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SYNTHESIS OF 2-*O*-α-, 3-*O*-α-, 3-*O*-β-, AND 4-*O*-α-L-RHAMNOPYRANOSYL-D-GALACTOSE

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ABSTRACT

Condensation of benzyl 3-*O*-benzoyl-4,6-*O*-benzylidene-, benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene- (**2**), and benzyl 2,3,6-tri-*O*-benzyl-β-D-galactopyranoside, separately, with tri-*O*-acetyl-α-L-rhamnopyranosyl bromide gave mainly α-linked disaccharide derivatives. An appreciable proportion of the β-linked disaccharide was also obtained from **2**. An anomalous deacylation reaction was found for the (1→3)-linked disaccharide, and the partially benzoylated products were isolated and characterised. The anomeric configuration of each disaccharide was established on the basis of $J_{C\text{-}1,H\text{-}1}$ values. The chemical shifts for the galactose moieties of the α- and β-L-rhamnopyranosyl derivatives differed in a systematic way.

INTRODUCTION

Both 2-*O*- and 6-*O*-α-L-rhamnopyranosyl-D-galactose[1,2] commonly occur in various plant glycosides, and 3-*O*-α-L-rhamnopyranosyl-D-galactose[3] is a constituent of several *Salmonella* cell-wall polysaccharides. To our knowledge, the fourth isomer (*i.e.*, 4-*O*-α-L-rhamnopyranosyl-D-galactose) has not been found in Nature.

For the preparation of robinobiose [the corresponding (1→6)-linked isomer], several methods have been reported[4–7] and 2-*O*-α-L-rhamnopyranosyl-D-galactose has been synthesised[8]. Two methods have been reported for the preparation of the (1→3)-linked isomer[9,10].

We now report on an essentially new route to 2-*O*-, 3-*O*-, and 4-*O*-α-L-rhamnopyranosyl-D-galactose, and on their ^{13}C-n.m.r. data in comparison with those of other disaccharides containing a β-rhamnopyranosyl linkage[11,12].

RESULTS AND DISCUSSION

The readily available benzyl 3-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranoside[13] (**1**), benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranoside[14] (**2**),

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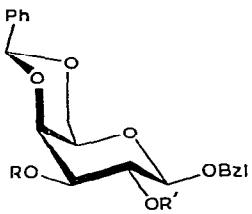
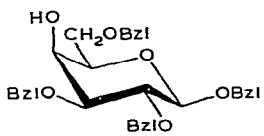
and benzyl 2,3,6-tri-*O*-benzyl-β-D-galactopyranoside[15] (**3**) were used as aglycons and condensed separately with tri-*O*-acetyl-α-L-rhamnopyranosyl bromide (**4**), according to the Helferich procedure. The reaction of **1** and **2** with **4** was complete within ~5 h, to give good yields of products. The reaction of **3** with **4** was fast and, after 1 h at 60°, **8** could be isolated in excellent yield. The chemical synthesis of 4-*O*-glycosyl-D-galactopyranosides has generally been considered to be difficult[16–18] due to HO-4 being axial. This hydroxyl group has relatively low reactivity if the neighbouring groups are esters, but an increased reactivity was observed in the case of partially benzylated derivatives[19].



1 R = Bz R' = H
2 R = H, R' = Bz



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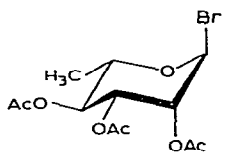

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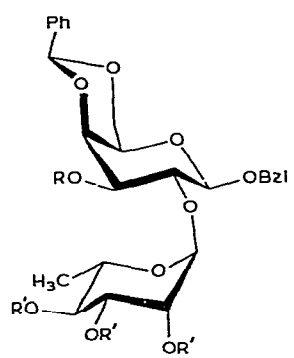
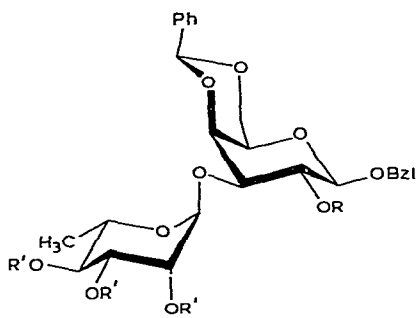


