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Note

Synthesis of methyl 3-*O*-(2-*O*-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranoside, methyl 3-*O*-α-L-rhamnopyranosyl-α-D-glucopyranoside, and methyl 3-*O*-[3-*O*-(2-*O*-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl]-α-L-rhamnopyranoside: di- and tri-saccharide segments of a lipo-oligosaccharide (LOS-1) of *Mycobacterium szulgai* *

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Phenolic glycolipids, glycopeptidolipids, and lipo-oligosaccharides are the major serological species in Mycobacteria[1]. The so-called lipo-oligosaccharides (LOS) are rare examples of the presence of trehalose units as structural elements[2]. LOS have been explored little and only recently have asignments of structure of their glycolipid fractions appeared[2]. *Mycobacterium szulgai* causes opportunistic pulmonary infection[3], six non-reducing oligosaccharides (Ose 1–6) have been isolated from its glycolipid fraction, and complete or partial structures have been assigned[4].

The simplest of the oligosaccharides in *M. Szulgai* (Ose 1) has been assigned the structure **1** based on chemical and spectroscopic studies. We now report the synthesis of di- (**2** and **3**) and tri-saccharide (**4**) glycosides related to segments of Ose 1. The crucial *O*-glycosylation reactions involved[5] boron trifluoride etherate as the catalyst and 1-*O*-acetyl derivatives as the glycosyl donors. This methodology circumvented the use of glycosyl halides and provided a high degree of α-selectivity, but with moderate yields.

Methyl 3-O-(2-O-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranoside (**2**).—The glycosyl donor was 1,3,4-tri-*O*-acetyl-2-*O*-methyl-α,β-L-fucopyranose (**5**, α,β-ratio 1:1), obtained by conventional treatment of 2-*O*-methyl-L-fucopyranose[6] with acetic anhydride and pyridine. Reaction of **5** with methyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside[7] (**6**) in the presence of a catalytic amount of boron trifluoride

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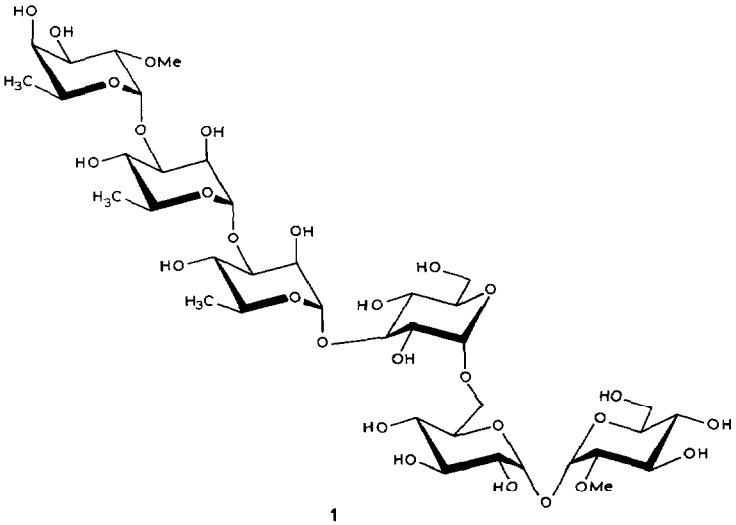

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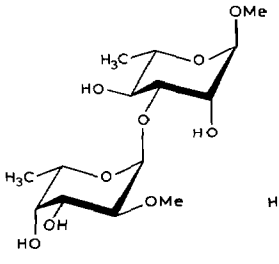

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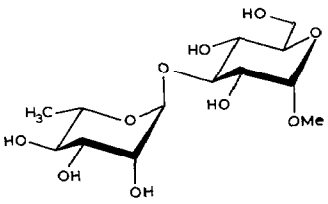

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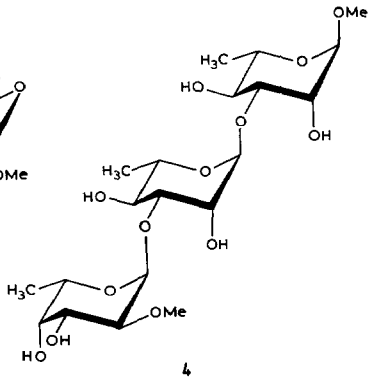
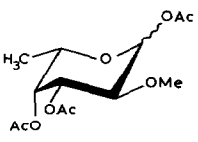


