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*Erratum**

Note

Synthesis of methyl 3-*O*-*a*-D-galactopyranosyl-6-*O*-*a*-D-mannopyranosyl-*a*-D-mannopyranoside, methyl 3-*O*-*a*-D-glucopyranosyl-6-*O*-*a*-D-mannopyranosyl-*a*-D-mannopyranoside, methyl 6-*O*-*a*-D-galactopyranosyl-3-*O*-*a*-D-mannopyranosyl-*a*-D-mannopyranoside, and methyl 6-*O*-*a*-D-glucopyranosyl-3-*O*-*a*-D-mannopyranosyl-*a*-D-mannopyranoside

Per J. Garegg, Stefan Oscarson, and Anna-Karin Tidén
Department of Organic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm (Sweden)

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The title trisaccharide glycosides were needed for studies of the interactions of lectins, receptor sites for bacteriophages with *Salmonella* lipopolysaccharide core-specificity, and correlation of n.m.r. chemical shifts and structure.

The methods used in the syntheses were conventional. Thus, 2,3,4,6-tetra-*O*-benzoyl-*a*-D-mannopyranosyl bromide[1] was reacted with methyl 2,3,4-tri-*O*-benzyl-*a*-D-mannopyranoside[2] in dichloromethane in the presence of silver triflate[3,4] to yield the (1→6)-linked disaccharide derivative, catalytic hydrogenolysis of which gave 89% of **1**. Treatment of **1**, first with trimethyl orthoacetate, then with acetic anhydride followed by acidic opening of the cyclic 2,3-orthoester[5], afforded 94% of methyl 2,4-di-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-*a*-D-mannopyranosyl)-*a*-D-mannopyranoside (**2**). Glycosylation of the HO-3 of **2** with 2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl bromide[6] under halide-assisted conditions[7] afforded 83% of the trisaccharide derivative **3**, whereas the corresponding reaction of **2** with 2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl bromide[7] afforded 79% of **4**. Deprotection of **3** and **4** then gave the first two of the title trisaccharides, **5** and **6**.

Similarly, methyl 2-*O*-benzyl-4,6-*O*-benzylidene-*a*-D-mannopyranoside[8,9] was glycosylated with tetra-*O*-benzoyl-*a*-D-mannopyranosyl bromide[1] in dichloromethane in the presence of silver triflate to yield 82% of the (1→3)-linked disaccharide derivative **7**. Removal of the 4,6-*O*-benzylidene group of **7** by acid hydrolysis afforded 92% of **8**. Selective glycosylation of HO-6 in **8** with 2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl

* Owing to a computer error, a number of lines were not taken over from the original text at the bottom of the first page and on page 478 of this article as it was published in Volume 200. This replacement text provides the correct version.

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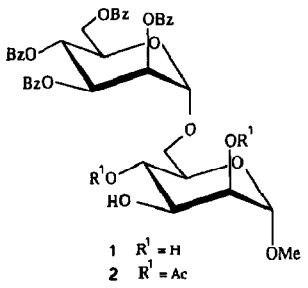
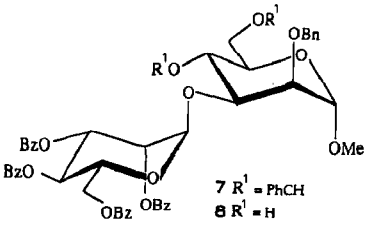
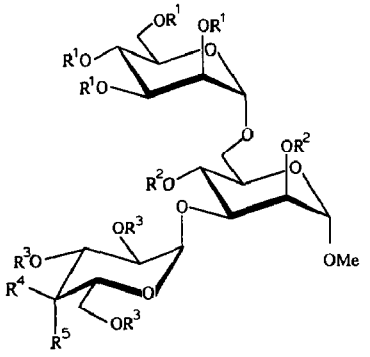


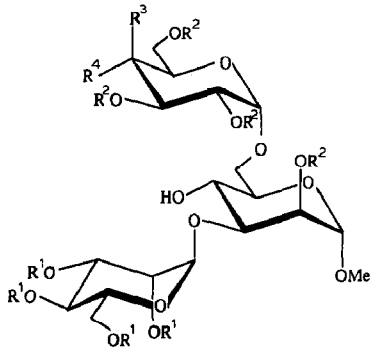
1 R^1 = H
2 R^1 = Ac



7 R^1 = PhCH
8 R^1 = H



3 R^1 = Bz, R^2 = Ac, R^3 = Bn, R^4 = H, R^5 = OBn
4 R^1 = Bz, R^2 = Ac, R^3 = Bn, R^4 = OBn, R^5 = H
5 R^1 = R^2 = R^3 = R^4 = H, R^5 = OH
6 R^1 = R^2 = R^3 = R^5 = H, R^4 = OH



