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Note

Synthesis of a tri- and a tetradeoxy analogue of methyl 3,6-di-*O*-α-D-mannopyranosyl-α-D-mannopyranoside for investigation of the binding site of various plant lectins

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Abstract

The synthesis of the 2,4,3′-trideoxy and 2,4,3′,4′-tetradeoxy analogues of the trimannoside part of the core structure of N-linked glycoproteins, methyl 3,6-di-*O*-α-D-mannopyranosyl-α-D-mannopyranoside, is described. A 2,4-dideoxy (1→6)-linked disaccharide was used as a common intermediate acceptor, which was coupled with a 3-deoxy and a 3,4-dideoxy benzochlorosugar donor, the latter prepared from methyl α-D-mannopyranoside in five steps. Despite the acid-sensitive donors and acceptor, acceptable glycosylation yields were obtained of both the trideoxy- and the tetradeoxy trisaccharide using silver triflate as a promoter (65 and 51%, respectively). Deprotection in one step then gave the target products.

Keywords: Deoxysugars; Oligosaccharide synthesis; N-Linked glycoproteins; Concanavalin A

The branched core trisaccharide of N-linked glycoproteins, 3,6-di-*O*-α-D-mannopyranosyl-D-mannopyranose, binds selectively to a number of legume lectins, i.e., the well-known jack bean lectin Concanavalin A (Con A) [1]. To investigate these bindings on a molecular level all the possible monodeoxy derivatives of the methyl α-glycoside of the core trisaccharide were synthesised [2]. Results from binding studies of these with Con A showed that apart from the 3, 4 and 6-hydroxyl groups of the 6-substituted mannose, which binds to the lectin in the ''monosaccharide binding site'', additional binding was found to the 2- and 4-hydroxyl groups of the central mannose unit and the 3- and 4-hydroxyl groups of the 3-substituted mannose. Synthesis and binding studies of the 2,3′- and the 4,3′-dideoxy derivatives corroborated these findings [2–4]. To even further look into this binding the 2,4,3′-trideoxy and the 2,4,3′,4′-tetradeoxy analogues would be an asset. The synthesis of these derivatives is described in this article and isothermal titration microcalorimetry (ITC) measurements of their binding to ConA has been performed to give a very detailed picture of this carbohydrate-protein interaction [4]. The thermodynamic solution data also agrees well with the

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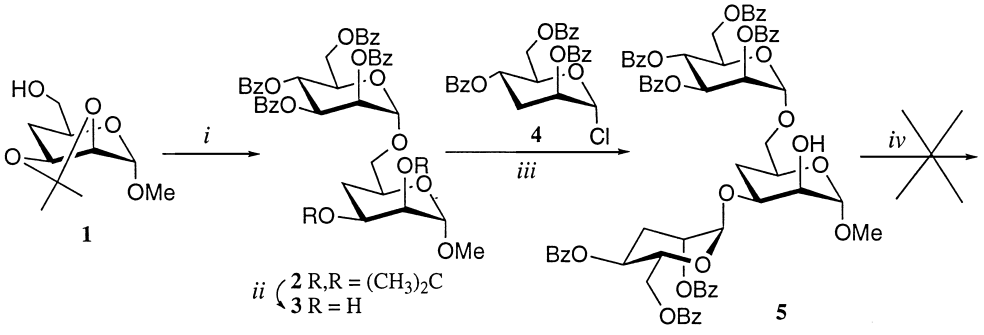
recent X-ray crystal structure of ConA complexed with the trimannoside [5].