4

etherate and 4A molecular sieves in dry dichloromethane at 0°C for 3 h gave 31% of the disaccharide derivative **7**, Zemplén *O*-deacetylation of which gave **8**. The ^{13}C NMR spectrum of **8** contained C-1 resonances at 97.14 and 98.36 ppm. Debenzylation (Pd/C) of **8** gave 86% of **2**, whose ^{1}H NMR spectrum contained resonances for H-1 at δ 4.65 ($J_{1,2}$ 1.5 Hz) and H-1′ at δ 5.16 ($J_{1',2'}$ 4.0 Hz), which indicated that each sugar residue was α.



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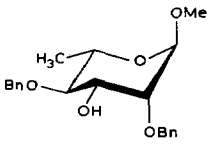

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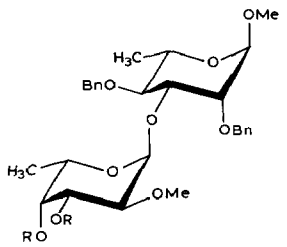
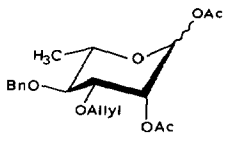


7 R = Ac

8 R = H



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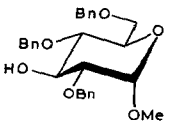

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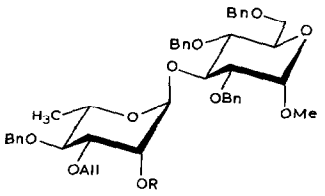
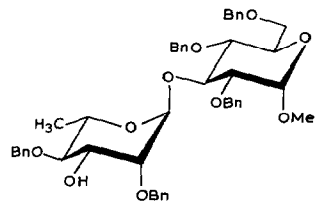


11 R = Ac
12 R = H
13 R = Bn



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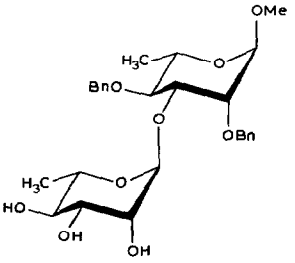

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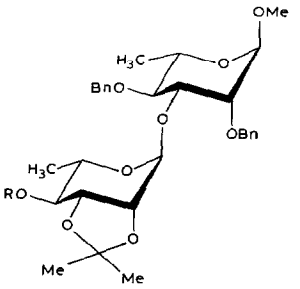


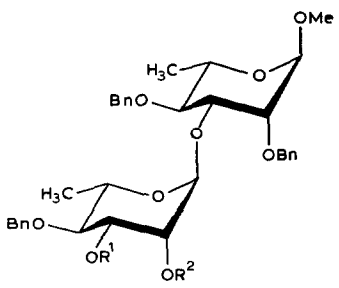
16 R = H
17 R = Bn

Methyl 3-O-α-L-rhamnopyranosyl-α-D-glucopyranoside (**3**).—The glycosyl donor 1,2-di-*O*-acetyl-3-*O*-allyl-4-*O*-benzyl-L-rhamnopyranose (**9**, α,β-ratio 4:1) was prepared from methyl 3-*O*-allyl-4-*O*-benzyl-α-L-rhamnopyranoside[8] by conventional acid hydrolysis, then acetylation (acetic anhydride–pyridine). The coupling of **9** and methyl 2,4,6-tri-*O*-benzyl-α-D-glucopyranoside[9] (**10**) in the presence of boron trifluoride etherate gave 44% of the disaccharide **11**. Zemplén *O*-deacetylation of **11** gave **12**, the ^{13}C NMR spectrum of which contained C-1 signals at 100.0 and 97.50 ppm, and the $J_{C\text{-}1,H\text{-}1}$ and $J_{C\text{-}1',H\text{-}1'}$ values of 174 and 166 Hz, respectively, indicated[10] each sugar residue to be α.

