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Anomalous Zemplén deacylation reactions of 2-*O*-acyl-3-*O*-alkyl or -3-*O*-glycosyl derivatives of D-galactose and D-glucose: synthesis of *O*-α-D-mannopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→3)-D-galactose and an intermediate for the preparation of 2-*O*-glycosyl-3-*O*-(α-D-mannopyranosyl)-D-glucoses

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ABSTRACT

Treatment of 2-*O*-benzoyl (**1**) and 2-*O*-acetyl (**5**) derivatives of benzyl 4,6-*O*-benzylidene-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside under Zemplén conditions (catalytic amount of sodium methoxide in methanol) gave partially deacylated disaccharides in which the 2-*O*-acyl groups were retained. Likewise, a similar result was obtained with the β-L-rhamnopyranosyl analogue (**3**) of **1**. This anomalous reaction was used in a synthesis of the title trisaccharide (**17**) and of methyl 4,6-*O*-benzylidene-3-*O*-(2,3:4,6-di-*O*-isopropylidene-α-D-mannopyranosyl)-α-D-glucopyranoside, an intermediate for the synthesis of 2-*O*-glycosyl-3-*O*-(α-D-mannopyranosyl)-D-glucoses.

INTRODUCTION

During the synthesis of 3-*O*-α-L-rhamnopyranosyl-D-galactose[1], it was found that conventional Zemplén deacylation of benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside (**1**) gave a partially deacylated disaccharide (**2**). This finding was extended to the corresponding AcO-2 derivative and used for the preparation of 2-*O*-acetyl-3-*O*-(α-L-rhamnopyranosyl)-D-galactose, a constituent of bacterial cell-wall polysaccharides[2].

There are few data[3–5] on this type of anomalous deacylation, but the reaction appears to be general and was found[6] in a series of 3-*O*-substituted-D-glucosides. We now summarise our data and report the application of the reaction for the synthesis of *O*-α-D-mannopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→3)-D-galactose and methyl 2-*O*-glycosyl-3-*O*-(α-D-mannopyranosyl)-α-D-glucopyranosides. The former trisaccharide is a constituent of the repeating unit of the O-antigenic polysaccharides of *Salmonella* bacteria and syntheses have been reported[7–10].

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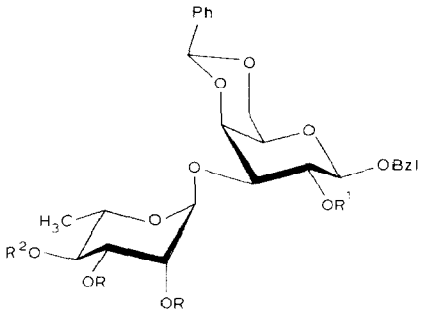
RESULTS AND DISCUSSION

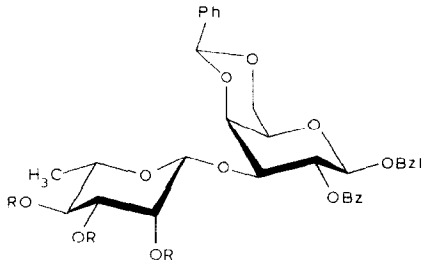
Treatment of benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosyl)-β-D-galactopyranoside (**1**) under Zemplén conditions (catalytic amount of sodium methoxide in methanol) removed the acetyl groups and gave **2** in which BzO-2 was retained. Removal of BzO-2 required an equimolar amount of sodium methoxide and prolonged reaction time at reflux temperature. Likewise, the AcO-2 derivative (**5**) gave 96% of benzyl 2-*O*-acetyl-4,6-*O*-benzylidene-3-*O*-(α-L-rhamnopyranosyl)-β-D-galactopyranoside (**6**), and **3** gave benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(β-L-rhamnopyranosyl)-β-D-galactopyranoside (**4**). The presence and the position of acyl groups in **2**, **4**, and **6** were indicated by i.r. and ^{1}H-n.m.r. data.