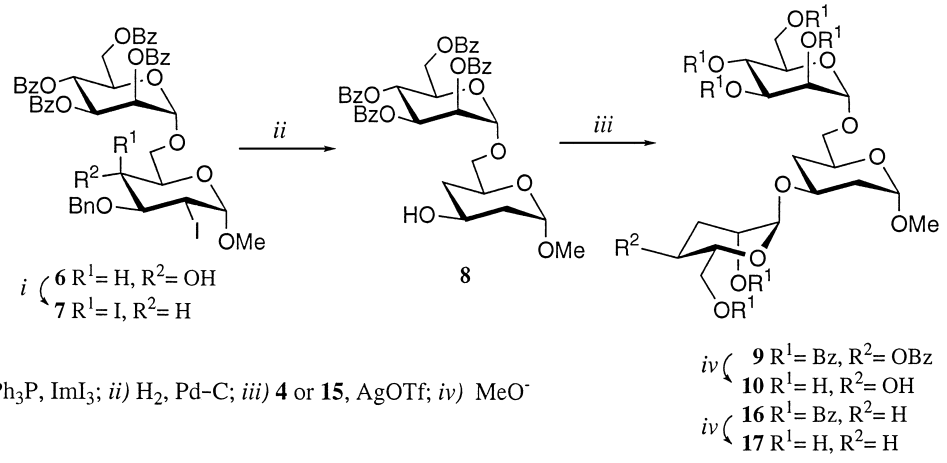
Although a 2-deoxy acceptor had been used with success in the earlier synthesis of the 2,3′-dideoxy analogue [2], the supposed further enhanced acid lability of 2,4-dideoxy glycosides [6] made us first try different pathways to the target structures in which the deoxy functions on the central moiety were planned to be introduced as late as possible and preferably at the trisaccharide level after glycosylations with their acidic conditions. However, all these attempts failed since the deoxygenation of the various selectively protected trisaccharide structures proved not to be possible. For example, the 2-hydroxyl group in trisaccharide **5**, constructed from the known 4-deoxy monosaccharide precursor **1** [7] by two subsequent glycosylations using halide donors and silver trifluoromethanesulfonate (triflate) promotion (Scheme 1), proved to be inert both to treatment with triphenylphosphine-triiodoimidazole [8] and thiocarbonyldiimidazole [9]. Hence, new pathways were envisaged exploiting the glycosylation of a common 2,4-dideoxy disaccharide acceptor intermediate (**8**).

The known 4-OH disaccharide **6** [2] was treated with triphenylphosphine and triiodoimidazole to give the inverted 4-iodo compound **7** (90%) (Scheme 2). Hydrogenolysis then gave the key intermediate, the 2,4-dideoxy acceptor disaccharide **8** (42%) with a free 3-OH group. The rather low yield in the hydrogenation is explained by the concomitant ring contraction reaction, which is almost always a side-product in the hydrogenolysis of these 4-iodo derivatives [10]. The fear of hydrolysis of the methyl glycoside in **8** during glycosylations turned out to be more or less without justification. Using ordinary conditions (0.6 equiv of base) for a silver triflate-promoted glycosylation, with 2,4,6-tri-*O*-benzoyl-3-deoxy-α-D-*arabino*-hexopyranosyl chloride (**4**) (prepared from the methyl glycoside as



i) Bz_4ManBr, AgOTf; *ii)* CF_3COOH (90%, aq); *iii)* AgOTf; *iv)* Ph_3P, ImI_3 or $C(S)Im_2$

Scheme 1.



i) Ph_3P, ImI_3; *ii)* H_2, Pd–C; *iii)* **4** or **15**, AgOTf; *iv)* MeO^-

Scheme 2.

described for the corresponding acetylated analogue [11]) as donor and **8** as acceptor, a 65% yield of the trisaccharide **9** was obtained. Debenzoylation using methanolic sodium methoxide then gave the first target compound **10** (73%).

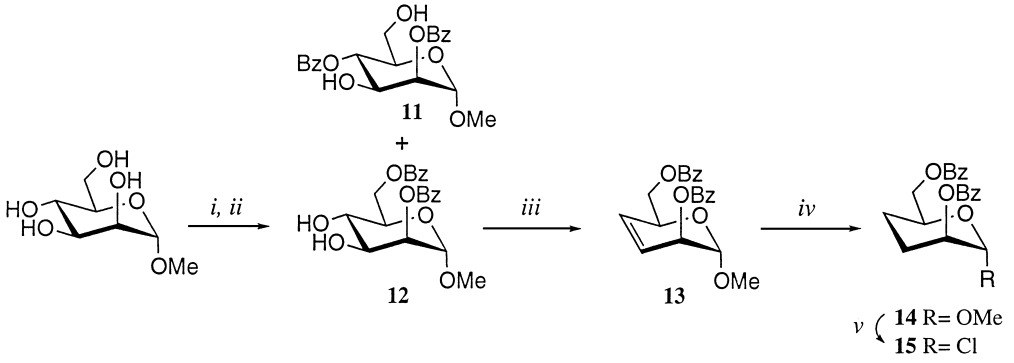
For the synthesis of the tetradeoxy analogue, a 3,4-dideoxy donor first had to be synthesised (Scheme 3). To obtain a 2,6-protected mannose derivative a simple one pot-procedure was used [12]. Treatment of methyl α-D-mannopyranoside with triethylorthobenzoate and acid catalysts gave the 2,3;4,6-diorthoester derivative, which was immediately treated with aqueous trifluoroacetic acid to open up the orthoesters and give a mixture of the 2,4- and the 2,6-di-*O*-benzoyl derivatives **11** and **12** (45 and 34%, respectively), which could easily be separated on a silica gel column. Use of orthoacetates instead of benzoates could give a better yield of the desired 2,6-acyl protected compound, owing to acid-catalyzed 4- to 6-acetyl migration [13]. However, when this was tried it was found that other acetyl migrations were as fast and a complex mixture of products was obtained. Compound **12** was treated with the triphenylphosphine-triiodoimidazole reagent [14] to give the 3,4-unsaturated derivative **13** (47%), which was hydrogenated to yield the 3,4-dideoxy compound **14** (60%).