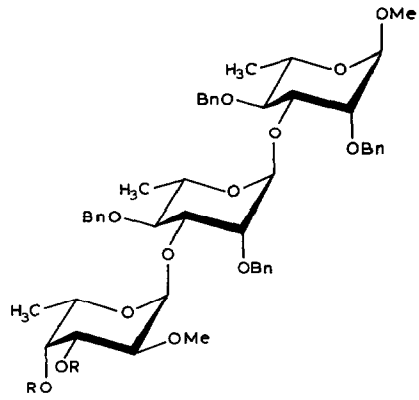
The free hydroxyl group (HO-2′) in **12** was benzylated (sodium hydride–benzyl bromide) to afford **13** from which the 3′-*O*-allyl group was removed by isomerisation[11] with tris(triphenylphosphine)rhodium(I) chloride in refluxing ethanol–benzene–water, followed by hydrolysis with mercuric chloride–mercuric oxide in aqueous acetone to give **14** (53%).

Debenzylation (Pd/C) of **14** gave **3**[12], the ^1H NMR spectrum of which contained signals for H-1 at δ 4.52 ($J_{1,2}$ 4.0 Hz) and H-1′ at δ 4.96 ($J_{1',2'}$ 1.5 Hz).

Methyl 3-O-[3-O-(2-O-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl]-α-L-rhamnopyranoside (**4**).—The triol **15**, obtained by Zemplén *O*-deacetylation of methyl 2,4-di-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside[13] was treated with 2,2-dimethoxypropane in the presence of a catalytic



18 $R^1 = R^2 = H$
19 $R^1 = H, R^2 = Bn$



20 R = Ac
21 R = H

amount of *p*-toluenesulfonic acid to give the 2′,3′-*O*-isopropylidene derivative **16**. Benzylation of HO-4′ then gave **17**. Removal of the isopropylidene group in **17** with aqueous 70% acetic acid at 70°C gave **18**, O-2′ of which was selectively benzylated[7], with tetrabutylammonium bromide as the phase-transfer catalyst and benzyl bromide in aqueous 5% sodium hydroxide and dichloromethane, to afford **19** (73%).

Condensation of **19** with **9** in the presence of boron trifluoride etherate gave the trisaccharide derivative **20** contaminated with **19**. Zemplén *O*-deacetylation of the mixture followed by chromatography gave **21** (47%). Debenzylation (Pd/C) of **21** gave **4**, the ^{1}H NMR spectrum of which contained a signal for H-1″ at δ 5.36 (d, $J_{1'',2''}$ 4.0 Hz) which indicated that the fucopyranose residue was α.

EXPERIMENTAL

General methods.—Solvents were dried by conventional procedures. 4A Molecular sieves were activated by heating to 400°C. Solvents were evaporated under diminished pressure at 40°C. Optical rotations were measured with a JASCO DIP 360 digital polarimeter. NMR spectra (internal standard Me_4Si) were recorded with a Varian FT 200 spectrometer. Reactions were monitored by TLC on silica gel (Merck) with detection by 1-naphthol. Column chromatography was performed on silica gel (mesh 60–120) purchased from the Acme Chemical Company, Bombay.

Methyl 3-O-(2-O-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranoside (**2**).—To a stirred mixture of **6**[7] (0.25 g, 0.70 mmol), **5** (0.25 g, 0.82 mmol; α,β-ratio 1:1) [prepared (76%) by conventional treatment of 2-*O*-methyl-L-fucose[6] with pyridine–acetic anhydride], and 4A molecular sieves (0.5 g) in dry CH_2Cl_2 (10 mL) at 0°C was added freshly distilled boron trifluoride etherate (100 μL). After 3 h,

K_2CO_3 was added, and the mixture was filtered, washed with water, dried, and concentrated. Column chromatography (1:5 EtOAc–light petroleum) of the residue and treatment of the product **7** (0.13 g, 31%) with methanolic NaOMe (5 mL of MeOH and 10 mg of Na) for 3 h, followed by conventional workup and column chromatography (100:1 $CHCl_3$–MeOH) gave methyl 2,4-di-*O*-benzyl-3-*O*-(2-*O*-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranoside (**8**; 80 mg, 72%), isolated as a syrup; $[\alpha]_D$ −47° (*c* 0.9, $CHCl_3$). NMR data ($CDCl_3$): ^1H, δ 1.10, 1.27 (2 d, 6 H, *J* 6.5 Hz, H-6,6,6 and H-6′,6′,6′), 3.19, 3.33 (2 s, 6 H, 2 OMe), 4.44, 4.54, 4.71, 5.04 (2 ABq, 4 H, 2 PhCH_2), 4.67 (d, 1 H, $J_{1,2}$ 1.0 Hz, H-1), 5.10 (d, 1 H, $J_{1',2'}$ 4.0 Hz, H-1′), 7.4 (m, 10 H, 2 Ph); ^{13}C δ 97.14 (C-1), 98.36 (C-1′).

