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SYNTHESIS AND ^{13}C-N.M.R. SPECTROSCOPY OF 2-*O*- AND 6-*O*-ACETYL-3-*O*-α-L-RHAMNOPYRANOSYL-D-GALACTOSE, CONSTITUENTS OF BACTERIAL CELL-WALL POLYSACCHARIDES

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ABSTRACT

Benzyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside (**11**) has been synthesised by two routes. Partial deacetylation of **11** and then acid hydrolysis yielded benzyl 2-*O*-acetyl-3-*O*-α-L-rhamnopyranosyl-β-D-galactopyranoside, catalytic hydrogenolysis of which gave the first title compound in excellent yield. Benzyl 4,6-*O*-benzylidene-3-*O*-α-L-rhamnopyranosyl-β-D-galactopyranoside was benzylated, and hydrogenolysis ($LiAlH_4$–$AlCl_3$) of the product gave the disaccharide derivative **16** with only HO-6 unsubstituted. Acetylation of **16** followed by catalytic hydrogenolysis gave the crystalline, second title compound. As model compounds for comparative n.m.r. studies, 2-*O*-, 3-*O*-, and 6-*O*-acetyl-D-galactose were also synthesised.

INTRODUCTION

Because of the frequent occurrence of partially acetylated carbohydrates in Nature, mainly in oligo- and poly-saccharides that are constituents of immunodeterminant bacterial capsules and lipopolysaccharides[1] and also as components of plant glycosides[2,3], their chemical synthesis is important. The chemical methods[4,5] for locating the position of acetyl groups in oligo- and poly-saccharides are limited due to possible acetyl migration, and ^{13}C-n.m.r. spectroscopy[6–10] should be more reliable. However, the ^{13}C-n.m.r. method is limited at present, because relatively few such derivatives have been investigated[11–13].

Apparently, no syntheses of oligosaccharides having only one acetyl group in a given position have been described, and the two title disaccharides were chosen as models because they are constituents of the immunodeterminant repeating-unit of the O-specific side-chains in *Salmonella* lipopolysaccharides belonging to sero-group[14] B and sero-group[15] E_1.

RESULTS AND DISCUSSION

The partial deacylation of benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2,3,4-

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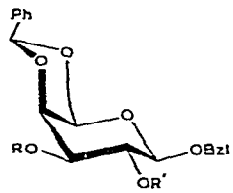
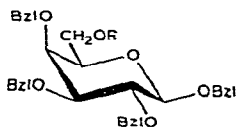
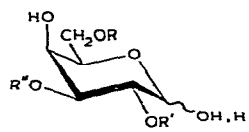
tri-*O*-acetyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside to give benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-α-L-rhamnopyranosyl-β-D-galactopyranoside has been reported[16]. Similar results have been encountered[17] with galactose-containing oligosaccharides. These findings suggested a new route for the synthesis of 2-*O*-acetyl-3-*O*-α-L-rhamnopyranosyl-D-galactose (**14**) from benzyl 4,6-*O*-benzylidene-3-*O*-α-L-rhamnopyranosyl-β-D-galactopyranoside[16] (**10**). Conventional acetylation of **10** gave **11**.



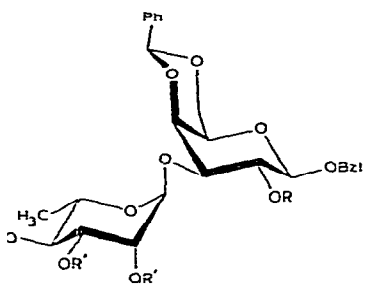
1 R = R′ = H
2 R = R′ = Ac
3 R = H,R′ = Ac
4 R = Ac,R′ = H



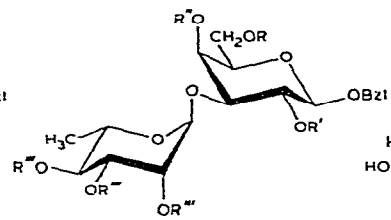
5 R = H
6 R = Ac



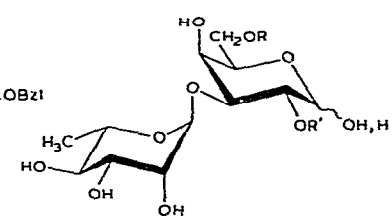
7 R = R‴ = H,R′ = Ac
8 R = R′ = H,R‴ = Ac
9 R = Ac,R′ = R‴ = H