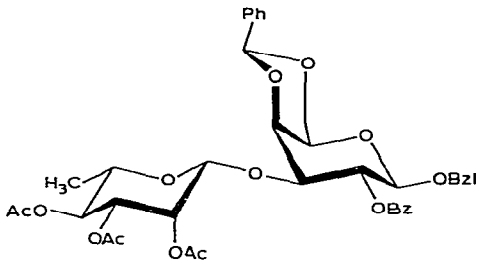
5 R = Bz, R' = Ac
9 R = R' = H



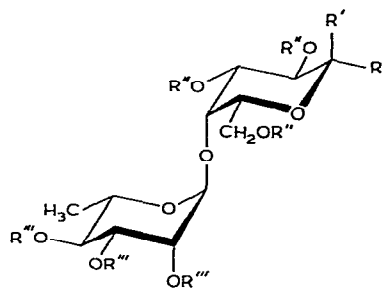
6 R = Bz, R' = Ac
10 R = Bz, R' = H
11 R = R' = H

The stereoselectivity of the rhamnosylation was excellent for **1** and **3** in giving **5** and **8**, respectively; no β anomers were detected (t.l.c.) in the reaction mixture. However, for **2**, two coupled products, **6** (α) and **7** (β), were detected in the ratio 9:1 (t.l.c.). Compounds **6** and **7** had different chromatographic mobilities and could also be separated by fractional crystallisation.

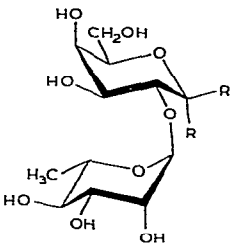
Determination of the anomeric configuration of L-rhamnosides cannot be based unambiguously on p.m.r. data, because the $J_{1,2}$ values are similar for α and β configurations. Only slight differences were found between the ^{13}C chemical shifts of



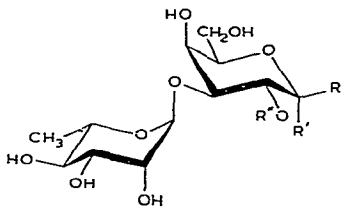
7



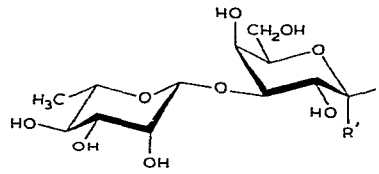
8 R = OBzl, R′ = H, R″ = Bzl, R‴ = Ac
12 R = OBzl, R′ = R‴ = H, R″ = Bzl
21 α R = R″ = R‴ = H, R′ = OH
21 β R = OH, R′ = R = R‴ = H



13 R = OBzl, R′ = H
17 α R = H, R′ = OH
17 β R = OH R′ = H



14 R = OBzl, R′ = H R″ = Bz
15 R = OBzl, R′ = R″ = H
18 α R = H R′ = OH, R″ = Bz
18 β R = OH R′ = H, R″ = Bz
19 α R = R″ = H, R′ = OH
19 β R = OH, R′ = R″ = H



16 R = OBzl R′ = H
20 α R = H, R′ = OH
20 β R = OH, R = H

C-1 for α- and β-L-rhamnosides, except for derivatives with relatively hindered aglycons[20–22]. However, the $J_{C\text{-}1,H\text{-}1}$ values[21] are characteristic in being ~10 Hz smaller when H-1 is axial than when it is equatorial. The $J_{C\text{-}1,H\text{-}1}$ values for **6** and **7** were consistent with the assigned configurations.

Zemplén deacylation of **5** and **8** proceeded smoothly, to give the crystalline **9** and syrupy **12**, respectively. Similar treatment of **6** gave **10**, in which BzO-2 was retained. Compound **10** had a strong i.r. absorption for carbonyl at 1740 cm^{-1}, and its ^1H-n.m.r. spectrum contained signals for three Ph groups but none for AcO groups.