A solution of **8** (80 mg, 0.15 mmol) in EtOH (5 mL) was stirred under H_2 for 48 h in the presence of 10% Pd/C (15 mg), then filtered, and concentrated. Column chromatography (20:1 $CHCl_3$–MeOH) of the residue gave **2** (45 mg, 86%), isolated as a syrup; $[\alpha]_D$ −60° (*c* 0.3, $CHCl_3$). ^1H-NMR data ($CDCl_3$): δ 1.26, 1.31 (2 d, 6 H, *J* 6.0 Hz, H-6,6,6 and H-6′,6′,6′), 3.38, 3.54 (2 s, 6 H, 2 OMe), 4.65 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 5.16 (d, 1 H, $J_{1',2'}$ 4.0 Hz, H-1′). Anal. Calcd for $C_{14}H_{26}O_9$: C, 49.7; H, 7.7. Found: C, 49.3; H, 7.6.

Methyl 3-O-(3-O-allyl-4-O-benzyl-α-L-rhamnopyranosyl)-2,4,6-tri-O-benzyl-α-D-glucopyranoside (**12**).—A mixture of methyl 3-*O*-allyl-4-*O*-benzyl-α-L-rhamnopyranoside[8] (2.3 g, 7.47 mmol), 1.5 M H_2SO_4 (10 mL), and 1,4-dioxane (30 mL) was heated at 100°C for 18 h, then neutralised ($BaCO_3$), filtered, and concentrated. Toluene was evaporated from the residue in order to remove traces of moisture, and the residue was then treated with acetic anhydride (5 mL) and pyridine (7 mL) to afford 1,2-di-*O*-acetyl-3-*O*-allyl-4-*O*-benzyl-α,β-L-rhamnopyranose (**9**; 2.51 g, 89%; α,β-ratio 4:1). ^1H NMR data ($CDCl_3$): δ 1.32 (d, 3 H, *J* 6.0 Hz, H-6,6,6), 2.10, 2.18 (2 s, 6 H, 2 Ac), 3.38 (t, 1 H, $J_{3,4} = J_{4,5} = 10.0$ Hz, H-4), 4.60, 4.88 (ABq, 2 H, PhCH_2), 5.1–5.3 (m, 2 H, CH_2=), 5.22 (dd, 1 H, $J_{1,2}$ 1.5, $J_{2,3}$ 3.0 Hz, H-2), 5.75–6.00 (m, 1 H, CH=), 5.92 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 7.3 (m, 5 H, Ph).

To a solution of **9** (0.98 g, 2.60 mmol), **10**[9] (0.80 g, 1.72 mmol), and 4A molecular sieves (1.0 g) in CH_2Cl_2 at 0°C was added boron trifluoride etherate (0.2 mL). After 3 h, the reaction was worked up as described above. Column chromatography (1:7 EtOAc–light petroleum) of the product gave **11** (0.60 g, 44%) which was dissolved in MeOH (10 mL), Na (25 mg) was added, and, after 2 h, the mixture was worked up in the usual way. Column chromatography (1:4 EtOAc–light petroleum) of the product gave **12** (0.45 g, 80%), isolated as a syrup; $[\alpha]_D$ +20° (*c* 1.5, $CHCl_3$). NMR data ($CDCl_3$): ^1H, δ 1.07 (d, 3 H, *J* 6.5 Hz, H-6′,6′,6′), 3.27 (s, 3 H, OMe), 4.55 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1), 5.28 (d, 1 H, $J_{1',2'}$ 1.3 Hz, H-1′); ^{13}C, δ 97.50 (*J* 166 Hz, C-1′), 100.0 (*J* 174 Hz, C-1). Anal. Calcd for $C_{44}H_{52}O_{10}$: C, 71.35; H, 7.0. Found: C, 71.0; H, 7.15).