Transformation of the methyl glycoside **14** into the glycosyl chloride donor **15** was performed using zinc chloride and dichloromethyl methyl ether [11,15] and immediately before the coupling to acceptor **8**. Once more a good yield (51%) of the coupling product (**16**) was obtained using silver triflate as a promoter (Scheme 2). The one-step deprotection of **16** then gave the tetradeoxy target product **17** (77%).

1. Experimental

General methods.—TLC was carried out on Merck precoated 60 F_{254} plates using UV light and/or 8% H_2SO_4 for visualization. Column chromatography was performed on silica gel (0.040–0.063 mm, Amicon). NMR spectra were recorded in $CDCl_3$ (internal Me_4Si, δ 0.00) or D_2O (internal acetone ^{13}C δ 31.0, ^1H δ 2.21) at 25 °C. Optical rotations were determined at room temperature with a Perkin–Elmer 241 polarimeter. Organic phases were dried over Na_2SO_4 before concentration, which was performed under reduced pressure.

Methyl (2,4,6-tri-O-*benzoyl-3-deoxy*-α-D-arabino-*hexopyranosyl)-(1→3)-[(2,3,4,6-tetra*-O-*benzoyl*-α-D-*mannopyranosyl)-(1→6)]-4-deoxy*-α-D-lyxo-*hexopyranoside* (**5**).—Silver triflate (869 mg, 3.38 mmol) dissolved in dry toluene (10 mL) was added at 0 °C to a stirred solution of **1** [7] (434 mg, 1.99 mmol) and benzobromomannose (1.70 g, 2.58 mmol) in CH_2Cl_2 (50 mL) containing 4 Å crushed molecular sieves. After 1 h, NEt_3 (3 mL) was added and the stirring was continued for 15 min, whereafter the mixture was diluted with CH_2Cl_2, filtered through Celite, concentrated, and purified by silica gel chromatography (9:1 toluene–EtOAc) to give crude **2** (1.36 g, 86%), which was directly treated with 90% CF_3COOH for 2 h at 0 °C before concentration. Co-concentration twice with toluene followed by silica gel chromatography (1:2 toluene–EtOAc) of the residue afforded methyl (2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-(1→6)-4-deoxy-α-D-*lyxo*-hexopyranoside (**3**; 1.15 g, 90%). ^{13}C NMR: δ 30.8 (C-4), 55.2 (OMe), 63.0, 65.8, 67.0, 67.2, 69.0, 70.1, and 70.7 (C-2,3,5,6,2′–6′), 97.4 and 101.5 (C-1,1′), 128.4–133.7 (Ph), 165.6–166.3 (PhCO). Silver triflate (40 mg, 0.16 mmol)



i) $PhC(OEt)_3$, pTsOH; *ii)* CF_3COOH (90%, aq); *iii)* Ph_3P, Im, I_2; *iv)* H_2, Pd-C; *v)* $ZnCl_2$, $CHCl_2OMe$

Scheme 3.

dissolved in dry toluene (2 mL) was added at −30 °C to a stirred solution of **3** (70 mg, 0.093 mmol) and 2,4,6-tri-*O*-benzoyl-3-deoxy-α-D-*arabino*-hexopyranosyl chloride [11] (**4**; 55 mg, 0.11 mmol) in CH_2Cl_2 (5 mL) containing crushed 4 Å molecular sieves. After 2 h, NEt_3 (0.2 mL) was added and the stirring was continued for 15 min. The mixture was diluted with CH_2Cl_2, filtered through Celite, concentrated, and purified by silica gel chromatography (6:1 toluene–EtOAc) to give **5** (44 mg, 39%) together with unreacted **3** (18 mg, 26%). ^{13}C NMR: δ 27.3 and 29.6 (C-4,3′), 55.2 (OMe), 63.0, 64.1, 65.7, 67.1, 67.3, 68.4, 69.0, 69.6, 70.1, 70.3, 70.7, and 72.9 (C-2,3,5,6,2′,4′–6′,2″–6″), 95.2, 97.4, and 101.5 (C-1,1′,1″), 128.5–133.6 (Ph), 165.6–166.5 (PhCO).