Removal of BzO-2 from **10** required an equimolar amount of sodium methoxide and, after 40 h at reflux temperature, crystalline **11** was obtained. Compound **11** was more conveniently prepared by saponification of **6** with sodium hydroxide in acetone–water. Saponification of **7** proceeded within 6 h to give the acyl-free disaccharide derivative, which was then treated with dilute sulphuric acid to obtain **16**. The different reactivity of BzO-2 in **6** and **7** suggests that it is sterically more crowded in **6**.

TABLE I

^{13}C-N.M.R.[a] CHEMICAL SHIFTS (p.p.m.) AND COUPLING CONSTANTS (Hz)

Carbon atom	*Compound*[b]																					
Galactose	**A**	**1**	**2**	**5**	**6**	**7**	**B**	**13**	**15**	**16**	**17**		**18**		**19**		**20**		**21**		**C**	
C-1	102.7	100.6	99.5	100 5	99.9	101.2	102.9	101.8	102.6	102.5	92.6	96.1	90.9	95 4	93.1	97.1	92.8	97.1	91 8	96.0	93 1	97.3
				160.5	159	160	159				170.7	161			170	160	171.1	163	168 5	160.1	170	160.5
C-2	70.6	68.8	73.1	75.4	69.0	69.8[c]	71.7	77 8	71.0[c]	70.0	77.8	79.6	71.9	74.2	68.5	72.1	67.7	71.1	70.2	71.4	69.1	72.7
C-3	72.6	74.4	72.0	73.1	80.0	76.1	73.8	74.6	81.2	80.5	69.1	74.2	76.1	79.8	77.9	81.2	76.9	80 2	68.0	73.0	69.8	73.6
C-4	76.0	73.7	75.9	73 8	75 7	73.4	69.5	69.6	69.3	66.6	70.3	69.4	70.1	69 4	70.0	69.3	67.4	66.6	76.2	75.5	70.2	69.6
C-5	66.5	66.5	66.8	66.4	66.8	66.9	75.9	75.6	75.7	75.6		75.6	71.3	75.8	71.2	75.7	71.0	75 6	69.4	74.5	69.9	74.2
C-6	69.0	69.0	69.1	69.0	69.3	69.2[c]	61.7	61.7	61.6	61.6	61.9	61 7	61.8	61.6	61.8	61.6	61.8	61.6	60.9	61.0	68.1	67.7
Ph-CH		102.1	101.6	100.5	101.3																	
Ph-CH_2	70.1	70.8	70.1	69.6	70.3	70.2	71.9	72.1[c]	71.8[c]	71.8												
Rhamnose																						
C-1				98.2	99.2	95.9		101.5	102.9	97.9	103.2	101.8	102.7		102.9		97.7	97.8	101.1		101.3	101.2
				174	170.2	158					169.7	171.2			171		159		171.2		169.7	
C-2				71.1	70.3	69.0		71.2[c]	71.0	71.7	70.9		71.9		70.9[c]		71.8	71.7	69.8		70.8	
C-3				69.0	70.0	71.1		71.3	71.0	73 5	70.1		71.1		71 0[c]		73.4	73.5	69.7		71.1	
C-4				71.1	71.5	71.0		73.0	72.9	72.8	72.8	72.9	72.8		72.9		72.8		71.4		72.9	
C-5				66.7	67.1	70.7		70.0	69.8	73 1	69 8		70.0		69.8		73.0		68.8		69.4	
C-6				16.86	17.51	17.30		17.4	17.56	17.56	17.49	17.31	17.51		17.43		17.46		16.18		17.42	

[a]Solvents: $CDCl_3$ for compounds **1**, **2**, and **5–7**; $CDCl_3$-$(CD_3)_2SO$ (1:1) for compound **A**; D_2O for compounds **B**, **C**, **13**, and **15–21**. [b]**A** = Benzyl 4,6-*O*-benzylidene-β-D-galactopyranoside. **B** = Benzyl β-D-galactopyranoside. **C** = 6-*O*-α-L-Rhamnopyranosyl-D-galactose (robinobiose). [c]Assignments may be reversed.