10 R = R′ = H
11 R = R′ = Ac
12 R = Ac,R′ = H
15 R = R′ = Bzl



13 R = R″ = R‴ = H,R′ = Ac
16 R = H,R′ = R″ = R‴ = Bzl
17 R = Ac,R′ = R″ = R‴ = Bzl



14 R = H,R′ = Ac
18 R = Ac,R′ = H

Zemplén deacetylation of **11** gave **12** in excellent yield and in which AcO-2 was retained. Mild, acid hydrolysis of **12** afforded benzyl 2-*O*-acetyl-3-*O*-α-L-rhamnopyranosyl-β-D-galactopyranoside (**13**), hydrogenolysis of which gave **14**.

An alternative route to **11** was as follows. Benzyl 4,6-*O*-benzylidene-β-D-galactopyranoside[18] (**1**) was acetylated with *N*-acetylimidazole under the conditions used by Chittenden[19] for the benzoylation of **1** with *N*-benzoylimidazole. Column chromatography of the product mixture gave the diacetate **2** and the acetates (**3** and **4**) of **1**. The ^{1}H-n.m.r. spectrum of **4** contained a low-field doublet of doublets with $J_{2,3}$ 10.4 and $J_{3,4}$ 3.6 Hz, clearly demonstrating the structure to be benzyl 3-*O*-acetyl-4,6-*O*-benzylidene-β-D-galactopyranoside (**4**). In the spectrum of **3**, H-2 resonated at δ 5.14 ($J_{1,2}$ 8.4, $J_{2,3}$ 10.4 Hz).

TABLE I

^{13}C-N.M.R. CHEMICAL SHIFTS (P.P.M.)

Carbon atom	*Compound*																							
	A[a]		**7**				**8**				**9**				**B**[a]		**14**				**18**			
	α	β	α	Δδ	β	Δδ	α	Δδ	β	Δδ	α	Δδ	β	Δδ	α	β	α	Δδ	β	Δδ	α	Δδ	β	Δδ
Galactose																								
C-1	93.1	97.3	90.5	−2.6	95.4	−1.9	93.0	−0.1	97.2	−0.1	93.1	0	97.2	−0.1	93.1	97.1	90.6	−2.5	95.4	−1.7	93.2	+0.1	97.2	+0.1
C-2	69.1	72.7	72.2	+3.1	74.6	+1.9	66.9	−2.2	70.4	−2.3	69.0	−0.1	72.5	−0.2	68.5	72.1	71.2	+2.7	73.6	+1.5	68.3	−0.2	71.9	−0.2
C-3	69.8	73.6	67.8	−2.0	71.9	−1.7	73.7	+3.9	76.4	+2.8	69.7	−0.1	73.4	−0.2	77.9	81.2	76.0	−1.9	79.4	−1.8	77.6	−0.3	81.0	−0.2
C-4	70.2	69.6	70.1	−0.1	69.5	−0.1	68.0	−2.2	67.3	−2.3	70.0	−0.2	69.5	−0.1	70.0	69.3	69.8	−0.2	69.2	−0.1	70.9	+0.9	69.3	0
C-5	71.2	75.7	71.1	−0.1	76.0	+0.3	70.7	−0.5	75.5	−0.2	68.7	−2.5	73.1	−2.6	71.2	75.7	70.9	−0.3	75.3	−0.4	68.8	−2.4	73.0	−2.7
C-6	61.9	61.7	61.8	−0.1	61.6	−0.1	61.7	−0.2	61.5	−0.2	64.9	+3.0	64.7	+3.0	61.8	61.6	61.7	−0.1	61.5	−0.1	64.6	+2.8	64.4	+2.8
Rhamnose																								
C-1															102.9		102.6				103.0			
C-2															70.9[b]		70.9				70.9			
C-3															71.0[b]		71.0				71.0			
C-4															72.9		72.8				72.9			
C-5															69.8		69.9				69.8			
C-6															17.43		17.43				17.42			

[a]**A**, D-Galactose; **B**, 3-*O*-α-L-rhamnopyranosyl-D-galactose. [b]Assignments may be reversed.

Treatment of **3** with tri-*O*-acetyl-α-L-rhamnopyranosyl bromide, using Helferich conditions, gave **11** together with a small proportion of the β anomer.

