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Synthesis of structural elements of the capsular polysaccharides of *Streptococcus pneumoniae* types 6A and 6B

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ABSTRACT

O-α-D-Glucopyranosyl-(1→3)-α,β-L-rhamnopyranose (**15**), *O*-α-D-galactopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→3)-α,β-L-rhamnopyranose (**17**), *O*-α-D-galactopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→3)-D-ribitol (**23**), and *O*-α-D-galactopyranosyl-(1→3)-*O*-α-D-glucopyranosyl-(1→3)-*O*-α-L-rhamnopyranosyl-(1→4)-D-ribitol (**27**), which are structural elements of the capsular polysaccharides of *Streptococcus pneumoniae* types 6A and 6B {[→2)-α-D-Gal*p*-(1→3)-α-D-Glc*p*-(1→3)-α-L-Rha*p*-(1→X)-D-Rib-ol-(5-P→]$_n$; 6A X = 3, 6B X = 4}, have been synthesised. Ethyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside (**3**) was coupled with benzyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside (**4**), and subsequent deallylation (→**14**) and debenzylation gave **15**. Condensation of **14** with ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (**2**) followed by debenzylation gave **17**. Acetylation of **17** followed by removal of AcO-1, conversion into the imidate, coupling with 1,2,4,5-tetra-*O*-benzyl-D-ribitol (**11**), deacetylation, and debenzylation gave **23**. Coupling of the imidate with 1-*O*-allyloxycarbonyl-2,3,5-tri-*O*-benzyl-D-ribitol (**12**) followed by deallyloxycarbonylation, deacetylation, and debenzylation yielded **27**.

INTRODUCTION

As part of our studies on the development of synthetic vaccines, based on oligosaccharide conjugates, against infections by *Streptococcus pneumoniae* serotypes, we have described the synthesis of an essential building block for the preparation of higher oligomers corresponding with fragments of the capsular polysaccharide of types 6A and 6B, namely, 4-methoxybenzyl 2,4-di-*O*-benzyl-3-*O*-[2,4,6-tri-*O*-benzyl-3-*O*-(3,4,6-tri-*O*-benzyl-α-D-galactopyranosyl)-α-D-glucopyranosyl]-α-L-rhamnopyranoside[1].

We now report the synthesis of the repeating units of the capsular polysaccharides of the serotypes 6A and 6B, namely, α-D-Gal*p*-(1→3)-α-D-Glc*p*-(1→3)-α-L-Rha*p*-(1→3)-D-Rib-ol (**23**) and α-D-Gal*p*-(1→3)-α-D-Glc*p*-(1→3)-α-L-Rha*p*-(1→4)-D-Rib-ol (**27**), respectively, together with the structural elements α-D-Glc*p*-(1→3)-α,β-L-Rha*p* (**15**) and α-D-Gal*p*-(1→3)-α-D-Glc*p*-(1→3)-α,β-L-Rha*p* (**17**).

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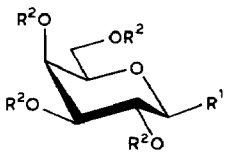
RESULTS AND DISCUSSION

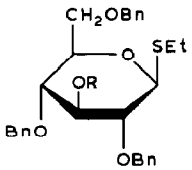
For the synthesis of **23** and **27**, the three monosaccharide synthons ethyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside[1] (**3**), benzyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside[2] (**4**), and 1-*O*-allyloxycarbonyl-2,3,5-tri-*O*-benzyl-D-ribitol[3] (**12**) were synthesised as described earlier, and the two monosaccharide synthons **2** for D-Gal and **11** for D-Rib-ol were prepared as follows.

Ethyl 1-thio-β-D-galactopyranoside[4-6] (**1**) was benzylated to yield ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-D-galactopyranoside (**2**, 81%).

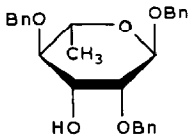
Methyl 5-*O*-benzyl-α,β-D-ribofuranoside[7] (**5**) was selectively benzylated at C-2, using a phase-transfer catalyst[1,2,8] (→**6**, 44%). Subsequent allylation (→**7**, 93%), demethylation with 1.2M hydrochloric acid in 1,4-dioxane (→**8**, 79%), reduction with sodium borohydride in ethanol (→**9**, 85%), benzylation (→**10**, 85%), deallylation with KO^{t}Bu in *N,N*-dimethylformamide, and acid hydrolysis gave 1,2,4,5-tetra-*O*-benzyl-D-ribitol (**11**, 71%).



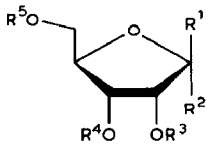
1 R^1 = SEt, R^2 = H
2 R^1 = SEt, R^2 = Bn



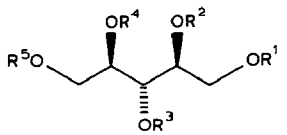
3 R = allyl



4



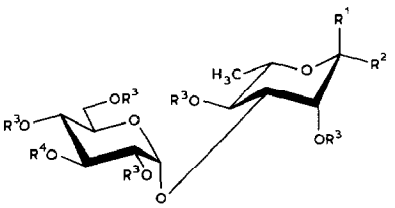
5 R^1, R^2 = H,OMe, R^3 = R^4 = H, R^5 = Bn
6 R^1 = OMe, R^2 = R^4 = H, R^3 = R^5 = Bn
7 R^1 = OMe, R^2 = H, R^3 = R^5 = Bn, R^4 = allyl
8 R^1, R^2 = H,OH, R^3 = R^5 = Bn, R^4 = allyl



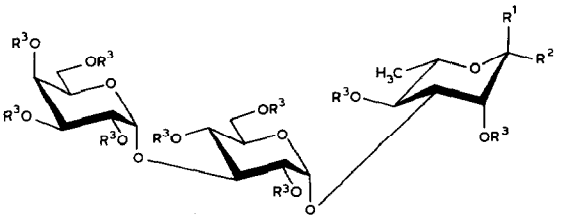
9 R^1 = R^4 = H, R^2 = R^5 = Bn, R^3 = allyl
10 R^1 = R^2 = R^4 = R^5 = Bn, R^3 = allyl
11 R^1 = R^2 = R^4 = R^5 = Bn, R^3 = H
12 R^1 = AOC, R^2 = R^3 = R^5 = Bn, R^4 = H
(AOC = allyloxycarbonyl)

