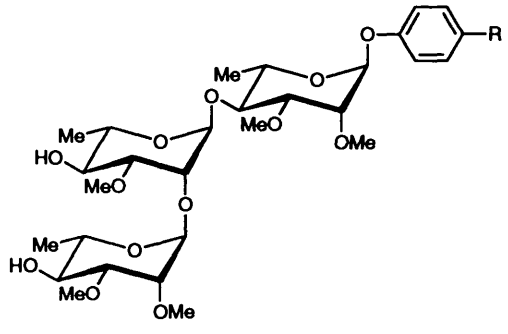
Synthesis of the Oligosaccharide Segment of a Novel Phenolic Glycolipid Antigen from *Mycobacterium haemophilum*

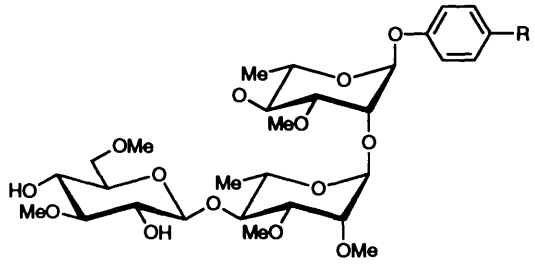
M. K. Gurjar* and K. Revathi Reddy
Indian Institute of Chemical Technology, Hyderabad 500 007, India

The synthesis of the trisaccharide segment from *Mycobacterium haemophilum* phenolic glucolipid has been described. The synthesis of the disaccharide derivative **12** containing a free hydroxy group at C-2′ was first examined by using 2-*O*-acetyl-4-*O*-benzyl-3-*O*-methyl-L-rhamnopyranosyltrichloroacetimidate **9** as a glycosyl donor and **10** as an aglycone followed by Zemplen deacetylation. The same glycosyl donor **9** was utilised for second coupling reaction with **12** to give the requisite trisaccharide **3** isolated after deacetylation, methylation and debenzylation. The high degrees of α-selectivity in both the coupling reactions were substantiated by using ^{1}H NMR, ^{13}C NMR and partially decoupled ^{13}C NMR spectral studies.

The isolation of species-specific antigens from *Mycobacterium* (*M.*) *leprae* and *M. tuberculosis* have renewed significant interest in mycobacterium glycolipids.[1] Recently it has also been observed that *M. kansasii*[2] and *M. avium*[3] serotype 4 are found in the majority of patients who are HIV-1 positive. The structure and antigenicity of the phenolic glycolipid **1** from *M.*



1



2

R = $CH_2(CH_2)_{15}CHCH_2CH(CH_2)_4CHCHCH_2CH_3$ (OMe, OMe, Me, OMe)

haemophilum that distinguished it from other mycobacteria has recently been described.[4] The oligosaccharide segment was established as 2,3-di-*O*-Me-L-Rhap-(α1→2)-3-*O*-Me-L-Rhap-(α1→4)-2,3-di-*O*-Me-L-Rhap-(α1→ which showed[4] novel structural similarities with that of the glycosyl residue: 3,6-di-*O*-Me-D-Glcp-(β1→4)-2,3-di-*O*-Me-L-Rhap-(α1→2)-3-*O*-Me-L-Rhap-(α1→ of *M. leprae* phenolic glycolipid **2**. For example, the glycolipids obtained from both *M. haemophilum* and *M. leprae* contained 2-linked 3-*O*-Me-α-L-Rhap and 4-linked 2,3-di-*O*-Me-L-Rhap but attached in a reverse sequence. It is also suggested[4] that this relationship may prove extremely useful in explaining the nonavailability and pathogenicity associated with *M. leprae*.

