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Synthesis of trisaccharide methyl glycosides related to fragments of the capsular polysaccharide of *Streptococcus pneumoniae* type 18C

Augusta M. P. van Steijn, Johannis P. Kamerling*, and Johannes F. G. Vliegenthart
Bijvoet Center, Department of Bio-Organic Chemistry, Utrecht University, P.O. Box 80.075, NL-3508 TB Utrecht (The Netherlands)

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ABSTRACT

The synthesis is reported of methyl 3-*O*-(4-*O*-β-D-galactopyranosyl-α-D-glucopyranosyl)-α-L-rhamnopyranoside (**1**), methyl 2-*O*-α-D-glucopyranosyl-4-*O*-β-D-glucopyranosyl-β-D-galactopyranoside (**3**), methyl 3-*O*-(4-*O*-β-D-galactopyranosyl-α-D-glucopyranosyl)-α-L-rhamnopyranoside 3″-(*sn*-glycer-3-yl sodium phosphate) (**2**), and methyl 2-*O*-α-D-glucopyranosyl-4-*O*-β-D-glucopyranosyl-β-D-galactopyranoside 3-(*sn*-glycer-3-yl sodium phosphate) (**4**), which are trisaccharide methyl glycosides related to fragments of the capsular polysaccharide of *Streptococcus pneumoniae* type 18C ($\{\rightarrow 4)$-β-D-Glc*p*-$(1\rightarrow 4)$-[α-D-Glc*p*-$(1\rightarrow 2)$]-[Glycerol-$(1\text{-P}\rightarrow 3)$]-β-D-Gal*p*-$(1\rightarrow 4)$-α-D-Glc*p*-$(1\rightarrow 3)$-α-L-Rha*p*-$(1\rightarrow\}_n$).

Ethyl 4-*O*-acetyl-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (**10**) was coupled with benzyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside (**6**). Deacetylation of the product, followed by condensation with 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-galactopyranosyl trichloroacetimidate (**18**), gave benzyl 2,4-di-*O*-benzyl-3-*O*-[2,3,6-tri-*O*-benzyl-4-*O*-(2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-D-galactopyranosyl)-α-D-glucopyranosyl]-α-L-rhamnopyranoside (**19**). Acetolysis of **19**, followed by methylation, deallylation (→**22**), and further deprotection afforded **1**.

Condensation of methyl 2,4-di-*O*-benzyl-3-*O*-[2,3,6-tri-*O*-benzyl-4-*O*-(2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-α-D-glucopyranosyl]-α-L-rhamnopyranoside (**22**) with 1,2-di-*O*-benzyl-*sn*-glycerol 3-(triethylammonium phosphonate) (**24**), followed by oxidation and deprotection, yielded **2**.

Condensation of ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside (**27**) with methyl 3-*O*-allyl-4,6-*O*-benzylidene-β-D-galactopyranoside (**28**), selective benzylidene ring-opening of the product, coupling with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (**31**), and deallylation afforded methyl 6-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)-β-D-galactopyranoside (**33**). Deprotection of **33** gave **3**, and condensation of **33** with **24**, followed by oxidation and deprotection, gave **4**.

INTRODUCTION

The current polysaccharide vaccine Pneumovax 23 against such pneumococcal diseases as pneumonia, otitis media, and meningitis contains the capsular polysaccharides isolated from 23 species of *Streptococcus pneumoniae*. In view of the immunological problems associated with this vaccine, much attention has been paid to the preparation of better alternatives based on polysaccharide or oligosaccharide conjugates,

* Author for correspondence.

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having proteins as the carrier[1]. We now report the synthesis of the trisaccharide methyl glycosides **1**–**4**, which are related to fragments of the capsular polysaccharide (**5**) of *S. pneumoniae* serotype 18C (ref. 2), one of the constituents of the vaccine[3].

β-D-Gal*p*-(1→4)-α-D-Glc*p*-(1→3)-α-L-Rha*p*-OMe

1

sn-Glycerol-(3-P→3)-β-D-Gal*p*-(1→4)-α-D-Glc*p*-(1→3)-α-L-Rha*p*-OMe

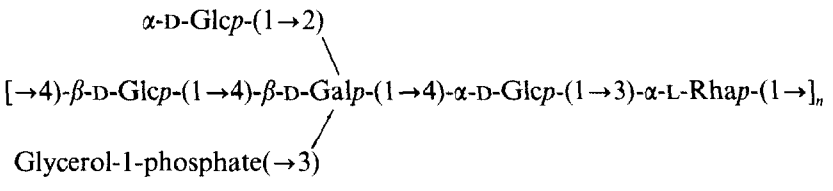
2

α-D-Glc*p*-(1→2)-[β-D-Glc*p*-(1→4)]-β-D-Gal*p*-OMe

3

α-D-Glc*p*-(1→2)-[*sn*-Glycerol-(3-P→3)]-[β-D-Glc*p*-(1→4)]-β-D-Gal*p*-OMe

4



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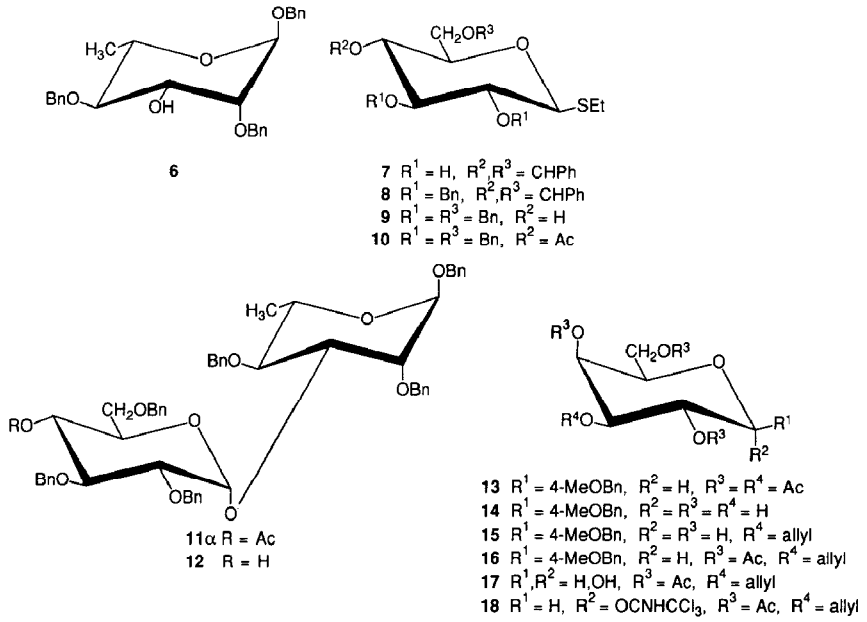
RESULTS AND DISCUSSION

The syntheses of **1** and **2** involved the synthons benzyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside[4] (**6**), ethyl 4-*O*-acetyl-2,3,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (**10**), and 2,4,6-tri-*O*-acetyl-3-*O*-allyl-α-D-galactopyranosyl trichloroacetimidate (**18**). Benzylidenation of ethyl 1-thio-β-D-glucopyranoside[5] with α,α-dimethoxytoluene[6] (→**7**, 69%; lit.[5] 47%), followed by benzylation (→**8**, 81%), regioselective reductive opening of the 4,6-*O*-benzylidene ring using the borane–trimethylamine complex and aluminium(III) chloride in tetrahydrofuran[7] (→**9**, 73%), and acetylation afforded **10**. Condensation of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl trichloroacetimidate[8] with 4-methoxybenzyl alcohol in dichloromethane, using trimethylsilyl triflate as a catalyst (→**13**, 73%), followed by deacetylation (→**14**), selective allylation with allyl bromide in the presence of tetrabutylammonium iodide[9] (→**15**), and acetylation gave crystalline **16** (42% from **13**). Removal of the 4-methoxybenzyl group from **16** in the presence of ceric ammonium nitrate[10] (→**17**, 81%) and imidation gave **18**. A synthesis of

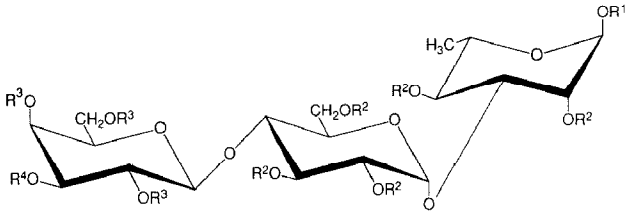


17 (and **18**) from methyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-D-galactopyranoside has been described[11]; however, the acetolysis of MeO-1 remained a problem.

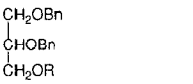
Condensation of **10** with **6** in ether, using methyl triflate[12] as a promoter, gave the disaccharide derivatives **11α** (57%) and **11β** (31%). Deacetylation of **11α** yielded **12** (98%). Coupling of **18** with **12** in dry dichloromethane at −30°, using trimethylsilyl triflate as a catalyst, afforded the trisaccharide derivative **19** (73%).

The synthesis of the methyl α-glycoside of **19**, using a non-participating group at C-2 of the rhamnose residue, was studied in order to identify the best conditions for the introduction of a spacer element. Acetolysis of **19** with sulfuric acid in acetic anhydride–acetic acid replaced BnO-1 by AcO-1 and gave **20** (78%). Replacement of the axial AcO-1 in **20** by an axial MeO-1 (→**21**, 62%) was carried out in dichloromethane using methanol with trimethylsilyl triflate as the promoter[13]. Attempts to prepare **21** via the corresponding glycosyl imidates or glycosyl bromide failed. Removal of AcO-1 of **20** with hydrazine acetate, followed by conversion of the resulting trisaccharide derivative into the corresponding glycosyl imidates (1,8-diazabicyclo[5.4.0]undec-7-ene, potassium carbonate) or glycosyl bromide (Vilsmeier–Haack reagent), and condensation with methanol applying different promoters in different solvents afforded always α,β-mixtures of the methyl glycosides. Deallylation of **21** using palladium(II) chloride[14] in acetic acid (→**22**, 75%), then deacetylation, and debenzylation yielded the target methyl glycoside **1**. The ^{1}H-n.m.r. data of **1**, obtained by 2D COSY[15] and HOHAHA[16] measurements, are given in Table I.

