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Syntheses of specifically deoxygenated methyl α-isomaltotriosides

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ABSTRACT

Specifically deoxygenated methyl α-isomaltotriosides were synthesized by the silver perchlorate-mediated condensation of a protected α-isomaltosyl chloride with suitably blocked derivatives of methyl α-D-glucopyranoside deoxygenated respectively at positions 2, 3, and 4, followed by deprotection.

INTRODUCTION

This laboratory has investigated the binding of carbohydrate ligands to monoclonal antigalactan and antidextran antibodies using mono- and oligo-saccharides and their deoxy and deoxyfluoro analogues[1–3]. Changes in binding resulting from the replacement of a hydroxyl group by fluorine or hydrogen in a saccharide indicate a role of hydrogen bonding by either H donation or H acceptance. As a continuation of this work we are studying anti-α-(1 → 6)-dextran IgG 35.8.2H, isolated by Kabat and coworkers[4], which is capable of binding internal epitopes of its homologous carbohydrate antigen. In experiments to be described elsewhere we used as ligands methyl α-D-glucopyranoside and the methyl α-glycosides of the isomalto-oligosaccharides up to and including the octasaccharide[5]. We observed a protein fluorescence change[6] with methyl α-isomaltotrioside and higher oligosaccharides, but not with methyl α-D-glucopyranoside or methyl α-isomaltoside. This suggests that the highest affinity subsite is well removed from a perturbable tryptophanyl residue. In the methyl α-trioside that does induce a protein fluorescence change, either the glucoside residue or the glucosyl group — respectively

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the "aglyconic terminus" or the "glyconic terminus" * — could occupy the highest affinity subsite. We decided to first elucidate the possible contribution to hydrogen bonding of the glucopyranoside residue. Thus, the syntheses of the specifically deoxygenated trisaccharides **28**, **29**, and **30** were undertaken.

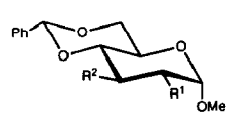
RESULTS AND DISCUSSION

For the synthesis of the trisaccharides **28–30** we used nucleophiles derived from methyl α-D-glucopyranoside deoxygenated at position 2, 3, or 4, and appropriately substituted at the other carbons, except C-6, the position to be condensed with the isomaltosyl donor **21**. Nucleophiles **6**, **14**, and **17** were prepared in the following way. Methyl 6-*O*-benzyl-2,3-di-*O*-benzoyl-α-D-glucopyranoside (**3**), obtained as described[8], was treated with *N*,*N*′-thiocarbonyldiimidazole[9–11] to give the 4-*O*-(imidazol-1-ylthiocarbonyl) derivative **4** in 97% yield. The reaction of the latter with tributyltin hydride gave the expected methyl 6-*O*-benzyl-2,3-di-*O*-benzoyl-4-deoxy-α-D-*xylo*-hexopyranoside (**5**, 52%), and two byproducts. With the aid of NMR spectroscopy, these were identified as methyl 6-*O*-benzyl-2,3-di-*O*-benzoyl-α-D-glucopyranoside (**3**, 9%) and methyl 2,3-di-*O*-benzoyl-4-deoxy-α-D-*xylo*-hexopyranoside (**6**, 12%). When 2,2′-azobis(2-methylpropionitrile)[12] was used in catalytic amounts in the hydride reaction, the deoxygenation of the imidazole derivative **4** was faster (1 h) and gave **5** in a better yield (72%). On debenzylation of **5** the target compound **6** was obtained in an almost quantitative yield.

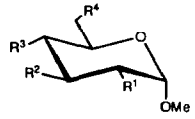
The yield of **6** could be improved using a 4-*O*-(phenoxythiocarbonyl)[13] derivative (**7**) as the substrate for deoxygenation. Compound **7** was prepared from **3** using phenyl chlorothionocarbonate as the reagent. Of the catalyst/acid scavengers (pyridine, 4-dimethylaminopyridine, and *N*-hydroxysuccinimide)[13–15] and solvents (dichloromethane, acetonitrile, toluene) tried for the conversion, the best yield of product **7** (71%) was obtained when the reaction was conducted with *N*-hydroxysuccinimide and pyridine in toluene. Reduction with tributyltin hydride then gave the desired material (**5**) in 91% yield.

Methyl 2-*O*- (**8**) and 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside[18] (**9**) were converted (> 93%) into phenoxythiocarbonyl derivatives **10** and **11**, respectively, as described for the conversion **3** → **7**. The reduction with tributyltin hydride in the presence of 2,2′-azobis(2-methylpropionitrile) smoothly afforded **12** and **13** in yields of > 92%. The opening of the 4,6-*O*-benzylidene ring in **12** and **13** with

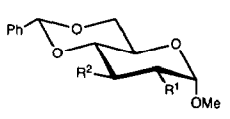
* These terms are used in place of the traditional "nonreducing end" and "reducing end", the latter referring to the terminus that *would* be the reducing end *if* the oligosaccharide were terminated by a hemiacetal glycose unit instead of an alkyl-bearing glycose unit. We consider that terminology fundamentally incorrect, and especially confusing to those not conversant with carbohydrate chemistry. We agree with, and urge adherence to, the rule that in an oligosaccharide such as β-D-Glc*p*NAc-(1 → 3)-β-D-Gal*p*-(1 → 4)-β-D-Glc*p*-1 → OCH_3, for instance, we have a 2-acetamido-2-deoxy-β-D-glucopyranosyl group, a β-D-galactopyranosyl residue and a β-D-glucopyranoside residue, respectively[7].