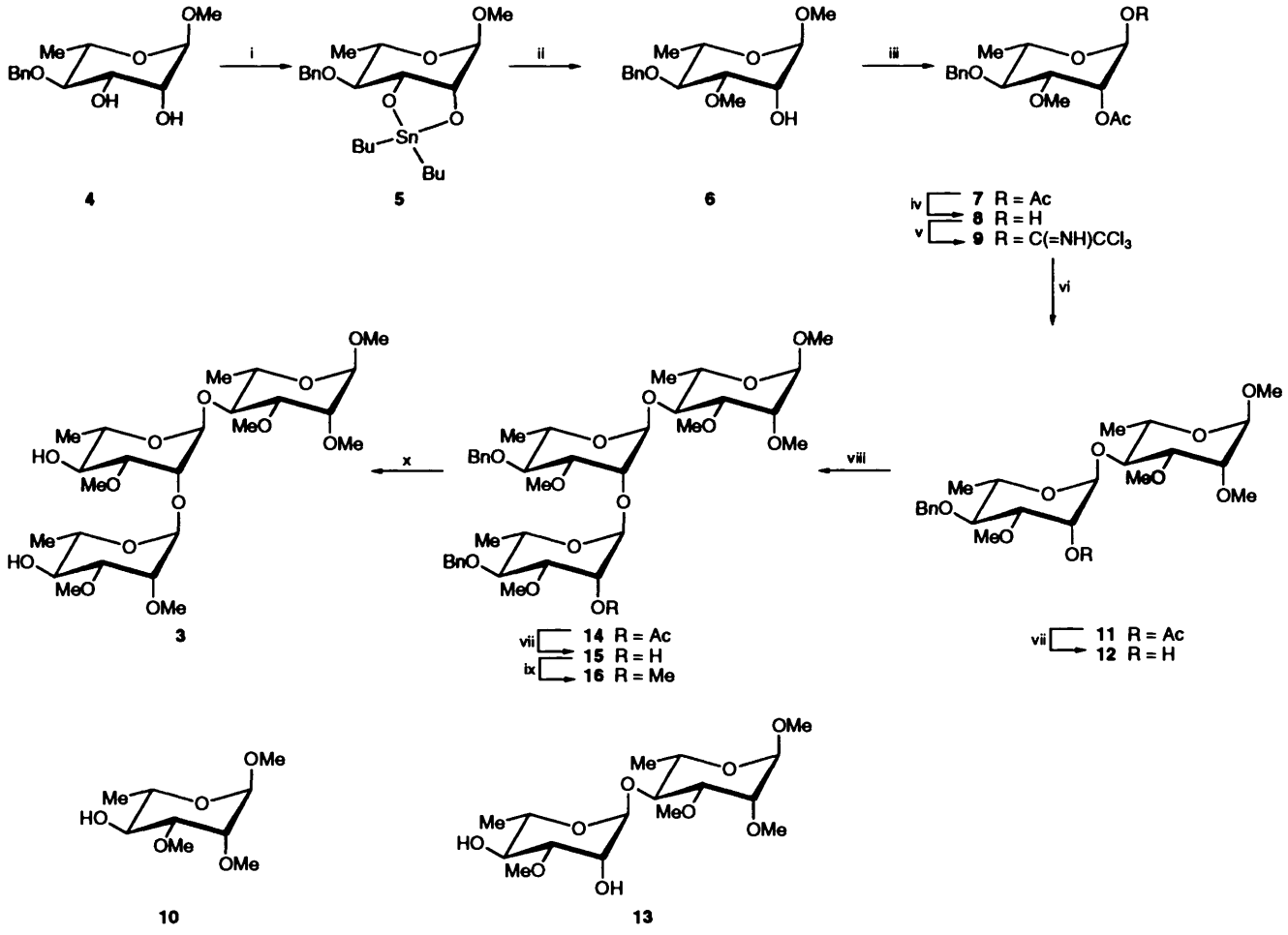
Development of an efficient strategy for the oligosaccharide preparation of a mycobacterium genus is a major objective of our laboratory.[5] Although a plethora of synthetic approaches[6] for *O*-glycosylation have been described with variable degrees of anomeric selectivity, we used Schmidt's trichloroacetimidate approach[7] because of its simplicity and reliability. In addition, synthesis of the antigenic oligosaccharide was basic to an understanding of the structure–activity relationship necessary for the development of a synthetic antigen required for serodiagnosis and vaccination.[8] We described herein our synthetic studies on the oligosaccharide obtained from *M. haemophilum*.