This anomalous Zemplén deacylation reaction was observed in the *gluco* series. Thus, on Zemplén deacylation of **7**, AcO-4′,6′ were removed but not BzO-2 and AcO-2′, and methyl 3-*O*-(2-*O*-acetyl-3-*O*-methyl-β-D-glucopyranosyl)-2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-glucopyranoside (**8**, 49%) was isolated after column chromatography[6]. Likewise, **9**[6] and **11**[13] gave the monoacetates **10** and **12**, respectively, in good yield.

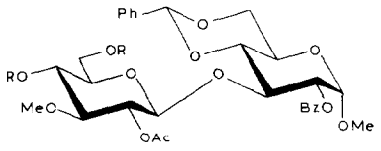
Thus, in the appropriate compounds, acyl groups can be used as temporary protecting groups in the synthesis of oligosaccharides as illustrated by the synthesis of the title trisaccharide (**17**). Reaction of benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(α-L-rhamnopyranosyl)-β-D-galactopyranoside (**2**) with 2,2-dimethoxypropane in acetone in the presence of a cation-exchange (H^+) resin gave 76% of benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2,3-*O*-isopropylidene-α-L-rhamnopyranosyl)-β-D-galactopyranoside (**13**). In compound **13**, HO-4′ was glycosylated with 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide by the Helferich method. On Zemplén deacetylation of the crude product, BzO-2 was retained, and crystalline benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-[2,3-*O*-isopropylidene-4-*O*-(α-D-mannopyranosyl)-α-L-rhamnopyranosyl]-β-D-galactopyranoside (**14**) was obtained. Hydrolysis of **14** with dilute sulfuric



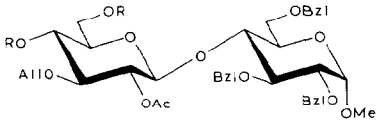
1 R^1 = Bz, R = R^2 = Ac
2 R^1 = Bz, R = R^2 = H
5 R = R^1 = R^2 = Ac
6 R^1 = Ac, R = R^2 = H
13 R^1 = Bz, R, R = $>CMe_2$, R^2 = H



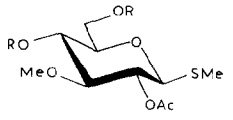
3 R = Ac
4 R = H



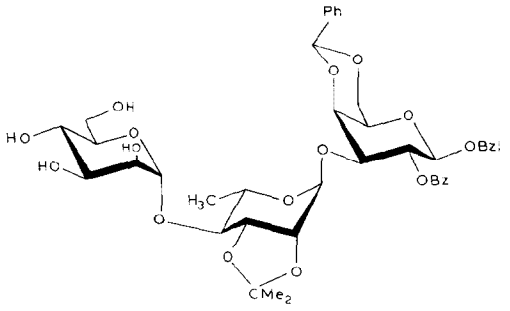
7 R = Ac
8 R = H



9 R = Ac
10 R = H



11 R = Ac
12 R = H



14

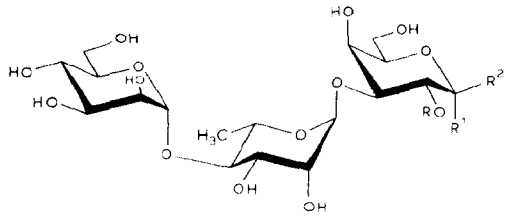
acid cleaved the acetal groups to give crystalline **15**, from which BzO-2 was removed by sodium methoxide in boiling methanol to give crystalline benzyl 3-*O*-[4-*O*-(*α*-D-mannopyranosyl)-*α*-L-rhamnopyranosyl]-*β*-D-galactopyranoside (**16**). Catalytic hydrogenolysis of **16** gave *O*-*α*-D-mannopyranosyl-(1→4)-*O*-*α*-L-rhamnopyranosyl-(1→3)-D-galactose (**17**). The structures of **16** and **17** were verified by their ^{13}C-n.m.r. spectra.

Another example of the above synthesis strategy is the preparation of methyl 4,6-*O*-benzylidene-3-*O*-(2,3:4,6-di-*O*-isopropylidene-*α*-D-mannopyranosyl)-*α*-D-glucopyranoside having a HO-2 unsubstituted. Methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-*α*-D-glucopyranoside[11] was condensed with 2,3,4,6-tetra-*O*-acetyl-*α*-D-mannopyranosyl bromide according to the Helferich procedure. The stereoselectivity of the reaction was excellent, and crystalline **18** was obtained in good yield.