Coupling of ethyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside[1] (**3**) and benzyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside[2] (**4**) in ether, using methyl triflate[9] as the promoter, gave **13** (61%). The allyl group of **13** was removed using KO^{t}Bu in *N,N*-dimethylformamide followed by acid hydrolysis to yield **14** (93%). Catalytic hydrogenolysis of **14** over Pd–C removed the benzyl groups and gave disaccharide **15** (80%). Condensation of **14** with the Gal synthon **2** in ether, using methyl triflate[9] as the promoter, afforded **16** (57%). After catalytic hydrogenolysis of **16** (→**17**, 89%) and acetylation in pyridine/acetic anhydride in the presence of a trace of dimethylaminopyridine at 50° (→**18**), AcO-1 was removed with hydrazine acetate in *N,N*-dimethylforma-

mide[10] (→**19**, 88%). Subsequent imidation using trichloroacetonitrile and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base[11] afforded 2,4-di-*O*-acetyl-3-*O*-[2,4,6-tri-*O*-acetyl-3-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl)-α-D-glucopyranosyl]-α-L-rhamnopyranosyl trichloroacetimidate (**20**, 81%).



13 R^1 = OBn, R^2 = H, R^3 = Bn, R^4 = allyl
14 R^1 = OBn, R^2 = R^4 = H, R^3 = Bn
15 R^1, R^2 = H,OH, R^3 = R^4 = H



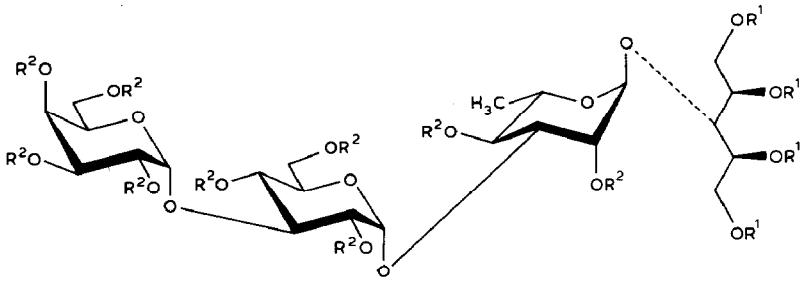
16 R^1 = OBn, R^2 = H, R^3 = Bn
17 R^1, R^2 = H,OH, R^3 = H
18 R^1, R^2 = H,OAc, R^3 = Ac
19 R^1 = OH, R^2 = H, R^3 = Ac
20 R^1 = OC=NH, R^2 = H, R^3 = Ac
CCl_3

Coupling of **20** with the Rib-ol synthon **11** in dichloromethane, using trimethylsilyl triflate as the promoter, gave **21** (90%), which was saponified (→**22**) and debenzylated to afford **23** (93%). In a similar way, **20** was condensed with the Rib-ol synthon **12** (ref. 3) to yield **24** (91%). Subsequent removal of the allyloxycarbonyl group with palladium tetrakis[triphenylphosphine][3] (→**25**, 82%), deacetylation (→**26**), and catalytic hydrogenolysis gave **27** (90%). The ^{1}H- and ^{13}C-n.m.r. data of the tetrasaccharide-alditol **27** were identical to those of the tetrasaccharide-alditol isolated[12] from the capsular polysaccharide 6B by hydrolysis with HF.

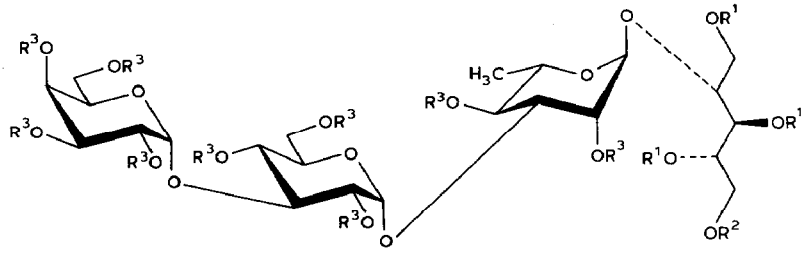
The di- and tri-saccharides **15**, **17**, **23**, and **27** are being tested in immunological inhibition experiments in order to evaluate the precise antigenic determinant of 6A and 6B.

EXPERIMENTAL

General methods. — ^{1}H-N.m.r. spectra (60, 360, and 500 MHz) were recorded at 25° with a Varian 360, Bruker HX 360, or Bruker AM 500 spectrometer. The ^{13}C-n.m.r. spectra (50 MHz) were recorded at 25° with a Bruker WP-200 spectrometer. Chemical shifts (δ) are given in p.p.m. relative to internal Me_4Si ($CDCl_3$) or internal sodium 4,4-dimethyl-4-silapentane-1-sulfonate (D_2O; indirectly to internal acetone, δ 2.225) for ^{1}H, and to internal Me_4Si ($CDCl_3$; indirectly to $CDCl_3$, δ 76.9) and external Me_4Si (D_2O; indirectly to internal acetone, δ 31.55) for ^{13}C data.



21 R^1 = Bn, R^2 = Ac
22 R^1 = Bn, R^2 = H
23 R^1 = R^2 = H



24 R^1 = Bn, R^2 = AOC, R^3 = Ac
25 R^1 = Bn, R^2 = H, R^3 = Ac
26 R^1 = Bn, R^2 = R^3 = H
27 R^1 = R^2 = R^3 = H

(AOC = allyloxycarbonyl)

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 sulfuric acid after examination under u.v. light. Optical rotations were measured at 20° with a Perkin–Elmer 241 polarimeter, using a 10-cm microcell. Evaporations were conducted *in vacuo* at 40° (bath). All solvents were distilled from appropriate drying agents.