Results and Discussion

The first stage in a route to the trisaccharide **3** involved preparation of the disaccharide derivative **12** containing a free 2′-hydroxy group. The glycosyl donor, namely, 2-*O*-acetyl-4-*O*-benzyl-3-*O*-methyl-L-rhamnopyranosyl trichloroacetimidate **9** was used for the two successive glycosylations and the presence of acetyl group at *O*-2 was expected to provide a high degree of α-selectivity.

Methyl 4-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranoside **6** was synthesised by a modified route in which the methyl 4-*O*-benzyl-α-L-rhamnopyranoside[9] **4** was first transformed into the corresponding dibutyltin acetal derivative **5** by using dibutyltin oxide in refluxing benzene for 5 h followed by treatment with methyl iodide in the same solvent at reflux temperature for an additional 5 h to afford **6** (90%).[10] Hydrolysis of the *O*-glycoside bond by heating of the compound with 1.5 mol dm^{-3} sulfuric acid and dioxane at 100 °C for 3 h and then conventional acetylation with acetic anhydride, pyridine and dimethylaminopyridine (catalytic) at room temperature gave the diacetate **7**[11] obtained as a mixture of α-and β-anomers (7:3; 65%). With a view to removing the acetyl group at the anomeric position, **7** was treated with freshly prepared tributyltin ethoxide in refluxing 1,2-dichloroethane for 3 h to give **8** (93%). Subsequently, **8** was converted[12] into the trichloroacetimidate derivative **9** by employing trichloroacetonitrile, 1,8-diazabicyclo[5.4.0]undec-7-ene in methylene dichloride at room temperature for 30 min.

The coupling reaction between **9** and the methyl 2,3-di-*O*-methyl-α-L-rhamnopyranoside[13] **10** in the presence of a catalytic amount of boron trifluoride–diethyl ether and 4 Å molecular sieves in methylene dichloride at 0 °C afforded the disaccharide **11** (80%). The ^{1}H NMR spectrum of **11** revealed anomeric protons at δ 4.72 (d, $J_{1,2}$ 1.2 Hz) and 5.12 (d, $J_{1',2'}$



Scheme 1 *Reagents and conditions:* i, Bu_2SnO, C_6H_6, heat, 5 h; ii, MeI, Bu_4NI, C_6H_6, heat, 5 h; iii, 1.5 mol dm^{-3} H_2SO_4, dioxane, heat, 3 h, then Ac_2O, Py, DMAP, 24 h; iv, Bu_3SnOEt, $ClCH_2CH_2Cl$, heat, 3 h; v, DBU, CCl_3CN, CH_2Cl_2, 30 min; vi, **10**, BF_3·OEt_2, CH_2Cl_2, 0 °, 30 min; vii, NAOMe, MeOH, 2 h; viii, **9**, BF_3·OEt_2, CH_2Cl_2, 0 °, 30 min; ix, NaH, MeI, THF, 3 h; x, 10% Pd-C, H_2, MeOH, 1 atm, 20 h.

1.5 Hz), whilst the remaining protons had chemical shifts as expected. The partially decoupled ^{13}C NMR spectrum of **11** provided satisfactory stereochemical information since the observed coupling constants ($J_{C\text{-}1,H\text{-}1}$ 167.0 and $J_{C\text{-}1',H\text{-}1'}$ 173.0 Hz) were greater than 165 Hz, an indication[14] of α-configurations at both anomeric centres. Zemplen deacetylation of **11** gave the requisite disaccharide **12** containing a 2'-OH group free for the next coupling reaction.

Compound **12** was also hydrogenolysed in the presence of 10% palladium on charcoal in methanol at normal temperature and pressure to give **13** which constituted the inner segment of the oligosaccharide framework of *M. haemophilum*. The structure of **13** was confirmed by ^1H NMR and partially decoupled ^{13}C NMR spectral studies.