For the introduction of the glycerol phosphate group at HO-3 of the galactose moiety of **22**, 1,2-di-*O*-benzyl-*sn*-glycerol 3-(triethylammonium phosphonate) (**24**, 23%) was prepared by converting 1,2-di-*O*-benzyl-*sn*-glycerol[17] (**23**) into the corre-



19 $R^1 = R^2 = Bn$, $R^3 = Ac$, $R^4 = allyl$
20 $R^1 = R^3 = Ac$, $R^2 = Bn$, $R^4 = allyl$
21 $R^1 = Me$, $R^2 = Bn$, $R^3 = Ac$, $R^4 = allyl$
22 $R^1 = Me$, $R^2 = Bn$, $R^3 = Ac$, $R^4 = H$
1 $R^1 = Me$, $R^2 = R^3 = R^4 = H$
25 $R^1 = Me$, $R^2 = Bn$, $R^3 = Ac$, $R^4 = PH(O)OCH_2CHOBnCH_2OBn$
26 $R^1 = Me$, $R^2 = Bn$, $R^3 = Ac$, $R^4 = P(O)(O^-{}^+NHEt_3)OCH_2CHOBnCH_2OBn$
2 $R^1 = Me$, $R^2 = R^3 = H$, $R^4 = P(O)(O^-Na^+)OCH_2CHOHCH_2OH$



23 R = H
24 R = $PH(O)(O^-{}^+NHEt_3)$

sponding phosphonate using 2-chloro-4*H*-1,3,2-benzodioxaphosphorin-4-one in acetonitrile–pyridine[11,18]. Condensation of **24** with **22** gave 74% of the phosphonic diester **25** in two enantiomeric forms [^{1}H-n.m.r. data: δ 6.853 ($J_{H,P}$ 715 Hz) and 6.701 ($J_{H,P}$ 726 Hz), PH]. Mild oxidation of **25** with iodine in water–pyridine (→**26**, 92%), followed by deacetylation, debenzylation, and treatment with Dowex-50 (Na^+) resin, afforded the target methyl glycoside **2**, which was very labile under mild alkaline conditions. The ^{1}H-n.m.r. data for **2** are given in Table I.

The syntheses of **3** and **4** involved the synthons ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside[19] (**27**), methyl 3-*O*-allyl-4,6-*O*-benzylidene-β-D-galactopyranoside (**28**), and 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate[8] (**31**). Benzylidenation of methyl 3-*O*-allyl-β-D-galactopyranoside[20] using α,α-dimethoxytoluene afforded crystalline **28** (70%), which was condensed with **27** in ether, using methyl triflate[12] as the promoter, to give the disaccharide derivatives **29**α (56%) and **29**β (33%). Regioselective reductive opening of the 4,6-*O*-benzylidene ring in **29**α, as described for **9**, yielded **30** (76%), coupling of which with **31** in dichloromethane at −30°, using trimethylsilyl triflate as the catalyst, gave the trisaccharide derivative **32** (90%). Deallylation[21] of **32** (→**33**, 49%) followed by further deprotection yielded the target methyl glycoside **3**. Coupling of **33** with **24** afforded two enantiomers of the phosphonic diester **34** (70%) [^{1}H-n.m.r. data: δ 6.959 ($J_{H,P}$ 707 Hz) and 6.901 ($J_{H,P}$ 726 Hz), PH]. Mild oxidation of **34** with iodine in water–pyridine (→**35**, 99%), followed by deacetylation, debenzylation, and treatment with Dowex-50 (Na^+) resin gave the target methyl glycoside **4**. The ^{1}H-n.m.r. data for **3** and **4** are given in Table I.

The results of immunological inhibition experiments with **1**–**4** will be reported elsewhere.

EXPERIMENTAL

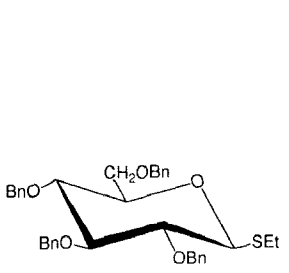
General methods. — ^{1}H-N.m.r. spectra (360 and 500 MHz) were recorded at 25° with a Bruker HX 360 or AM 500 spectrometer (Bijvoet Center, Utrecht University). 2D double-quantum-filtered ^{1}H–^{1}H correlation spectra (2D DQF ^{1}H–^{1}H COSY) were

TABLE I

500-MHz ^{1}H-N.m.r. data[a] for the trisaccharide methyl glycosides **1–4**

Residue	*Proton (J)*	*δ (p.p.m.) (J in Hz)*			
		1	**2**	**3**	**4**
α-Rha	H-1 ($J_{1,2}$)	4.744 (1.8)	4.744 (2.1)		
	H-2 ($J_{2,3}$)	4.134 (2.5)	4.13[b]		
	H-3 ($J_{3,4}$)	3.77 (9.8)	3.80		
	H-4 ($J_{4,5}$)	3.549 (9.8)	3.55		
	H-5 ($J_{5,6}$)	3.71 (6.2)	3.72 (6.5)		
	H-6	1.321	1.322		
α-Glc	H-1 ($J_{1,2}$)	5.056 (3.9)	5.055 (4.0)		
	H-2 ($J_{2,3}$)	3.630 (9.9)	3.63		
	H-3 ($J_{3,4}$)	3.910 (9.5)	3.92		
	H-4 ($J_{4,5}$)	3.72 (10.1)	3.73		
	H-5 ($J_{5,6a}$)	4.083 (2.4)	4.09		
	($J_{5,6b}$)	(3.6)			
β-Gal	H-1 ($J_{1,2}$)	4.471 (7.8)	4.553 (7.9)	4.474 (7.9)	4.529 (7.9)
	H-2 ($J_{2,3}$)	3.547 (10.0)	3.67	3.637 (9.8)	3.917 (9.9)
	H-3 ($J_{3,4}$)	3.668 (3.4)	4.11	3.836 (3.3)	4.262[c] (2.9)
	H-4 ($J_{4,5}$)	3.929 (<1)	4.14	4.173 (<1)	4.405 (<1)
	H-5	n.d.	n.d	3.704	3.737
α-Glc	H-1 ($J_{1,2}$)			5.251 (3.9)	5.331 (3.9)
	H-2 ($J_{2,3}$)			3.523 (9.9)	3.503 (9.9)
	H-3 ($J_{3,4}$)			3.726 (9.3)	3.811 (9.3)
	H-4 ($J_{4,5}$)			3.457 (10.2)	3.392 (10.2)
	H-5 ($J_{5,6a}$)			4.025 (2.7)	4.101 (2.4)
	($J_{5,6b}$)			(3.9)	(4.5)
β-Glc	H-1 ($J_{1,2}$)			4.664 (8.0)	4.767 (7.9)
	H-2 ($J_{2,3}$)			3.370 (9.3)	3.319 (9.4)
	H-3 ($J_{3,4}$)			3.505 (8.7)	3.529 (8.6)
	H-4 ($J_{4,5}$)			3.396 (9.8)	3.398 (9.8)
	H-5 ($J_{5,6a}$)			3.440 (2.1)	3.445 (2.2)
	H-6a ($J_{6a,6b}$)			3.908 (−12.3)	3.909 (−12.2)
	H-6b ($J_{5,6b}$)			3.730 (5.4)	3.728 (5.6)
OCH_3		3.406	3.406	3.564	3.570
Glycerol	H-1a ($J_{1a,2}$)		3.68		3.689 (4.3)
	($J_{1a,1b}$)				(−11.8)
	H-1b ($J_{1b,2}$)		3.61		3.607 (5.8)
	H-2		3.90		3.92
	H-3a/H-3b		4.01/3.90		3.996/3.92

[a] Chemical shifts are relative to the signal of internal acetone (δ 2.225 p.p.m. in D_2O). [b] Chemical shift values with two decimals are deduced directly from 2D COSY and HOHAHA measurements. [c] $J_{3,P}$ 9.5 Hz.



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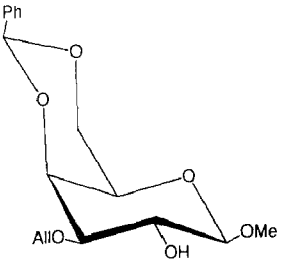

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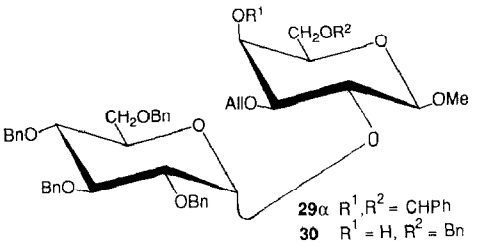
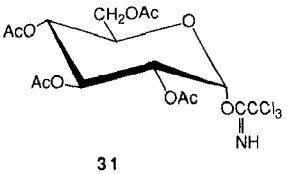


29α R^1,R^2 = CHPh
30 R^1 = H, R^2 = Bn



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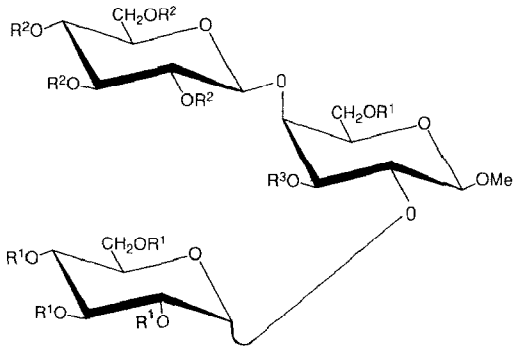

32 R^1 = Bn, R^2 = Ac, R^3 = allyl
33 R^1 = Bn, R^2 = Ac, R^3 = H
3 R^1 = R^2 = R^3 = H
34 R^1 = Bn, R^2 = Ac, R^3 = PH(O)$OCH_2CHOBnCH_2OBn$
35 R^1 = Bn, R^2 = Ac, R^3 = P(O)($O^-{}^+NHEt_3$)$OCH_2CHOBnCH_2OBn$
4 R^1 = R^2 = H, R^3 = P(O)(O^-Na^+)$OCH_2CHOHCH_2OH$

recorded in the phase-sensitive mode[15], and 2D homonuclear Hartmann–Hahn spectra (2D HOHAHA) with a MLEV-17 mixing sequence of 120 ms[16]. ^{13}C-N.m.r. spectra (APT, 50 MHz) were recorded at 25° with a Bruker WP 200 spectrometer. Chemical shifts (δ) are given in p.p.m. relative to the signal for internal Me_4Si ($CDCl_3$) or sodium 4,4-dimethyl-4-silapentane-1-sulfonate (D_2O; indirectly to internal acetone, δ 2.225) for ^{1}H, and to the signal for internal Me_4Si ($CDCl_3$; indirectly to $CDCl_3$, δ 76.9) or external Me_4Si (D_2O; indirectly to internal acetone, δ 31.55) for ^{13}C.