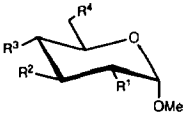
	R^1	R^2
1	OH	OH
2	OBz	OBz



	R^1	R^2	R^3	R^4
3	OBz	OBz	OH	OBn
4	OBz	OBz	Oltc	OBn
5	OBz	OBz	H	OBn
6	OBz	OBz	H	OH
7	OBz	OBz	OPtc	OBn



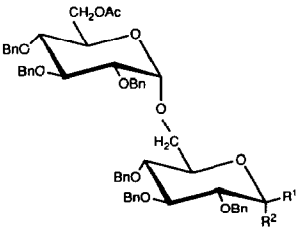
	R^1	R^2
8	OBn	OH
9	OH	OBn
10	OBn	OPtc
11	OPtc	OBn
12	OBn	H
13	H	OBn



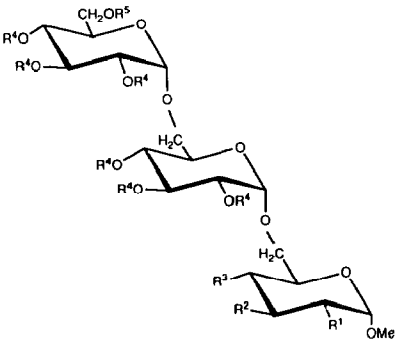
	R^1	R^2	R^3	R^4
14	OBn	H	OBn	OH
15	OBn	H	OAc	OBn
16	OBn	H	OBn	OAc
17	H	OBn	OBn	OH
18	OBn	H	OH	OBn

Itc = imidazol-1-ylthiocarbonyl
Ptc = phenoxythiocarbonyl

borane–trimethylamine complex and aluminium chloride in toluene then afforded methyl 2,4-di-*O*-benzyl-3-deoxy-α-D-*ribo*-hexopyranoside (**14**) and methyl 3,4-di-*O*-benzyl-2-deoxy-α-D-*arabino*-hexopyranoside (**17**), respectively. Opening of the 4,6-



	R^1	R^2
19	H	OMe
20	H, Ac	
21	H	Cl



	R^1	R^2	R^3	R^4	R^5
22	OBz	OBz	H	Bn	Ac
23	OBn	H	OBn	Bn	Ac
24	H	OBn	OBn	Bn	Ac
25	OH	OH	H	Bn	H
26	OBn	H	OBn	Bn	H
27	H	OBn	OBn	Bn	H
28	OH	OH	H	H	H
29	OH	H	OH	H	H
30	H	OH	OH	H	H

benzylidene ring in compound **12** was not regiospecific, and methyl 2,6-di-*O*-benzyl-3-deoxy-α-D-*ribo*-hexopyranoside (**18**) was also formed along with **14**. Separation of these two compounds failed, but the corresponding *O*-acetyl derivatives **15** and **16** could be resolved by column chromatography. Deacetylation of **16** then gave **14** in a final yield of 53%.

Methyl *O*-(6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1 → 6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[17] (**19**) was treated with acetic acid, acetic anhydride, and sulfuric acid to give *O*-(6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1 → 6)-1-*O*-acetyl-2,3,4-tri-*O*-benzyl-α,β-D-glucopyranose (**20**) in 81% yield (α : β 8 : 1). The reaction of **20** with ethereal hydrogen chloride gave the isomaltosyl donor **21** (76%) used for glycosylation reactions with the respective nucleophiles. The condensation of the benzoyl derivative **6** and chloride **21** in ether at −30°, using silver perchlorate as the promoter, gave the trisaccharide **22** in 72% yield. Subsequent deacetylation and debenzylation of **22** gave the target trisaccharide **28**. Similarly, trisaccharide **23** (83%) and **24** (78%) were prepared using chloride **21** and nucleophiles **14** and **17**, respectively. Deblocking then gave the deoxygenated trisaccharides **29** and **30**.

EXPERIMENTAL

General methods.—Melting points were determined on a Kofler hot stage. Optical rotations were measured at 25° 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 F254 (Analtech). Detection was effected by charring with 5% H_2SO_4 in EtOH and, when applicable, with UV light. Preparative chromatography was performed by gradient 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 spectrometers, operating at 300 MHz for protons and 75 MHz for ^{13}C. Chemical shifts (δ) recorded for solutions in $CDCl_3$ and D_2O were measured, respectively, against Me_4Si and MeOH (δ_C 49.0) as internal standards. Proton-signal assignments were done by homonuclear decoupling experiments. The nonequivalent geminal proton resonating at a lower field is denoted H-a and the one resonating at a higher field is denoted H-b. Chemical ionization mass spectra (CIMS) generated with ammonia as the reactive gas were recorded with a Finigan 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 anhydrous sodium sulfate, and concentrated at 2 kPa and 40°. 2,2′-Azobis(2-methylpropionitrile) (99%) from Eastman Kodak Company was used as supplied.

All compounds were pure as judged by TLC and ^1H as well as ^{13}C NMR spectroscopy.

Methyl 2,3-di-O-benzoyl-6-O-benzyl-4-O-(imidazol-1-ylthiocarbonyl)-α-D-gluco-

pyranoside (**4**).—A mixture of methyl 2,3-di-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside[8] (4.43 g, 9 mmol) and *N*,*N*′-thiocarbonyldiimidazole (2.7 g, 14.4 mmol) in toluene (135 mL) was heated under reflux overnight, when the reaction mixture contained only traces of starting material (TLC, 6:1 toluene–acetone). After concentration, chromatography gave 5.89 g (98%) of **4**; $[\alpha]_D$ +74° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.21–6.95 (18 H, 3 Ph, 1 imidazole), 6.20 (m, 2 H, H-3, 4), 5.33 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 9.6 Hz, H-2), 5.24 (d, 1 H, H-1), 4.53 (s, 2 H, PhCH_2), 4.37 (m, 1 H, H-5), 3.74 (dd, 1 H, $J_{5,6a}$ 3.4, $J_{6a,6b}$ 10.7 Hz, H-6a), 3.65 (dd, 1 H, $J_{5,6b}$ 4.4 Hz, H-6b), and 3.49 (s, 3 H, OCH_3); ^{13}C NMR ($CDCl_3$): δ 183.11 (*C*=S), 165.69, 165.64 (Ph*C*O), 97.03 (C-1), 77.70 (C-4), 73.89 (Ph*C*H_2), 71.65 (C-3), 70.41 (C-2), 68.75 (C-6), 68.25 (C-5), and 55.80 (O*C*H_3).