The second coupling reaction of **12** with **9** under the same conditions, as described earlier, provided the trisaccharide **14** (70%). In the ^1H NMR spectrum of **14**, three distinct singlets due to 1-H, 1'-H and 1''-H were located at δ 4.66, 5.04 and 5.13. Resonances characteristic of methoxy, benzyloxy and acetoxy groups appeared in the region expected of the assigned structure. However, further proof for **14** was gleaned from the ^{13}C NMR spectrum in which chemical shifts at δ 98.3 (C-1, $J_{C\text{-}1,1\text{-}H}$ 165.0 Hz), 98.5 (C-1, $J_{C\text{-}1',1'\text{-}H}$ 171.4 Hz) and 100.4 (C-1'', $J_{C\text{-}1'',1''\text{-}H}$ 171.5 Hz) confirmed α configurations. Removal of the acetyl group in **14** under Zemplen conditions gave **15** whose structure was also scrutinised by ^1H NMR, ^{13}C NMR and partially decoupled ^{13}C NMR spectral studies. The methylation of **15** with sodium hydride–methyl iodide in dry tetrahydrofuran at room temperature gave **16** which was finally debenzylated by hydrogenation over palladium-on-charcoal in methanol at normal temperature and pressure to give the crystalline trisaccharide **3** in whose NMR spectral analysis, resonances due to anomeric protons were located at δ 4.66, 5.08 and 5.16 whilst anomeric carbons appeared at δ 98.1 (C-1, $J_{C\text{-}1,1\text{-}H}$ 173.0 Hz), 98.4 (C-1', $J_{C\text{-}1',1'\text{-}H}$ 167.0 Hz) and 100.7 (C-1'', $J_{C\text{-}1'',1''\text{-}H}$ 174.0 Hz). In addition the chemical ionisation mass spectrum showed a molecular ion peak at *m/z* 540 (M^+).

Experimental

General Methods.—NMR spectra were recorded on a Varian Gemini 200 MHz spectrophotometer with tetramethylsilane as internal indicator. Chemical ionisation mass spectra were recorded on a VG MICROMASS 7070H instrument with acetone as ionisation molecule. Optical rotations were determined on a JASCO DIP 360 digital polarimeter and are expressed in units of 10^{-1} deg cm^2 g^{-1}.

Methyl 4-O-*Benzyl*-3-O-*methyl*-α-L-*rhamnopyranoside* **6**.—A solution of methyl 4-*O*-benzyl-α-L-rhamnopyranoside[9] **4** (3.0 g, 11.2 mmol) dibutyltin oxide (3.34 g, 13.4 mmol) and benzene (100 cm^3) was heated under reflux with azeotropic removal of water for 5 h. The solution was cooled to room temperature and methyl iodide (2.13 g, 15.0 mmol) and tetrabutylammonium iodide (1.5 g) were added to it. The reaction mixture was then further heated under reflux for 5 h, cooled to room temperature,

washed with water, dried and concentrated. The residue was chromatographed on silica gel by eluting with ethyl acetate–light petroleum (1:4), to afford pure **6** (2.85 g, 90%), isolated as a syrup: $[\alpha]_D$ −81.1 (*c* 0.6, chloroform) {lit.,[10] $[\alpha]_D$ −83 (chloroform)}; δ($CDCl_3$, 200 MHz) 1.21 (3 H, d, $J_{5,6}$ 6.5, 6-, 6′-, 6″-H), 3.36, 3.48 (6 H, 2 s, 2 × OMe), 3.36 (1 H, t, $J_{3,4} = J_{4,5}$ 90, 4-H), 3.50 (1 H, dd, $J_{2,3}$ 4.0, $J_{3,4}$ 9.0, 3-H), 4.04 (1 H, dd, $J_{1,2}$ 1.0, $J_{2,3}$ 4.0, 2-H), 4.62, 4.86 (2 H, 2d, *J* 12.0, PhCH_2), 4.68 (1 H, br s, 1-H) and 7.3 (5 H, m, Ph).