Methyl 3-O-α-L-rhamnopyranosyl-α-D-glucopyranoside (**3**).—To a solution of **12** (0.30 g, 0.40 mmol) in dry tetrahydrofuran (5 mL) was added NaH (100 mg, 60% dispersion in oil) followed, after 2 h, by benzyl bromide (0.2 mL). After the usual

workup, column chromatography (1:12 EtOAc–light petroleum) of the product afforded **13** (0.30 g, 89%), which was heated with tris(triphenylphosphine)-rhodium(I) chloride (45 mg) and 1,4-diazabicyclo[2.2.2]octane (70 mg) in 7:3:1 EtOH–benzene–water (10 mL) at 100°C for 20 h. The mixture was filtered, diluted with water, and extracted with $CHCl_3$. The extract was dried and concentrated, and to a solution of the residue in 1:1 acetone–water (10 mL) were added mercuric chloride (70 mg) and mercuric oxide (25 mg). The mixture was stirred vigorously for 1 h at room temperature, then filtered, and concentrated, and the residue was partitioned between water and $CHCl_3$. The $CHCl_3$ layer was dried and concentrated. Column chromatography (1:19 EtOAc–light petroleum) of the residue gave methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-α-D-glucopyranoside (**14**; 0.15 g, 53%), isolated as a syrup. ^1H NMR data ($CDCl_3$): δ 1.02 (d, 3 H, *J* 6.5 Hz, H-6′,6′,6′), 3.34 (s, 3 H, OMe), 4.77 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 5.43 (s, 1 H, H-1′), 7.26 (m, 25 H, 5 Ph).

Debenzylation of **14** (0.15 g, 0.19 mmol) with 10% Pd/C (50 mg) in EtOH (3 mL) under H_2 at ambient temperature for 48 h gave **3** (50 mg, 78%) as a syrup; $[\alpha]_D$ +38° (*c* 1.3, MeOH); lit.[12] $[\alpha]_D$ +37° (*c* 1.4, H_2O). ^1H NMR data (CD_3OD): δ 1.13 (d, 3 H, *J* 6.5 Hz, H-6′,6′,6′), 3.31 (s, 3 H, OMe), 4.52 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1), 4.96 (d, 1 H, $J_{1',2'}$ 1.5 Hz, H-1′).

*Methyl 2,4-di-O-benzyl-3-*O*-α-L-rhamnopyranosyl-α-L-rhamnopyranoside* (**15**).—Treatment of methyl 2,4-di-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside[13] (0.80 g) with MeOH (15 mL) containing Na (25 mg) and column chromatography (19:1 $CHCl_3$–MeOH) of the product gave **15** (0.60 g, 94%), isolated as a syrup; $[\alpha]_D$ −32° (*c* 0.7, $CHCl_3$). NMR data ($CDCl_3$): ^1H, δ 1.21, 1.29 (2 d, 6 H, *J* 6.4 Hz, H-6,6,6 and H-6′,6′,6′), 3.32 (s, 3 H, OMe), 3.97, 4.02 (ABq, 2 H, PhCH_2), 4.57, 4.70 (ABq, 5 H, 2 PhCH_2 and H-1), 5.02 (s, 1 H, H-1′), 7.5 (m, 10 H, 2 Ph); ^{13}C, δ 98.0 (*J* 167 Hz, C-1), 101.0 (*J* 168 Hz, C-1′).

*Methyl 2,4-di-*O*-benzyl-3-*O*-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside* (**19**).—A mixture of **15** (0.60 g, 1.19 mmol), 2,2-dimethoxypropane (0.3 mL), *p*-toluenesulfonic acid (15 mg), and dry CH_2Cl_2 was stirred for 3 h, then neutralised with triethylamine, and concentrated. Column chromatography (1:6 EtOAc–light petroleum) of the residue gave methyl 2,4-di-*O*-benzyl-3-*O*-(2,3-*O*-isopropylidene-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (**16**; 0.55 g, 85%), isolated as a syrup. ^1H NMR data ($CDCl_3$): δ 1.19, 1.31 (2 d, 6 H, *J* 6.0, 6.5 Hz, H-6,6,6 and H-6′,6′,6′), 1.31, 1.51 (2 s, 6 H, Me_2C), 3.34 (s, 3 H, OMe), 4.50 (s, 1 H, H-1), 4.60, 4.76 (ABq, 2 H, PhCH_2), 4.65 (s, 2 H, PhCH_2), 5.21 (s, 1 H, H-1′), 7.3 (m, 10 H, 2 Ph).