Anal. Calcd for $C_{32}H_{30}O_8N_2S$: C, 63.77; H, 5.02; N, 4.65; S, 5.32. Found: C, 63.65; H, 5.03; N, 4.67; S, 5.37.

Methyl 2,3-di-O-benzoyl-6-O-benzyl-4-deoxy-α-D-xylo-hexopyranoside (**5**).—(*a*) A solution of **4** (1.21 g, 2 mmol) in toluene (40 mL) was added to a refluxing solution of tributyltin hydride (1 mL, 3 mmol) in toluene (100 mL). After 4 h, TLC showed that no starting material was present. After concentration, chromatography (CCl_4–EtOAc) yielded, in order, **5** (0.467 g, 52%), methyl 2,3-di-*O*-benzoyl-6-*O*-benzyl-α-D-glucopyranoside (**3**, 0.076 g, 9%), starting compound **4** (0.103 g), and methyl 2,3-di-*O*-benzoyl-4-deoxy-α-D-*xylo*-hexopyranoside (**6**, 0.108 g, 13%). Compound **5** had $[\alpha]_D$ +136° (*c* 1.4, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.09–7.25 (m, 15 H, 3 Ph), 5.75 (m, 1 H, H-3), 5.29 (dd, 1 H, $J_{1,2}$ 3.6, $J_{2,3}$ 10.2 Hz, H-2), 5.16 (d, 1 H, H-1), 4.61 (s, 2 H, PhCH_2), 4.21–3.44 (m, 3 H, H-5,6a,6b), 3.39 (s, 3 H, OCH_3), 2.36 (ddd, 1 H, $J_{3,4}$ 5.2, $J_{4a,4b}$ 12.6, $J_{4a,5}$ 2.0 Hz, H-4a), and 1.86 (m, 1 H, H-4b); ^{13}C NMR ($CDCl_3$): δ 166.31, 166.05 (Ph*C*O), 98.15 (C-1), 73.74 (Ph*C*H_2), 73.08 (C-3), 72.29 (C-6), 68.97 (C-2), 66.78 (C-5), 55.53 (O*C*H_3), and 33.54 (C-4).

Anal. Calcd for $C_{28}H_{28}O_7$: C, 70.57; H, 5.92. Found: C, 70.34; H, 5.86.

(*b*) To a refluxing solution of **4** (2.194 g, 4.6 mmol) in toluene (50 mL) containing 0.084 g (0.5 mmol) of 2,2′-azobis(2-methylpropionitrile)[11,12], tributyltin hydride (1.83 mL, 6.9 mmol) was added dropwise over 10 min. Concentration followed by chromatography gave compound **5** in 72% yield.

(*c*) Tributyltin hydride (0.084 mL, 0.315 mmol), and 2,2′-azobis(2-methylpropionitrile) (0.004 g, 0.023 mmol) were added to a solution of phenoxythiocarbonyl derivative **7** (see below) in toluene (8 mL), and the mixture was stirred for 1 h at 110°. Chromatography (15:1 toluene–EtOAc) gave 0.94 g (91%) of **5**.

Methyl 2,3-di-O-benzoyl-4-deoxy-α-D-xylo-hexopyranoside (**6**).—A solution of **5** (0.447 g, 0.94 mmol) in MeOH was stirred under an H_2 atmosphere, in the presence of 5% Pd–C catalyst (0.08 g) for 5 h. The reaction mixture was processed conventionally, and the crude product was chromatographed (6:1 toluene–EtOAc) to give **6**, $[\alpha]_D$ +165.7° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 8.02–7.26 (m, 10 H, Ph), 5.77 (m, 1 H, H-3), 5.26 (dd, 1 H, $J_{1,2}$ 3.5, $J_{2,3}$ 10.1 Hz, H-2), 5.16 (d, 1 H, H-1), 4.14–4.07 (m, 1 H, H-5), 3.78–3.47 (m, 2 H, H-6a,b), 3.43 (s, 3 H, OCH_3), 2.31 (m, 2 H, H-4a, O*H*), and 1.86 (m, 1 H, H-4b); ^{13}C NMR ($CDCl_3$): δ 166.11,

165.82 (PhCO), 97.87 (C-1), 72.84 (C-3), 68.51 (C-2), 67.77 (C-5), 64.86 (C-6), 55.28 (OCH_3), and 32.41 (C-4).

Anal. Calcd for $C_{21}H_{22}O_7$: C, 65.28; H, 5.74. Found: C, 65.17; H, 5.77.

Methyl 2,3-di-O-benzoyl-6-O-benzyl-4-O-(phenoxythiocarbonyl)-α-D-glucopyranoside (**7**).—To a solution of **3** (0.492 g, 1 mmol) in toluene (6 mL) was added *N*-hydroxysuccinimide (0.075 g, 0.65 mmol), pyridine (0.1 mL, 1.2 mmol), and phenylchlorothionocarbonate[16] (0.2 mL, 1.1 mmol). The mixture was stirred for 14 h at 80° while six fresh portions of pyridine and phenylchlorothionocarbonate (original amounts) were added. The reaction mixture was concentrated, taken up in CH_2Cl_2–water, extracted with N HCl, satd $NaHCO_3$ solution, and water, dried, and concentrated. Chromatography (15 : 1 CCl_4–EtOAc) gave **7** (0.450 g, 72%), mp 135–136° (from MeOH); $[\alpha]_D$ +143° (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 8.03–7.18 (m, 20 H, 4 Ph), 5.30 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 9.9 Hz, H-2), 5.24 (d, 1 H, H-1), 4.27 (ddd, 1 H, $J_{4,5}$ 7.5, $J_{5,6a}$ 2.9, $J_{5,6b}$ 4.5 Hz, H-5), 3.80 (dd, 1 H, $J_{6a,6b}$ 10.9 Hz, H-6a), and 3.72 (dd, 1 H, H-6b); ^{13}C NMR ($CDCl_3$): δ 194.20 (PhO*C*S), 165.69, 165.50 (Ph*C*O), 97.05 (C-1), 78.56 (C-4), 73.87 (Ph*C*H_2), 71.88 (C-3), 70.85 (C-2), 68.65 (C-6), 68.47 (C-5), and 55.68 (O*C*H_3).