*Ethyl 2,3,4,6-tetra-*O*-benzyl-1-thio-β-*D*-galactopyranoside* (**2**). — To a suspension of sodium hydride (6 g, 8 equiv.) in *N,N*-dimethylformamide (50 mL) was added dropwise at 0° a solution of ethyl 1-thio-β-D-galactopyranoside[6] (**1**; 3.84 g, 17.1 mmol) and benzyl bromide (12.2 mL) in *N,N*-dimethylformamide (50 mL). The mixture was stirred for 2 h at room temperature [R_F 0.80, 9:1 light petroleum (b.p. 40–60°)–ethyl acetate], the excess of sodium hydride was destroyed with methanol, the mixture was poured onto crushed ice and extracted with ether (3 × 50 mL), and the combined extracts were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography [9:1 light petroleum (b.p. 40–60°)–ethyl acetate] to yield **2**, isolated as a syrup (8.10 g, 81%), $[\alpha]_D$ −4° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ

1.290 (t, 3 H, J_{CH_3,CH_2} 7.5 Hz, SCH_2CH_3), 2.729 (m, 2 H, SCH_2CH_3), 3.821 (t, 1 H, $J_{1,2} = J_{2,3}$ = 9.6 Hz, H-2), 3.951 (bd, 1 H, $J_{3,4}$ 2.8 Hz, H-4), 4.428 (d, 1 H, H-1), 4.399 (d), 4.475 (d), 4.609 (d), 4.723 (s), 4.788 (d), 4.875 (d), and 4.946 (d) (8 H, 4 $PhCH_2O$), 7.250–7.396 (m, 20 H, 4 Ph); ^{13}C, δ 14.9 (SCH_2CH_3), 24.6 (SCH_2CH_3), 68.6, 72.5, 73.4, 74.2, and 75.6 (C-6 and 4 $C_6H_5CH_2$), 73.5, 77.0, 78.3, 83.9, and 85.1 (C-1,2,3,4,5), 127.3–128.2 and 137.1–138.1 ($C_6H_5CH_2$).

Anal. Calc. for $C_{36}H_{40}O_5S$: C, 73.93; H, 6.91. Found: C, 73.80; H, 6.85.

*Methyl 2,5-di-*O*-benzyl-β-*D*-ribofuranoside* (**6**). — To a solution of methyl 5-*O*-benzyl-α,β-D-ribofuranoside[7] (**5**; 1.25 g, 4.92 mmol) in dichloromethane (49.3 mL) were added tetrabutylammonium bromide (396 mg), benzyl bromide (6.45 mL), and aqueous 10% sodium hydroxide (4.93 mL). After stirring overnight, the mixture (R_F 0.36, 5:1 toluene–ethyl acetate) was washed with water (30 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (5:1 toluene–ethyl acetate) to yield **6**, isolated as a syrup (750 mg, 44%), $[\alpha]_D$ +4° (*c* 1, dichloromethane). N.m.r. data ($CDCl_3$): ^1H, δ 3.331 (s, 3 H, OMe), 3.554 (dd, 1 H, $J_{5a,5b}$ 10.4 Hz, H-5b), 3.657 (dd, 1 H, H-5a), 3.859 (dd, 1 H, $J_{2,3}$ 5.0, $J_{1,2}$ 1.2 Hz, H-2), 4.097 (m, 1 H, $J_{4,5a}$ 3.7, $J_{4,5b}$ 6.2 Hz, H-4), 4.161 (m, 1 H, H-3), 4.596 (s), 4.622 (d), and 4.733 (d) (4 H, 2 $PhCH_2O$), 4.905 (d, 1 H, H-1), 7.265–7.368 (m, 10 H, 2 Ph); ^{13}C, δ 54.5 (OMe), 71.2 (C-3), 71.1, 72.1, and 72.7 (2 $C_6H_5CH_2$ and C-5), 81.4 and 82.5 (C-2,4), 105.3 (C-1), 127.0–128.0, 136.8, and 137.8 ($C_6H_5CH_2$).

Anal. Calc. for $C_{20}H_{24}O_5$: C, 69.74; H, 7.04. Found: C, 69.66; H, 7.24.

*Methyl 3-*O*-allyl-2,5-di-*O*-benzyl-β-*D*-ribofuranoside* (**7**). — A solution of **6** (780 mg, 2.27 mmol) and allyl bromide (0.3 mL, 1.5 equiv.) in *N,N*-dimethylformamide (5 mL) was added dropwise to a suspension of sodium hydride (110 mg, 2 equiv.) in *N,N*-dimethylformamide (5 mL) at 0°. The mixture was stirred for 2 h at room temperature (R_F 0.16, 95:5 toluene–acetone), the excess of sodium hydride was destroyed with methanol, the mixture was poured onto crushed ice and extracted with ether (3 × 20 mL), and the combined extracts were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (95:5 toluene–acetone) to yield **7**, isolated as a syrup (814 mg, 93%), $[\alpha]_D$ +25° (*c* 1, dichloromethane). N.m.r. data ($CDCl_3$): ^1H, δ 3.316 (s, 3 H, OMe), 3.547 (dd, 1 H, $J_{4,5b}$ 5.8, $J_{5a,5b}$ 10.6 Hz, H-5b), 3.646 (dd, 1 H, $J_{4,5a}$ 3.7 Hz, H-5a), 3.853 (dd, 1 H, $J_{2,3}$ 4.6, $J_{1,2}$ 0.8 Hz, H-2), 3.904–4.026 (m, 3 H, $OCH_2CH=CH_2$ and H-3), 4.230 (m, 1 H, H-4), 4.561, 4.605, 4.642, and 4.688 (4 d, 4 H, 2 $PhCH_2O$), 4.905 (bs, 1 H, H-1), 5.143 and 5.223 (2 m, 2 H, $OCH_2CH=CH_2$), 5.860 (m, 1 H, $OCH_2CH=CH_2$), 7.213–7.376 (m, 10 H, 2 Ph); ^{13}C, δ 54.8 (OMe), 71.2, 71.3, 72.1, and 73.0 (2 $C_6H_5CH_2$, $OCH_2CH=CH_2$, and C-5), 78.3, 79.6, and 80.3 (C-2,3,4), 106.2 (C-1), 117.1 ($OCH_2=CH_2$), 134.3 ($OCH_2CH\,CH=CH_2$), 127.3–128.2, 137.7, and 138.2 ($C_6H_5CH_2$).