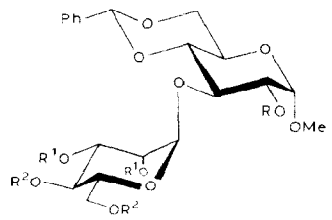
Zemplén deacylation of **18** afforded crystalline methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(*α*-D-mannopyranosyl)-*α*-D-glucopyranoside (**19**), which reacted with 2,2-dimethoxypropane containing *p*-toluenesulfonic acid[12] to give the isopropylidene derivative **20**. Treatment of **20** with > 1 mol. equiv. of sodium methoxide in methanol for 2 days was necessary to remove BzO-2 and afford crystalline methyl 4,6-*O*-benzylidene-3-*O*-(2,3:4,6-di-*O*-isopropylidene-*α*-D-mannopyranosyl)-*α*-D-glucopyranoside (**21**), which can be used for the synthesis of 2-*O*-glycosyl-3-*O*-(*α*-D-mannopyranosyl)-D-glucoses.

EXPERIMENTAL

General methods. — Melting points (uncorrected) were determined on a Kofler apparatus. Optical rotations were measured with a Perkin–Elmer 241 polarimeter. The ^{1}H- and ^{13}C-n.m.r. spectra were recorded with Jeol MH-100 (100 MHz) and Bruker



15 R = Bz, R^1 = H, R^2 = OBzl
16 R = R^1 = H, R^2 = OBzl
17 R = H, R^1, R^2 = H, OH



18 R = Bz, R^1 = R^2 = Ac
19 R = Bz, R^1 = R^2 = H
20 R = Bz, R^1, R^1 = R^2, R^2 = >CMe$_2$
21 R = H, R^1, R^1 = R^2, R^2 = >CMe$_2$

WP-200 SY spectrometers for solutions in $CDCl_3$ (internal Me_4Si), D_2O (internal 1,4-dioxane), or $(CD_3)_2SO$. Reactions were monitored by t.l.c. on Kieselgel $60F_{254}$ (Merck) with detection by charring with sulfuric acid. Both Kieselgel G and Kieselgel H (Reanal) were used for short-column chromatography.

Preparations of compounds **1**–**3**, **5** and **6**, **7**–**10**, and **11** and **12** have been described[1,2,6,13].

*Benzyl 2-O-benzoyl-4,6-O-benzylidene-3-O-(β-*L*-rhamnopyranosyl)-β-*D*-galactopyranoside (**4**).* — To a solution of benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-(2,3,4-tri-*O*-acetyl-β-L-rhamnopyranosyl)-β-D-galactopyranoside[1] (**3**, 85 mg) in dry methanol (60 mL) was added sodium methoxide (10 mg), and the mixture was stored for 3 h at room temperature, then neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated to yield **4** (65 mg, 92.3%). Recrystallisation from ethanol gave material with m.p. 220–222°, $[\alpha]_D$ +42° (*c* 0.9, chloroform). ^{1}H-N.m.r. data [$(CD_3)_2SO$]: δ 7.95 (d, 2 H, aromatic), 7.73–7.08 (m, 13 H, aromatic), 5.67 (s, 1 H, PhC*H*), 5.25 (dd, 1 H, H-2), 1.12 (d, 3 H, CH*Me*).

Anal. Calc. for $C_{33}H_{36}O_{11}$: C, 65.12; H, 5.96. Found: C, 65.08; H, 6.00.