Anal. Calcd for $C_{35}H_{32}O_9S$: C, 66.86; H, 5.13; S, 5.10. Found: C, 66.93; H, 5.10; S, 4.82.

Methyl 3-O-benzyl-4,6-O-benzylidene-2-O-(phenoxythiocarbonyl)-α-D-glucopyranoside (**11**).—Methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (0.372 g, 1 mmol)[18] was dissolved in toluene (6 mL) and *N*-hydroxysuccinimide (0.074 g, 0.64 mmol), pyridine (0.3 mL, 3.6 mmol), and phenylchlorothionocarbonate (0.6 mL, 3.3 mL) were added. The reaction mixture was stirred for 15 min at 80°, when no starting material remained. After the usual workup and chromatography (CCl_4–EtOAc), compound **11** (0.485 g, 95.5%) was obtained; $[\alpha]_D$ −4.9° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.52–7.07 (m, 15 H, 3 Ph), 5.60 (s, 1 H, PhC*H*), 5.46 (dd, 1 H, $J_{1,2}$ 3.8, $J_{2,3}$ 9.7 Hz, H-2), 5.19 (d, 1 H, H-1), 4.90 (d, 1 H, PhCH_2), 4.76 (d, 1 H, PhCH_2), and 4.23 (m, 1 H, H-3); ^{13}C NMR ($CDCl_3$): δ 194.80 (PhO*C*S), 101.48 (Ph*C*H), 96.89 (C-1), 81.93 (C-4), 81.64 (C-2), 76.30 (C-3), 74.99 (Ph*C*H_2), 68.93 (C-6), 62.50 (C-5), and 55.47 (O*C*H_3).

Anal. Calcd for $C_{28}H_{28}O_7S$: C, 66.12; H, 5.55; S, 6.30. Found: C, 66.13; H, 5.55; S, 6.25.

Methyl 2-O-benzyl-4,6-O-benzylidene-3-O-(phenoxythiocarbonyl)-α-D-glucopyranoside (**10**).—To a solution of **8** (0.372 g, 1 mmol)[18] in toluene (6 mL) was added *N*-hydroxysuccinimide (0.07 g, 20%), pyridine (0.3 mL, 3.6 mmol), and phenylchlorothionocarbonate (0.6 mL, 3.3 mmol), and the reaction mixture was stirred for 1 h at 80°. After processing, as described for the preparation of **7**, crystallization from MeOH gave **10** (0.474 g, 93%), mp 96–97.5°; $[\alpha]_D$ −3.3° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.50–7.01 (m, 15 H, 3 Ph), 5.53 (s, 1 H, PhC*H*), 5.84 (m, 1 H, H-3), 4.75 (2 H, PhCH_2), 4.73 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.30 (dd, 1 H, $J_{5,6a}$ 4.9, $J_{6a,6b}$ 10.1 Hz, H-6a), 3.94 (m, 1 H, H-5), and 3.75 (m, 3 H, H-2,4,6b); ^{13}C

NMR ($CDCl_3$): δ 194.40 (PhO*C*S), 101.51 (Ph*C*H), 98.91 (C-1), 80.54 (C-4), 79.51 (C-2), 77.65 (C-3), 73.26 (Ph*C*H_2), 68.93 (C-6), 62.29 (C-5), and 55.47 (O*C*H_3).

Anal. Calcd for $C_{28}H_{28}O_7S$: C, 66.12; H, 5.55; S, 6.30. Found: C, 66.04; H, 5.55; S, 6.35.

*Methyl 3-O-benzyl-4,6-O-benzylidene-2-deoxy-α-*D-arabino-*hexopyranoside* (**13**).—A mixture of the 2-phenoxythiocarbonyl derivative **11** (7.2 g, 14 mmol), 2,2′-azobis(2-methylpropionitrile) (1.8 g, 3.55 mmol), and tributyltin hydride (6.6 mL, 24.85 mmol) in toluene (250 mL) was stirred for 1.5 h at 110°. Since a small amount of the starting material **11** remained, further portions of 2,2′-azobis(2-methylpropionitrile) (0.056 g, 0.11 mmol) and tributyltin hydride (0.93 mL, 3.5 mL) were added. After 30 min at 110° the reaction was complete, and after workup chromatography gave 4.62 g (94%) of compound **13**, mp 105.5–106° (from MeOH); $[\alpha]_D$ +73.8° (*c* 0.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.52–7.19 (m, 10 H, 2 Ph), 5.62 (s, 1 H, PhC*H*), 4.82 (d, 1 H, PhCH_2), 4.79 (br d, 1 H, H-1), 4.67 (d, 1 H, PhCH_2), 4.26 (dd, 1 H, $J_{5,6a}$ 3.0, $J_{6a,6b}$ 9.0 Hz, H-6a), 4.04–3.97 (m, 1 H, H-3), 3.82–3.77 (m, 2 H, H-5,6b), 3.69 (m, 1 H, H-4), 2.26 (ddd, 1 H, $J_{1,2a}$ 0.8, $J_{2a,3}$ 5.2, $J_{2a,2b}$ 13.3 Hz, H-2a), and 1.79 (m, 1 H, H-2b); ^{13}C NMR ($CDCl_3$): δ 101.41 (Ph*C*H), 99.09 (C-1), 83.83 (C-4), 72.85 (2 C, C-3, Ph*C*H_2), 69.13 (C-6), 62.88 (C-5), 54.67 (O*C*H_3), and 36.41 (C-2).

Anal. Calcd for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79. Found: C, 70.53; H, 6.72.