Column chromatography was performed on Kieselgel 60 (Merck, <230 mesh) and fractions were monitored by t.l.c. on Kieselgel 60 F_{254} (Merck). Detection was effected by charring with H_2SO_4 after examination under u.v. light. Optical rotations

were measured at 20° with a Perkin–Elmer 241 polarimeter, using a 10-cm 1-mL cell. Melting points were determined with a Mettler FP 51 instrument. In the work-up procedures, washings were carried out three times with appropriate quantities of water or aq. 5% sodium hydrogencarbonate unless indicated otherwise. Solvents were evaporated under reduced pressure at 40° (bath). All solvents were distilled from appropriate drying agents.

*Ethyl 4,6-O-benzylidene-1-thio-β-*D*-glucopyranoside* (**7**). — A mixture of ethyl 1-thio-β-D-glucopyranoside[5] (2.88 g, 12.79 mmol) and *p*-toluenesulfonic acid (100 mg) in *N,N*-dimethylformamide (15 mL) and α,α-dimethoxytoluene (30 mL) was heated for 1 h at 60° under reduced pressure[6], then concentrated. The residue was crystallised from aq. saturated sodium hydrogencarbonate (75 mL) and recrystallised from EtOAc–light petroleum (b.p. 40–60°) to give **7** (2.77 g, 69%), m.p. 145°, $[\alpha]_D$ −65° (*c* 1, $CHCl_3$), R_F 0.06 (95:5 CH_2Cl_2–EtOAc); lit.[5] m.p. 144–147°, $[\alpha]_D$ +47° (*c* 1, $CHCl_3$). N.m.r. data ($CDCl_3$): ^{13}C, δ 136.5 and 129.2–126.2 (C_6H_5CH), 101.8 (PhCH), 86.4 (C-1), 80.2, 74.4, 73.1, and 70.4 (C-2,3,4,5), 68.5 (C-6), 24.6 (CH_3CH_2S), 15.1 (CH_3CH_2S); ^1H, δ 7.508–7.365 (m, 5 H, Ph), 5.551 (s, 1 H, PhC*H*), 4.478 (s, 1 H, H-1), 4.361 (dd, 1 H, H-6), 2.804–2.743 (m, 2 H, CH_3CH_2S), 1.337 (t, 3 H, CH_3CH_2S); $J_{1,2}$ 9.7, $J_{5,6}$ 4.9, $J_{6a,6b}$ −10.6, $J_{CH_2CH_3}$ 7.4 Hz.

Anal. Calc. for $C_{15}H_{20}O_5S$: C, 57.67; H, 6.45. Found: C, 57.53; H, 6.20.

*Ethyl 2,3-di-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-*D*-glucopyranoside* (**8**). — A solution of **7** (1.46 g, 4.68 mmol) and benzyl bromide (1.8 mL, 14.9 mmol) in dry *N,N*-dimethylformamide (6 mL) was added to a stirred suspension of sodium hydride (0.45 g, 1.88 mmol) in *N,N*-dimethylformamide (5 mL) at 0°. After 1 h, t.l.c. (95:5 CH_2Cl_2–EtOAc) indicated the disappearance of **7** and a product with R_F 0.75. Methanol was added to destroy the excess of sodium hydride, the mixture was poured into ice–water (300 mL) and extracted with ether (3 × 75 mL), and the combined extracts were dried (Na_2SO_4), filtered, and concentrated. The residue was crystallised from EtOH to yield **8** (1.86 g, 81%), m.p. 118° (from EtOH), $[\alpha]_D$ −43° (*c* 1, $CHCl_3$). Column chromatography (97:3 CH_2Cl_2–EtOAc) of the material in the mother liquour yielded more **8** (0.31 g, 13%). N.m.r. data ($CDCl_3$): ^{13}C, δ 128.1–125.9 ($C_6H_5CH_2O$ and C_6H_5CH), 101.0 (PhCH), 85.7 (C-1), 82.7, 81.5, 81.2, and 70.1 (C-2,3,4,5), 75.8 and 75.1 (2 $PhCH_2O$), 68.6 (C-6), 25.0 (CH_3CH_2S), 15.0 (CH_3CH_2S); ^1H, δ 7.491–7.252 (m, 15 H, 3 Ph), 5.574 (s, 1 H, PhC*H*), 4.945, 4.882, 4.808, and 4.795 (4 d, each 1 H, 2 $PhCH_2O$), 4.560 (d, 1 H, H-1), 4.354 (dd, 1 H, H-6), 3.463 (dd, 1 H, H-2), 2.810–2.716 (m, 2 H, CH_3CH_2S), 1.318 (t, 3 H, CH_3CH_2S); $J_{1,2}$ 9.8, $J_{2,3}$ 8.1, $J_{5,6}$ 5.0, $J_{6a,6b}$ −10.5, $J_{CH_2CH_3}$ 7.4 Hz.

Anal. Calc. for $C_{29}H_{32}O_5S$: C, 70.71; H, 6.55. Found: C, 70.72; H, 6.53.

*Ethyl 2,3,6-tri-*O*-benzyl-1-thio-β-*D*-glucopyranoside* (**9**). — A mixture of **8** (1.86 g, 3.77 mmol), borane–trimethylamine complex (1.68 g, 23.03 mmol), and powdered molecular sieves (4 Å, 5.0 g) in tetrahydrofuran[7] (50 mL) was stirred for 1 h. Aluminium (III) chloride (3.12 g, 23.40 mmol) was added at 0° and stirring was continued for 3 h, when t.l.c. (95:5 CH_2Cl_2–EtOAc) showed the ring opening to be complete (→**8**, R_F 0.48). The mixture was diluted with CH_2Cl_2 (350 mL), filtered through Celite, washed with M H_2SO_4 (3 × 50 mL), water, aq. 5% sodium hydrogencarbonate, and water, dried

(Na_2SO_4), filtered, and concentrated. Column chromatography of the residue gave **9** (1.37 g, 73%), m.p. 66° (from EtOH), $[\alpha]_D$ − 38° (*c* 1, $CHCl_3$). N.m.r. data ($CDCl_3$): ^{13}C, δ 138.4 and 128.4–127.6 ($C_6H_5CH_2O$), 85.8, 85.0, 81.1, 77.8, and 71.9 (C-1,2,3,4,5), 75.2 (2 C) and 73.5 (3 PhCH_2O), 70.4 (C-6), 24.8 (CH_3CH_2S); ^1H, δ 7.404–7.258 (m, 15 H, 3 Ph), 4.920, 4.788, 4.739, 4.594, and 4.555 (5 d, 2,1,1,1, and 1 H, 3 PhCH_2O), 4.485 (d, 1 H, H-1), 3.743 (dd, 1 H, H-6a), 3.717 (dd, 1 H, H-6b), 2.776–2.693 (m, 2 H, CH_3CH_2S), 1.321 (t, 3 H, CH_3CH_2S); $J_{1,2}$ 9.6, $J_{5,6a}$ 4.6, $J_{5,6b}$ 5.1, $J_{6a,6b}$ − 10.4, $J_{CH_2CH_3}$ 7.4 Hz.

Anal. Calc. for $C_{29}H_{34}O_5S$: C, 70.42; H, 6.93. Found: C, 70.47; H, 7.02.

*Ethyl 4-*O*-acetyl-2,3,6-tri-*O*-benzyl-1-thio-β-*D*-glucopyranoside* (**10**). — A solution of **9** (12.0 g, 24.3 mmol) in pyridine (60 mL) and acetic anhydride (60 mL) was stirred for 16 h at room temperature, then concentrated, and toluene, EtOH, and CH_2Cl_2 (each 3 × 50 mL) were evaporated from the residue. Column chromatography (97:3 CH_2Cl_2–EtOAc) then gave **10** (12.8 g, 99%), m.p. 67° (from EtOH), $[\alpha]_D$ − 19° (*c* 1, $CHCl_3$), R_F 0.70 (95:5 CH_2Cl_2–EtOAc). ^{13}C-N.m.r. data ($CDCl_3$): δ 138.1–137.6 and 128.2–127.5 ($C_6H_5CH_2O$), 84.8, 83.6, 81.3, 77.3, and 70.9 (C-1,2,3,4,5), 75.4, 75.2, and 73.4 (3 PhCH_2O), 69.8 (C-6), 24.8 (CH_3CH_2S), 20.6 ($COCH_3$), 15.0 (CH_3CH_2S).