Mild, acid hydrolysis of the benzylidene group in **9** and **10** gave **13** and **14**, respectively. Zemplén deacylation of **14** gave crystalline benzyl 3-*O*-α-L-rhamnopyranosyl-β-D-galactopyranoside (**15**).

A comparison of the ^{13}C-n.m.r. spectra of **15** and **16** shows that the change of the anomeric configuration of the L-rhamnopyranosyl moiety from α to β caused a marked downfield shift of the signals for C-3′ and C-5′, in accordance with the previous observations[11,21].

The chemical shifts of the C-1 signals for α- and β-rhamnopyranosides differ greatly (see Table I). The C-1 resonances of the β-rhamnosides are characteristic, appearing 3.3, 5, and 5.1 p.p.m. upfield for **7**, **16**, and **20**, respectively, as compared to the corresponding signals for the α anomers **6**, **15**, and **19**. These chemical shifts differ markedly from the data given by Kochetkov *et al.*[11] and Bundle *et al.*[12], but agree with those reported by Kasai *et al.*[21] for rhamnosides having relatively hindered aglycons. This discrepancy may be explained by the conformational properties of the glycosidic linkages[22].

There are characteristic differences also in the spectra of the aglycon part, the glycosylation shift caused by the α-rhamnopyranosyl moiety being larger than those observed for the β anomers. However, the β-effect is much larger for the β anomers, particularly at C-4.

Catalytic hydrogenolysis of the benzyl glycosides **13**, **16**, and **12** gave the disaccharides **17**, **20**, and **21**, respectively. Similar treatment of **14** gave **18**, in which BzO-2 was retained. Zemplén saponification of **18** afforded the disaccharide **19**. Thus, the stability of the benzoyl groups in **6** and **14** strongly depends on the presence of the aglycon and the 4,6-*O*-benzylidene group.

The values of the α-rhamnosylation shifts for **17** [(1→2)-linkage], **19** [(1→3)-linkage], **21** [(1→4)-linkage], and 6-*O*-α-L-rhamnopyranosyl-D-galactose are different. The highest values belong to the (1→2)-linked compound, and those for the (1→4)- and (1→6)-linked compounds are similar. Also, the values are higher for the α- than for the β-galactose moieties.

Conventional treatment of **17** with acetic anhydride–pyridine gave a crystalline hepta-acetate having physical parameters the same as those reported by van Niekerk and Koeppen[8], but different from those for the compound isolated by Kuhn *et al.*[1] and characterised as a hepta-acetate of 2-*O*-α-L-rhamnopyranosyl-D-galactose.

EXPERIMENTAL

General methods. — Melting points (uncorrected) were determined with a Kofler apparatus. Reactions were monitored by t.l.c. on DC Alurolle Kieselgel 60 F_{254} (Merck); detection was made possible by charring with sulfuric acid. Kieselgel G and Kieselgel 60 H (Reanal) were used for short-column chromatography. Optical rotations were measured with a Perkin–Elmer 241 automatic polarimeter; equilibrium values are given for compounds **17–21**. ^{1}H-N.m.r. spectra were recorded with a Jeol MH-100 (100 MHz) instrument (internal Me_4Si). ^{13}C-N.m.r. spectra were recorded

with a Varian XL-100-15 FT spectrometer for solutions in $CDCl_3$ (internal Me_4Si) or D_2O (internal 1,4-dioxane). I.r. spectra were recorded with a Perkin–Elmer 700 spectrometer.