Methyl (2,3,4,6-tetra-O-*benzoyl*-α-D-*mannopyranosyl)-(1→6)-2,4-dideoxy*-α-D-threo-*hexopyranoside* (**8**).—Triphenylphosphine (0.51 g, 1.94 mmol) and triiodoimidazole (0.43 g, 0.97 mmol) were added to solution of **6** [2] (0.63 g, 0.65 mmol) in toluene (10 mL). The mixture was heated to 110 °C and stirred overnight, then diluted with toluene, washed with aq $Na_2S_2O_3$ and water, dried, and concentrated. The residue was purified by silica gel chromatography (19:1 toluene–EtOAc) to give methyl (2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-(1→6)-3-*O*-benzyl-2,4-dideoxy-2,4-diiodo-α-D-galactopyranoside (**7**; 0.63 g, 90%). $[\alpha]_D$ +50° (*c* 1.0, $CHCl_3$); ^{13}C NMR: δ 30.3 and 39.6 (C-2,4), 55.9 (OMe), 63.2, 66.9, 67.4, 69.2, 69.9, 70.3, 71.3, 72.4, and 75.0 (C-3,5,6,2′–6′, CH_2Ph), 97.1 and 100.8 (C-1,1′), 127.7–136.7 (Ph), 165.4, 165.5, and 166.2 (PhCO). Compound **7** (250 mg, 0.23 mmol) was dissolved in 6:6:1 EtOAc–MeOH–water (13 mL), and solid $NaHCO_3$ (125 mg) and Pd-C (10%) were added. The solution was hydrogenolyzed at 100 psi for 4 h, whereafter the mixture was filtered through Celite and concentrated. The residue was dissolved in CH_2Cl_2, and the solution was washed twice with aq sat $Na_2S_2O_3$, dried, and concentrated. The residue was redissolved in 1:1 EtOAc–MeOH (12 mL) and water (10 drops). Then, Amberlite OH^- ion-exchange resin (250 mg) and new Pd-C catalyst were added, and the mixture was hydrogenolyzed overnight, then filtered through Celite, dried, and concentrated. Silica gel chromatography (5:1 toluene–EtOAc) gave **8** (72 mg, 42%); $[\alpha]_D$ −29° (*c* 0.9, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 36.8 and 39.1 (C-2,4), 54.8 (OMe), 62.9, 63.8, 66.8, 67.0, 68.9, 70.0, and 70.5 (C-3,5,6,2′–6′), 97.3 and 99.1 (C-1,1′), 128.3–133.5 (Ph), 165.5 and 166.2 (PhCO). Anal. Calcd for $C_{41}H_{40}O_{13}$: C, 66.48; H, 5.44. Found: C, 66.59; H, 5.48.