*3-*O*-Allyl-2,5-di-*O*-benzyl-α,β-*D*-ribofuranose* (**8**). — To a solution of **7** (694 mg, 1.81 mmol) in 1,4-dioxane (39 mL) was added 1.2M hydrochloric acid (9.8 mL), and the mixture was boiled under reflux until hydrolysis was complete (R_F 0.30, 95:5 dichloromethane–ethyl acetate). The mixture was neutralised with sodium hydrogencarbonate,

concentrated, diluted with dichloromethane (40 mL), washed with water (3 × 20 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (95:5 dichloromethane–ethyl acetate) to yield **8**, isolated as a syrup (530 mg, 79%; α,β-ratio 2:1), $[\alpha]_D$ +53° (*c* 1, dichloromethane). ^{13}C-N.m.r. data ($CDCl_3$): δ 96.0 (C-1α), 100.1 (C-1β), 117.1 and 117.2 ($OCH_2CH=CH_2$), 133.9 and 134.2 ($OCH_2CH=CH_2$), 127.3–128.2, 137.3, and 137.7 ($C_6H_5CH_2$).

Anal. Calc. for $C_{22}H_{26}O_5$: C, 71.32; H, 7.09. Found: C, 71.53; H, 6.85.

*3-O-Allyl-2,5-di-O-benzyl-*D*-ribitol* (**9**). — To a solution of **8** (700 mg, 1.89 mmol) in ethanol (9.4 mL) was added sodium borohydride (122 mg). After stirring overnight, the reaction was complete (R_F 0.36, 7:3 dichloromethane–ethyl acetate). The pH of the mixture was adjusted to 5 with aqueous 96% acetic acid, and the solution was concentrated, diluted with dichloromethane (30 mL), washed with M hydrochloric acid (2 × 10 mL) and water (3 × 10 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (7:3 dichloromethane–ethyl acetate) to yield **9**, isolated as a syrup (600 mg, 85%), $[\alpha]_D$ +11° (*c* 1, dichloromethane). N.m.r. data ($CDCl_3$): ^{1}H, 4.069 and 4.179 (2 m, 2 H, $OCH_2CH=CH_2$), 4.505, 4.538, 4.580, and 4.620 (4 d, 4 H, 2 $PhCH_2O$), 5.126 and 5.204 (2 m, 2 H, $OCH_2CH=CH_2$), 5.843 (m, 1 H, $OCH_2CH=CH_2$), 7.268–7.352 (m, 10 H, 2 Ph); ^{13}C, δ 60.9 (C-1), 70.5 (C-4), 71.0, 71.8, 72.7, and 73.3 (2 $C_6H_5CH_2$, $OCH_2CH=CH_2$, and C-5), 79.1 and 79.3 (C-2,3), 117.0 ($OCH_2CH=CH_2$), 134.5 ($OCH_2CH=CH_2$), 127.7–128.3, 137.8, and 137.9 ($C_6H_5CH_2$).

*3-O-Allyl-1,2,4,5-tetra-O-benzyl-*D*-ribitol* (**10**). — To a suspension of sodium hydride (100 mg, 4 equiv.) in *N,N*-dimethylformamide (5 mL) was added dropwise at 0° a solution of **9** (382 mg, 1.03 mmol) and benzyl bromide (0.4 mL, 3 equiv.) in *N,N*-dimethylformamide (5 mL). The stirring was continued for 2 h at room temperature when t.l.c. demonstrated that the reaction was complete (R_F 0.20, 98:2 dichloromethane–ethyl acetate). The excess of sodium hydride was destroyed with methanol, the mixture was poured onto crushed ice and extracted with ether (3 × 20 mL), and the combined extracts were dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (98:2 dichloromethane–ethyl acetate) to yield **10**, isolated as a syrup (488 mg, 85%). N.m.r. data ($CDCl_3$): ^{1}H, δ 4.118 (m, 2 H, $OCH_2CH=CH_2$), 4.493 (s), 4.584 (d), and 4.684 (d) (8 H, 4 $PhCH_2O$), 5.076 and 5.169 (2 m, 2 H, $OCH_2CH=CH_2$), 5.823 (m, 1 H, $OCH_2CH=CH_2$), 7.229–7.344 (m, 20 H, 4 Ph); ^{13}C, δ 70.2, 72.3, and 73.2 (4 $C_6H_5CH_2$, C-1,5), 72.2 ($OCH_2CH=CH_2$), 78.5 (C-2,4), 78.6 (C-3), 116.4 ($OCH_2CH=CH_2$), 135.0 ($OCH_2CH=CH_2$), 127.3–128.2, 138.4, and 138.7 ($C_6H_5CH_2$).

Anal. Calc. for $C_{36}H_{40}O_5$: C, 78.22; H, 7.31. Found: C, 78.12; H, 7.46.

*1,2,4,5-Tetra-O-benzyl-*D*-ribitol* (**11**). — A solution of **10** (488 mg, 0.884 mmol) in *N,N*-dimethylformamide (9.1 mL) was heated at 80°, and KO^{t}Bu (500 mg) was added. After 2.5 h, the isomerisation was complete (R_F 0.74, 40:1 toluene–acetone). The mixture was cooled, dichloromethane (40 mL) was added, and the organic phase was washed with water (3 × 20 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was dissolved in 9:1 acetone–0.1 M hydrochloric acid (36 mL) and boiled under reflux for 45 min when t.l.c. (R_F 0.37, 20:1 toluene–acetone) showed that the reaction was

complete. The mixture was neutralised with aqueous 25% ammonia, concentrated, diluted with dichloromethane (40 mL), washed with water (3 × 20 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (20:1 toluene–acetone) to yield **11**, isolated as a syrup (320 mg, 71%). ^{13}C-N.m.r. data ($CDCl_3$): δ 70.0, 71.9, and 73.3 (4 $C_6H_5CH_2$, C-1,5), 71.5 (C-3), 77.9 (C-2,4), 127.4–128.2, 138.0 and 138.2 ($C_6H_5CH_2$).

Anal. Calc. for $C_{33}H_{36}O_5$: C, 77.30; H, 7.09. Found: C, 77.11; H, 7.23.