*Benzyl 3-*O*-(4-*O*-acetyl-2,3,6-tri-*O*-benzyl-α,β-*D*-glucopyranosyl)-2,4-di-*O*-benzyl-α-*L*-rhamnopyranoside* (**11**αβ). — To a stirred solution of **10** (1.80 g, 3.36 mmol), benzyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside[4] (**6**; 1.47 g, 3.38 mmol), and powdered molecular sieves (4 Å, 10 g) in dry ether (60 mL) was added methyl triflate (1.9 mL, 16.8 mmol). After 18 h, when t.l.c. (95:5 CH_2Cl_2–EtOAc) indicated two products with R_F 0.69 (**11**β) and 0.64 (**11**α), triethylamine (8 mL) was added, and stirring was continued for 10 min. The mixture was then filtered through Celite and concentrated. Column chromatography (97:3 CH_2Cl_2–EtOAc) of the residue gave **11**β, isolated as a syrup (0.94 g, 31%), $[\alpha]_D$ − 32° (*c* 1, $CHCl_3$), and **11**α, isolated as a syrup (1.72 g, 57%), $[\alpha]_D$ + 10° (*c* 1, $CHCl_3$). N.m.r. data ($CDCl_3$): **11**β ^{13}C, δ 169.5 ($COCH_3$), 138.4–137.1 and 128.0–127.3 ($C_6H_5CH_2O$), 103.2 (C-1′), 97.5 (C-1), 20.6 ($COCH_3$), 17.7 (C-6); ^1H, δ 7.373–7.186 (m, 30 H, 6 Ph), 4.962 (t, 1 H, H-4′), 4.268 (dd, 1 H, H-3), 3.933 (dd, 1 H, H-2), 3.763 (m, 1 H, H-5), 1.827 (s, 3 H, Ac), 1.330 (d, 3 H, H-6,6,6); $J_{1,2}$ 1.8, $J_{2,3}$ 3.2, $J_{3,4} = J_{4,5}$ = 9.4, $J_{5,6}$ 6.1, $J_{3',4'} = J_{4',5'}$ = 9.4 Hz; **11**α ^{13}C, δ 169.3 ($COCH_3$), 138.2–137.7 and 128.2–127.4 ($C_6H_5CH_2O$), 97.0 (C-1), 94.4 (C-1′), 79.8, 79.2, 79.1, 75.8, 74.9, 70.1, 68.5, and 68.4 (C-2,3,4,5,2′,3′,4′,5′), 75.1, 74.8, 73.3, 73.1 (2 C), 68.7, and 68.1 (6 PhCH_2O and C-6′), 20.6 ($COCH_3$), 17.9 (C-6); ^1H, δ 7.324–7.188 (m, 30 H, 6 Ph), 5.153 (d, 1 H, H-1′), 5.113 (t, 1 H, H-4′), 4.818 (s, 1 H, H-1), 4.175 (dd, 1 H, H-3), 4.080 (m, 1 H, H-5′), 4.019 (t, 1 H, H-3′), 3.759 (m, 1 H, H-5), 3.908 (dd, 1 H, H-2), 3.679 (dd, 1 H, H-2′), 3.678 (t, 1 H, H-4), 3.328 (dd, 1 H, H-6′a), 3.193 (dd, 1 H, H-6′b), 1.716 (s, 3 H, Ac), 1.334 (d, 3 H, H-6,6,6); $J_{1,2} < 1$, $J_{2,3}$ 3.0, $J_{3,4} = J_{4,5}$ = 9.3, $J_{5,6}$ 6.1, $J_{1',2'}$ 3.4, $J_{2',3'}$ 9.6, $J_{3',4'} = J_{4',5'}$ = 9.5, $J_{5',6'a}$ 2.7, $J_{5',6'b}$ 4.1, $J_{6'a,6'b}$ − 11.0 Hz.

Anal. Calc. for $C_{56}H_{60}O_{11}$: C, 73.99; H, 6.65. Found **11**α: C, 73.65; H, 6.78. Found **11**β: C, 74.35; H, 6.94.

*Benzyl 2,4-di-*O*-benzyl-3-*O*-(2,3,6-tri-*O*-benzyl-α-*D*-glucopyranosyl)-α-*L*-rhamnopyranoside* (**12**). — To a solution of **11**α (6.5 g, 7.2 mmol) in methanol (60 mL) was added sodium methoxide to pH 10, and the mixture was stirred overnight. T.l.c.

(95:5 CH_2Cl_2–EtOAc) then showed the deacetylation to be complete (→**12**, R_F 0.59), Dowex-50 (H^+) resin was added, and the mixture was filtered and concentrated. Column chromatography (97:3 CH_2Cl_2–EtOAc) of the residue afforded **12**, isolated as a syrup (6.1 g, 98%), $[\alpha]_D$ −3° (*c* 0.7, $CHCl_3$). N.m.r. data ($CDCl_3$): ^{13}C, δ 138.5–137.2 and 128.3–127.5 ($C_6H_5CH_2O$), 97.1 (C-1), 95.0 (C-1′), 81.1, 79.9, 79.2, 76.1, 75.3, 70.9, 70.0, and 68.2 (C-2,3,4,5,2′,3′,4′,5′), 17.9 (C-6); ^1H, δ 7.402–7.127 (m, 30 H, 6 Ph), 5.170 (d, 1 H, H-1′), 4.152 (dd, 1 H, H-3), 3.987 (m, 1 H, H-5′), 3.595 (dd, 1 H, H-2′), 3.543 (dd, 1 H, H-6′b), 3.494 (dd, 1 H, H-6′a), 1.322 (d, 3 H, H-6,6,6); $J_{2,3}$ 2.9, $J_{3,4}$ 8.9, $J_{5,6}$ 6.0, $J_{1',2'}$ 3.4, $J_{2',3'}$ 9.6, $J_{4',5'}$ 9.8, $J_{5',6'a}$ 3.6, $J_{5',6'b}$ 3.8, $J_{6'a,6'b}$ −10.5 Hz.

Anal. Calc. for $C_{54}H_{58}O_{10}$: C, 74.81; H, 6.74. Found: C, 74.60; H, 6.81.

*4-Methoxybenzyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranoside* (**13**). — A solution of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl trichloroacetimidate[8] (5.1 g, 10.4 mmol), 4-methoxybenzyl alcohol (2.5 mL, 20.8 mmol), and molecular sieves (4 Å, 10 g) in dry CH_2Cl_2 (40 mL) was stirred for 1 h under N_2. A solution of trimethylsilyl triflate (38 μL, 0.21 mmol) in dry CH_2Cl_2 (1 mL) was added at −30°. After 10 min, t.l.c. (85:15 CH_2Cl_2–EtOAc) indicated the reaction to be complete (→**13**, R_F 0.25), pyridine (2 mL) was added, and the mixture was filtered through Celite and concentrated. Column chromatography (8:2 CH_2Cl_2–EtOAc) of the residue gave **13**, isolated as a syrup (3.5 g, 73%), $[\alpha]_D$ −24° (*c* 1, $CHCl_3$). N.m.r. data ($CDCl_3$): ^{13}C, δ 169.7 (2 C), 169.4, and 168.7 (4 $COCH_3$), 158.9, 128.9 (2 C), 128.2, and 113.3 (2 C) ($MeOC_6H_4CH_2O$), 98.8 (C-1), 70.4, 70.1, 68.3, and 66.6 (C-2,3,4,5), 69.8 ($MeOC_6H_4CH_2O$), 60.8 (C-6), 54.6 ($CH_3OC_6H_4CH_2O$), 20.1–19.9 ($COCH_3$); ^1H, δ 7.218 and 6.880 (2 d, each 2 H, $MeOC_6H_4CH_2O$), 5.382 (bd, 1 H, H-4), 5.256 (dd, 1 H, H-2), 4.976 (dd, 1 H, H-3), 4.835 and 4.575 (2 d, each 1 H, $MeOC_6H_4CH_2O$), 4.484 (d, 1 H, H-1), 4.219 (dd, 1 H, H-6a), 4.152 (dd, 1 H, H-6b), 3.875 (m, 1 H, H-5), 3.816 (s, 3 H, $CH_3OC_6H_4CH_2O$), 2.157, 2.072, 2.004, and 1.974 (4 s, each 1 H, 4 Ac); $J_{1,2}$ 7.9, $J_{2,3}$ 10.4, $J_{3,4}$ 3.5, $J_{4,5}$ < 1, $J_{5,6a}$ 6.5, $J_{5,6b}$ 6.9, $J_{6a,6b}$ −11.2 Hz.

Anal. Calc. for $C_{22}H_{28}O_{11}$: C, 56.41; H, 6.02. Found: C, 56.85; H, 6.07.