Methyl (3-deoxy-α-D-arabino-*hexopyranosyl)-(1→3)-[(*α-D-*mannopyranosyl)-(1→6)]-2,4-dideoxy*-α-D-threo-*hexopyranoside* (**10**).—Silver triflate (24 mg, 93 mmol) dissolved in dry toluene (1 mL) was added at −20 °C to a stirred solution of **8** (40 mg, 54 μmol), 2,6-di-*tert*-butylpyridine (12 μL, 0.054 mmol), and **4** (40 mg, 81 μmol) in CH_2Cl_2 (2 mL) containing crushed 4 Å molecular sieves. After 1.5 h, NEt_3 (200 μL) was added and the stirring was continued for 15 min. The mixture was diluted with CH_2Cl_2, filtered through Celite, concentrated, and the residue was purified by silica gel chromatography (9:1 toluene–EtOAc) to give methyl (2,4,6-tri-*O*-benzoyl-3-deoxy-α-D-*arabino*-hexopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-(1→6)]-2,4-dideoxy-α-D-*threo*-hexopyranoside (**9**; 42 mg, 65%); $[\alpha]_D$ +16° (*c* 1.0, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 29.7, 33.6, and 37.5 (C-2,4,3′), 55.0 (OMe), 63.2, 64.2, 65.9, 66.9, 67.3, 69.2, 69.5, 70.3, 70.4, and 70.7 (C-3,5,6,2′,4′–6′, 2″–6″), 94.9, 97.5, and 99.2 (C-1,1′,1″), 128.6–133.7 (Ph), 165.7–166.4 (PhCO). A solution of **9** (42 mg, 35 μmol) in MeOH (5 mL) was treated with a catalytic amount of 1 M methanolic NaOMe at room temperature overnight. Dowex 50 (H^+) ion-exchange resin was added and the mixture was then filtered and concentrated. Purification on a Bio-Gel P-2 column gave, after freeze-drying, **10** (12 mg, 73%); $[\alpha]_D$ +139° (*c* 0.7, H_2O); NMR (D_2O): ^{13}C, δ 33.0, 34.2, and 36.8 (C-2,4,3′), 55.1 (OMe), 61.7, 61.8, 62.2, 67.5, 67.6, 68.2, 69.5, 69.7, 70.7, 71.3, 73.6, and 74.7 (C-3,5,6,2′,4′–6′,2″–6″), 97.2, 99.8, and 100.2 (C-1,1′,1″); ^1H, δ 1.46 (1 H, H-4ax), 1.69 (1 H, H-2ax), 1.81 (1 H, H-3′ax), 2.02–2.21 (3 H, H-2eq,3′eq,4eq), 4.87 (2 H), 4.98 (1 H) (H-1,1′,1″). FABMS: *m*/*z* 471.3 [M + 1].

Methyl 2,6-di-O-*benzoyl-3,4-dideoxy*-α-D-threo-*hexopyranoside* (**14**).—4-Toluenesulfonic acid (1.0 mL, 10% in MeCN, 0.31 mmol) and CF_3COOH (30 μL, 0.39 mmol) were added to a stirred suspension of methyl α-D-mannopyranoside (1.0 g, 5.15 mmol) and triethylorthobenzoate (3.0 mL, 13.4 mmol) in MeCN (75 mL). After 1 h, the solution was concentrated and the residue dissolved in MeCN (50 mL). Aq 90% CF_3COOH (1.8 mL) was added and the mixture was stirred for 30 min, whereafter concentration and silica gel chromatography (3:1 toluene–EtOAc) of the residue yielded, first, methyl 2,4-di-*O*-benzoyl-α-D-mannopyranoside (**11**; 0.93 g, 45%); $[\alpha]_D$ −48.7°

(*c* 1.4, $CHCl_3$); NMR data: ^{13}C, δ 55.3 (OMe), 61.5 (C-6), 68.5, 70.3, 70.5, and 72.8 (C-2–5), 98.6 (C-1), 128.5–133.6 (Ph), 166.1 and 167.2 (PhCO); ^1H, δ 3.77 (2 H, H-6a,6b), 3.92 (1 H, H-5), 4.41 (1 H, H-3), 4.92 (1 H, H-1), 5.41 (1 H, H-2), 5.48 (1 H, H-4); followed by methyl 2,6-di-*O*-benzoyl-α-D-mannopyranoside (**12**; 0.70 g, 34%); $[\alpha]_D$ +10.8° (*c* 0.9, $CHCl_3$); NMR data: ^{13}C, δ 55.2 (OMe), 63.6 (C-6), 67.9, 70.0, 70.7, and 72.3 (C-2–5), 98.8 (C-1), 128.4–133.3 (Ph), 166.1 and 167.1 (PhCO); ^1H, δ 3.91 (2 H, H-4,5), 4.15 (1 H, H-3), 4.53 (1 H, H-6a), 4.83 (2 H, H-1,6b), 5.37 (1 H, H-2). Triphenylphosphine (1.49 g, 5.67 mmol), imidazole (0.39 g, 5.67 mmol) and iodine (1.08 g, 4.25 mmol) were added to a solution of **12** (0.57 g, 1.42 mmol) in toluene (100 mL). The mixture was heated to 110 °C and stirred overnight, then diluted with toluene, washed with aq $Na_2S_2O_3$ and water, dried, and concentrated. The residue was purified by silica gel chromatography (9:1 toluene–EtOAc) to give methyl 2,6-di-*O*-benzoyl-3,4-dideoxy-α-D-*threo*-hex-3-enopyranoside (**13**, slightly contaminated; 0.25 g, 47%); $[\alpha]_D$ +58° (*c* 1.1, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 56.1 (OMe), 65.5, 65.6, and 66.5 (C-2,5,6), 98.9 (C-1), 122.3 and 131.4 (C-3,4), 128.4–133.2 (Ph), 165.4 and 165.8 (PhCO). Compound **13** (0.60 g, 1.63 mmol) was dissolved in 6:6:1 EtOAc–MeOH–water (13 mL), and Pd-C (10%) was added. The solution was hydrogenolyzed at 100 psi overnight, then filtered, concentrated, and redissolved in 6:6:1 EtOAc–MeOH–water (13 mL). Some new catalyst was added and the solution was hydrogenolyzed for another night, then filtered through Celite, dried, and concentrated. Silica gel chromatography (50:1 toluene–EtOAc) of the residue gave **14** (0.36 g, 60%); $[\alpha]_D$ +51° (*c* 0.9, $CHCl_3$); ^{13}C NMR ($CDCl_3$): δ 22.0 and 22.9 (C-3,4), 54.9 (OMe), 66.7, 67.2, and 67.8 (C-2,5,6), 98.1 (C-1), 128.4–133.1 (Ph), 165.7 and 166.4 (PhCO). Anal. Calcd for $C_{21}H_{22}O_6$: C, 68.10; H, 5.99. Found: C, 68.05; H, 6.06.