The synthesis of the second, title disaccharide derivative, 6-*O*-acetyl-3-*O*-α-L-rhamnopyranosyl-D-galactose (**18**) was accomplished as follows. Benzylation of **10** and regioselective hydrogenolysis[20] of the benzylidene group of the product **15** with $LiAlH_4$–$AlCl_3$ gave **16**, which was converted into the acetate **17**. Hydrogenolysis of the benzyl groups in **17** then gave **18**.

Catalytic hydrogenolysis of **3** and **4** gave crystalline 2-*O*-acetyl- (**7**) and 3-*O*-acetyl-D-galactose (**8**), respectively. Benzyl 2,3,4-tri-*O*-benzyl-β-D-galactopyranoside[20] (**5**) was acetylated and the product (**6**) was hydrogenolysed, to give crystalline 6-*O*-acetyl-D-galactose (**9**).

The assignment of the ^{13}C-n.m.r. signals of the disaccharide derivatives **14** and **18** was relatively straightforward on the basis of the data for 3-*O*-α-L-rhamnopyranosyl-D-galactose[16]. A solution of **14** in D_2O had an α,β-ratio of 7:5. The carbons of the α- and β-galactopyranose moieties gave well-separated signals consistent with this ratio. The signals of the rhamnopyranosyl moiety appeared with almost double intensities, reflecting independence of the anomeric configuration at the reducing end. Acetylation at O-2 in 3-*O*-α-L-rhamnopyranosyl-D-galactose only slightly influences the chemical shift of the signals for C-4,5,6 in both the α and β anomers. The change of the chemical shift of the signal for C-3 does not depend markedly upon the anomeric configuration of the galactopyranose moiety (−1.9 and −1.8 p.p.m. for the α and β anomers, respectively). The change (β-shift) in the chemical shift of the signal for C-1 depends on the anomeric configuration (α −2.5 p.p.m., β −1.7 p.p.m.), suggesting that the α anomer is the more crowded. Similar shifts (α-shifts) occur for the C-2 signal (α 2.7 p.p.m., β 1.5 p.p.m.). These data show that no acetyl migration took place during the catalytic hydrogenation and that the acetyl group must be located at O-2.

A similar situation was found for the ^{13}C-n.m.r. spectrum of **18**. Acetylation at O-6 resulted in a 2.8-p.p.m. downfield shift of the signal for C-6 in both anomers. The β-shifts are also similar (α −2.4 p.p.m., β −2.7 p.p.m.). Acetylation of HO-6 does not influence the chemical shifts of the other carbon atoms. An α,β-ratio of 3:4 was found for **18**.

The above assignments for **14** and **18** were supported by the ^{13}C-n.m.r. data for **7**–**9** (Table I). For each compound, the α-shift values are positive and independent of the anomeric configuration. The β-shifts are negative and in the range 1.7–2.6 p.p.m.

It is well established[7,11] that acetylation β-shifts are negative, and they are useful for the assignment of the ^{13}C-n.m.r. spectra. The α-shifts noted above involve downfield shifts and are also very characteristic parameters.

EXPERIMENTAL

General methods. — Melting points (uncorrected) were determined with a Kofler apparatus. Reactions were monitored by t.l.c. on Kieselgel 60 F_{254} (Merck), with

detection by charring with sulfuric acid. Kieselgel G (Reanal) was used for short-column chromatography. Optical rotations were measured with a Perkin–Elmer 241 automatic polarimeter; equilibrium values are given for compounds **7–9**, **14**, and **18**. ^{1}H-N.m.r. spectra were recorded with a Jeol MH-100 (100 MHz) instrument (internal Me_4Si) and ^{13}C-n.m.r. spectra with a Varian XL-100-15 FT spectrometer for solutions in D_2O (internal 1,4-dioxane, δ 67.4 relative to the signal for Me_4Si). I.r. spectra were recorded with a Perkin–Elmer 700 instrument.