*4-Methoxybenzyl 2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-*D*-galactopyranoside* (**16**). — To a solution of **13** (14.7 g, 32.4 mmol) in MeOH (125 mL) was added sodium methoxide to pH 10. After 16 h, Dowex-50 (H^+) resin was added, and the solution was filtered and concentrated. A solution of the product **14** (R_F 0.25, 9:1 CH_2Cl_2–MeOH) and dibutyltin oxide (8.1 g, 32.4 mmol) in benzene (150 mL) was boiled under reflux for 16 h in a Soxhlet apparatus containing molecular sieves (3 Å). Then tetrabutylammonium iodide (11.8 g, 32.4 mmol) and allyl bromide (4.8 mL, 55.8 mmol) were added, and boiling was continued for 2 h, when t.l.c. (7:3 CH_2Cl_2–acetone) showed the formation of **15** (R_F 0.61). The mixture was concentrated and column chromatography of the residue afforded **15**. A solution of **15** in pyridine (75 mL) and acetic anhydride (40 mL) was stirred overnight to yield **16** as indicated by t.l.c. (8:2 CH_2Cl_2–EtOAc, R_F 0.70). The mixture was concentrated, and toluene, EtOH, and CH_2Cl_2 (each 3 × 50 mL) were evaporated from the residue. Crystallisation from EtOH afforded **16** (5.2 g, 35%), m.p. 87° (from EtOH), $[\alpha]_D$ −26° (*c* 0.6, $CHCl_3$). Column chromatography (85:15 CH_2Cl_2–acetone) of the material in the mother liquour afforded more **16** (1.1 g, 7%). N.m.r. data

($CDCl_3$): ^{13}C, δ 170.2, 170.1, and 169.2 (3 $COCH_3$), 159.2, 129.2 (2 C), 128.7, and 113.6 (2 C) ($MeOC_6H_4CH_2O$), 133.9 ($H_2C=CHCH_2O$), 117.0 ($H_2C=CHCH_2O$), 99.1 (C-1), 76.4, 70.7, 70.2, and 65.9 (C-2,3,4,5), 70.3 and 69.8 ($H_2C=CHCH_2O$ and $MeOC_6H_4CH_2O$), 61.8 (C-6), 55.0 ($CH_3OC_6H_4CH_2O$), 20.6–20.5 ($COCH_3$); ^1H, δ 7.220 and 6.872 (2 d, each 2 H, $MeOC_6H_4CH_2O$), 5.763 (m, 1 H, $H_2C=CHCH_2O$), 5.405 (bd, 1 H, H-4), 4.819 and 4.568 (2 d, each 1 H, $MeOC_6H_4CH_2O$), 4.410 (d, 1 H, H-1), 4.103 and 3.885 (2 m, each 1 H, $H_2C=CHCH_2O$), 3.807 (s, 3 H, $CH_3OC_6H_4CH_2O$), 3.774 (m, 1 H, H-5), 3.471 (dd, 1 H, H-3), 2.142, 2.090, and 2.036 (3 s, each 3 H, 3 Ac); $J_{1,2}$ 8.1, $J_{2,3}$ 10.0, $J_{3,4}$ 3.5, $J_{4,5} < 1$, $J_{5,6a} \approx J_{5,6b} \approx 6.5$ Hz.

Anal. Calc. for $C_{23}H_{30}O_{10}$: C, 59.22; H, 6.48. Found: C, 58.81; H, 6.33.

*2,4,6-Tri-*O*-acetyl-3-*O*-allyl-*α*,*β*-*D*-galactopyranose* (**17**). — To a solution of **16** (2.0 g, 4.4 mmol) in acetonitrile (45 mL) and water (5 mL) was added ceric ammonium nitrate (4.9 g, 8.8 mmol). When t.l.c. (8:2 CH_2Cl_2–EtOAc) indicated the reaction to be complete (3 h; **17**, R_F 0.26), the mixture was diluted with CH_2Cl_2 (300 mL), washed with water, aq. concentrated sodium hydrogensulfite (2 × 50 mL), aq. 5% sodium hydrogencarbonate (2 × 50 mL), and water, dried (Na_2SO_4), filtered, and concentrated. Column chromatography of the residue afforded **17**, isolated as a syrup (1.2 g, 81%), having analytical data as reported previously[11].

*Benzyl 2,4-di-*O*-benzyl-3-*O*-[2,3,6-tri-*O*-benzyl-4-*O*-(2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-*D*-galactopyranosyl)-α-*D*-glucopyranosyl]-α-*L*-rhamnopyranoside* (**19**). — To a solution of **18** (ref. 11) (0.55 g, 0.63 mmol) and **12** (0.39 g, 0.80 mmol) in dry CH_2Cl_2 containing molecular sieves (4 Å, 3 g) was added a solution of trimethylsilyl triflate (43 μL, 0.24 mmol) in CH_2Cl_2 (2 mL) at −30°. When t.l.c. (29:2 CH_2Cl_2–EtOAc) indicated the disappearance of **18** (R_F 0.78), pyridine (2 mL) was added, and the mixture was filtered through Celite and concentrated. Column chromatography of the residue gave **19**, isolated as a syrup (0.57 g, 73%), $[\alpha]_D$ −1° (*c* 1, $CHCl_3$), R_F 0.59. N.m.r. data ($CDCl_3$): ^{13}C, δ 169.8 (2 C) and 168.6 (3 $COCH_3$), 138.9–137.2 and 128.1–126.8 ($C_6H_5CH_2O$), 133.8 ($H_2C=CHCH_2O$), 116.5 ($H_2C=CHCH_2O$), 99.9 (C-1″), 97.0 (C-1), 96.2 (C-1′), 20.5 and 20.3 (2 C) (3 $COCH_3$), 17.6 (C-6); ^1H, δ 7.311–7.055 (m, 30 H, 6 Ph), 5.680 (m, 1 H, $H_2C=CHCH_2O$), 5.200 (bd, 1 H, H-4″), 5.070 (d, 1 H, H-1′), 4.925 (dd, 1 H, H-2″), 4.394 (d, 1 H, H-1″), 3.107 (dd, 1 H, H-3″), 1.996, 1.937, and 1.810 (3 s, each 3 H, 3 Ac), 1.174 (d, 3 H, H-6,6,6), $J_{1',2'}$ 3.6, $J_{1'',2''}$ 8.1, $J_{2'',3''}$ 10.0, $J_{3'',4''}$ 3.4, $J_{4'',5''} < 1$ Hz.

Anal. Calc. for $C_{69}H_{78}O_{18}$: C, 69.33; H, 6.58. Found: C, 69.19; H, 6.30.

*1-*O*-Acetyl-2,4-di-*O*-benzyl-3-*O*-[2,3,6-tri-*O*-benzyl-4-*O*-(2,4,6-tri-*O*-acetyl-3-*O*-allyl-β-*D*-galactopyranosyl)-α-*D*-glucopyranosyl]-α-*L*-rhamnopyranose* (**20**). — A solution of H_2SO_4 (10 μL) in acetic anhydride (0.99 mL) was added to a solution of **19** (0.57 g, 0.54 mmol) in acetic anhydride (9 mL) and acetic acid (5 mL) at 0°. The mixture was stirred for 2 h at room temperature, poured into ice–water containing aq. concentrated sodium hydrogencarbonate (300 mL), and, after 16 h, extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were washed with water, dried (Na_2SO_4), filtered, and concentrated. Column chromatography (9:1 CH_2Cl_2–EtOAc) of the residue gave **20**, isolated as a syrup (0.48 g, 78%), $[\alpha]_D$ +12° (*c* 1, $CHCl_3$), R_F 0.35. N.m.r. data ($CDCl_3$): ^{13}C, δ 170.1–168.9 ($COCH_3$), 139.1–137.8 and 128.4–127.1 ($C_6H_5CH_2O$), 134.0

(H_2C = $CHCH_2O$), 116.9 (H_2C = $CHCH_2O$), 100.2 (C-1″), 96.2 (C-1′), 91.6 (C-1), 20.8–20.6 ($COCH_3$), 17.9 (C-6); ^1H, δ 7.370–7.193 (m, 25 H, 5 Ph), 6.070 (d, 1 H, H-1), 5.764 (m, 1 H, H_2C = $CHCH_2O$), 5.279 and 5.145 (2 d, each 1 H, H-1′,4″), 5.015 (dd, 1 H, H-2″), 4.496 (d, 1 H, H-1″), 3.208 (dd, 1 H, H-3″), 2.068, 2.003, 1.938, and 1.900 (4 s, each 3 H, 4 Ac); $J_{1,2}$ 2.2, $J_{1',2'} \approx 3$, $J_{1'',2''}$ 8.1, $J_{2'',3''}$ 9.9, $J_{3'',4''}$ 3.4, $J_{4'',5''} < 1$ Hz.

Anal. Calc. for $C_{64}H_{74}O_{14}$: C, 67.00; H, 6.50. Found: C, 67.04; H, 6.72.

Methyl 2,4-di-O-benzyl-3-O-[2,3,6-tri-O-benzyl-4-O-(2,4,6-tri-O-acetyl-3-O-allyl-β-D-galactopyranosyl)-α-D-glucopyranosyl]-α-L-rhamnopyranoside (**21**). — To a solution of **20** (105 mg, 92 μmol) in dry CH_2Cl_2 (6 mL), containing MeOH (40 μL, 0.98 mmol) and powdered molecular sieves (3 Å, 150 mg), was added trimethyl triflate[13] (53 μL, 0.29 mmol). After 15 min, t.l.c. [7:3 light petroleum (b.p. 40–60°)–EtOAc] indicated the conversion of **20** (R_F 0.20) into **21** (R_F 0.36), pyridine was added (5 mL), and the mixture was diluted with CH_2Cl_2 (50 mL), filtered through Celite, and concentrated. Column chromatography of the residue afforded **21**, isolated as a syrup (64 mg, 62%), $[\alpha]_D$ +21° (*c* 1, $CHCl_3$). N.m.r. data ($CDCl_3$): ^{13}C, δ 170.2–168.9 ($COCH_3$), 139.1–137.9 and 128.3–127.0 ($C_6H_5CH_2O$), 134.0 (H_2C = $CHCH_2O$), 116.8 (H_2C = $CHCH_2O$), 100.2 (C-1″), 99.1 (C-1), 96.1 (C-1′), 54.5 (OCH_3), 20.7–20.6 ($COCH_3$), 17.8 (C-6), $J_{C\text{-}1,H\text{-}1}$ 167, $J_{C\text{-}1',H\text{-}1'}$ 167, $J_{C\text{-}1'',H\text{-}1''}$ 160 Hz; ^1H, δ 7.378–7.208 (m, 25 H, 5 Ph), 5.759 (m, 1 H, H_2C = $CHCH_2O$), 5.272 (bd, 1 H, H-4″), 5.219 and 5.155 (2 m, each 1 H, H_2C = $CHCH_2O$), 5.157 (d, 1 H, H-1′), 4.998 (dd, 1 H, H-2″), 4.485 (d, 1 H, H-1″), 3.271 (s, 3 H, OMe), 3.190 (dd, 1 H, H-3″), 2.063, 2.001, and 1.880 (3 s, each 3 H, 3 Ac), 1.237 (d, 3 H, H-6,6,6); $J_{5,6}$ 5.6, $J_{1',2'}$ 3.7, $J_{1'',2''}$ 8.1, $J_{2'',3''}$ 9.9, $J_{3'',4''}$ 3.4, $J_{4'',5''} < 1$ Hz.