*Methyl 2-O-benzyl-4,6-O-benzylidene-3-deoxy-α-*D-ribo-*hexopyranoside* (**12**).—2,2′-Azobis(2-methylpropionitrile) (0.004 g, 0.02 mmol) and tributyltin hydride (0.084 mL, 0.35 mmol) were added to a solution of the 3-*O*-(phenoxythiocarbonyl)derivative **10** (0.101 g, 0.20 mmol) in toluene (8 mL), and the resulting mixture was stirred for 2.5 h at 110°. Further portions of 2,2′-azobis(2-methylpropionitrile) (0.005 g, 0.03 mmol) and tributyltin hydride (0.028 mL, 0.117 mmol) were added, and heating and stirring were continued for 1.5 h. The reaction mixture was concentrated, and chromatography (15:1 toluene–EtOAc) gave the 3-deoxy derivative **12** (0.064 g, 94%), mp 107–107.5° (from MeOH); $[\alpha]_D$ +23° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.49–7.25 (m, 10 H, 2 Ph), 5.49 (s, 1 H, PhC*H*), 4.68 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.62 (dd, 2 H, PhCH_2), 4.24 (dd, 1 H, $J_{5,6a}$ 4.5, $J_{6a,6b}$ 9.9 Hz, H-6a), 3.81–3.73 (m, 1 H, H-5), 3.69–3.47 (m, 3 H, H-6b,2,4), 3.45 (s, 3 H, O*C*H_3), 2.31–2.24 (m, 1 H, H-3a), and 2.11–1.99 (m, 1 H, H-3b); ^{13}C NMR ($CDCl_3$): δ 101.78 (Ph*C*H), 98.02 (C-1), 76.72 (C-4), 73.91 (C-2), 71.03 (Ph*C*H_2), 69.39 (C-6), 63.94 (C-5), 55.06 (O*C*H_3), and 30.11 (C-3).

Anal. Calcd for $C_{21}H_{24}O_5$: C, 70.77; H, 6.79. Found: C, 70.85; H, 6.86.

*Methyl 3,4-di-O-benzyl-2-deoxy-α-*D-arabino-*hexopyranoside* (**17**).—Borane–trimethylamine complex (1.44 g, 20 mmol) and molecular sieves 4A (2.4 g) were added to a solution of benzylidene derivative **13** (0.71 g, 2 mmol) in toluene (30 mL). The mixture was stirred for 30 min and cooled to 0°, and aluminium chloride (1.06 g, 8 mmol) was added portionwise over 1 h. When the reaction was complete (TLC, 3:1 toluene–EtOAc), M H_2SO_4 (100 mL) was added, and the mixture was stirred for 30 min. It was extracted with satd aq $NaHCO_3$ and water, dried,

concentrated, and chromatographed (4:1 → 3:1 toluene–EtOAc). Compound **17** (0.45 g, 63%) was obtained as an oil, $[\alpha]_D$ +84° (*c* 0.7, $CHCl_3$); ^1H NMR (CD_3COCD_3): δ 4.92 (d, 1 H, PhCH_2), 4.77 (br d, 1 H, H-1), 4.69 (d, 2 H, PhCH_2), 4.61 (d, 1 H, PhCH_2), 3.88 (ddd, 1 H, $J_{2a,3}$ 5.1, $J_{2b,3}$ 11.5, $J_{3,4}$ 8.1 Hz, H-3), 3.79–3.67 (m, 2 H, H-5,6a), 3.58–3.44 (m, 2 H, H-4,6b), 3.26 (s, 3 H, OCH_3), 2.27 (ddd, 1 H, $J_{1,2a}$ 1.4, $J_{2a,2b}$ 12.9 Hz, H-2a), and 1.56 (ddd, 1 H, $J_{1,2b}$ 3.7 Hz, H-2b); ^{13}C NMR ($CDCl_3$): δ 98.56 (C-1), 78.37 (C-3), 74.92 (C-4), 71.77 (C-5), 71.78, 71.18 (2 PhCH_2), 62.42 (C-6), 54.61 (OCH_3), and 35.54 (C-2).

Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.30; H, 7.32.

*Methyl 2,4-di-O-benzyl-3-deoxy-α-*D-ribo-*hexopyranoside* (**14**).—To a solution of **12** (0.676 g, 1.9 mmol) in toluene (30 mL) were added borane–trimethylamine complex (1.38 g, 18.9 mmol) and molecular sieves 4A (2.4 g). The mixture was stirred for 30 min, then cooled to 0°, and aluminium chloride (1.01 g, 7.6 mmol) was added portionwise over 1 h. TLC (5:1 toluene–EtOAc) showed that no starting material remained, and the mixture was worked up as described for the preparation of compound **17**. Chromatography gave a main fraction (0.491 g, 72%) shown by NMR analysis to be a mixture of two components. It was treated overnight with pyridine (10 mL) and acetic anhydride (4 mL) and, after the usual workup and chromatography (CCl_4–EtOAc), methyl 4-*O*-acetyl-2,6-di-*O*-benzyl-3-deoxy-α-D-*ribo*-hexopyranoside (**15**) (0.059 g, 11%) was obtained; ^1H NMR ($CDCl_3$): δ 7.25–7.16 (m, 10 H, 2 Ph), 4.75 (m, 1 H, H-4), 4.61 (d, 1 H, $J_{1,2}$ 3.4 Hz, H-1), 4.55, 4.53, 4.44, 4.36 (4 d, 4 H, PhCH_2), 3.70 (m, 1 H, H-5), 3.51 (dddd, 1 H, $J_{2,3a}$ 4.6, $J_{2,3b}$ 8.1 Hz, H-2), 3.42 (m, 2 H, H-6a,6b), 3.35 (s, 3 H OCH_3), 2.26 (m, 1 H, H-3a), 1.82 (s, 3 H, CH_3CO), and 1.77 (m, 1 H, H-3b); ^{13}C NMR ($CDCl_3$): δ 169.69 (CH_3CO), 97.36 (C-1), 73.39 (PhCH_2), 73.26 (C-2), 71.17 (PhCH_2), 69.07 (C-5), 68.49 (C-6), 66.92 (C-4), 55.06 (OCH_3), 29.82 (C-3), and 20.90 (CH_3CO).