*Benzyl 3-*O*-(3-*O*-allyl-2,4,6-tri-*O*-benzyl-α-*D*-glucopyranosyl)-2,4-di-*O*-benzyl-α-*L*-rhamnopyranoside (***13***).* — A solution of ethyl 3-*O*-allyl-2,4,6-tri-*O*-benzyl-1-thio-β-D-glucopyranoside[1] (**3**; 6.74 g, 12.63 mmol) and benzyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside[2] (**4**; 2.58 g, 5.92 mmol) in dry ether (50 mL) containing molecular sieves 4 Å (12.5 g) was stirred for 2 h in the dark. Methyl triflate (1.30 mL, 11.85 mmol) was added and the mixture was stirred overnight when t.l.c. showed that the reaction was not complete. More methyl triflate (0.62 mL, 5.93 mmol) was added and, after 4 h, t.l.c. showed the reaction to be complete [R_F 0.33, 65:35 light petroleum (b.p. 40–60°)–ether]. Triethylamine (5.20 mL) was added, the mixture was filtered through Celite and diluted with dichloromethane (75 mL), and the organic phase was washed with aqueous saturated sodium hydrogencarbonate (2 × 75 mL) and water (3 × 75 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography [65:35 light petroleum (b.p. 40–60°)–ether] to yield **13**, isolated as a syrup (3.27 g, 61%), $[\alpha]_D$ +22° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 1.337 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6,6,6), 3.411 (dd, 1 H, $J_{6a',6b'}$ 10.7, $J_{5',6a'}$ 1.9 Hz, H-6a'), 3.539 (dd, 1 H, $J_{5',6b'}$ 2.8 Hz, H-6b'), 3.584 (dd, 1 H, $J_{1',2'}$ 3.5, $J_{2',3'}$ 9.7 Hz, H-2'), 3.884 (dd, 1 H, $J_{2,3}$ 2.6 Hz, H-2), 3.990 (t, 1 H, $J_{3',4'}$ 9.7 Hz, H-3'), 4.142 (dd, 1 H, $J_{3,4}$ 9.7 Hz, H-3), 4.339 and 4.402 (2 m, 2 H, $OCH_2CH=CH_2$), 4.284, 4.394, 4.432, 4.540, 4.547, 4.556, 4.621, 4.696, 4.744, 4.811, 4.824, and 4.878 (12 d, 12 H, 6 $PhCH_2O$), 4.777 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 5.120 and 5.261 (2 m, 2 H, $OCH_2CH=CH_2$), 5.133 (d, 1 H, H-1'), 5.973 (m, 1 H, $OCH_2CH=CH_2$), 7.060–7.342 (m, 30 H, 6 Ph); ^{13}C, δ 17.9 (C-6), 68.0, 68.6, 73.1 (2 C), 73.2, 74.1, 74.8, and 75.4 (C-6', 6 $C_6H_5CH_2$, and $OCH_2CH=CH_2$), 68.3, 70.2, 75.1, 76.1, 77.7, 79.3, 80.0, and 81.8 (C-2,3,4,5,2',3',4',5'), 95.0 and 97.2 (C-1,1'), 116.3 ($OCH_2CH=CH_2$), 127.3–128.3 and 137.9–138.5 ($C_6H_5CH_2$), 135.2 ($OCH_2CH=CH_2$).

Anal. Calc. for $C_{58}H_{64}O_{11}$: C, 75.46; H, 6.90. Found: C, 75.45; H, 7.04.

*Benzyl 2,4-di-*O*-benzyl-3-*O*-(2,4,6-tri-*O*-benzyl-α-*D*-glucopyranosyl)-α-*L*-rhamnopyranoside* (**14**). — A solution of **13** (1.20 g, 1.33 mmol) in *N,N*-dimethylformamide (13 mL) was heated at 90° and KO^{t}Bu (700 mg) was added. After 45 min, the reaction was complete (R_F 0.60, 25:1 toluene–acetone). The mixture was cooled, dichloromethane (50 mL) was added, and the organic phase washed with water (13 mL), dried ($MgSO_4$), filtered, and concentrated. A solution of the residue in acetone (12 mL) and 0.1M hydrochloric acid (1.3 mL) was boiled under reflux for 45 min when t.l.c. (R_F 0.22, 25:1 toluene–acetone) showed that the reaction was complete. The mixture was neutralised with aqueous 25% ammonia, diluted with dichloromethane (25 mL), washed with water (3 × 25 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (95:5 toluene–acetone) to yield **14**, isolated as a syrup (1.07 g,

93%), $[\alpha]_D$ +30° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 1.328 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6,6,6), 3.476 (dd, 1 H, $J_{6a',6b'}$ 10.6, $J_{5',6a'}$ 2.2 Hz, H-6a'), 3.488 (dd, 1 H, $J_{1',2'}$ 3.5, $J_{2',3'}$ 9.5 Hz, H-2'), 3.555 (dd, 1 H, $J_{5',6b'}$ 3.1 Hz, H-6b'), 3.745 (m, 1 H, H-5), 3.905 (t, 1 H, $J_{2,3}$ 2.6 Hz, H-2), 4.018 (m, 1 H, H-5'), 4.156 (dd, 1 H, $J_{3,4}$ 9.0 Hz, H-3), 4.213 (t, 1 H, $J_{3',4'}$ 9.5 Hz, H-3'), 4.321, 4.423, 4.481, 4.538, 4.566, 4.581, 4.644, 4.725, 4.769, 4.791, 4.824, and 4.859 (12 d, 12 H, 6 PhCH_2O), 4.843 (bs, 1 H, H-1), 5.227 (d, 1 H, H-1'), 7.103–7.355 (m, 30 H, 6 Ph); ^{13}C, δ 17.7 (C-6), 67.9, 68.5, 72.4, 72.7, 73.0, 74.2, and 75.1 (C-6' and 6 $C_6H_5CH_2$), 68.1, 69.6, 73.6, 74.9, 75.4, 77.5, 78.8, and 79.8 (C-2,3,4,5,2',3',4',5'), 93.8 and 96.8 (C-1,1'), 127.4–128.1, and 137.5–138.4 ($C_6H_5CH_2$).