Anal. Calc. for $C_{63}H_{74}O_{18}$: C, 67.61; H, 6.66. Found: C, 67.64; H, 6.85.

Methyl 2,4-di-O-benzyl-3-O-[2,3,6-tri-O-benzyl-4-O-(2,4,6-tri-O-acetyl-β-D-galactopyranosyl)-α-D-glucopyranosyl]-α-L-rhamnopyranoside (**22**). — A mixture of **21** (61 mg, 54 μmol), palladium(II) chloride[14] (54 mg, 0.30 mmol), and sodium acetate (47 mg, 0.57 mmol) in acetic acid (1.4 mL) was sonicated for 22 h. The mixture was diluted with CH_2Cl_2 (50 mL), filtered through Celite, washed with water, aq. 5% sodium hydrogencarbonate, and aq. 5% sodium chloride, dried (Na_2SO_4), filtered, and concentrated. Column chromatography (9:1 CH_2Cl_2–acetone) of the residue gave **22**, isolated as a syrup (44 mg, 75%), $[\alpha]_D$ +5° (*c* 1, $CHCl_3$), R_F 0.42. N.m.r. data ($CDCl_3$): ^{13}C, δ 171.2, 170.6, and 170.2 (3 $COCH_3$), 139.1–137.8 and 128.3–127.1 ($C_6H_5CH_2O$), 99.8 (C-1″), 99.0 (C-1), 95.7 (C-1′), 54.6 (OCH_3), 20.8–20.6 ($COCH_3$), 17.9 (C-6); ^1H, δ 7.358–7.217 (m, 25 H, 5 Ph), 5.184 (bd, 1 H, H-4″), 5.162 (d, 1 H, H-1′), 4.473 (d, 1 H, H-1″), 3.278 (s, 3 H, OMe), 2.095, 1.999, and 1.888 (3 s, each 3 H, 3 Ac), 1.266 (d, 3 H, H-6,6,6); $J_{5,6}$ 5.8, $J_{1',2'}$ 3.6, $J_{1'',2''}$ 7.9, $J_{3'',4''}$ 3.6, $J_{4'',5''} < 1$ Hz.

Methyl 3-O-(4-O-β-D-galactopyranosyl-α-D-glucopyranosyl)-α-L-rhamnopyranoside (**1**). — To a solution of **22** (21 mg, 20 μmol) in MeOH (5 mL) was added sodium methoxide to pH 10. After 24 h, the mixture was neutralised with Dowex-50 (H^+) resin, filtered, and concentrated. A solution of the residue in EtOH (5 mL) containing 10% Pd/C (20 mg) was hydrogenolysed for 20 h at 4 kg/cm^2, filtered through Celite, and concentrated to give **1**, isolated as a white powder (8 mg, 79%), $[\alpha]_D$ +80° (*c* 0.7, H_2O). ^{13}C-N.m.r. data (D_2O): δ 104.2 and 101.8 (C-1′,1″), 96.8 (C-1), 79.4, 77.2, 76.7, 73.9,

72.9, 72.4, 72.3, 71.7, 71.5, 69.9 (2 C), and 68.0 (C-2,3,4,5,2′,3′,4′,5′,2″,3″,4″,5″), 62.4 and 60.9 (C-6′,6″), 56.1 (OCH_3), 18.0 (C-6). For the ^{1}H-n.m.r. data, see Table I.

*1,2-Di-O-benzyl-*sn*-glycerol 3-(triethylammonium phosphonate)* (**24**). — To a solution of 1,2-di-*O*-benzyl-*sn*-glycerol[17] (157 mg, 0.58 mmol) in 4:1 acetonitrile–pyridine (3 mL) was added a solution of 2-chloro-4*H*-1,3,2-benzodioxaphosphorin-4-one (145 mg, 0.72 mmol) in acetonitrile (0.6 mL). After1 h, t.l.c. (9:1 CH_2Cl_2–acetone) indicated a partial conversion of the starting compound into **24** (R_F 0), which could not be improved. Water (1 mL) was added, and the mixture was diluted with CH_2Cl_2 (100 mL), washed with M triethylammonium hydrogencarbonate (2 × 15 mL), dried (Na_2SO_4), filtered, and concentrated. Column chromatography (9:1:0.1 CH_2Cl_2–acetone–triethylamine, followed by 9:1:0.1 CH_2Cl_2–MeOH–triethylamine) of the residue yielded **24**, isolated as a syrup (58 mg, 23%). N.m.r. data ($CDCl_3$): ^{13}C, δ 138.2, 137.8, and 127.7–127.1 ($C_6H_5CH_2O$), 77.1 (d, C-2), 72.9, 71.6, and 69.6 (2 PhCH_2O and C-1), 62.9 (d, C-3), 45.3 [N(CH_2CH_3)$_3$], 8.2 [N(CH_2CH_3)$_3$]; $^2J_{C,P}$ 4.5, $^3J_{C,P}$ 7.0 Hz; ^{1}H, δ 7.367–7.244 (m, 10 H, 2 Ph), 6.868 (d, 1 H, PH), 4.725 and 4.669 (2 d, each 1 H, PhCH_2O), 4.307 (s, 2 H, PhCH_2O), 4.071 (dq, 1 H, H-3a), 4.010 (dq, 1 H, H-3b), 3.825 (q, 1 H, H-2), 3.663 (dd, 1 H, H-1a), 3.611 (dd, 1 H, H-1b), 3.045 [q, 6 H, N(CH_2CH_3)$_3$], 1.326 [t, 9 H, N(CH_2CH_3)$_3$]; $^1J_{H,P}$ 632 Hz; ^{31}P, δ 5.5 (dt, $^1J_{P,H}$ 640, $^3J_{P,H}$ 8 Hz).

*Methyl 2,4-di-O-benzyl-3-O-[2,3,6-tri-O-benzyl-4-O-(2,4,6-tri-O-acetyl-β-D-galactopyranosyl)-α-D-glucopyranosyl]-α-L-rhamnopyranoside 3″-(1,2-di-O-benzyl-*sn*-glycer-3-yl phosphonate)* (**25**). — Pyridine (2 × 5 mL) was evaporated from a mixture of **22** (31 mg, 29 μmol) and **24** (44 mg, 0.10 mmol), and the residue was dissolved in pyridine (2 mL). Pivaloyl chloride (18 μL, 0.14 mmol) was added, and the mixture was stirred for 2 h, when t.l.c. (9:1 CH_2Cl_2–acetone) revealed the formation of **25** (R_F 0.63). The mixture was diluted with CH_2Cl_2 (50 mL), washed with M triethylammonium hydrogencarbonate (2 × 10 mL), dried (Na_2SO_4), filtered, and concentrated. Column chromatography of the residue afforded **25**, isolated as a syrup (30 mg, 74%). ^{1}H-N.m.r. data ($CDCl_3$): δ 6.853 (d, 0.5 H, $J_{H,P}$ 715 Hz, PH) and 6.701 (d, 0.5 H, $J_{H,P}$ 726 Hz, PH) of two enantiomers.

*Methyl 2,4-di-O-benzyl-3-O-[2,3,6-tri-O-benzyl-4-O-(2,4,6-tri-O-acetyl-β-D-galactopyranosyl)-α-D-glucopyranosyl]-α-L-rhamnopyranoside 3″-(1,2-di-O-benzyl-*sn*-glycer-3-yl triethylammonium phosphate)* (**26**). — To compound **25** (30 mg, 21 μmol) was added a 0.2M solution of iodine in 9:1:1 tetrahydrofuran–pyridine–water (1.5 mL). The mixture was stirred for 3 h, when t.l.c. (9:1 CH_2Cl_2–acetone) indicated the absence of **25** and the formation of **26** (R_F 0). The excess of iodine was destroyed with aq. 5% sodium hydrogensulfite, and the mixture was washed with M triethylammonium hydrogencarbonate (2 × 10 mL), dried (Na_2SO_4), filtered, and concentrated. Column chromatography (9:1 CH_2Cl_2–acetone followed by 9:1 CH_2Cl_2–MeOH) of the residue gave **26**, isolated as a syrup (30 mg, 92%). N.m.r. data ($CDCl_3$): ^{1}H, δ 7.357–7.201 (m, 35 H, 7 Ph), 5.469 (d, 1 H, H-4″), 5.152 (d, 1 H, H-1′), 3.256 (OMe), 2.906 [q, 6 H, N(CH_2CH_3)$_3$], 1.988, 1.925, and 1.897 (3 s, each 3 H, 3 Ac), 1.184 [t, 9 H, N(CH_2CH_3)$_3$]; $J_{1',2'}$ 3.5, $J_{3'',4''}$ 3.1, $J_{4'',5''}$ < 1 Hz; ^{31}P, δ −0.28.