1,2-*Di*-O-*acetyl*-4-O-*benzyl*-3-O-*methyl*-α,β-L-*rhamnopyranose* **7**.—A mixture of compound **6** (2.85 g, 10.1 mmol), dioxane (10 cm^3) and 1.5 mol dm^{-3} sulfuric acid (10 cm^3) was heated on a boiling water-bath for 3 h after which it was neutralised with solid barium carbonate. The solid was filtered off and washed with methanol and the combined filtrate and washings were concentrated, traces of moisture being removed by co-distillation with toluene. Acetic anhydride (3 cm^3), pyridine (10 cm^3) and 4,4-dimethylaminopyridine (30 mg) were added to the residue and the mixture stored for 24 h. Ice–water (5 cm^3) was added to the reaction mixture which was then extracted with ethyl acetate. The ethyl acetate layer was washed with 1 mol dm^{-3} HCl, water, aqueous sodium carbonate and water and then dried. The residue obtained after concentration was purified by column chromatography on silica gel with ethyl acetate–light petroleum (1:9) to give **7** (2.3 g, 65%) (α:β = 7:3) isolated as a syrup: δ($CDCl_3$, 200 MHz) 1.30 (d, $J_{5,6}$ 6.5, 5α-CH_3), 1.34 (d, $J_{5,6}$ 6.5, 5β-CH_3), 2.12, 2.18 (2 s, α-CH_3CO_2), 2.10, 2.22 (2 s, β-CH_3CO_2), 3.42 (s, β-OMe), 3.44 (s, α-OMe), 4.62, 4.88 (2 H, 2d, *J* 12.0, PhCH_2), 5.26 (m, 2α-H), 5.50 (m, 2β-H), 5.68 (s, 1β-H), 5.94 (d, *J* 1.0, 1α-H) and 7.3 (5 H, m, Ph).

Methyl 2,3-*Di*-O-*methyl*-4-O-(2-O-*acetyl*-4-O-*benzyl*-3-O-*methyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranoside* **11**.—A solution of compound **7** (2.3 g, 6.51 mmol), tributyltin ethoxide (2.5 cm^3) and 1,2-dichloroethane (20 cm^3) was heated under reflux for 3 h and then concentrated. The residue was purified on silica gel by eluting with ethyl acetate–light petroleum (2:3) to give **8** (1.95 g) which was treated with 1,8-diazabicyclo-[5.4.0]undec-7-ene (0.9 cm^3) and trichloroacetonitrile (1.5 cm^3) in methylene dichloride (20 cm^3) at room temperature for 30 min. The solution was passed through a small column of silica gel and eluted with methylene dichloride to give **9** (2.75 g, 93%).

Compound **9** (2.75 g, 6.0 mmol) was added to a stirred solution of methyl 2,3-di-*O*-methyl-α-L-rhamnopyranoside[13] **10** (0.83 g, 40 mmol), 4 Å molecular sieves (2.0 g) in dichloromethane (30 cm^3) and the mixture cooled to 0 °C. Boron trifluoride–diethyl ether (50 mm^3) was added to the mixture which, after 30 min, was quenched with triethylamine (0.1 cm^3). The solution was filtered, washed with water, dried and concentrated. The residue was chromatographed on silica gel by eluting with ethyl acetate–light petroleum (1:4), to give **11** (1.6 g, 80%), isolated as a crystalline solid, m.p. 125–127 °C; $[\alpha]_D$ −53.2 (*c* 1.2, chloroform) (Found: C, 60.0; H, 7.5. Calc. for $C_{25}H_{38}O_{10}$: C, 60.2; H, 7.6%); δ_H($CDCl_3$) 1.29 (6 H, d, *J* 6.5, 5,5′-CH_3), 2.12 (3 H, s, CH_3CO_2), 3.37, 3.44, 3.46, 3.50 (12 H, 4 s, 4 × OMe), 4.61, 4.91 (2 H, 2d, *J* 11.7, PhCH_2), 4.72 (1 H, d, $J_{1,2}$ 1.2, 1-H), 5.12 (1 H, d, $J_{1',2'}$ 1.5, 1′-H), 5.40 (1 H, dd, $J_{2',3'}$ 4.0, 2′-H) and 7.3 (5 H, m, Ph); δ_C 98.1 (C-1, $J_{C\text{-}1,1\text{-}H}$ 167.0) and 99.4 (C-1′, $J_{C\text{-}1',1\text{-}H}$ 173.0).