*Partial acetylation of benzyl 4,6-*O*-benzylidene-β-*D*-galactopyranoside with N-acetylimidazole.* — To a solution of recrystallised imidazole (1.36 g) in alcohol-free chloroform (15 mL) at 5° was added a solution of acetyl chloride (0.785 g) in alcohol-free chloroform (5 mL). The imidazole hydrochloride was removed, the filtrate was added to a solution of benzyl 4,6-*O*-benzylidene-β-D-galactopyranoside[18] (**1**, 3.28 g) in alcohol-free chloroform (20 mL), and the mixture was boiled under reflux for 18 h. The cooled mixture was diluted with dichloromethane (100 mL), washed with aqueous $NaHCO_3$ (2 × 15 mL) and water (2 × 15 mL), dried (Na_2SO_4), and concentrated. The residue was eluted from Kieselgel G with 6:4 dichloromethane–ethyl acetate.

Eluted first was benzyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-β-D-galactopyranoside (**2**; 360 mg, 8.9%), m.p. 193–194° (from ethanol), $[\alpha]_D$ +26° (*c* 0.7, chloroform). Eluted second was benzyl 3-*O*-acetyl-4,6-*O*-benzylidene-β-D-galactopyranoside (**4**; 1.23 g, 33.6%), and third, a mixture (1.33 g) of **4** and benzyl 2-*O*-acetyl-4,6-*O*-benzylidene-β-D-galactopyranoside (**3**).

Repeated chromatography of this mixture gave more **4** (610 mg) and **3** (560 mg, 15.3%), m.p. 170–171° (from ethanol), $[\alpha]_D$ −27° (*c* 0.7, chloroform), R_F 0.45 (dichloromethane–ethyl acetate, 6:4), ν_{max} 1745 cm^{-1} (C=O). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.50–7.10 (m, 10 H, aromatic protons), 5.49 (s, 1 H, PhC*H*), 5.14 (dd, 1 H, H-2), 4.75 (q, 2 H, PhCH_2), 4.43 (d, 1 H, H-1), 4.41–3.90 (m, 3 H, H-5,6,6), 3.65 (ddd, 1 H, H-3), 3.36 (m, 1 H, H-4), 2.66 (d, 1 H, OH), and 2.00 (s, 3 H, OAc); $J_{1,2}$ 8.4, $J_{2,3}$ 10.4, $J_{3,4}$ 4.0, $J_{H,OH}$ 11.6 Hz.

Anal. Calc. for $C_{22}H_{24}O_7$: C, 65.99; H, 6.04. Found: C, 65.80; H, 6.11.

Compound **4** (total yield, 1.84 g; 50.2%) had m.p. 122–123° (from cyclohexane–ethanol), $[\alpha]_D$ +28° (*c* 0.8, chloroform), R_F 0.56, ν_{max} 1760 cm^{-1} (C=O). ^{1}H-N.m.r. data: δ 7.45–7.15 (m, 10 H, aromatic protons), 5.45 (s, 1 H, PhC*H*), 4.81 (dd, 1 H, H-3), 4.76 (q, 2 H, PhCH_2), 4.39 (d, 1 H, H-1), 4.37–3.89 (m, 4 H, ring protons), 3.37 (m, 1 H, H-4), 2.72 (d, 1 H, OH), and 2.00 (s, 3 H, OAc); $J_{1,2}$ 8.1, $J_{2,3}$ 10.4, $J_{3,4}$ 3.6, $J_{H,OH}$ 2.8 Hz.

Anal. Found: C, 65.75; H, 6.00.

*Benzyl 6-*O*-acetyl-2,3,4-tri-*O*-benzyl-β-*D*-galactopyranoside* (**6**). — To a solution of benzyl 2,3,4-tri-*O*-benzyl-β-D-galactopyranoside[20] (**5**, 400 mg) in pyridine (20 mL) was added acetic anhydride (20 mL), and, after storage overnight at room temperature, ethanol (10 mL) was added. After 20 min, the mixture was concentrated and benzene (3 × 15 mL) was distilled from the residue. Recrystallisation of the crude product (410 mg, 95.1%) from ethanol (4 mL) gave **6** (215 mg, 49.9%), m.p.

100–101°, $[\alpha]_D$ −41.5° (*c* 0.6, chloroform), R_F 0.59 (light petroleum–ethyl acetate, 7:3).

Anal. Calc. for $C_{36}H_{38}O_7$: C, 74.21; H, 6.57. Found: C, 73.89; H, 6.65.