Continued elution gave methyl 6-*O*-acetyl-2,4-di-*O*-benzyl-3-deoxy-α-D-*ribo*-hexopyranoside (**16**, 0.429 g, 78%); ^1H NMR ($CDCl_3$): δ 7.26–7.15 (m, 10 H, 2 Ph), 4.57 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 4.51 (d, 1 H, PhCH_2), 4.49 (2 d, 2 H, PhCH_2), 4.30 (1 H, PhCH_2), 4.17 (m, 2 H, H-6a,6b), 3.69 (m, 1 H, H-5), 3.41 (m, 1 H, H-2), 3.31 (s, 3 H, OCH_3), 3.26 (m, 1 H, H-4), 2.27 (m, 1 H, H-3a). 1.91 (s, 3 H, CH_3CO), and 1.77 (m, 1 H, H-3b); ^{13}C NMR ($CDCl_3$): δ 170.71 (CH_3CO), 97.12 (C-1), 73.71 (C-2), 71.70 (C-4), 71.14 (PhCH_2), 70.43 (PhCH_2), 69.08 (C-5), 63.44 (C-6), 54.86 (OCH_3), 29.88 (C-3), and 20.77 (CH_3CO). Compound **16** was deacetylated (Zemplén) to give the title compound **14** (0.359 g, 53%), $[\alpha]_D$ +92.9° (*c* 1.2, $CHCl_3$); ^1H NMR (CD_3COCD_3): δ 4.72 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 4.60 (s, 2 H, PhCH_2), 4.59 (dd, 2 H, PhCH_2), 3.78 (m, 1 H, H-5), 3.62 (dd, 1 H, $J_{5,6a}$ 4.6, $J_{6a,6b}$ 11.6 Hz, H-6a), 3.56–3.37 (m, 3 H, H-6b,4,2), 3.36 (s, 3 H, OCH_3), 2.42 (m, 1 H, H-3a), and 1.76 (m, 1 H, H-3b); ^{13}C NMR ($CDCl_3$): δ 97.22 (C-1), 73.94 (C-2), 72.42 (C-4), 71.12 (C-5), 70.97, 70.68 (2 PhCH_2), 62.44 (C-6), 54.91 (OCH_3), and 29.85 (C-3).

Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.11; H, 7.30. Deacetylation of **15** gave methyl 2,6-di-*O*-benzyl-3-deoxy-α-D-*ribo*-hexopyranoside (**18**); ^1H NMR ($CDCl_3$): δ 7.29–7.16 (m, 10 H, 2 Ph), 4.55 (d, 1 H, $J_{1,2}$ 3.4 Hz,

H-1), 4.49 (dd, 2 H, PhCH_2), 4.46 (d, 2 H, PhCH_2), 3.65–3.56 (m, 1 H, H-5), 3.53–3.49 (m, 3 H, H-4,6a,6b), 3.42 (ddd, 1 H, $J_{2,3a}$ 4.5, $J_{2,3b}$ 7.9 Hz, H-2), 2.14–2.07 (m, 1 H, H-3a), and 1.82–1.70 (m, 1 H, H-3b); ^{13}C NMR ($CDCl_3$): δ 97.22 (C-1), 73.77 (PhCH_2), 73.64 (C-2), 71.02 (C-6, PhCH_2), 70.34 (C-5), 67.90 (C-4), 55.00 (OCH_3), and 32.72 (C-3).

O-*(6-O-Acetyl-2,3,4-tri-O-benzyl-α-D-glucopyranosyl)-(1 → 6)-1-O-acetyl-2,3,4-tri-O-benzyl-α,β-D-glucopyranose* (**20**).—Methyl *O*-(6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1 → 6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (**19**) (ref. 17) (3.864 g, 4 mmol) was dissolved in a mixture of acetic anhydride (26.4 mL), acetic acid (8.8 mL), and H_2SO_4 (0.032 mL). After 30 min, when no starting material was present, sodium acetate trihydrate (0.9 g) was added and the mixture was concentrated to dryness by azeotropic distillation with toluene. The residue was swirled with CH_2Cl_2, dried with anhyd sodium sulfate, and filtered, and the filtrate was concentrated. Chromatography (4:1 CCl_4–acetone) gave 3.22 g (81%) of sirupy **20** (α:β 8:1), ^{1}H NMR (α anomer, $CDCl_3$): δ 6.27 (δ, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 2.1 (s, 3 H, CH_3CO), and 1.97 (s, 3 H, CH_3CO); ^{13}C NMR (α anomer, $CDCl_3$): δ 170.65, 169.41 (2 CH_3CO), 97.34 (C-1′), 89.87 (C-1), 81.67, 81.58 (C-3, C-3′), 80.08, 79.21 (C-2, C-2′), 77.25, 76.85 (C-4, C-4′), 75.61, 75.27, 74.91, 73.27 (5 C, PhCH_2), 73.06 (C-5), 72.17 (PhCH_2), 68.82 (C-5′), 65.78 (C-6), 63.02 (C-6′), and 20.79 (CH_3CO); CIMS: *m/z* 984 ([M + NH_4]$^+$).

Anal. Calcd for $C_{58}H_{62}O_{13}$: C, 72.03; H, 6.46. Found C, 72.14; H, 6.49.

Methyl O-(6-O-acetyl-2,3,4-tri-O-benzyl-α-D-glucopyranosyl)-(1 → 6)-O-(2,3,4-tri-O-benzyl-α-D-glucopyranosyl)-(1 → 6)-2,3-di-O-benzoyl-4-deoxy-α-D-xylo-hexopyranoside (**22**).—To a solution of **20** (1.44 g, 1.49 mmol) in ether (5 mL) ethereal hydrogen chloride (0.2 g/ml, 4.5 mL) was added. After 48 h at room temperature, when no starting material remained, chromatography (15:1 CCl_4–acetone) gave *O*-(6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl)-(1 → 6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranosyl chloride (**21**, 1.11 g, 76%); ^{1}H NMR ($CDCl_3$): δ 5.98 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), and 1.96 (s, 3 H, CH_3CO); ^{13}C NMR ($CDCl_3$): δ 170.59 (CH_3CO), 97.08 (C-1′), 93.28 (C-1), 81.61, 81.33 (C-3′, C-3), 80.16, 79.98 (C-2′, C-2), 77.30, 76.49 (C-4, C-4′), 75.79, 75.59, 75.18, 74.95, 73.40 (PhCH_2), 72.95 (C-5), 72.24 (PhCH_2), 68.90 (C-5′), 65.65 (C-6), 63.01 (C-6′), and 20.75 (CH_3CO).