9 R^1 = Bz, R^2 = Bn, R^3 = OBn, R^4 = H
10 R^1 = Bz, R^2 = Bn, R^3 = H, R^4 = OBn
11 R^1 = R^2 = R^4 = H, R^3 = OH
12 R^1 = R^2 = R^3 = H, R^4 = OH

bromide[6] under halide-assisted conditions[7] gave 70% of the trisaccharide derivative **9** and glycosylation with 2,3,4,6-tetra-*O*-benzyl-*α*-D-glucopyranosyl bromide[7] gave 78% of **10**. The "open" strategy was preferred to more circuituous routes involving, for example, regioselective reductive opening of the 4,6-*O*-benzylidene acetal ring of **8**, to leave HO-6 unsubstituted, followed by halide-assisted glycosylation as described above. Deprotection of **9** and **10** then gave the other two title trisaccharides, **11** and **12**.

The various structures were assigned on the basis of elemental analyses, n.m.r. data including $J_{C\text{-}1,H\text{-}1}$ values, and the results of methylation analysis[10,11].

EXPERIMENTAL

General methods. – These were the same as described[12,13]. ^{13}C-N.m.r. spectra for solutions in D_2O were obtained at 70° and referenced relative to internal acetone (δ 31.00).

Methyl 6-O-(2,3,4,6-tetra-O-benzoyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**1**). — A solution of silver triflate (0.62 g) in toluene (4 mL) was added dropwise at 0° to a stirred mixture of methyl 2,3,4-tri-*O*-benzyl-*α*-D-mannopyranoside[2] (0.74 g) and 2,3,4,6-tetra-*O*-benzoyl-D-mannopyranosyl bromide[1] (1.5 g) in dichloromethane containing molecular sieves. The mixture was allowed to attain room temperature, then

filtered through Celite, diluted with toluene, and washed with saturated aqueous sodium hydrogencarbonate and water, dried (Na_2SO_4), and concentrated. A solution of the residue in ethyl acetate (20 mL) was hydrogenolyzed in a Parr apparatus over 10% Pd–C (0.1g). After 2 days at 400 kPa pressure, the mixture was filtered and concentrated. Column chromatography (silica gel, 1:1 toluene–ethyl acetate) of the residue gave **1** (1.1 g, 89%), $[\alpha]_D$ −15° (*c* 1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 55.0 (OMe), 62.8, 66.8, 67.6, 68.8, 70.4, 70.6, 70.9, 71.4, 72.2 (C-2,3,4,5,6, C-2′,3′,4′,5′,6′, one overlap), 97.6, 101.1 (C-1,1′), 128.3–133.4 (aromatic carbons), 165.5, 166.0, and 166.3 (carbonyl C).

Anal. Calc. for $C_{41}H_{40}O_{15}$: C, 63.7; H, 5.2. Found: C, 63.3; H, 5.5.

*Methyl 2,4-di-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranoside* (**2**). — Trimethyl orthoacetate (1 mL) and *p*-toluenesulfonic acid (100 μL of a 5% solution in acetonitrile) were added to a solution of **1** (1.1 g) in acetonitrile (50 mL). After 5 min, pyridine (3 mL), acetic anhydride (3 mL), and a catalytic amount of 4-dimethylaminopyridine were added. When t.l.c. (toluene–ethyl acetate, 2:1) showed acetylation to be complete, the mixture was concentrated and co-concentrated twice with toluene. The residue was dissolved in acetonitrile (50 mL), aqueous 90% trifluoroacetic acid (100 μL) was added, and, after 15 min, the mixture was concentrated. Column chromatography (2:1 toluene–ethyl acetate) of the residue gave **2** (1.15 g, 94%), $[\alpha]_D$ −22° (*c* 1.3, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 20.9, 21.0 (CH_3CO), 55.3 (OMe), 62.8, 66.6, 66.8, 68.6, 69.0, 69.1, 69.6, 70.0, 70.4, 72.4 (C-2,3,4,5,6, C-2′,3′,4′,5′,6′), 97.6, 98.6 (C-1,1′), 125.8–133.5 (aromatic C), 165.3, 165.4, 165.5, 166.2, 170.8, and 171.1 (carbonyl C).