2-O-Acetyl-D-galactose (**7**). — A mixture of 10% Pd/C (100 mg) and ethanol (5 mL) was stirred under hydrogen for 15 min, and a solution of **3** (280 mg) in a mixture of ethanol (10 mL) and acetic acid (5 mL) was then added. The mixture was stirred overnight under hydrogen, the catalyst was then collected and washed with ethanol (2 × 5 mL), and the combined filtrate and washings were concentrated. Benzene (3 × 10 mL) was distilled from the residue (151 mg, 97.2%), which was crystallised from methanol–ethyl acetate to obtain **7** (96 mg, 61.8%), m.p. 130–132°, $[\alpha]_D$ +91° (*c* 1.3, water), R_F 0.59 (1-butanol–methanol–water, 2:1:1), ν_{max} 1760 cm^{-1} (C=O).

Anal. Calc. for $C_8H_{14}O_7$: C, 43.25; H, 6.35. Found: C, 43.45; H, 6.30.

3-O-Acetyl-D-galactose (**8**). — Catalytic hydrogenation of **4** (280 mg), as described for **3**, gave a crude product (153 mg, 98.5%) that was crystallised from methanol–ethyl acetate, to yield **8** (85 mg, 54.7%), m.p. 128–131°, $[\alpha]_D$ +81° (*c* 1.4, water), R_F 0.58 (1-butanol–methanol–water, 2:1:1), ν_{max} 1750 cm^{-1} (C=O).

Anal. Calc. for $C_8H_{14}O_7$: C, 43.25; H, 6.35. Found: C, 42.94; H, 6.46.

6-O-Acetyl-D-galactose (**9**). — Catalytic hydrogenation of **6** (200 mg), as described for **3**, with recrystallisation of the product (75 mg, 98.3%) from methanol–ethyl acetate, gave **9**, m.p. 141–143°, $[\alpha]_D$ +9° (*c* 0.3, water), R_F 0.58 (1-butanol–methanol–water, 2:1:1), ν_{max} 1775 cm^{-1} (C=O).

Anal. Calc. for $C_8H_{14}O_7$: C, 43.25; H, 6.35. Found: C, 43.50; H, 6.26.

Benzyl 2-O-acetyl-4,6-O-benzylidene-3-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside (**11**). — (*a*) A solution of **3** (260 mg) in benzene (20 mL) and nitromethane (20 mL) was concentrated to half volume at atmospheric pressure. Powdered $Hg(CN)_2$ (164 mg) and tri-*O*-acetyl-α-L-rhamnopyranosyl bromide (229 mg) were then added and the mixture was stirred at 45°. After 15, 30, and 45 min, more $Hg(CN)_2$ (41 mg) and glycosyl bromide (57 mg) were added, and stirring was continued for 1 h.

The cooled mixture was filtered and concentrated. The residue was extracted with dichloromethane (50 mL), the extract was filtered, washed with aqueous 5% potassium iodide (2 × 10 mL) and water (2 × 10 mL), dried (Na_2SO_4), and concentrated. The residue was crystallised from ethanol (8 mL) to obtain, first, the β anomer of **11** (15 mg, 3.4%), m.p. 268–270°, $[\alpha]_D$ +38° (*c* 0.8, chloroform), R_F 0.24 (ethyl acetate–light petroleum, 6:4). ^{1}H-N.m.r. data ($CDCl_3$, 200 MHz): δ 7.45–7.27 (m, 10 H, aromatic protons), 5.53 (s, 1 H, PhC*H*), 5.39 (dd, 1 H, H-2), 5.36 (dd, 1 H, H-2'), 5.01–4.64 (m, 5 H, H-1',3',4' and PhCH_2), 4.54 (d, 1 H, H-1), 4.29 (m, 1 H, H-5), 4.24 (m, 2 H, 2 H-6), 3.91 (dd, 1 H, H-3), 3.42 (m, 1 H, H-4), 3.31 (m, 1 H, H-5'), 2.10, 2.08, 2.04, and 1.99 (4 s, 12 H, 4 OAc), and 1.22 (d, 3 H, C-Me); $J_{1,2}$ 8.0, $J_{2,3}$ 10.5, $J_{3,4}$ 3.5, $J_{5',6'}$ 6.0 Hz.