Benzyl 3-O-benzoyl-4,6-O-benzylidene-2-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside (**5**). — A solution of benzyl 3-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranoside[13] (**1**, 3.0 g) in a mixture of dry benzene (100 ml) and nitromethane (100 ml) was concentrated at atmospheric pressure to ~100 ml and cooled to 60°. $Hg(CN)_2$ (1.97 g) and, after stirring for 15 min, tri-*O*-acetyl-α-L-rhamnopyranosyl bromide (**4**, 2.75 g) were added, and the mixture was stirred at 60°. After 1, 2, 3, and 4 h, more $Hg(CN)_2$ (0.39 g) and **4** (0.55 g) were added and stirring was continued for 5 h. After cooling, the mixture was concentrated, diluted with dichloromethane (250 ml), washed with 5% aqueous potassium iodide (2 × 50 ml) and water (2 × 50 ml), dried (Na_2SO_4), and concentrated. The residue (6.12 g) was purified by short-column chromatography on Kieselgel G (250 g) with 95.5 dichloromethane–ethyl acetate. The crystalline product (3.26 g, 68.4%) was recrystallised from ethanol (20 ml), to give **5** (1.98 g, 41.5%), m.p. 104–106°, $[\alpha]_D$ +31° (*c* 0.7, chloroform), R_F 0.55 (dichloromethane–ethyl acetate, 95:5). ^{1}H-N.m.r. ($CDCl_3$): δ 8.02–7.20 (m, 15 H, aromatic), 5.44 (s, 1 H, PhC*H*), 3.52 (m, 1 H, H-4), 1.91, 1.81, and 1.78 (3 s, 9 H, 3 OAc), and 0.82 (d, 3 H, CH_3)

Anal. Calc. for $C_{39}H_{42}O_{14}$ (734.76): C, 63.75; H, 5.76. Found: C, 63.84; H, 5.81.

Benzyl 2-O-benzoyl-4,6-O-benzylidene-3-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside (**6**) *and benzyl 2-O-benzoyl-4,6-O-benzylidene-3-O-(2,3,4-tri-O-acetyl-β-L-rhamnopyranosyl)-β-D-galactopyranoside* (**7**). — Benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranoside[14] (**2**, 6.50 g) was treated with **4**, as described for the preparation of **5**. Work-up gave a crystalline residue (13.04 g) which contained **6** and **7** in a ratio of ~9:1 (t.l.c.). Crystallisation from ethanol (100 ml) gave a product (0.66 g, 6.4%) which was recrystallised from ethanol (66 ml), to give **7** (0.56 g, 5.4%), m.p. 226°, $[\alpha]_D$ +50° (*c* 0.75, chloroform), R_F 0.38 (ethyl acetate–light petroleum, 6:4). ^{1}H-N.m.r. ($CDCl_3$): δ 8.04–7.00 (m, 15 H, aromatic), 5.48 (s, 1 H, PhC*H*), 1.91, 1.85, and 1.69 (3 s, 9 H, 3 OAc), and 0.97 (d, 3 H, CH_3).

Anal. Calc. for $C_{39}H_{42}O_{14}$ (734.76): C, 63.75; H, 5.76. Found: C, 63.60; H, 5.83.

The mother liquor from the first crystallisation, after storage overnight, gave **6** (5.70 g, 55.2%), m.p. 98–100°, $[\alpha]_D$ +24° (*c* 0.5, chloroform), R_F 0.46 (ethyl acetate–light petroleum, 6:4). ^{1}H-N.m.r. ($CDCl_3$): δ 8.10–7.15 (m, 15 H, aromatic), 5.71 (dd, 1 H, H-2), 5.56 (s, 1 H, PhC*H*), 5.24 (dd, 1 H, H-3′), 3.88 (dd, 1 H, H-3), 3.48 (m, 1 H, H-4), 1.92 and 1.84 (2 s, 6 H and 3 H, 3 OAc), 1.01 (d, 3 H, CH_3); $J_{1,2}$ 8.0, $J_{2,3}$ 10.0, $J_{3,4}$ 3.4, $J_{2',3'}$ 3.1, and $J_{3',4'}$ 10.0 Hz.

Anal. Calc. for $C_{39}H_{42}O_{14}$ (734.76): C, 63.75; H, 5.76. Found: C, 63.55; H, 5.69.