Anal. Calc. for $C_{54}H_{58}O_{10}$: C, 74.81; H, 6.74. Found: C, 74.34; H, 6.83.

O-α-D-*Glucopyranosyl-(1→3)-α,β*-L-*rhamnopyranose* (**15**). — A solution of **14** (245 mg, 0.284 mmol) in ethanol (20 mL) was hydrogenolysed in the presence of 10% Pd–C (700 mg) at 4 atm. overnight, filtered through Celite, and concentrated to yield **15**, isolated as a syrup (74 mg, 80%; α,β-ratio 2:1), $[\alpha]_D$ +38° (*c* 1, water). N.m.r. data (D_2O): ^1H, δ 1.294 and 1.311 (2 d, together 3 H, $J_{5,6}$ 6.3 Hz, H-6,6,6), 4.867 (s) and 5.154 (d, $J_{1,2}$ 2.0 Hz) (together 1 H, H-1αβ), 5.079 and 5.106 (2 d, together 1 H, $J_{1',2'}$ 3.8 Hz, H-1'); ^{13}C, δ 18.2 (C-6), 61.5 (C-6'), 94.7 and 94.9 (C-1), 96.5 and 96.8 (C-1').

Anal. Calc. for $C_{12}H_{22}O_{10}\cdot H_2O$: C, 41.85; H, 7.04. Found: C, 42.05; H, 7.08.

Benzyl 2,4-di-O-*benzyl-3*-O-*[2,4,6-tri*-O-*benzyl-3*-O-*(2,3,4,6-tetra*-O-*benzyl-α*-D-*galactopyranosyl)-α*-D-*glucopyranosyl]-α*-L-*rhamnopyranoside* (**16**). — A mixture of **14** (479 mg, 0.553 mmol), **2** (650 mg, 1.11 mmol), and molecular sieves 4 Å (3 g) in ether (15 mL) was stirred for 2 h in the dark at room temperature. Methyl triflate (120 μL, 1.11 mmol) was added, and the mixture was stirred for 2 h, when t.l.c. showed that the reaction was not complete. More methyl triflate (60 μL, 0.553 mmol) was added and, after 1 h, the reaction was complete (R_F 0.52, 95:5 toluene–acetone). Triethylamine (650 μL) was added, and the mixture was filtered through Celite, diluted with dichloromethane (25 mL), washed with aqueous saturated sodium hydrogencarbonate (2 × 25 mL) and water (3 × 25 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (98.5:1.5 toluene–acetone) to yield **16**, isolated as a syrup (440 mg, 57%), $[\alpha]_D$ +38° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 1.320 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6,6,6), 4.868 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 5.220 (d, 1 H, $J_{1',2'}$ 3.4 Hz, H-1'), 5.626 (d, 1 H, $J_{1'',2''}$ 3.4 Hz, H-1''), 7.056–7.311 (m, 50 H, 10 Ph); ^{13}C, δ 17.8 (C-6), 93.5, 96.9, and 97.4 (C-1,1',1''), 126.7–128.3 and 137.3–138.6 ($C_6H_5CH_2$).

Anal. Calc. for $C_{89}H_{92}O_{15}$: C, 76.26; H, 6.61. Found: C, 76.28; H, 6.56.

O-α-D-*Galactopyranosyl-(1→3)*-O-α-D-*glucopyranosyl-(1→3)-α,β*-L-*rhamnopyranose* (**17**). — A solution of **16** (452 mg, 0.326 mmol) in ethanol (20 mL) was hydrogenolysed in the presence of 10% Pd–C (700 mg) at 4 atm. overnight, filtered through Celite, and concentrated to yield **17**, isolated as a syrup (142 mg, 89%; α,β-ratio 7:3), $[\alpha]_D$ +1° (*c* 1, water). N.m.r. data (D_2O): ^1H, δ 1.297 and 1.313 (2 d, together 3 H, $J_{5,6}$ 6.3 Hz, H-6,6,6), 4.866 (s) and 5.154 (d, $J_{1,2}$ 1.7 Hz) (together 1 H, H-1αβ), 5.101 and 5.129 (2 d, together 1 H, $J_{1',2'}$ 3.8 Hz, H-1'), 5.396 (d, 1 H, $J_{1'',2''}$ 3.7 Hz, H-1''); ^{13}C, δ 18.3 (C-6), 61.4 and 62.2 (C-6',6''), 94.7 and 94.9 (C-1), 96.5 and 96.8 (C-1'), 100.6 (C-1'').

Anal. Calc. for $C_{18}H_{32}O_{15}\cdot 2H_2O$: C, 41.21; H, 6.93. Found: C, 41.32; H, 6.98.

2,4-Di-O-acetyl-3-O-[2,4,6-tri-O-acetyl-3-O-(2,3,4,6-tetra-O-acetyl-α-D-galacto-pyranosyl)-α-D-glucopyranosyl]-α-L-rhamnopyranose (**19**). — To a solution of **17** (615 mg, 1.26 mmol) in acetic anhydride–pyridine (1:1, 20 mL) was added a catalytic amount of 4-dimethylaminopyridine. After stirring overnight at 50°, the reaction was complete (R_F 0.34, 98:2 dichloromethane–methanol). The mixture was thrice co-concentrated with toluene (30 mL), ethanol (30 mL), and dichloromethane (30 mL) to yield **18**, isolated quantitatively as a syrup, $[\alpha]_D$ +97° (*c* 1, chloroform); α,β-ratio 1:1.

Anal. Calc. for $C_{38}H_{52}O_{25}$: C, 50.21; H, 5.78. Found: C, 49.83; H, 5.80.

To a solution of **18** (1.26 g, 1.39 mmol) in *N,N*-dimethylformamide (14 mL) was added hydrazine acetate (163 mg, 1.77 mmol). The mixture was stirred for 6 h when the deacetylation was complete (R_F 0.39, 6:4 dichloromethane–ethyl acetate). Ethyl acetate (50 mL) was added, and the mixture was diluted with dichloromethane (50 mL), washed with aqueous 5% sodium chloride (3 × 100 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (7:3 dichloromethane–ethyl acetate) to yield **19**, isolated as a syrup (1.06 g, 88%), $[\alpha]_D$ + 102° (*c* 1, chloroform). ^{13}C-N.m.r. data ($CDCl_3$): δ 17.2 (C-6), 20.3–20.6 (CH_3CO), 60.6 and 61.4 (C-6′,6″), 91.7 ($J_{C,H}$ 170.8 Hz), 92.9 ($J_{C,H}$ 173.9 Hz), and 95.8 ($J_{C,H}$ 175.9 Hz) (C-1,1′,1″), 169.2–170.4 (CH_3CO).