From the mother liquor, **11** (115 mg, 26.3%) crystallised upon storage for 1 h. Column chromatography yielded more (80 mg) **11** (overall yield, 195 mg; 44.6%);

m.p. 189–191°, $[\alpha]_D$ +6° (*c* 0.7, chloroform), R_F 0.30 (ethyl acetate–light petroleum, 6:4). Characteristic ^{1}H-n.m.r. data ($CDCl_3$): δ 7.60–7.20 (m, 10 H, aromatic protons), 5.50 (s, 1 H, PhC*H*), 5.43 (dd, 1 H, H-2), 5.24 (dd, 1 H, H-3'), 5.17 (bs, 1 H, H-1'), 5.12 (dd, 1 H, H-2'), 4.76 (q, 2 H, PhCH_2), 4.54 (d, 1 H, H-1), 3.64 (dd, 1 H, H-3), 3.39 (m, 1 H, H-4), 2.10, 1.95, and 1.93 (3 s, 6 H, 3 H, 3 H, 4 OAc), and 1.01 (d, 3 H, C-Me).

Anal. Calc. for $C_{34}H_{40}O_{14}$: C, 60.71; H, 5.99. Found: C, 60.43; H, 5.81.

(*b*) Acetylation of benzyl 4,6-*O*-benzylidene-3-*O*-α-L-rhamnopyranosyl-β-D-galactopyranoside[16] (**10**, 400 mg), as described above for the preparation of **6**, gave a crude product (510 mg, 95.6%) that was recrystallised from ethanol (16 mL), to obtain **11** (204 mg, 38.3%), m.p. 192–193°, $[\alpha]_D$ +4.5° (*c* 0.8, chloroform), R_F 0.30 (ethyl acetate–light petroleum, 6:4).

Benzyl 2-O-acetyl-4,6-O-benzylidene-3-O-α-L-rhamnopyranosyl-β-D-galactopyranoside (**12**). — To a solution of **11** (320 mg) in dry methanol (100 mL) was added sodium methoxide (5 mg). The solution was kept at room temperature for 2 h, neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. The residue (251 mg, 96.5%) was recrystallised from ethanol, to obtain **12**, m.p. 215–218°, $[\alpha]_D$ +16° (*c* 0.3, pyridine), R_F 0.39 (dichloromethane–methanol, 9:1), ν_{max} 1770 cm^{-1} (C=O). ^{1}H-N.m.r. data ($CDCl_3$ + Me_2SO-d_6): δ 7.60–7.00 (m, 10 H, aromatic protons), 5.48 (s, 1 H, PhC*H*), 5.17 (t, 1 H, H-2), 1.96 (s, 3 H, OAc), and 1.22 (d, 3 H, C-Me).

Anal. Calc. for $C_{28}H_{34}O_{11}$: C, 61.53; H, 6.27. Found: C, 61.40; H, 6.35.

Benzyl 2-O-acetyl-3-O-α-L-rhamnopyranosyl-β-D-galactopyranoside (**13**). — A mixture of crude **12** (200 mg), ethanol (20 mL), and 0.5M sulfuric acid (20 mL) was boiled under reflux for 4 h, and then neutralised with barium carbonate, filtered, and concentrated. The product (157 mg, 93.6%) was recrystallised from ethanol (8 mL), to yield **13** (112 mg, 66.8%), m.p. 202–206°, $[\alpha]_D$ −48° (*c* 0.5, pyridine), R_F 0.67 (1-butanol–methanol–water, 2:1:1), ν_{max} 1730 cm^{-1} (C=O).

Anal. Calc. for $C_{21}H_{30}O_{11}$: C, 55.02; H, 6.60. Found: C, 55.31; H, 6.51.

2-O-Acetyl-3-O-α-L-rhamnopyranosyl-D-galactose (**14**). — Compound **13** (100 mg) was catalytically hydrogenated as described for **7**. The amorphous product (79 mg, 98.3%) was crystallised from dry methanol–ethyl acetate, to obtain **14**, m.p. 141–143°, $[\alpha]_D$ +9° (*c* 0.3, water), R_F 0.58 (1-butanol–methanol–water, 2:1:1), ν_{max} 1775 cm^{-1} (C=O).

Anal. Calc. for $C_{14}H_{24}O_{11}$: C, 45.65; H, 6.57. Found: C, 45.81; H, 6.50.