Methyl 3-O-(4-O-β-D-galactopyranosyl-α-D-glucopyranosyl)-α-L-rhamnopyranoside 3''-(sn-glycer-3-yl sodium phosphate) (**2**). — To a solution of **26** (30 mg, 20 μmol) in CH_2Cl_2 (1 mL) was added methanolic 7M ammonia (4 mL). After 3 days, t.l.c. (9:1 CH_2Cl_2–MeOH) showed the deacetylation to be complete, and the mixture was concentrated. Column chromatography of the residue afforded deacetylated **26**, isolated as a syrup, R_F 0.57. A solution of the residue in 2-propanol (3 mL) and methanol (2 mL), containing 10% Pd/C (15 mg), was hydrogenolysed for 65 h at 4 kg/cm^2, filtered, and concentrated. Column chromatography (2:1:1 1-butanol–EtOH–water) of 50% of the residue afforded **2**, isolated as a white powder (2.1 mg, 3 μmol). ^{13}C-N.m.r. data (D_2O): δ 103.9 and 101.8 (C-1′,1″), 96.8 (C-1), 67.8 (d, C-3‴, $^2J_{C,P}$ 6.1 Hz), 63.4 (C-1‴), 62.3 and 60.8 (C-6′,6″), 56.1 (OCH_3), 18.0 (C-6). For the ^{1}H-n.m.r. data, see Table I.

Methyl 3-O-allyl-4,6-O-benzylidene-β-D-galactopyranoside (**28**). — To a solution of methyl 3-*O*-allyl-β-D-galactopyranoside[20] (7.60 g, 32.49 mmol) in *N,N*-dimethylformamide (10 mL) were added α,α-dimethoxytoluene (25 mL) and *p*-toluenesulfonic acid (100 mg). After 30 min, when t.l.c. (9:1 CH_2Cl_2–EtOAc) showed the formation of **28** (R_F 0.13) to be complete, solid sodium hydrogencarbonate was added, and the mixture was diluted with CH_2Cl_2, washed with water, dried (Na_2SO_4), filtered, and concentrated. Crystallisation from EtOH gave **28** (7.32 g, 70%), m.p. 181°, $[\alpha]_D$ +54° (*c* 1, $CHCl_3$). N.m.r. data ($CDCl_3$): ^{13}C, δ 137.6 and 128.7–126.2 (C_6H_5CH), 134.6 ($H_2C=CHCH_2O$), 117.5 ($H_2C=CHCH_2O$), 103.7 (C-1), 100.8 (PhCH), 78.8, 72.8, 69.7, and 66.4 (C-2,3,4,5), 70.4 ($H_2C=CHCH_2O$), 69.1 (C-6), 56.7 (OCH_3); ^{1}H, δ 7.531–7.325 (m, 5 H, Ph), 5.974 (m, 1 H, $H_2C=CHCH_2O$), 5.545 (s, 1 H, PhCH), 5.330 and 5.219 (2 m, each 1 H, $H_2C=CHCH_2O$), 4.357 (dd, 1 H, H-6a), 4.267 (d, 1 H, H-1), 4.090 (dd, 1 H, H-6b), 3.953 (dd, 1 H, H-2), 3.587 (s, 3 H, OMe), 3.475 (dd, 1 H, H-3), 3.431 (m, 1 H, H-5); $J_{1,2}$ 7.8, $J_{2,3}$ 9.7, $J_{3,4}$ 3.5, $J_{4,5}$ < 1, $J_{5,6a}$ 1.6, $J_{5,6b}$ 1.9, $J_{6a,6b}$ −12.4 Hz.

Anal. Calc. for $C_{17}H_{22}O$: C, 63.34; H, 6.88. Found: C, 63.15; H, 7.15.

Methyl 3-O-allyl-4,6-O-benzylidene-2-O-(2,3,4,6-tetra-O-benzyl-α,β-D-glucopyranosyl)-β-D-galactopyranoside (**29αβ**). — To a stirred solution of ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-glucopyranoside[19] (**27**; 1.54 g, 4.80 mmol), **28** (2.50 g, 4.24 mmol), and powdered molecular sieves (4 Å, 10 g) in dry ether (100 mL) was added methyl triflate (2.3 mL, 21.2 mmol). After 18 h, t.l.c. (25:2 toluene–acetone) indicated the absence of **28** (R_F 0.03) and the presence of **29α** (R_F 0.23) and **29β** (R_F 0.15). Triethylamine (9 mL) was added, stirring was continued for 10 min, and the mixture was filtered through Celite and concentrated. Column chromatography (97:3 CH_2Cl_2–EtOAc) of the residue yielded **29α** (2.02 g, 56%), m.p. 127° (from EtOH), $[\alpha]_D$ +97° (*c* 1, $CHCl_3$), followed by **29β** (1.20 g, 33%), m.p. 162° (from EtOH), $[\alpha]_D$ +42° (*c* 1, $CHCl_3$). N.m.r. data ($CDCl_3$): **29α** ^{13}C, δ 138.9–135.5 and 128.7–126.4 ($C_6H_5CH_2O$ and C_6H_5CH), 134.7 ($H_2C=CHCH_2O$), 117.5 ($H_2C=CHCH_2O$), 104.5 (C-1), 101.1 (PhCH), 95.7 (C-1′), 81.9, 79.5, 78.2, 77.7, 73.1, 72.3, 69.8, and 66.3 (C-2,3,4,5,2′,3′,4′,5′), 75.4, 74.4, 69.7, 72.2, 70.8, 69.1, and 68.4 (4 $PhCH_2O$, $H_2C=CHCH_2O$, and C-6,6′), 56.4 (OCH_3); ^{1}H, δ 7.534–7.118 (m, 25 H, 5 Ph), 5.914 (m, 1 H, $H_2C=CHCH_2O$), 5.579 (d, 1 H, H-1′), 5.534 (s, 1 H, PhCH), 5.247 and 5.084 (2 m, each 1 H, $H_2C=CHCH_2O$), 4.967, 4.832, 4.800, 4.787, 4.703, 4.619, 4.498, and 4.932 (8 d, each 1 H, 4 $PhCH_2O$), 4.483 (d, 1 H, H-1),

4.240 (d, 1 H, H-4), 3.532 (s, 3 H, OMe), 3.386 (bs, 1 H, H-5); $J_{1,2}$ 7.8, $J_{3,4}$ 3.6, $J_{4,5} < 1$, $J_{1',2'}$ 3.7 Hz; **29***β* ^{13}C, *δ* 138.7–136.0 and 128.8–127.3 ($C_6H_5CH_2O$ and C_6H_5CH), 134.9 ($H_2C=CHCH_2O$), 117.2 ($H_2C=CHCH_2O$), 102.5 (2 C) and 101.3 (C-1,1′ and PhCH), 55.5 (OCH_3); ^{1}H, *δ* 7.161–7.533 (m, 25 H, 5 Ph), 5.854 (m, 1 H, $H_2C=CHCH_2O$), 5.515 (s, 1 H, PhCH), 5.174 and 5.046 (2 m, each 1 H, $H_2C=CHCH_2O$), 5.046, 4.913, 4.807, 4.784, 4.727, 4.644, 4.561, and 4.542 (8 d, each 1 H, 4 $PhCH_2O$), 4.917 (d, 1 H, H-1′), 4.422 (d, 1 H, H-1), 3.521 (s, 3 H, OMe), 3.378 (bs, 1 H, H-5); $J_{1,2}$ 7.7, $J_{1',2'}$ 8.0 Hz.

Anal. Calc. for $C_{51}H_{56}O_{11}$: C, 72.49; H, 6.68. Found **29**α: C, 72.57; H, 6.65. Found **29***β*: C, 72.45; H, 6.76.

*Methyl 3-*O*-allyl-6-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-*α*-*D*-glucopyranosyl)-*β*-*D*-galactopyranoside* (**30**). — A solution of **29**α (2.02 g, 2.39 mmol), borane–trimethylamine complex (1.05 g, 14.39 mmol), and powdered molecular sieves (4 Å, 5.0 g) in tetrahydrofuran[7] (50 mL) was stirred for 1 h. Aluminium(III) chloride (1.89 g, 14.17 mmol) was added at 0° and the mixture was stirred for 16 h at room temperature. T.l.c. (95:5 CH_2Cl_2–EtOAc) then showed the conversion of **29**α (R_F 0.62) into **30** (R_F 0.47). The mixture was diluted with CH_2Cl_2 (400 mL), filtered through Celite, washed with M H_2SO_4 (3 × 50 mL), water, aq. 5% sodium hydrogencarbonate, and water, dried (Na_2SO_4), filtered, and concentrated. Column chromatography of the residue yielded **30**, isolated as a syrup (1.54 g, 76%), $[\alpha]_D$ + 51° (*c* 1, $CHCl_3$). N.m.r. data ($CDCl_3$): ^{13}C, *δ* 138.8–137.3 and 128.2–127.3 ($C_6H_5CH_2O$), 133.9 ($H_2C=CHCH_2O$), 118.3 ($H_2C=CHCH_2O$), 104.4 (C-1), 95.7 (C-1′), 75.5, 74.5, 73.7, 73.3, 72.2, 71.0, 69.0, and 68.4 (5 $PhCH_2O$, $H_2C=CHCH_2O$, and C-6,6′), 56.4 (OCH_3); ^{1}H, *δ* 7.358–7.136 (m, 25 H, 5 Ph), 5.889 (m, 1 H, $H_2C=CHCH_2O$), 5.542 (d, 1 H, H-1′), 5.220 and 5.094 (2 m, each 1 H, $H_2C=CHCH_2O$), 4.411 (d, 1 H, H-1), 3.505 (s, 3 H, OMe), 3.478 (dd, 1 H, H-3); $J_{1,2}$ 7.9, $J_{2,3}$ 9.6, $J_{3,4}$ 3.4, $J_{1',2'}$ 3.7 Hz.

Anal. Calc. for $C_{51}H_{58}O_{11}$: C, 72.32; H, 6.90. Found: C, 72.24; H, 7.07.