Anal. Calc. for $C_{36}H_{50}O_{24}$: C, 49.87; H, 5.82. Found: C, 49.41; H, 5.95.

2,4-Di-O-acetyl-3-O-[2,4,6-tri-O-acetyl-3-O-(2,3,4,6-tetra-O-acetyl-α-D-galacto-pyranosyl)-α-D-glucopyranosyl]-α-L-rhamnopyranosyl trichloroacetimidate (**20**). — To a solution of **19** (155 mg, 0.179 mmol) in dichloromethane (2.0 mL) and trichloroacetonitrile (225 μL, 2.24 mmol) was added at −5° a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 30 μL, 0.20 mmol) in dichloromethane (1.0 mL). The mixture was stirred for 1 h when the reaction was complete (R_F 0.47, 9:1 dichloromethane–acetone) and, after concentration, the residue was purified by column chromatography (9:1 toluene–acetone) to yield **20**, isolated as a syrup (146 mg, 81%), $[\alpha]_D$ +33° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^{1}H, δ 1.257 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6,6,6), 1.964, 2.052, 2.060, 2.080, 2.100, 2.105, 2.107, 2.120, and 2.194 (9 s, each 3 H, 9 Ac), 4.854 (dd, 1 H, $J_{1',2'}$ 3.4, $J_{2',3'}$ 10.2 Hz, H-2′), 5.191 (d, 1 H, H-1′), 5.220 (dd, 1 H, H-3″), 5.285 (d, 1 H, $J_{1'',2''}$ 3.7 Hz, H-1″), 5.399 (dd, 1 H, $J_{4'',5''}$ 0.9, $J_{3'',4''}$ 3.4 Hz, H-4″), 5.438 (t, 1 H, H-2), 6.193 (d, 1 H, $J_{1,2}$ 2.7 Hz, H-1); ^{13}C, δ 17.1 (C-6), 20.1–20.3 (CH_3CO), 60.4 and 61.4 (C-6′,6″), 90.2 ($OC{=}NHCCl_3$), 93.1, 94.5, and 95.6 (C-1,1′,1″), 159.1 ($OC{=}NHCCl_3$), 169.0–170.2 (CH_3CO).

1,2,4,5-Tetra-O-benzyl-3-O-{*2,4-di-O-acetyl-3-O-[2,4,6-tri-O-acetyl-3-O-(2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl)-α-D-glucopyranosyl]-α-L-rhamnopyranosyl*}-D-*ribitol* (**21**). — A suspension of **20** (200 mg, 0.20 mmol), **11** (130 mg, 0.30 mmol), and molecular sieves 4 Å (2 g) in dichloromethane (5 mL) was stirred for 2 h at room temperature. Then, at −30°, trimethylsilyl triflate (15.4 μL) was added and the mixture was stirred for 5 min, when t.l.c. showed the reaction to be complete (R_F 0.46, 8:2 dichloromethane–ethyl acetate). Pyridine (1.0 mL) was added, and the mixture was filtered through Celite, diluted with dichloromethane (50 mL), washed with water (3 ×

10 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by column chromatography (8:2 dichloromethane–ethyl acetate) to yield **21**, isolated as a syrup (242 mg, 90%), $[\alpha]_D$ +46° (*c* 1, dichloromethane). N.m.r. data ($CDCl_3$): ^1H, δ 0.998 (d, 3 H, $J_{5',6'}$ 6.2 Hz, H-6',6',6'), 1.954, 2.031, 2.043, 2.048, 2.051, 2.070, 2.073, 2.092, and 2.110 (9 s, each 3 H, 9 Ac), 4.853 (dd, 1 H, $J_{1'',2''}$ 3.4, $J_{2'',3''}$ 10.1 Hz, H-2''), 4.990 (d, 1 H, $J_{1',2'}$ 1.7 Hz, H-1'), 5.139 (d, 1 H, H-1''), 5.257 (d, 1 H, $J_{1''',2'''}$ 3.6 Hz, H-1'''), 5.383 (dd, 1 H, $J_{3''',4'''}$ 3.3 Hz, H-4'''), 7.190–7.321 (m, 20 H, 4 Ph); ^{13}C, δ 17.1 (C-6'), 20.4–20.7 (CH_3CO), 60.7 and 61.4 (C-6'',6'''), 68.2 and 69.7 (C-1,5), 71.7 and 71.9 (4 $C_6H_5CH_2$), 93.1, 95.9, and 97.4 (C-1',1'',1'''), 127.3–128.2 and 137.9–138.1 ($C_6H_5CH_2$), 169.2–170.5 (CH_3CO).

O-α-D-*Galactopyranosyl-(1→3)*-O-α-D-*glucopyranosyl-(1→3)*-O-α-L-*rhamnopyranosyl-(1→3)*-D-*ribitol* (**23**). — To a solution of **21** (200 mg, 0.15 mmol) in dry methanol (4 mL) was added sodium methoxide (pH 10). After stirring for 48 h at room temperature, deacetylation was complete (R_F 0.12, 9:1 dichloromethane–methanol). The mixture was neutralised with Dowex-50 (H^+) resin, filtered, and concentrated to yield **22**, isolated as a syrup (145 mg, 98%), $[\alpha]_D$ +55° (*c* 1, methanol). A solution of **22** in methanol (20 mL) was hydrogenolysed overnight in the presence of 10% Pd–C (700 mg) at 4 atm., then filtered through Celite, and concentrated to yield **23**, isolated as a syrup (85 mg, 93%), $[\alpha]_D$ +26° (*c* 1, water). N.m.r. data (D_2O): ^1H, δ 5.019 (bs, 1 H, H-1'), 5.110 (d, 1 H, $J_{1'',2''}$ 3.7 Hz, H-1''), 5.396 (d, 1 H, $J_{1''',2'''}$ 3.8 Hz, H-1'''); ^{13}C, δ 18.0 (C-6'), 96.7 (C-1''), 100.5 (C-1'''), 101.4 (C-1').