Benzyl 2,3,6-tri-O-benzyl-4-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside (**8**). — Benzyl 2,3,6-tri-*O*-benzyl-β-D-galactopyranoside[15] (**3**, 2.20 g) was treated with **4**, as described for the preparation of **5**, but for 60 min. Work-up gave a syrupy residue (4.14 g) which was purified by short-column chromatography on Kieselgel G (200 g) with 9:1 dichloromethane–ethyl acetate, to give **8** (3.11 g,

94%) as a syrup, $[\alpha]_D$ −36° (*c* 1, chloroform), R_F 0.81 (dichloromethane–ethyl acetate, 9·1). ^{1}H-N.m.r. ($CDCl_3$): δ 7.45–7.00 (m, 20 H, aromatic), 5.55–4.36 (m, 13 H, 4 PhC*H*$_2$, H-1,1′,2′,3′,4′), 4.16–3.28 (m, 7 H, skeleton protons of galactose moiety and H-5′), 1.94 and 1.89 (2 s, 9 H, 3 OAc), and 1.11 (d, 3 H, CH_3).

Anal. Calc. for $C_{46}H_{52}O_{13}$ (812.92): C, 67.97; H, 6.45. Found: C, 69.72; H, 6.22.

Benzyl 4,6-O-benzylidene-2-O-α-L-rhamnopyranosyl-β-D-galactopyranoside (**9**). — To a solution of **5** (1.50 g) in dry methanol (50 ml) was added sodium methoxide (10 mg). After 24 h at room temperature, the mixture was neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. The crystalline residue (1.07 g) was recrystallised from ethanol (15 ml), to yield **9** (0.96 g, 93.2%), m.p. 206–209°, $[\alpha]_D$ −34.5° (*c* 0.6, pyridine), R_F 0.34 (dichloromethane–methanol, 9:1). ^{1}H-N.m.r. [$CDCl_3$ + $(CD_3)_2SO$]: δ 7.60–7.20 (m, 10 H, aromatic), 5.52 (s, 1 H, PhC*H*), 5.17 (s, 1 H, H-1′), 4.74 (q, 2 H, PhC*H*$_2$), and 1.07 (d, 3 H, CH_3).

Anal. Calc. for $C_{26}H_{32}O_{10}$ (504.54): C, 61.89; H, 6.39. Found: C, 62.01; H, 6.46.

Benzyl 2-O-benzoyl-4,6-O-benzylidene-3-O-α-L-rhamnopyranosyl-β-D-galactopyranoside (**10**). — Compound **6** (3.12 g) was deacetylated, as described for the preparation of **9**, to give a crystalline product. Recrystallisation from ethanol (60 ml) and hexane (60 ml) yielded **10** (1.83 g, 70.8%), m.p. 202–204°, $[\alpha]_D$ +26° (*c* 0.5, pyridine), R_F 0.42 (dichloromethane–methanol, 9:1), ν_{max} 1740 cm^{-1} (C=O). ^{1}H-N.m.r. [$CDCl_3$ + $(CD_3)_2SO$]: δ 8.00–7.00 (m, 15 H, aromatic), 5.50 (s, 1 H, PhC*H*), 5.60–5.34 (m, 1 H, H-2), 2.68 (broad s, 3 H, 3 OH), and 1.21 (d, 3 H, CH_3); after the addition of D_2O, the singlet at δ 2.68 disappeared.

Anal. Calc. for $C_{33}H_{36}O_{11}$ (608.65): C, 65.12; H, 5.96. Found: C, 65.30; H, 5.61.

Benzyl 4,6-O-benzylidene-3-O-α-L-rhamnopyranosyl-β-D-galactopyranoside (**11**). — A mixture of **6** (1.0 g), acetone (60 ml), and 0.1M NaOH (40 ml) was boiled under reflux for 8 h, and then cooled, neutralised (acetic acid), decolourised, and concentrated. A solution of the residue in methanol (30 ml) was filtered, concentrated to ~10 ml, and eluted from a column of Kieselgel G, to give **11** (0.65 g, 94.7%). Recrystallisation from ethanol (20 ml) gave 0.32 g of **11** (46.6%), m.p. 217–220°, $[\alpha]_D$ −8° (*c* 0.6, pyridine), R_F 0.34 (dichloromethane–methanol, 9:1). ^{1}H-N.m.r. [$CDCl_3$ + $(CD_3)_2SO$]: δ 7.60–7.20 (m, 10 H, aromatic), 5.50 (s, 1 H, PhC*H*), 5.00–4.56 (m, 3 H, H-1′ and PhC*H*$_2$), and 1.21 (d, 3 H, CH_3).