Methyl 2,3-*Di*-O-*methyl*-4-O-(4-O-*benzyl*-3-O-*methyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranoside* **12**.—Sodium (0.1 g) was added to a solution of **11** (1.6 g, 3.2 mmol) in methanol (20 cm^3) and the mixture stirred at room temperature for 2 h. It was then deionised with Amberlite IR 120 (H) resin, filtered and concentrated. The residue was purified on silica gel by using ethyl acetate–light petroleum (2:3) to give **12** (1.39 g, 95%), isolated as a syrup: $[\alpha]_D$ −73.8 (*c* 1.41, chloroform); δ($CDCl_3$) 1.26 (3 H, d, $J_{5,6}$ 6.5, 5-CH_3), 1.30 (3 H, $J_{5',6'}$ 6.5, 5′-CH_3), 2.40 (1 H, br s, OH), 3.38, 3.46, 3.50, 3.52 (12 H, 4 s, 4 × OMe), 4.62, 4.88 (2 H, 2d, *J* 11.6, PhCH_2), 4.72 (1 H, d, $J_{1,2}$ 2.0, 1-H), 5.10 (1 H, d, $J_{1',2'}$ 2.1, 1′-H) and 7.35 (5 H, m, Ph); δ 97.6 (C-1, $J_{C\text{-}1,1\text{-}H}$ 165.0) and 98.7 (C-1′, $J_{C\text{-}1',1'H}$ 173.0).

Methyl 2,3-*Di*-O-*methyl*-4-O-(3-O-*methyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranoside* **13**.—A solution of **12** (0.10 g, 0.219 mmol), 10% palladium-on-charcoal (20 mg) in methanol (5 cm^3) was stirred under an atmosphere of hydrogen at normal pressure and room temperature for 12 h after which the catalyst was filtered off and the filtrate concentrated. The residue was purified by column chromatography on silica gel by using ethyl acetate–hexane (9:1) to give **13** (0.075 g, 93%), isolated as a syrup; $[\alpha]_D$ −65 (*c* 1.0, chloroform) (Found: C, 52.15; H, 8.0. Calc. for $C_{16}H_{30}O_9$: C, 52.45; H, 8.2%); δ_H($CDCl_3$) 1.28 (6 H, d, *J* 6.0, 5,5′-CH_3), 3.34, 3.42, (6 H, 2s, 2 × OMe), 3.48 (6 H, s, 2 × OMe), 4.04 (1 H, m, 2-H), 4.66 (1 H, d, $J_{1,2}$ 1.0, 1-H), 5.14 (1 H, d, $J_{1',2'}$ 1.0, 1′-H); δ_C 98.0 (C-1, $J_{C\text{-}1,1\text{-}H}$ 165.0) and 101.1 (C-1′, $J_{C\text{-}1',1'\text{-}H}$ 170.2).

Methyl 2,3-*Di*-O-*methyl*-4-O-[4-O-*benzyl*-3-O-*methyl*-2-O-(2-O-*acetyl*-4-O-*benzyl*-3-O-*methyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranosyl*]-α-L-*rhamnopyranoside* **14**.—Boron trifluoride-diethyl ether (30 mm^3) was added to a stirred solution of **12** (1.0 g, 2.19 mmol), **9** (1.5 g, 3.3 mmol) and 4 Å molecular sieves (2.0 g) in dichloromethane (20 cm^3) at 0 °C. After 30 min the reaction mixture was worked-up and the residue chromatographed on silica gel with ethyl acetate–light petroleum (1:3) as eluent to afford **14** (1.15 g, 70%), isolated as a syrup; $[\alpha]_D$ −57.3 (*c* 2.48, chloroform): δ_H($CDCl_3$) 1.20, 1.26, 1.30 (9 H, 3d, *J* 6.4, 5,5′,5″-CH_3), 2.15 (3 H, s, CH_3CO_2), 3.32, 3.38, 3.43, 3.46, 3.48 (15 H, 5s, 5 × OMe), 4.58, 4.60, 4.83, 4.86 (4 H, 4d, *J* 11.5, 2 × PhCH_2), 4.66 (1 H, s, 1-H), 5.04 (1 H, s, 1′-H), 5.13 (1 H, s, 1″-H), 5.40 (1 H, m, 2″-H), 7.3 (10 H, m, 2 × Ph); δ_C 98.3 (C-1, $J_{C\text{-}1,1\text{-}H}$ 165.0), 98.5 (C-1′, $J_{C\text{-}1',1'\text{-}H}$ 171.4) and 100.4 (C-1″, $J_{C\text{-}1'',1''\text{-}H}$ 171.5).