To a solution of **6** (0.15 g, 0.388 mmol), chloride **21** (0.5 g, 0.53 mmol), and 2,4,6-trimethylpyridine (0.08 mL) in ether (5 mL) was added with stirring at −30° 0.08 M ethereal silver perchlorate (8 mL). After 10 min, TLC (5:1 CCl_4–acetone) indicated the absence of **6**. The mixture was filtered, the filtrate was concentrated and diluted with CH_2Cl_2, washed with aq sodium thiosulfate and water, dried, concentrated, and chromatographed (10:1 toluene–EtOAc) to give 0.363 g (72%) of **22**, $[\alpha]_D$ +97° (*c* 0.7, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 170.64 (CH_3CO), 166.07, 165.79 (2 PhCO), 97.75, 97.04 (2 C) (C-1, C-1′, C-1″), 81.87, 81.71 (C-3′, C-3″), 80.38, 80.15 (C-2′, C-2″), 77.72, 77.30 (C-4′, C-4″), 75.56, 74.93, 73.03 (5 C, PhCH_2), 72.93 (C-3), 72.34 (PhCH_2), 70.75 (C-2), 69.19 (C-6), 68.81, 68.60 (C-5′,

C-5″), 66.40 (C-5), 65.93 (C-6′), 63.09 (C-6″), 55.32 (O*C*H$_3$), 33.28 (C-4), and 20.80 (*C*H$_3$CO): CIMS: *m/z* 1310 ([M + NH$_4$]$^+$).

Anal. Calcd for $C_{77}H_{80}O_{18}$: C, 71.50; H, 6.23. Found: C, 71.54; H, 6.27.

Methyl O-*(6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1 → 6)-*O*-(2,3,4-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1 → 6)-2,4-di-*O*-benzyl-3-deoxy-α-*D*-ribo-hexopyranoside* (**23**).—A solution of **14** (0.14 g, 0.4 mmol) and glycosyl chloride **21** (0.5 g, 0.53 mmol) in ether (5 mL) was treated with silver perchlorate and 2,4,6-trimethylpyridine, as described for the preparation of **22**, to give sirupy **23** (0.405 g, 83%), $[\alpha]_D$ +64.6° (*c* 1.2, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 170.67 (CH$_3$*C*O), 97.03 (2 C), 96.90 (C-1, C-1′, C-1″), 81.79, 81.65 (C-3′, C-3″), 80.47, 80.16 (C-2′, C-2″), 77.68, 77.24 (C-4′, C-4″), 75.56, 75.46, 74.95 (4 C, Ph*C*H$_2$), 74.19 (C-2), 72.32, 72.21 (2 C, Ph*C*H$_2$), 71.80 (C-4), 71.08, 70.74 (2 C, Ph*C*H$_2$), 70.96, 70.63 (C-5, C-5′), 68.77 (C-5″), 65.95, 65.80 (C-6, C-6′), 63.08 (C-6″), 54.44 (O*C*H$_3$), 30.22 (C-3), and 20.81 (*C*H$_3$CO); CIMS: *m/z* 1282 ([M + NH$_4$]$^+$).

Anal. Calcd for $C_{77}H_{84}O_{16}$: C, 73.08; H, 6.69. Found: C, 73.24; H, 6.76.

Methyl O-*(6-*O*-acetyl-2,3,4-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1 → 6)-*O*-(2,3,4-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1 → 6)-3,4-di-*O*-benzyl-2-deoxy-α-*D*-arabino-hexopyranoside* (**24**).—A solution of **17** (0.14 g, 0.4 mmol) and glycosyl chloride **21** (0.5 g, 0.53 mmol) in ether (5 mL) was treated with silver perchlorate, as described for the preparation of **22**, to afford **24** (0.38 g, 78%), $[\alpha]_D$ +85.6° (*c* 1.0, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 170.93 (CH$_3$*C*O), 98.60, 97.34 (2 C) (C-1, C-1′, C-1″), 81.96 (2 C, C-3′, C-3″), 80.75, 80.42 (C-2′, C-2″), 78.66, 77.92, 77.58 (4 C, C-3, C-4, C-4′, C-4″), 75.83, 75.73, 75.16, 72.76, 72.47, 71.96 (8 C, Ph*C*H$_2$), 71.31, 70.95 (C-5, C-5′), 69.02 (C-5″), 66.61, 66.10 (C-6, C-6′), 63.36 (C-6″), 54.84 (O*C*H$_3$), 35.75 (C-2), and 21.07 (*C*H$_3$CO); CIMS: *m/z* 1282 ([M + NH$_4$]$^+$).

Anal. Calcd for $C_{77}H_{84}O_{16}$: C, 73.08; H, 6.69. Found: C, 72.83; H, 6.64.

Methyl O-*(2,3,4-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1 → 6)-*O*-(2,3,4-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1 → 6)-4-deoxy-α-*D*-xylo-hexopyranoside* (**25**).—To a solution of **22** (0.25 g) in toluene (2 mL) and MeOH (5 mL) was added M methanolic NaOMe until the solution was strongly alkaline. After 3.5 h the mixture was neutralized with Amberlite IR 120 (H$^+$) resin. Chromatography (15:1 CH_2Cl_2–MeOH) gave **25** (0.185 g, 92%), $[\alpha]_D$ +94.5° (*c* 0.5, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 99.7 (C-1), 97.25, 97.08 (C-1′, C-1″), 81.98 (C-3′), 81.67 (C-3″), 80.40 (C-2′), 80.33 (C-2″), 77.86, 77.71 (C-4′, C-4″), 75.61, 75.01, 73.11 72.47 (6 C, Ph*C*H$_2$), 74.50 (C-3), 70.98 (C-2), 70.79 (C-5), 69.92 (C-6), 69.10, 67.23 (C-5′, C-5″), 66.22 (C-6′), 62.04 (C-6″), 55.38 (O*C*H$_3$), and 34.81 (C-4).