Anal. Calc. for $C_{26}H_{32}O_{10}$ (504.54): C, 61.89; H, 6.39. Found: C, 62.01; H, 6.30.

Benzyl 2,3,6-tri-O-benzyl-4-O-α-L-rhamnopyranosyl-β-D-galactopyranoside (**12**). — Compound **8** (2.90 g) was deacetylated, as described for the preparation of **9**. Purification of the product by short-column chromatography on Kieselgel G gave syrupy **12** (2.20 g, 89.8%), $[\alpha]_D$ −17° (*c* 0.9, pyridine), R_F 0.50 (dichloromethane–methanol, 9:1).

Anal. Calc. for $C_{40}H_{46}O_{10}$ (686.81): C, 69.95; H, 6.75. Found: C, 70.23; H, 6.95.

Benzyl 2-O-α-L-rhamnopyranosyl-β-D-galactopyranoside (**13**). — A solution of **9** (0.60 g) in a mixture of ethanol (30 ml) and 0.05M sulfuric acid (30 ml) was boiled for 2 h, and the boiling solution was neutralised with $BaCO_3$, filtered, and concentrated. The residue (0.40 g) was purified by short-column chromatography on Kieselgel

60 H (15 g) with 2:1:1 1-butanol–methanol–water, to give amorphous **13** (0.32 g, 64.6%), $[\alpha]_D$ −34° (*c* 0.8, water), R_F 0.60 (1-butanol–methanol–water, 2:1:1).

Anal. Calc. for $C_{19}H_{28}O_{10}$ (416.43). C, 54.80, H, 6.78. Found: C, 54.21; H, 6 50.

Benzyl 2-O-benzoyl-3-O-α-L-rhamnopyranosyl-β-D-galactopyranoside (**14**). — Compound **10** (1.65 g) was hydrolysed, as described for the preparation of **13**, to give a crystalline residue (1.21 g). Recrystallisation from ethanol (120 ml) gave **14** (0.67 g, 47 5%), m.p 236–237°, $[\alpha]_D$ −43° (*c* 1.3, pyridine), R_F 0.18 (dichloromethane–methanol, 9:1). ν_{max} 1710 cm^{-1} (C=O). ^{1}H-N.m.r. [$CDCl_3$ + $(CD_3)_2SO$]: δ 8 00–7.05 (m, 10 H, aromatic), 5.36 (dd, 1 H, H-2), and 1.18 (d, 3 H, CH_3).

Anal. Calc for $C_{26}H_{32}O_{11}$ (520.54): C, 59.99, H, 6.20. Found: C, 60.31; H, 6.32.

Benzyl 3-O-α-L-rhamnopyranosyl-β-D-galactopyranoside (**15**). — To a solution of **14** (230 mg) in dry methanol (30 ml) was added sodium methoxide (20 mg), and the reaction mixture was boiled for 8 h, cooled, neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated, to give a crystalline product (205 mg). Recrystallisation from methanol (3 ml) yielded **15** (100 mg, 54.3%), m.p. 180–184°, $[\alpha]_D$ −45° (*c* 0 3, water), R_F 0 63 (1-butanol–methanol–water, 2:1:1).

Anal. Calc. for $C_{19}H_{28}O_{10}$ (416 43): C, 54 80; H, 6.78. Found: C, 54.00, H, 6.95.

Benzyl 3-O-β-L-rhamnopyranosyl-β-D-galactopyranoside (**16**). — To a solution of 7 (400 mg) in dry methanol (40 ml) was added sodium methoxide (20 mg), and the mixture was boiled for 6 h, cooled, neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. A solution of the residue (380 mg) in ethanol (10 ml) and 0.05M sulfuric acid (10 ml) was boiled for 4 h. The boiling solution was neutralised with $BaCO_3$, filtered, and concentrated. The syrupy product was purified by short-column chromatography on Kieselgel 60 H (20 g) with 2:1:1 1-butanol–methanol–water, to give **16** (147 mg, 64.8%), which, after crystallisation from methanol–ether, had m.p. 198–202°, $[\alpha]_D$ +30° (*c* 0.4, water), R_F 0.62 (1-butanol–methanol–water, 2:1:1).