Anal. Calc. for $C_{45}H_{44}O_{17}$: C, 63.1; H, 5.2. Found: C, 62.9; H, 5.0.

*Methyl 2,4-di-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-galactopyranosyl)-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranoside* (**3**) *and methyl 2,4-di-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranoside* (**4**). — A solution of 2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl bromide[6] (1 g) in dichloroethane (1.5 mL) was added to a mixture of **2** (0.36 g) and tetraethylammonium bromide (0.12 g) in dichloroethane (2 mL) containing *N*,*N*-dimethylformamide (0.5 mL) and molecular sieves. The mixture was stirred for 24 h at 35°, then filtered through Celite onto the top of a column of silica gel, and eluted with 16:1 toluene–ethyl acetate to give **3** (0.48 g, 83%), $[\alpha]_D$ +4° (*c* 1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 20.7, 20.9 (CH_3CO), 55.3 (OMe), 62.8 (C-6″), 66.8, 67.2, 68.5, 68.9, 69.4, 70.1, 70.4, 71.5, 72.9, 73.4, 73.6, 74.8, 74.9, 76.2, 76.6, 78.8 (C-2,3,4,5,6, C-2′,3′,4′,5′,6′, C-2″,3″,4″,5″, and 4 PhCH_2, overlap), 97.5, 98.1, 100.2 (C-1,1′,1″), 127.5–138.9 (aromatic C), 165.3, 165.5, 166.2, 170.0, 170.7 (carbonyl C).

Anal. Calc. for $C_{79}H_{78}O_{22}$: C, 68.8; H, 5.7. Found: C, 68.8; H, 5.7.

Compound **4** (0.46 g, 79%), prepared as described above for **3** except that the glucosyl bromide[7] was used and the reaction was worked-up after 48 h, had m.p. 78–79° [from toluene–light petroleum (b.p. 40–60°)], $[\alpha]_D$ +6° (*c* 1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 20.7, 21.1 (CH_3CO), 55.4 (OMe), 62.8 (C-6″), 66.8, 66.9, 67.0, 68.2, 68.9, 69.5, 70.1, 70.4, 71.5, 71.7, 73.4, 73.5, 74.9, 75.6, 77.3, 77.5, 80.1, 81.5 (C-2,3,4,5,6,

C-2′,3′,4′,5′,6′, C-2″,3″,4″,5″, and 4 Ph*C*H$_2$), 97.4, 98.0, 100.0 (C-1,1′,1″), 127.5–138.8 (aromatic C), 165.3, 166.1, 169.9, 170.6 (carbonyl C).

Anal. Calc. for $C_{79}H_{78}O_{22}$: C, 68.8; H, 5.7. Found: C, 68.6; H, 5.7.

*Methyl 3-*O*-α-*D*-galactopyranosyl-6-*O*-α-*D*-mannopyranosyl-α-*D*-mannopyranoside* (**5**) *and methyl 3-*O*-α-*D*-glucopyranosyl-6-*O*-α-*D*-mannopyranosyl-α-*D*-mannopyranoside* (**6**). — A catalytic amount of methanolic sodium methoxide was added to a solution of **3** (135 mg) in methanol (5 mL). The mixture was stirred for 48 h at room temperature, then neutralised with Dowex (H^+) resin, and filtered. 10% Pd–C (40 mg) was added to the filtrate, and the mixture was hydrogenolyzed in a Parr apparatus (400 kPa) overnight, then filtered, and concentrated. A solution of the residue in water was washed with dichloromethane and ethyl acetate, then concentrated, and the residue was purified on a column of Bio-Gel P-2 and freeze-dried to give **5** (47 mg, 93%), $[\alpha]_D$ +118° (*c* 1.1, water). ^{13}C-N.m.r. data (D_2O): δ 55.0 (OMe), 61.2, 61.3 (C-6′,6″), 65.8, 66.0, 67.0, 68.9, 69.5, 69.6, 69.8, 70.2, 70.9, 71.1, 71.5, 72.9, 79.4 (C-2,3,4,5,6, C-2′,3′,4′,5′, C-2″,3″,4″,5″), 99.7 ($J_{C\text{-}1,H\text{-}1}$ 170 Hz), 100.9 ($J_{C\text{-}1,H\text{-}1}$ 171 Hz), and 101.1 ($J_{C\text{-}1,H\text{-}1}$ 171 Hz) (C-1,1′,1″).