*Benzyl 2-O-benzoyl-4,6-O-benzylidene-3-O-(2,3-O-isopropylidene-α-*L*-rhamnopyranosyl)-β-*D*-galactopyranoside (**13**).* — A mixture of benzyl 2-*O*-benzoyl-4,6-*O*-benzylidene-3-*O*-α-L-rhamnopyranosyl-β-D-galactopyranoside[1] (**2**, 1.0 g), Amberlite IR-120 (H^+) resin (1 g), acetone (20 mL), and 2,2-dimethoxypropane (10 mL) was stirred at room temperature for 40 min. The resin was collected and washed with acetone (3 x 10 mL), the combined filtrate and washings were concentrated, and the residue was crystallised from ethanol (30 mL) to yield **13** (810 mg, 76.0%), m.p. 222–223°, $[\alpha]_D$ +25° (*c* 0.8, chloroform), R_F 0.86 (dichloromethane–methanol, 9:1). ^{1}H-N.m.r. data ($CDCl_3$): δ 8.10–7.05 (m, 15 H, aromatic), 5.61 (dd, 1 H, H-2), 5.51 (s, 1 H, PhC*H*), 4.97 (s, 1 H, H-1'), 3.45 (m, 1 H, H-4), 3.28 (m, 1 H, H-4'), 2.47 (d, 1 H, OH), 1.35 and 1.04 (2 s, each 3 H, CMe_2), 1.21 (d, 3 H, CH*Me*).

Anal. Calc. for $C_{36}H_{40}O_{11}$: C, 66.65; H, 6.22. Found: C, 66.58; H, 6.19.

Benzyl 2-O-benzoyl-4,6-O-benzylidene-3-O-[2,3-O-isopropylidene-4-O-(α-D-mannopyranosyl)-α-L-rhamnopyranosyl]-β-D-galactopyranoside (**14**). — To a solution of **13** (700 mg) in benzene–nitromethane (1:1, 140 mL) was added $Hg(CN)_2$ (328 mg), and 70 mL of the solvent was distilled off at atmospheric pressure. The mixture was cooled to 60°, 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide (533 mg) was added, and the mixture was stirred at 60°. After 5, 10, and 15 h, more $Hg(CN)_2$ (164 mg) and bromide (266 mg) were added, and stirring was continued for 5 h. The mixture was then concentrated, diluted with dichloromethane (100 mL), washed with aq. 5% KI (2 x 20 mL) and water (2 x 20 mL), dried (Na_2SO_4), and concentrated. To a solution of the residue in dry methanol (100 mL) was added sodium methoxide (10 mg). After storage overnight, the solution was neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. Recrystallisation of the residue from ethanol gave **14** (330 mg, 37.7%), m.p. 264–268°, $[\alpha]_D$ +82° (*c* 0.5, pyridine), R_F 0.48 (dichloromethane–methanol, 9:1). ^{1}H-N.m.r. data [$(CD_3)_2SO$]: δ 7.99 (d, 2 H, aromatic), 7.70–7.05 (m, 13 H, aromatic), 5.57 (s, 1 H, PhC*H*), 5.53 (dd, 1 H, H-2), 5.06 (s, 1 H, H-1'), 1.35 and 0.97 (2 s, each 3 H, CMe_2), 1.21 (d, 3 H, CH*Me*).

Anal. Calc. for $C_{42}H_{50}O_{16}$: C, 62.21; H, 6.22. Found: C, 62.16; H, 6.24.

Column chromatography (dichloromethane–methanol, 9:1) of the mother liquor gave more **14** (200 mg; total yield, 60.6%).

Benzyl 2-O-benzoyl-3-O-[4-O(α-D-mannopyranosyl)-α-L-rhamnopyranosyl]-β-D-galactopyranoside (**15**) *and benzyl 3-O-[4-O-(α-D-mannopyranosyl)-α-L-rhamnopyranosyl]-β-D-galactopyranoside* (**16**). — A solution of **14** (480 mg) in ethanol (20 mL) and 0.05M sulfuric acid (20 mL) was boiled for 2 h, and the boiling solution was neutralised with $BaCO_3$, filtered, and concentrated. Recrystallisation of a sample of the residue from ethanol gave **15**, m.p. 214–218°, $[\alpha]_D$ −12.5° (*c* 0.6, pyridine). To a solution of crude **15** in dry methanol (60 mL) was added sodium methoxide (30 mg), and the mixture was boiled for 8 h. After the usual work-up, the crude **16** was eluted from a column of Kieselgel H (1-butanol–methanol–water, 2:1:1) to give **16** (182 mg, 53.1%), m.p. 178–179° (from ethanol), $[\alpha]_D$ −5.9° (*c* 1, water), R_F 0.61 (1-butanol–methanol–water, 2:1:1). See Table I for the ^{13}C-n.m.r. data.