Anal. Calc. for $C_{19}H_{28}O_{10}$ (416.43): C, 54.80; H, 6.78. Found: C, 55.03; H, 6.72.

2-O-α-L-Rhamnopyranosyl-D-galactose (**17**) — A solution of **13** (210 mg) in a mixture of ethanol (30 ml), acetic acid (2 ml), and water (10 ml) was hydrogenated in the presence of 10% palladium-on-carbon (100 mg) for 12 h at room temperature, and then filtered and concentrated. The residue (160 mg) was purified by short-column chromatography on Kieselgel 60 H (10 g) with 2:1:1 1-butanol–methanol–water, to give amorphous **17** (120 mg, 72.9%), $[\alpha]_D$ +5° (*c* 0.6, water), R_F 0 45 (1-butanol–methanol–water, 2:1:1); lit.[8] $[\alpha]_D$ +10.19° (*c* 2.03, water), m.p. 125–126° (dec.).

Compound **17** was conventionally acetylated with acetic anhydride in pyridine, to give the crystalline hepta-acetate of **17**, which, after recrystallisation, had m.p. 200–204°, $[\alpha]_D$ +43° (*c* 0 2, methanol); lit.[8] m.p. 196–198°, $[\alpha]_D$ +49.4° (*c* 1.74, methanol).

2-O-Benzoyl-3-O-α-L-rhamnopyranosyl-D-galactose (**18**). — Compound **14** (400 mg) was hydrogenated, as described for the preparation of **17**, to yield a crystalline product (325 mg). Recrystallisation from ethanol (4 ml) gave **18** (126 mg, 38.1%),

m.p. 126–128°, $[\alpha]_D$ +39.5° (*c* 0 5, water), R_F 0.63 (1-butanol–methanol–water, 2:1:1), ν_{max} 1750 cm^{-1} (C=O).

Anal. Calc. for $C_{19}H_{26}O_{11}$ (430.41): C, 53.02; H, 6.09. Found. C, 53.29; H, 5.95.

3-O-α-L-Rhamnopyranosyl-D-galactose (**19**). — To a solution of **18** (240 mg) in dry methanol (30 ml) was added sodium methoxide (10 mg) After 12 h at room temperature, the mixture was neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. The syrupy product (177 mg) was crystallised from 2:1 1-butanol–methanol (5 ml), to yield **19** (65 mg, 35.7%), m.p. 146–150°, $[\alpha]_D$ +7.5° (*c* 0 45, water), R_F 0.44 (1-butanol–methanol–water, 2:1:1); lit.[10] $[\alpha]_D$ +8.1° (*c* 1 30, water).

Anal. Calc for $C_{12}H_{22}O_{10}$ (326.30)· C, 44 17; H, 6.79. Found: C, 43.89. H, 6.69.

3-O-β-L-Rhamnopyranosyl-D-galactose (**20**). — Compound **16** (60 mg) was hydrogenated, as described for the preparation of **17**, to give amorphous **20** (39 mg, 82.9%), $[\alpha]_D$ +41° (*c* 0 4, water), R_F 0.42 (1-butanol–methanol–water, 2.1.1).

4-O-α-L-Rhamnopyranosyl-D-galactose (**21**) — Compound **12** (1.75 g) was hydrogenated, as described for the preparation of **17**, to give a syrup. Purification by short-column chromatography on Kieselgel 60 H (25 g) with 2:1·1 1-butanol–methanol–water gave **21** (668 mg, 80.3%) as a foam, $[\alpha]_D$ +6° (*c* 0.35, water), R_F 0.41 (1-butanol–methanol–water, 2:1·1).

Anal. Ca'c. for $C_{12}H_{22}O_{10}$ (326.30): C, 44 17; H, 6.79 Found: C, 44.71; H, 6 90.

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