Methyl 2,3-*Di*-O-*methyl*-4-O-[4-O-*benzyl*-3-O-*methyl*-2-O-(4-O-*benzyl*-3-O-*methyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranosyl*]-α-L-*rhamnopyranoside* **15**.—Compound **14** (0.70 g, 0.94 mmol) was dissolved in methanol (10 cm^3) and sodium (40 mg) was added to the solution. After 2 h at room temperature, the reaction mixture was neutralised with Amberlite IR 120 (H) resin, filtered and concentrated. The residue was purified on a column of silica gel with ethyl acetate–light petroleum (2:3) as eluent to give **15** (0.62 g, 94%), isolated as a solid, m.p. 51–53 °C; $[\alpha]_D$ −64.4 (*c* 1.5, chloroform) (Found: C, 63.3; H, 7.45. Calc. for $C_{37}H_{54}O_{13}$: C, 62.9; H, 7.6%); δ_H($CDCl_3$) 1.3 (9 H, m, 5-, 5′-, 5″-CH_3), 3.37, 3.42, 3.49, 3.51, 3.54 (15 H, 5 s, 5 × OMe), 4.60, 4.62, 4.87, 4.90 (4 H, 4 d, *J* 11.7, 2 × PhCH_2), 4.70 (d, $J_{1,2}$ 1.0, 1-H), 5.14 (1 H, s, 1′-H), 5.19 (d, $J_{1'',2''}$ 1.0, 1″-H) and 7.3 (10 H, m, 2 × Ph); δ_C 98.5 (C-1, $J_{C\text{-}1,1\text{-}H}$ 166.0), 100.5 (C-1′ + C-1″, *J* 169.0).

Methyl 2,3-*Di*-O-*methyl*-4-O-[4-O-*benzyl*-3-O-*methyl*-2-O-(4-O-*benzyl*-2,3-*di*-O-*methyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranosyl*]-α-L-*rhamnopyranoside* **16**.—Methyl iodide (0.3 cm^3) was added to a solution of compound **15** (0.40 g, 0.56 mmol) sodium hydride (0.15 g) and dry tetrahydrofuran (5 cm^3) and the mixture stirred for 3 h at room temperature. Methanol (1 cm^3) was then added to it to decompose sodium hydride after which it was concentrated and partitioned between water–ethyl acetate (1:1; 60 cm^3). The ethyl acetate layer was dried and concentrated and the residue chromatographed on silica gel with ethyl acetate–light petroleum (1:2) as eluent to give **16** (0.38 g, 93%), isolated as a syrup: $[\alpha]_D$ −78.5 (*c* 0.6, chloroform): δ_H($CDCl_3$)

1.24, 1.27, 1.30 (9 H, 3 d, *J* 6.0, 5-, 5'-, 5''-CH_3), 3.35, 3.40, 3.48, 3.50 (12 H, 4 s, 4 × OMe), 3.56 (6 H, s, 2 × OMe), 4.59, 4.61, 4.85, 4.89 (4 H, 4 d, *J* 10.6, PhCH_2), 4.78 (1 H, d, $J_{1,2}$ 1.5, 1-H), 5.12 (2 H, d, *J* 1.2, 1'-H, 1''-H) and 7.3 (10 H, m, 2 × Ph).

