 (m, 1 H, H-3'), 5.36 (m, 1 H, H-3), 5.11 (br d, 1 H, H-1'), 4.85 (br d, $J_{1,2b}$ 3.2 Hz, H-1), 4.89–4.63 (m, 4 H, 2 CH_2Ph), 4.00 (br d, $J_{6a,6b}$ 11.2 Hz, H-6a), 3.93–3.78 (m, 4 H, H-4, H-5', H-5, H-4'), 3.76–3.64 (m, 3 H, H-6'a, H-6'b, H-6b), 2.57 (br dd, 1 H, $J_{2'a,3'}$ 5.3, $J_{2'a,2'b}$ 12.8 Hz, H-2'a), 2.41 (m, 1 H, $J_{2a,3}$ 5.4, $J_{2a,2b}$ 12.7 Hz, H-2a), and 1.92–1.74 (m, 2 H, H-2b, H-2'b); ^{13}C NMR ($CDCl_3$): δ 165.54 (2 C, *C*OPh), 98.08 (C-1), 97.62 (C-1'), 76.46 (C-4), 76.25 (C-4'), 74.79, 74.54 (*C*H_2Ph), 72.81 (C-3), 72.65 (C-3'), 71.25 (C-5), 70.22 (C-5'), 65.96 (C-6), 61.69 (C-6'), 54.73 (O*C*H_3), and 35.28 (2 C, C-2, C-2'); CIMS: *m/z* 730 ($[M + NH_4]^+$).

Methyl O-*(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* (**16**).—Trisaccharide **15** [8] (0.07 g, 0.06 mmol), was deacylated as described under general methods, using toluene (0.5 mL), MeOH (0.5 mL), and NaOMe (0.01 mL) for 15 min. The mixture was purified (10:1 toluene–acetone) giving 0.067 g (90%) of the target compound **16**; $[\alpha]_D$ +67° (*c* 0.65, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.19–8.15 (m, 4 H, Ph), 7.72–7.28 (m, 31 H, Ph), 5.80–5.70 (m, 2 H, H-3', H-3''), 5.12 (br d, 3 H, H-1', H-1'', 1/2 CH_2Ph), 4.95–4.72 (m, 8 H, 4 CH_2Ph), 4.71 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 3.99–3.55 (m, 14 H, H-4', H-4'', H-3, H-6a, H-6b, H-6'a, H-6'b, H-4, H-2, H-5, H-5', H-5'', H-6''a, H-6''b), 3.51 (s, 3 H, OCH_3), 2.64–2.53 (m, 2 H, H-2'a, H-2''a), 2.00–1.85 (m, 2 H, H-2'b, H-2''b), and 1.77 (br s, 1 H, O*H*); ^{13}C NMR ($CDCl_3$): δ 165.52 (2 C, *C*OPh), 97.97 (C-1), 97.55, 97.29 (C-1', C-1''), 82.29 (C-3), 80.11 (C-2), 77.79 (C-4), 76.39, 76.22 (C-4', C-4''), 75.65, 74.91, 74.83, 74.55, 73.42 (*C*H_2Ph), 72.86, 72.64 (C-3', C-3''), 71.19, 70.32, 69.84 (C-5, C-5', C-5''), 65.87, 65.71 (C-6', C-6), 61.71 (C-6''), 55.17 (O*C*H_3), and 35.27 (2 C, C-2', C-2''); CIMS: *m/z* 1163 ($[M + NH_4]^+$).

Methyl O-*(2,3,4-tri-O-benzyl-α-*D-*glucopyranosyl)-(1 → 6)-(3-O-benzoyl-4-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranosyl)-(1 → 6)-2,3,4-tri-O-benzyl-α-*D-*glucopyranoside* (**18**).—Trisaccharide **17** [8] (0.1 g, 0.078 mmol) was deacylated using toluene (3 mL), MeOH (3 mL), and NaOMe (0.1 mL). After 3 h the mixture was purified (10:1

toluene–acetone) to give 0.09 g of **18** (93%); $[\alpha]_D$ +81° (*c* 1.45, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 7.69–7.93 (d, 2 H, Ph), 7.60–7.16 (m, 38 H, Ph), 5.55 (ddd, 1 H, $J_{2',3'}$ 5.4, $J_{3',4'}$ 9.2, $J_{2'b,3'}$ 11.4 Hz, H-3'), 5.15 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1''), 4.93 (br d, 1 H, H-1'), 4.69 (d, 1 H, $J_{1,2}$ 3.1 Hz, H-1), 5.16–4.60 (m, 14 H, 7 CH_2Ph), 4.07 (br dd, 1 H, $J_{3'',4''}$ 9.2 Hz, H-3''), 4.01 (dd, 1 H, $J_{3,4}$ 9.3 Hz, H-3), 3.93 (dd, 1 H, $J_{4',5'}$ 9.5 Hz, H-4'), 3.85–3.53 (m, 13 H, H-5', H-5'', H-6'a, H-4'', H-6a, H-6b, H-6'b, H-6''a, H-6''b, H-4, H-5, H-2, H-2''), 3.39 (s, 3 H, OCH_3), 2.36 (m, 1 H, H-2'a), and 1.60 (m, 1 H, H-2'b); ^{13}C NMR ($CDCl_3$): δ 165.50 (*C*OPh), 98.01 (C-1), 97.34 (C-1'), 96.91 (C-1''), 82.26, 81.60 (C-3, C-3''), 80.52, 80.14 (C-2, C-2''), 77.82, 77.44 (C-4, C-4''), 76.18 (C-4'), 75.65, 75.54, 75.09, 74.94, 74.51, 73.44, 72.40 (CH_2Ph), 72.33 (C-3'), 71.37 (C-5), 70.89, 69.85 (C-5', C-5''), 65.86, 65.07 (C-6, C-6'), 61.91 (C-6''), 55.19 (OCH_3), and 35.23 (C-2'); CIMS: *m/z* 1254 ($[M + NH_4]^+$). Anal. Calcd for $C_{75}H_{80}O_{16}$: C, 72.80; H, 6.52. Found: C, 72.55; H, 6.55.

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