Anal. Calc. for $C_{25}H_{38}O_{15}$: C, 51.90; H, 6.62. Found: C, 51.95; H, 6.58.

O-α-D-Mannopyranosyl-(1→4)-O-α-L-rhamnopyranosyl-(1→3)-D-galactose (**17**). — A solution of **16** (140 mg) in ethanol (15 mL), acetic acid (5 mL), and water (5 mL) was hydrogenated in the presence of 10% Pd–C (70 mg) for 48 h at room temperature, then filtered, and concentrated. The residue (116 mg, 98.1%) was purified by column chromatography on Kieselgel H with 2:1:1 1-butanol–methanol–water, to give amorphous **17** (81, mg, 68.5%), $[\alpha]_D$ +20° (*c* 0.6, water), R_F 0.39; lit.[9] $[\alpha]_D$ +27.2° (water). See Table I for the ^{13}C-n.m.r. data.

Anal. Calc. for $C_{18}H_{32}O_{15}$: C, 44.26; H, 6.60. Found: C, 44.32; H, 6.64.

Methyl 2-O-benzoyl-4,6-O-benzylidene-3-O-(2,3,4,6-tetra-O-acetyl-α-D-mannopyranosyl)-α-D-glucopyranoside (**18**). — To a solution of methyl 2-*O*-benzoyl-4,6-*O*-

TABLE I

^{13}C-n.m.r. data for solutions of **16** and **17** in D_2O

Residue	*Atom*	**16**	**17**	
		β	*α*	*β*
D-Gal	C-1	102.24	92.58	96.59
	C-2	69.43	70.42	71.54
	C-3	80.84	77.49	80.82
	C-4	68.82	67.94	68.80
	C-5	75.34	69.29	75.28
	C-6	61.19	61.30	61.13
α-L-Rha	C-1	102.09	102.19	
	C-2	70.87	70.64	
	C-3	70.57	69.42	
	C-4	81.64	81.53	
	C-5	68.43	68.34	
	C-6	17.31	17.17	
α-D-Man	C-1	101.66	101.59	
	C-2	70.70	70.71	
	C-3	70.70	70.71	
	C-4	67.06	66.89	
	C-5	73.51	73.38	
	C-6	61.19	61.03	
	$PhCH_2$	71.68		

benzylidene-α-D-glucopyranoside[11] (3.86 g, 10 mmol) in toluene–nitromethane (1:1, 80 mL) was added $Hg(CN)_2$ (3.789 g; 15 mmol), and 40 mL of the solvent was distilled off at atmospheric pressure. The mixture was cooled to 60°, 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide (4.934 g, 12 mmol) was added, and the mixture was stirred for 5 h at 60°, then concentrated. A solution of the residue in dichloromethane (250 mL) was washed with aq. 5% KI (2 × 20 mL) and water (2 × 20 mL), dried (Na_2SO_4), and concentrated. The syrupy residue was eluted from a column of Kieselgel G (350 g) with dichloromethane–ethyl acetate (9:1) to give **18** (6.721 g, 93.8%). Recrystallisation from ethanol yielded material (3.925 g, 54.8%) with m.p. 168–170°, $[\alpha]_D$ +116° (*c* 0.95, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 8.08 (d, 2 H, aromatic), 7.66–7.22 (m, 8 H, aromatic), 5.60 (s, 1 H, PhC*H*), 5.38–5.33 (m, 2 H, H-1′,2′), 5.23 (dd, 1 H, H-2), 5.17–5.06 (m, 2 H, H-3′,4′), 5.02 (d, 1 H, H-1), 4.50–4.31 (m, 2 H, H-6′,6′), 3.99–3.76 (m, 6 H, H-3,4,5,5′,6,6), 3.41 (s, 3 H, OMe), 2.07, 2.05, 1.92, and 1.72 (4 s, each 3 H, 4 OAc), $J_{1,2}$ 3.8 Hz.