Benzyl 2-O-benzyl-4,6-O-benzylidene-3-O-(2,3,4-tri-O-benzyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside (**15**). — A mixture of benzyl 4,6-*O*-benzylidene-3-*O*-α-L-rhamnopyranosyl-β-D-galactopyranoside[16] (**10**, 750 mg), powdered KOH (3.75 g), and benzyl chloride (15 mL) was stirred overnight at 100°. The cooled mixture was diluted with dichloromethane (50 mL), the residue was extracted with dichloromethane, and the solvent was decanted. To the combined organic phases was added $NaHCO_3$, and the mixture was steam distilled. After cooling, the residue was extracted with dichloromethane (3 × 30 mL), and the combined extracts were dried (Na_2SO_4)

and concentrated. The syrupy residue was purified by column chromatography (9:1 dichloromethane–ethyl acetate), to obtain **15** (850 mg, 66.1%), wnich, after crystallisation from cyclohexane, had m.p. 108–110°, $[\alpha]_D$ +18° (*c* 0.9, chloroform), R_F 0.77 (dichloromethane–ethyl acetate, 9:1). Characteristic ^{1}H-n.m.r. data ($CDCl_3$): δ 7.50–7.10 (m, 30 H, aromatic protons), 5.52 (s, 1 H, PhC*H*), 3.34 (m, 1 H, H-4), and 1.29 (d, 3 H, C-Me).

Anal. Calc. for $C_{54}H_{56}O_{10}$: C, 74.98; H, 6.53. Found: C, 75.11; H, 6.45.

*Benzyl 2,4-di-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-benzyl-α-*L*-rhamnopyranosyl)-β-*D*-galactopyranoside* (**16**). — To a solution of **15** (500 mg) in dichloromethane (15 mL) and ether (5 mL) were added $LiAlH_4$ (88 mg) and a solution of $AlCl_3$ (154 mg) in ether (10 mL). The mixture was boiled under reflux for 4 h, more $LiAlH_4$ (88 mg) and $AlCl_3$ (154 mg) were then added, and boiling was continued for 4 h. After cooling, the excess of $LiAlH_4$ was decomposed with ethyl acetate (3 mL), and $Al(OH)_3$ was precipitated by addition of water (5 mL). The solution was decanted and the precipitate was washed with ether (5 × 10 mL). The combined organic solutions were washed with water (2 × 10 mL), dried (Na_2SO_4), and concentrated. The residue was eluted from Kieselgel G with 9:1 dichloromethane–ethyl acetate, to give amorphous **16** (402 mg, 80.2%), $[\alpha]_D$ −26° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.50–6.90 (m, 30 H, aromatic protons), 5.26 (s, 1 H, H-1′), 5.10–4.28 (m, 13 H, H-1 and 6 PhCH_2), 3.96–3.28 (m, 10 H, ring protons), 1.72 (bs, 1 H, OH, disappeared on addition of D_2O), and 1.29 (d, 3 H, C-Me).

Anal. Calc. for $C_{54}H_{58}O_{10}$: C, 74.80; H, 6.74. Found: C, 74.98; H, 6.53.

*Benzyl 6-*O*-acetyl-2,4-di-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-benzyl-α-*L*-rhamnopyranosyl)-β-*D*-galactopyranoside* (**17**). — Acetylation of **16** (300 mg), as described for the preparation of **6**, and chromatography (7:3 light petroleum–ethyl acetate) of the product gave syrupy **17** (285 mg, 90.6%), $[\alpha]_D$ −26° (*c* 1.2, chloroform), R_F 0.53 (light petroleum–ethyl acetate, 7:3). Characteristic ^{1}H-n.m.r. data ($CDCl_3$): δ 7.40–7.05 (m, 30 H, aromatic protons), 5.20 (s, 1 H, H-1′), 1.86 (s, 3 H, OAc), and 1.24 (d, 3 H, C-Me).

Anal. Calc. for $C_{56}H_{60}O_{11}$: C, 73.99; H, 6.65. Found: C, 73.66; H, 6.81.

*6-*O*-Acetyl-3-*O*-α-*L*-rhamnopyranosyl-*D*-galactose* (**18**). — Compound **17** (230 mg) was catalytically hydrogenated as described for the preparation of **7**. The product (91 mg, 97.7%) was crystallised from dry methanol–ethyl acetate, to yield **18**, m.p. 178–181°, $[\alpha]_D$ +10° (*c* 0.6, water), R_F 0.58 (1-butanol–methanol–water, 2:1:1), ν_{max} 1765 cm^{-1} (C=O).

Anal. Calc. for $C_{14}H_{24}O_{11}$: C, 45.65; H, 6.57. Found: C, 45.79; H, 6.41.

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