*Methyl (3,4-dideoxy-*α*-D-*threo*-hexopyranosyl)-(1→3)-[*α*-D-mannopyranosyl-(1→6)]-2,4-dideoxy-*α*-D-*threo*-hexopyranoside* (**17**).—A catalytic amount of dry zinc chloride was added to a solution of **14** (100 mg, 0.27 mmol) in dichloromethyl methyl ether (2 mL). The mixture was heated to 70 °C and stirred for 1.5 h, then diluted with CH_2Cl_2 and washed with sat $NaHCO_3$ and water. The organic phase was dried, filtered, and concentrated to give glycosyl chloride **15**, which was used without further purification in the next step. Silver triflate (32 mg, 0.124 mmol) dissolved in dry toluene (1 mL) was added at 0 °C to a stirred solution of **8** (54 mg, 0.073 mmol), **15** (41 mg, 0.11 mmol) and 2,6-di-*tert*-butylpyridine (49 μL, 0.22 mmol) in CH_2Cl_2 (5 mL) containing crushed 4 Å molecular sieves. After 30 min NEt_3 (0.3 mL) was added and stirring was continued for 15 min. The mixture was diluted with CH_2Cl_2, filtered through Celite, and evaporated. Silica gel chromatography (90:9:1 toluene–EtOAc–pyridine) gave the crude trisaccharide methyl (2,6-di-*O*-benzoyl-3,4-dideoxy-α-D-*threo*-hexopyranosyl)-(1→3)-[(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-(1→6)]-2,4-dideoxy-α-D-*threo*-hexopyranoside (**16**; 40 mg, 51%); ^{13}C NMR ($CDCl_3$): δ 22.0 and 22.8 (C-3′,4′), 33.4 and 37.3 (C-2,4), 54.7 (OMe), 62.9, 66.6, 67.0, 67.1, 67.3, 68.3, 68.9, 69.3, 70.0, 70.2, and 70.4 (C-3,5,6,2′,5′,6′,2″–6″), 95.2, 97.1, and 99.0 (C-1,1′,1″), 128.3–133.4 (Ph), 165.4–166.6 (PhCO), which was deprotected following the same protocol as described for compound **9**. Purification on a Bio-Gel P-2 column gave, after freeze-drying, **17** (13 mg, 77%); $[\alpha]_D$ +130° (*c* 1.3, H_2O); NMR (D_2O): ^{13}C, δ 21.1, 24.7, 33.1, and 36.8 (C-2,4,3′,4′), 55.1 (OMe), 61.7, 65.1, 65.9, 67.5, 67.7, 69.3, 69.7, 70.7 (2 C), 71.3, and 73.6 (C-3,5,6,2′,5′,6′,2″–6″), 98.0, 99.8, and 100.2 (C-1,1′,1″); ^1H (70 °C), δ 1.35–2.22 (8 H, H-2ax,2eq,3′ax,3′eq,4ax,4eq,4′ax,4′eq), 4.87 (1 H) and 4.96 (2 H) (H-1,1′,1″). FABMS: *m*/*z* 455.3 [M + 1].

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