*Methyl 3-*O*-allyl-6-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-2-*O*-(2,3,4,6-tetra-*O*-benzyl-α-*D*-glucopyranosyl)-β-*D*-galactopyranoside* (**32**). — To a stirred mixture of **30** (1.54 g, 1.81 mmol), 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl trichloroacetimidate (**31**; 1.49 g, 3.02 mmol), and powdered molecular sieves (4 Å, 1.0 g) in dry CH_2Cl_2 (40 mL) was added trimethylsilyl triflate (250 μL, 1.38 mmol) at − 30°. The temperature was gradually raised to − 10° and, when t.l.c. [7:3 light petroleum (b.p. 40–60°)–EtOAc] showed the absence of **30** (R_F 0.31) and a new u.v.-positive product (**32**, R_F 0.18), pyridine (2 mL) was added, and the mixture was filtered through Celite and concentrated. Column chromatography [6:4 light petroleum (b.p. 40–60°)–EtOAc] of the residue afforded **32**, isolated as a syrup (1.92 g, 90%), $[\alpha]_D$ + 34° (*c* 1, $CHCl_3$). N.m.r. data ($CDCl_3$): ^{13}C, *δ* 170.4–169.3 ($COCH_3$), 138.8–138.0 and 128.3–127.3 ($C_6H_5CH_2O$), 133.9 ($H_2C=CHCH_2O$), 117.6 ($H_2C=CHCH_2O$), 104.4 (C-1), 99.3 (C-1″), 96.0 (C-1′), 56.3 (OCH_3), 20.6 ($COCH_3$); ^{1}H, *δ* 7.365–7.126 (m, 25 H, 5 Ph), 5.879 (m, 1 H, $H_2C=CHCH_2O$), 5.501 (d, 1 H, H-1′), 3.459 (OMe), 2.037, 2.030, 2.022, and 2.008 (4 s, each 3 H, 4 Ac); $J_{1',2'}$ 3.7 Hz.

Anal. Calc. for $C_{65}H_{76}O_{20}$: C, 66.31; H, 6.51. Found: C, 65.85; H, 6.51.

*Methyl 6-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-2-*O*-(2,3,4,*

6-tetra-O-benzyl-α-D-glucopyranosyl)-β-D-galactopyranoside (**33**). — To a solution of **32** (0.75 g, 0.49 mmol) in 7:3:1 EtOH–toluene–water (10 mL) was added tris(triphenylphosphine)rhodium(I) chloride[21] (95 mg, 0.1 mmol). The mixture was boiled under reflux for 30 h (t.l.c., 9:1 CH_2Cl_2–EtOAc, **33** R_F 0.26), then concentrated. Column chromatography (85:15 CH_2Cl_2–EtOAc) of the residue yielded **33**, isolated as a glass (0.27 g, 49%), $[\alpha]_D$ +28° (*c* 0.9, $CHCl_3$). N.m.r. data ($CDCl_3$): ^{13}C, δ 170.3–169.2 ($COCH_3$), 138.5–137.5 and 128.2–127.3 ($C_6H_5CH_2O$), 103.1 (C-1), 100.7 (C-1″), 97.5 (C-1′), 56.6 (OCH_3), 20.4 ($COCH_3$); ^1H, δ 7.385–7.092 (m, 25 H, 5 Ph), 5.198 (d, 1 H, H-1′), 4.331 (d, 1 H, H-1), 3.422 (s, 3 H, OMe), 2.043, 2.018, and 2.001 (3 s, 3, 6, 3 H, 4 Ac); $J_{1,2}$ 7.6, $J_{1',2'}$ 3.9 Hz.

Anal. Calc. for $C_{62}H_{70}O_{20}$: C, 65.60; H, 6.21. Found: C, 65.39; H, 6.47.

Methyl 2-O-α-D-glucopyranosyl-4-O-β-D-glucopyranosyl-β-D-galactopyranoside (**3**). — To a solution of **33** (58.4 mg, 51.4 μmol) in MeOH (4 mL) was added sodium methoxide to pH 10. The mixture was stirred for 16 h, neutralised with Dowex-50 (H^+) resin, filtered, and concentrated. The residue was taken up in EtOH (9 mL) and EtOAc (1 mL), and 10% Pd/C (25 mg) was added. Hydrogenolysis was performed for 16 h at 4 kg/cm^2, and the solution was filtered, concentrated, and lyophilised to afford **3**, isolated as a white powder (25 mg, 95%), $[\alpha]_D$ +65° (*c* 1, H_2O). N.m.r. data (D_2O): ^{13}C, δ 105.5 and 105.2 (C-1,1″), 99.7 (C-1′), 79.7, 77.9, 77.2, 77.1, 75.4, 75.0, 74.1, 73.2, 72.9, 72.7, 70.9, and 70.6 (C-2,3,4,5,2′,3′,4′,5′,2″,3″,4″,5″), 62.0 (2 C), 61.5 (C-6,6′,6″), 58.6 (OCH_3). For the ^1H-n.m.r. data, see Table I.

Methyl 6-O-benzyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-β-D-galactopyranoside 3-(1,2-di-O-benzyl-sn-glycer-3-yl phosphonate) (**34**). — Pyridine (2 × 5 mL) was evaporated from a mixture of **33** (112 mg, 99 μmol) and **24** (66 mg, 150 μmol), and the residue was dissolved in dry pyridine (2 mL). Pivaloyl chloride (46 μL, 375 μmol) was added and the mixture was stirred for 2 h, when t.l.c. (8:2 CH_2Cl_2–EtOAc) showed that **33** (R_F 0.51) had been converted almost completely into **34** (R_F 0.41). Water was added, and the solution was concentrated, diluted with CH_2Cl_2 (100 mL), washed with M triethylammonium hydrogencarbonate (2 × 25 mL), dried (Na_2SO_4), filtered, and concentrated. Column chromatography of the residue yielded the two enantiomers of **34**, isolated as a syrup (100 mg, 70%). N.m.r. data ($CDCl_3$): ^1H, δ 6.959 (d, 0.5 H, $J_{H,P}$ 707 Hz, PH), 6.901 (d, 0.5 H, $J_{H,P}$ 726 Hz, PH); ^{31}P, δ 11.10 (dq, $^1J_{P,H}$ 707, $^3J_{P,H}$ 10 Hz) and 8.87 (dq, $^1J_{P,H}$ 726, $^3J_{P,H}$ 10 Hz).

Methyl 6-O-benzyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-2-O-(2,3,4,6-tetra-O-benzyl-α-D-glucopyranosyl)-β-D-galactopyranoside 3-(1,2-di-O-benzyl-sn-glycer-3-yl triethylammonium phosphate) (**35**). — To a solution of **34** (80 mg, 55 μmol) in tetrahydrofuran (2 mL) was added 0.35M iodine in 1:1 pyridine–water (700 μL). After 1 h, t.l.c. (8:2 CH_2Cl_2–EtOAc) indicated complete formation of **35** (R_F 0), and aq. 10% sodium hydrogensulfite was added to destroy the excess of iodine. The mixture was diluted with CH_2Cl_2 (100 mL), washed with M triethylammonium hydrogencarbonate (2 × 20 mL), dried (Na_2SO_4), filtered, and concentrated. Column chromatography (2:1 CH_2Cl_2–MeOH) of the residue on LH-20 gave **35**, isolated as a syrup (86 mg, 99%), $[\alpha]_D$ +36° (*c* 1, $CHCl_3$). N.m.r. data ($CDCl_3$): ^{13}C, δ 170.5–169.3 (4 $COCH_3$), 138.8–138.2

and 128.1–127.3 ($C_6H_5CH_2O$), 103.8 (C-1), 100.0 (C-1″), 96.9 (C-1′), 65.3 (d, C-3 glycerol, $^2J_{C,P}$ 6.3 Hz), 56.1 (OCH_3), 44.9 [$N(CH_2CH_3)_3$], 20.8–20.4 ($COCH_3$), 8.2 [$N(CH_2CH_3)_3$]; ^1H, δ 7.348–7.114 (m, 35 H, 7 Ph), 5.437 (d, 1 H, H-1′), 5.379 (d, 1 H, H-1″), 4.271 (d, 1 H, H-1), 3.379 (s, 3 H, OMe), 2.649 [q, 6 H, $N(CH_2CH_3)_3$], 2.124, 2.005, 1.996, and 1.954 (4 s, each 3 H, 4 Ac), 1.008 [t, 9 H, $N(CH_2CH_3)_3$]; $J_{1,2}$ 7.7, $J_{1',2'}$ 3.8, $J_{1'',2''}$ 8.1 Hz; ^{31}P, δ −0.51.

*Methyl 2-O-α-D-glucopyranosyl-4-O-β-D-glucopyranosyl-β-D-galactopyranoside 3-(*sn*-glycer-3-yl sodium phosphate)* (**4**). — To a solution of **35** (59 mg, 38 μmol) in 1:1 CH_2Cl_2–MeOH (2 mL) was added methanolic 7M ammonia (3 mL). After 48 h, the solvent was evaporated, and the residue was purified by column chromatography (2:1 CH_2Cl_2–MeOH) on Sephadex LH-20 to yield deacetylated **35**, isolated as a syrup (40 mg, 80%). An aliquot (33 mg, 25 μmol) of this product was dissolved in 2-propanol (3 mL), and MeOH (2 mL) and 10% Pd/C (25 mg) were added. Hydrogenolysis was performed for 16 h at 4 kg/cm^2, the mixture was filtered through Celite and concentrated, and a solution of the residue in water was treated with Dowex-50 (Na^+) resin. Lyophilisation of the filtrate afforded **4**, isolated as a white powder (17.7 mg, 98%), $[\alpha]_D$ +40° (*c* 1, H_2O). N.m.r data (D_2O): ^{13}C, δ 105.7 and 104.0 (C-1,1″), 99.1 (C-1′), 67.7 (d, C-3‴, $^2J_{C,P}$ 5.2 Hz), 63.5 (C-1‴), 72.1 (d, C-2‴, $^3J_{C,P}$ 7.7 Hz), 62.1, 61.8, and 61.7 (C-6,6′,6″), 58.6 (OCH_3); ^{31}P, δ 3.10. For the ^1H-n.m.r. data, see Table I.

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