Anal. Calcd for $C_{61}H_{70}O_{15}$: C, 70.23; H, 6.76. Found: C, 70.33; H, 6.76.

Methyl O-*(2,3,4-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1 → 6)-*O*-(2,3,4-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1 → 6)-2,4-di-*O*-benzyl-3-deoxy-α-*D*-ribo-hexopyranoside* (**26**).—Compound **23** (0.26 g) was deacetylated, as described for the preparation of trisaccharide **25**, to give 0.231 g (92%) of **26**, $[\alpha]_D$ +81.9 (*c* 0.8, $CHCl_3$); ^{13}C NMR ($CDCl_3$): 97.06 (2 C), 96.98 (C-1, C-1′, C-1″), 81.78, 81.53 (C-3′, C-3″), 80.47, 80.27 (C-2′, C-2″), 77.60, 77.35 (C-4′, C-4″), 74.16 (2 C), 75.46, 74.96, 72.37, 72.28, 71.10,

70.67 (8 C, PhCH$_2$), 71.81 (C-4), 70.89 (2 C, C-5′, C-5″), 70.61 (C-5), 66.00, 65.80 (C-6, C-6′), 61.97 (C-6″), 54.87 (OCH$_3$), and 30.19 (C-3).

Anal. Calcd for $C_{75}H_{82}O_{15}$: C, 73.63; H, 6.76. Found: C, 73.46; H, 6.81.

Methyl O-*(2,3,4-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1 → 6)-*O*-(2,3,4-tri-*O*-benzyl-α-*D*-glucopyranosyl)-(1 → 6)-3,4-di-*O*-benzyl-2-deoxy-α-*D*-*arabino*-hexopyranoside* (**27**).—Trisaccharide **24** (0.110 g) was deacetylated, as described for the preparation of **25**, to give (0.13 g, 90%) of **27**, $[\alpha]_D$ +93.4° (*c* 0.9, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 98.34, 97.13 (2 C) (C-1, C-1′, C-1″), 81.73, 81.57 (C-3′, C-3″), 80.50, 80.29 (C-2′, C-2″), 78.41, 77.66, 77.54 (4 C, C-3, C-4, C-4′, C-4″), 75.50, 74.98, 74.89, 72.54, 72.30, 71.71 (8 C, PhCH$_2$), 71.01, 70.92, 70.70 (C-5, C-5′, C-5″), 66.45, 65.86 (C-6, C-6′), 61.99 (C-6″), 54.59 (OCH$_3$), and 35.48 (C-2).

Anal. Calcd for $C_{75}H_{82}O_{15}$: C, 73.63; H, 6.76. Found: C, 73.57; H, 6.77.

Deprotection of **25** *to methyl* O-α-*D*-*glucopyranosyl-(1 → 6)*-O-α-*D*-*glucopyranosyl-(1 → 6)-4-deoxy-α-*D*-xylo-*hexopyranoside* (**28**).—A solution of compound **25** (0.15 g, 0.123 mmol) in 95% EtOH containing 5% Pd–C catalyst (0.15 g) was stirred under H_2 overnight. After conventional processing the crude product was chromatographed (2:1:1 2-propanol–EtOAc–water), passed through a column of Biogel P-2 (200–400 mesh, 10% EtOH in water), and lyophilized to yield amorphous, hygroscopic **28** (51 mg, 83%). In neither the ^1H nor the ^{13}C NMR spectrum were signals observed that indicated the presence of aromatic residues. ^{13}C NMR (D_2O): δ 100.03 (C-1), 97.93, 97.85 (C-1′, C-1″), 73.43, 73.21 (C-3′, C-3″), 72.98, 71.93, 71.57, 71.45, 70.44, 67.38, 67.05 (C-2, C-2′, C-2″, C-3, C-5, C-5′, C-5″), 69.59 (2 C, C-4′, C-4″), 69.10 (C-6), 65.54 (C-6′), 60.59 (C-6″), 55.22 (OCH$_3$), and 34.36 (C-4).

Deprotection of **26** *to methyl* O-α-*D*-*glucopyranosyl-(1 → 6)*-O-α-*D*-*glucopyranosyl-(1 → 6)-3-deoxy-α-*D*-ribo-*hexopyranoside* (**29**).—The benzyl derivative **26** (0.05 g, 0.04 mmol) was hydrogenolyzed and purified as described for the preparation of **28**, and lyophilized to give amorphous, hygroscopic **29** (17.7 mg, 86%), whose ^1H and ^{13}C NMR spectra also failed to reveal any aromatic residues. ^{13}C NMR (D_2O): δ 98.4 (C-1), 97.87, 97.79 (C-1′, C-1″), 73.44, 73.17 (C-3′, C-3″), 71.91, 71.58, 71.49, 70.9, 70.31, 66.31, 65.67, 65.59, 64.02 (C-2, C-2′, C-2″, C-4, C-5, C-5′, C-5″, C-6, C-6″), 69.58 (2 C, C-4′, C-4″), 60.57 (C-6″), 55.05 (OCH$_3$), and 34.93 (C-3).

Deprotection of **27** *to methyl* O-α-*D*-*glucopyranosyl-(1 → 6)*-O-α-*D*-*glucopyranosyl-(1 → 6)-2-deoxy-α-*D*-arabino-*hexopyranoside* (**30**).—Compound **27** (0.06 g, 0.05 mmol) was debenzylated and purified as described for trisaccharide **28**, and lyophilized to give amorphous, hygroscopic **30** (22 mg, 88%), whose ^1H and ^{13}C NMR spectra failed to show any aromatic impurities. ^{13}C NMR (D_2O): δ 98.45 (C-1), 97.87, 97.79 (C-1′, C-1″), 73.44, 73.14 (C-3′, C-3″), 71.91, 71.57, 71.5, 70.97, 70.54, 70.33, 68.62 (C-2′, C-2″, C-3, C-4, C-5, C-5′, C-5″), 69.60 (2 C, C-4′, C-4″), 65.78 (C-6′), 65.63 (C-6), 60.57 (C-6″), 54.66 (OCH$_3$), and 36.75 (C-2).

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