Methyl 2,3-*Di*-O-*methyl*-4-O-[3-O-*methyl*-2-O-(2,3-*di*-O-*methyl*-α-L-*rhamnopyranosyl*)-α-L-*rhamnopyranosyl*]-α-L-*rhamnopyranoside* **3**.—A solution of compound **16** (0.30 g, 0.41 mmol), 10% palladium-on-charcoal (30 mg) in methanol (5 cm^3) was stirred under an atmosphere of hydrogen at normal pressure and room temperature for 20 h. The residue was purified by column chromatography on silica gel by using ethyl acetate–methanol (30:1) to give crystalline solid **3** (0.195 g, 86%), m.p. 158–159 °C; $[\alpha]_D$ −97.3 (*c* 1.0, chloroform) (Found: C, 52.9; H, 8.0. Calc. for $C_{24}H_{44}O_{13}$: C, 53.3; H, 8.1%); δ_H($CDCl_3$) 1.26, 1.28, 1.30 (9 H, 3 d, *J* 6.5, 5-, 5'-, 5''-CH_3), 3.36, 3.44 (6 H, 2 s, 2 × OMe), 3.48 (12 H, br s, 4 × OMe), 4.66 (1 H, s, 1-H), 5.08 (1 H, s, 1'-H) and 5.16 (1 H, s, 1''-H); δ_C 98.1 (C-1, $J_{C\text{-}1,1\text{-}H}$ 173.0), 98.4 (C-1', $J_{C\text{-}1',1'\text{-}H}$ 167.0) and 100.7 (C-1'', $J_{C\ 1'',1''\text{-}H}$ 174.0); *m/z* (CIMS) 540 (M^+).

References

1 P. J. Brennan, *Microbial Lipids*, 1988, vol. 1, Academic Press, London, p. 203; P. J. Brennan, in *The Mycobacteria. A Source Book*, Part A, eds. G. B. Kubica and G. L. Wayne, Marcel Dekker, New York, 1984, 467.
2 G. T. Valainis, I. M. Cardona and D. L. Greer, *J. Acquired Immune Defic. Syndr.*, 1991, **4**, 516.
3 M. K. Gurjar and G. Viswanadham, *Tetrahedron Lett.*, 1991, **32**, 6194.
4 S. B. Gurdyal, M. McNeil, E. M. David, P. Francoise, M. Ridell and P. J. Brennan, *Biochemistry*, 1991, **30**, 7772.
5 M. K. Gurjar and K. Revathi Reddy, *Carbohydr. Res.*, 1992, **226**, 233; M. K. Gurjar, M. K. and A. S. Mainkar, *Tetrahedron*, 1992, **48**, 6729; M. K. Gurjar and P. S. Mainkar, *Carbohydr. Res.*, 1993, **293**, 297.
6 H. Paulsen, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 155.
7 R. R. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 212.
8 D. Chatterjee, S. N. Cho, C. Stewart, J. T. Douglas, T. Fujiwara and P. J. Brennan, *Carbohydr. Res.*, 1988, **183**, 241.
9 V. Pozsgay, *Carbohydr. Res.*, 1969, **10**, 466.
10 V. Pozsgay, *Carbohydr. Res.*, 1979, **69**, 284.
11 T. Fujiwara and S. Izumi, *Agric. Biol. Chem.*, 1987, **51**, 2539.
12 M. K. Gurjar and U. K. Saha, *Tetrahedron Lett.*, 1992, **33**, 4979.
13 K. Bock, T. Hvidt, J. Marino-Albernas and V. Verez-Bencomo, *Carbohydr. Res.*, 1990, **200**, 33.
14 V. Pozsgay and A. Neszmely, *Carbohydr. Res.*, 1980, **80**, 196; R. Kasai, M. Okihara, J. Asakawa, K. Mizuyani and D. Tanaka, *Tetrahedron*, 1979, **35**, 1427.

Paper 3/00091E
Received 6th *January* 1993
Accepted 25th *February* 1993