Anal. Calc. for $C_{19}H_{34}O_{16}\cdot H_2O$: C, 42.5; H, 6.8. Found: C, 42.7; H, 6.5.

Compound **4** (160 mg) was deprotected, as described above for **3**, to give **6** (55 mg, 92%), $[\alpha]_D$ +111° (*c* 1.2, water). ^{13}C-N.m.r. data (D_2O): δ 55.2 (OMe), 61.1, 61.4 (C-6′,6″), 66.0, 66.2, 66.2, 67.3, 70.1, 70.5, 71.1, 71.4, 72.2, 72.8, 73.1, 73.4, 79.5 (C-2,3,4,5,6, C-2′,3′,4′,5′, C-2″,3″,4″,5″), 100.0 ($J_{C\text{-}1,H\text{-}1}$ 171 Hz), 100.9 ($J_{C\text{-}1,H\text{-}1}$ 171 Hz), and 101.3 ($J_{C\text{-}1,H\text{-}1}$ 171 Hz) (C-1,1′,1″).

Anal. Calc. for $C_{19}H_{34}O_{16}\cdot H_2O$: C, 42.5; H, 6.8. Found: C, 42.1; H, 6.5.

*Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranoside* (**7**). — Silver triflate (0.66 g) in toluene (4 mL) was added dropwise at 0° to a stirred mixture of methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-mannopyranoside[8,9] (0.48 g) and 2,3,4,6-tetra-*O*-benzoyl-D-mannopyranosyl bromide[1] (1.7 g) in dichloromethane (10 mL) containing molecular sieves. The mixture was allowed to attain room temperature, and, after 1 h thereat, the mixture was filtered through Celite onto the top of a column of silica gel which was eluted with 19:1 toluene–ethyl acetate to give **7** (1.01 g, 82%), m.p. 203–205° (from ethanol–ethyl acetate), $[\alpha]_D$ −23° (*c* 1.3, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 54.9 (OMe), 63.0, 64.0, 67.2, 68.6, 69.3, 69.8, 70.3, 73.2, 74.1, 77.1, 78.8 (C-2,3,4,5,6, C-2′,3′,4′,5′,6′, and Ph*C*H$_2$), 98.8, 99.8, 101.1 (C-1,1′, and Ph-*C*H), 125.9–137.8 (aromatic C), 165.0, 165.4, and 166.1 (carbonyl C).

Anal. Calc. for $C_{55}H_{49}O_{15}$: C, 69.5; H, 5.2. Found: 69.6; H, 5.2.

*Methyl 2-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-*D*-mannopyranosyl)-α-*D*-mannopyranoside* (**8**). — A solution of **7** (0.6 g) in aq. 70% acetic acid (15 mL) was stirred at 70° until t.l.c. (toluene–ethyl acetate, 3:1) showed complete reaction (3–4 h). The mixture was then concentrated and co-concentrated twice with toluene. Column chromatography (3:1 toluene–ethyl acetate) of the residue gave **8** (0.5 g, 92%), $[\alpha]_D$ −19° (*c* 1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 54.9 (OMe), 62.5, 63.0, 66.9, 67.3, 69.3, 70.1, 70.4, 72.3, 72.5, 77.4, 79.7 (C-2,3,4,5,6, C-2′,3′,4′,5′,6′, and Ph*C*H$_2$), 98.4, 99.5 (C-1,1′), 125.3–137.9 (aromatic C), 165.4, 165.7, and 166.2 (carbonyl C).

Anal. Calc. for $C_{48}H_{45}O_{15}$: C, 66.9; H, 5.3. Found: C, 66.5; H, 5.3.