To a solution of **16** (0.55 g, 1.01 mmol) in tetrahydrofuran (15 mL) was added NaH (0.20 g, 60% dispersion in oil). After 2 h, benzyl bromide (0.5 mL) was introduced. The usual workup was carried out after 18 h. Column chromatography (1:9 EtOAc–light petroleum) of the product gave methyl 2,4-di-*O*-benzyl-3-*O*-(4-*O*-benzyl-2,3-*O*-isopropylidene-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (**17**; 0.50 g, 78%).

Hydrolysis of **17** (0.50 g, 0.79 mmol) with aq 70% acetic acid (10 mL) at 70°C for 18 h followed by the usual workup gave methyl 2,4-di-*O*-benzyl-3-*O*-(4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (**18**; 0.40 g, 85%). ^{1}H NMR data ($CDCl_3$): δ 1.27, 1.33 (2 d, 6 H, *J* 6.0 Hz, H-6,6,6 and H-6′,6′,6′), 3.21 (s, 3 H, OMe), 5.08 (s, 1 H, H-1), 7.25 (m, 15 H, 3 Ph).

A mixture of **18** (0.25 g, 0.42 mmol), aq 5% NaOH (2 mL), tetrabutylammonium bromide (36 mg), benzyl bromide (90 mg), and CH_3Cl_2 (10 mL) was stirred vigorously at room temperature for 48 h. The organic layer was separated, washed with water, dried and concentrated. Column chromatography (1:6 EtOAc–light petroleum) of the residue gave **19** (0.21 g, 73%), isolated as a syrup; $[\alpha]_D$ -12° (*c* 0.3, $CHCl_3$). ^{1}H NMR data ($CDCl_3$): δ 1.25, 1.31 (2 d, 6 H, *J* 6.5 Hz, H-6,6,6 and H-6′,6′,6′), 3.34 (s, 3 H, OMe), 5.16 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 7.33 (m, 20 H, 4 Ph). Anal. Calcd for $C_{41}H_{48}O_9$: C, 71.9; H, 7.0. Found: C, 71.6; H, 6.9.

Methyl 3-O-[3-O(2-O-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl]-α-L-rhamnopyranoside (**4**).—To a stirred solution of **19** (0.15 g, 0.22 mmol), **5** (80 mg, 0.26 mmol), 4A molecular sieves (100 mg), and dry CH_2Cl_2 (5 mL) at 0°C was added boron trifluoride etherate (30 μL). After 3 h at room temperature, the mixture was worked up as described above. Column chromatography (1:4 EtOAc–light petroleum) of the product gave **20** (70 mg) contaminated with **19**. *O*-Deacetylation of the mixture with MeOH (3 mL) and Na (10 mg) and column chromatography (50:1 $CHCl_3$–MeOH) of the product gave methyl 2,4-di-*O*-benzyl-3-*O*-[2,4-di-*O*-benzyl-3-*O*-(2-*O*-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl]-α-L-rhamnopyranoside (**21**; 30 mg, 47%), isolated as a syrup; $[\alpha]_D$ −35° (*c* 1.8, $CHCl_3$). ^{1}H NMR data ($CDCl_3$): δ 1.02, 1.26, 1.32 (3 d, 9 H, *J* 6.0, 6.5 Hz, H-6,6,6, H-6′,6′,6′, and H-6″,6″,6″), 3.20, 3.34 (2 s, 6 H, 2 OMe), 7.25 (m, 20 H, 4 Ph).

Compound **21** (18 mg, 0.02 mmol) was hydrogenolysed in the presence of 10% Pd/C (7 mg) in EtOH (2 mL) for 72 h. Column chromatography (10:1 $CHCl_3$–MeOH) of the product gave **3** (8 mg, 80%), isolated as a syrup, $[\alpha]_D$ −75° (*c* 0.8, MeOH). ^{1}H NMR data (CD_3OD): δ 4.64 (d, 1 H, *J* 1.5 Hz, H-1), 5.09 (d, 1 H, $J_{1',2'}$ 1.5 Hz, H-1′), 5.36 (d, 1 H, $J_{1'',2''}$ 4.0 Hz, H-1″). Anal. Calcd for $C_{20}H_{36}O_{13}$: C, 49.6; H, 7.4. Found: C, 49.1; H, 7.25.

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