Anal. Calc. for $C_{35}H_{40}O_{16}$: C, 58.66; H, 5.63. Found: C, 58.71; H, 5.69.

Methyl 2-O-benzoyl-4,6-O-benzylidene-3-O-(α-D-mannopyranosyl)-α-D-glucopyranoside (**19**). — Compound **18** (3.00 g) was deacetylated as described for the preparation of **4**. Recrystallisation of the product from ethyl acetate–light petroleum gave **19**

(1.558 g, 67.9%), m.p. 198–201°, $[\alpha]_D$ +143° (*c* 0.95, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 8.04 (d, 2 H, aromatic), 7.58–7.21 (m, 8 H, aromatic), 5.36 (s, 1 H, PhC*H*), 5.18 (s, 1 H, H-1'), 5.08 (dd, 1 H, H-2), 5.00 (d, 1 H, H-1), 3.40 (s, 3 H, OMe).

Anal. Calc. for $C_{27}H_{32}O_{12}$: C, 59.12; H, 5.88. Found: C, 59.19; H, 5.81.

Methyl2-O-benzoyl-4,6-O-benzylidene-3-O-(2,3:4,6-di-O-isopropylidene-α-D-mannopyranosyl)-α-D-glucopyranoside (**20**). — A mixture of **19** (1.20 g), 2,2-dimethoxypropane (40 mL), and *p*-toluenesulfonic acid (100 mg) was stirred for 2 h at room temperature, then diluted with dichloromethane (70 mL), washed with aq. 5% $NaHCO_3$ (2 x 15 mL) and water (2 x 15 mL), dried (Na_2SO_4), and concentrated. Recrystallisation of the residue (1.28 g, 93.1%) from cyclohexane–ethyl acetate gave **20** (675 mg, 49.1%), m.p. 173–174°, $[\alpha]_D$ +89° (*c* 0.7, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 8.09 (d, 2 H, aromatic), 7.65–7.30 (m, 8 H, aromatic), 5.62 (s, 1 H, PhC*H*), 5.52 (s, 1 H, H-1'), 5.14 (dd, 1 H, H-2), 5.04 (d, 1 H, H-1), 4.49 (t, 1 H, H-4'), 4.34 (dd, 1 H, H-3'), 4.22 (d, 1 H, H-2'), 4.00–3.46 (m, 8 H), 3.41 (s, 3 H, OMe), 1.49, 1.41, 1.26, and 1.21 (4 s, each 3 H, 2 CMe_2); $J_{1,2}$ 3.8 Hz.

Anal. Calc. for $C_{33}H_{40}O_{12}$: C, 63.05; H, 6.41. Found: C, 63.11; H, 6.37.

Methyl 4,6-O-benzylidene-3-O-(2,3:4,6-di-O-isopropylidene-α-D-mannopyranosyl)-α-D-glucopyranoside (**21**). — To a solution of **20** (580 mg) in dry methanol (40 mL) was added sodium methoxide (30 mg), and the mixture was kept at room temperature for 2 days, neutralised with Amberlite IR-120 (H^+) resin, filtered, and concentrated. Column chromatography of the product with dichloromethane–acetone (9:1) afforded **21** (405 mg, 83.7%). After crystallisation from ethanol, it had m.p. 171–172°, $[\alpha]_D$ +50° (*c* 1, chloroform). ^{1}H-N.m.r. data ($CDCl_3$): δ 7.50–7.30 (m, 5 H, aromatic), 5.56 (s, 1 H, PhC*H*), 5.38 (s, 1 H, H-1'), 4.82 (d, 1 H, H-1), 4.34–3.53 (m, 12 H), 3.46 (s, 3 H, OMe), 2.42 (d, 1 H, OH), 1.53, 1.51, 1.42, and 1.32 (4 s, each 3 H, 2 CMe_2); $J_{1,2}$ 3.9 Hz.

Anal. Calc. for $C_{26}H_{36}O_{11}$: C, 59.53; H, 6.92. Found: C, 59.48; H, 6.95.

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