Methyl 2-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-α-D-galactopyranosyl)-3-O-(2,3,4,6-tetra-O-benzoyl-α-D-mannopyranosyl)-α-D-mannopyranoside (**9**) *and methyl 2-O-benzyl-6-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-3-O-*(2,3,4,6-tetra-O-*benzoyl-α-D-mannopyranosyl)-α-D-mannopyranoside* (**10**). — A solution of 2,3,4,6-tetra-*O*-benzyl-D-galactopyranosyl bromide[6] (0.6 g) in dichloromethane (2 mL) was added at 0° to a mixture of **8** (0.36 g) and tetraethylammonium bromide (0.12 g) in dichloromethane (3 mL) containing *N*,*N*-dimethylformamide (0.5 mL) and molecular sieves. The mixture was allowed to attain room temperature, stirred overnight, then filtered through Celite onto the top of a column of silica gel which was eluted with 14:1 toluene–ethyl acetate to give **9** (0.41 g, 70%), $[\alpha]_D$ +10° (*c* 0.7, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 54.9 (OMe), 63.2 (C-6′), 67.2, 69.2, 69.6, 69.9, 70.1, 70.2, 70.4, 70.5, 72.5, 73.1, 73.5, 73.6, 74.6, 74.9, 76.2, 76.9, 77.7, 79.0 (C-2,3,4,5,6, C-2′,3′,4′,5′, C-2″,3″,4″,5″,6″, and 5 Ph*C*H$_2$, one overlap), 98.5 (2 C), 99.4 (C-1,1′,1″), 127.5–138.7 (aromatic C), 165.2, and 165.5 (carbonyl C). A satisfactory elemental analysis was not obtained for this compound, but its purity was established by t.l.c. (toluene–ethyl acetate, 9:1) and by ^{13}C-n.m.r. spectroscopy.

Compound **10** (0.53 g, 78%) [prepared from **8** (0.40 g), as described above for **9**, except that no ice-bath was used, and the glucosyl bromide[7] was used] was obtained after purification on a column of silica gel (chloroform–acetone, 50:1); $[\alpha]_D$ +21° (*c* 0.8, chloroform). ^{13}C-N.m.r. data: δ 54.9 (OMe), 63.1 (C-6′), 67.1, 68.4, 69.2, 69.6, 70.0, 70.3, 70.4, 70.5, 72.5, 73.3, 73.4, 74.9, 75.6, 76.8, 77.4, 78.0, 79.6, 81.9 (C-2,3,4,5,6, C-2′,3′,4′,5′, C-2″,3″,4″,5″,6″, and 5 Ph*C*H$_2$, one overlap), 97.9, 98.5, 99.3 (C-1,1′,1″), 127.5–138.7 (aromatic C), 165.1, 165.4, and 166.1 (carbonyl C).

Anal. Calc. for $C_{82}H_{79}O_{20}$: C, 71.1; H, 5.9. Found: C, 71.5; H, 6.0.

Mehyl 6-O-α-D-galactopyranosyl-3-O-α-D-mannopyranosyl-α-D-mannopyranoside (**11**) *and methyl 6-O-α-D-glucopyranosyl-3-O-α-D-mannopyranosyl-α-D-mannopyranoside* (**12**). — Compound **9** (120 mg) was deprotected, as described above for **3** (except that 24 h was allowed for the deacylation), to give **11** (40 mg, 89%), $[\alpha]_D$ +184° (*c* 0.9, water). ^{13}C-N.m.r. data (D_2O): δ 55.8 (OMe), 62.0 (2 C) (C-6′,6″), 66.7 (2 C), 67.8, 69.4, 70.2, 70.4, 70.5, 71.0, 71.4, 71.8, 72.1, 74.2, 79.4 (C-2,3,4,5,6, C-2′,3′,4′,5′, C-2″,3″,4″,5″), 99.0 ($J_{C\text{-}1,H\text{-}1}$ 171 Hz), 101.9 ($J_{C\text{-}1,H\text{-}1}$ 170 Hz), and 103.1 ($J_{C\text{-}1,H\text{-}1}$ 171 Hz) (C-1,1′,1″).

Anal. Calc. for $C_{19}H_{34}O_{16}\cdot 1.5H_2O$: C, 41.7; H, 6.9. Found: C, 41.6; H, 6.5.

Compound **10** (255 mg) was deprotected, as described above for **9**, to give **12** (85 mg, 89%), $[\alpha]_D$ +122° (*c* 1.2, water). ^{13}C-N.m.r. data (D_2O): δ 55.1 (OMe), 61.0, 61.2 (C-6′,6″), 65.9, 66.0, 67.1, 69.7, 70.0, 70.3, 70.7, 71.3, 71.7, 72.0, 73.4, 73.5, 78.7 (C-2,3,4,5,6, C-2′,3′,4′,5′, C-2″,3″,4″,5″), 98.1 ($J_{C\text{-}1,H\text{-}1}$ 170 Hz), 101.2 ($J_{C\text{-}1,H\text{-}1}$ 171 Hz), and 102.4 ($J_{C\text{-}1,H\text{-}1}$ 171 Hz) (C-1,1′,1″).

Anal. Calc. for $C_{19}H_{34}O_{16}\cdot 0.5H_2O$: C, 43.2; H, 6.7. Found: C, 43.4; H, 6.7.

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