Anal. Calc. for $C_{23}H_{42}O_{19}\cdot 3H_2O$: C, 40.83; H, 7.15. Found: C, 41.19; H, 7.09.

1-O-*Allyloxycarbonyl-2,3,5-tri*-O-*benzyl-4*-O-{*2,4-di*-O-*acetyl-3*-O-*[2,4,6-tri*-O-*acetyl-3*-O-*(2,3,4,6-tetra*-O-*acetyl*-α-D-*galactopyranosyl)*-α-D-*glucopyranosyl]*-α-L-*rhamnopyranosyl*}-D-*ribitol* (**24**). — A suspension of **12** (ref. 3) (75 mg, 0.16 mmol), **20** (127 mg, 0.126 mmol), and powdered molecular sieves 4Å (2 g) in dichloromethane (4.5 mL) was stirred for 2 h under nitrogen at room temperature. Then, at −30°, trimethylsilyl triflate (12 μL) was added, and the mixture was stirred for 5 min, when t.l.c. showed the reaction to be complete (R_F 0.48, 8:2 dichloromethane–ethyl acetate). Pyridine (1.0 mL) was added, and the mixture was filtered through Celite, and co-concentrated thrice each with toluene (10 mL), ethanol (10 mL), and dichloromethane (10 mL). The residue was purified by column chromatography (9:1 dichloromethane–ethyl acetate) to yield **24**, isolated as a syrup (150 mg, 91%), $[\alpha]_D$ +29° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 1.035 (d, 3 H, $J_{5',6'}$ 6.2 Hz, H-6',6',6'), 1.964, 2.023, 2.049, 2.065, 2.077, 2.085, 2.122, and 2.146 (8 s, 3,3,6,3,3,3,3, and 3 H, 9 Ac), 4.382, 4.425, 4.477, 4.567, 4.643, and 4.655 (6 d, 6 H, 3 $PhCH_2O$), 4.870 (dd, 1 H, H-2''), 5.121 (d, 1 H, $J_{1',2'}$ 1.8 Hz, H-1'), 5.177 (d, 1 H, $J_{1'',2''}$ 3.4 Hz, H-1''), 5.271 (d, 1 H, $J_{1''',2'''}$ 3.3 Hz, H-1'''), 5.392 (dd, 1 H, $J_{3''',4'''}$ 3.3 Hz, H-4'''), 5.911 (m, 1 H, $OCOOCH_2CH=CH_2$), 7.221–7.337 (m, 15 H, 3 Ph); ^{13}C, δ 17.2 (C-6'), 20.5–20.8 (CH_3CO), 60.7 and 61.5 (C-6'',6'''), 93.2, 96.0, and 96.8 (C-1',1'',1'''), 118.8 ($OCOOCH_2CH=CH_2$), 127.6–128.3 and 137.5–137.8 ($C_6H_5CH_2$), 131.5 ($OCOOCH_2CH=CH_2$), 154.7 ($OCOOCH_2CH=CH_2$), 169.3–170.6 (CH_3CO).

2,3,5-Tri-O-*benzyl-4*-O-{*2,4-di*-O-*acetyl-3*-O-*[2,4,6-tri*-O-*acetyl-3*-O-*(2,3,4,6-tetra*-O-*acetyl*-α-D-*galactopyranosyl)*-α-D-*glucopyranosyl]*-α-L-*rhamnopyranosyl*}-D-*ribitol* (**25**). — To a solution of **24** (182 mg, 0.135 mmol) in tetrahydrofuran (1.7 mL) was

added palladium tetrakis[triphenylphosphine] (16 mg, 14 μmol), and the mixture was boiled under reflux for 2.5 h. T.l.c. (R_F 0.35, 9:1 dichloromethane–ethyl acetate) then showed complete conversion into **25**. The mixture was cooled and thrice co-concentrated with 1,4-dioxane (10 mL). The residue was purified by column chromatography (9:1 dichloromethane–ethyl acetate) to yield **25**, isolated as a syrup (141 mg, 82%), $[\alpha]_D$ +50° (*c* 1, chloroform). N.m.r. data ($CDCl_3$): ^1H, δ 1.057 (d, 3 H, $J_{5',6'}$ 6.8 Hz, H-6',6',6'), 1.962, 2.022, 2.047, 2.064, 2.076, 2.091, 2.119, and 2.151 (8 s, 3,3,6,3,3,3,3, and 3 H, 9 Ac), 4.398, 4.444, 4.505, 4.574, 4.596, and 4.679 (6 d, 6 H, 3 PhCH_2O), 4.866 (dd, 1 H, $J_{1'',2''}$ 3.4, $J_{2'',3''}$ 10.2 Hz, H-2''), 5.142 (d, 1 H, $J_{1',2'}$ 1.8 Hz, H-1'), 5.192 (d, 1 H, H-1''), 5.279 (d, 1 H, $J_{1''',2'''}$ 3.5 Hz, H-1'''), 5.397 (dd, 1 H, $J_{3''',4'''}$ 3.4 Hz, H-4'''), 7.231–7.347 (m, 15 H, 3 Ph); ^{13}C, δ 17.3 (C-6'), 20.5–20.7 (CH_3CO), 60.7 and 61.5 (C-6'',6'''), 61.0 (C-1), 70.1, 72.1, 73.2, and 73.5 (C-5 and 3 $C_6H_5CH_2$), 93.0, 95.9, and 96.9 (C-1',1'',1'''), 127.6–128.3 and 137.6–137.8 ($C_6H_5CH_2$), 169.2–170.5 (CH_3CO).

O-α-D-*Galactopyranosyl-(1→3)*-O-α-D-*glucopyranosyl-(1→3)*-O-α-L-*rhamnopyranosyl-(1→4)*-D-*ribitol* (**27**). — To a solution of **25** (103 mg, 81 μmol) in dry methanol (1.0 mL) was added sodium methoxide (pH 10). After stirring overnight at room temperature, deacetylation was complete (R_F 0.73, 1:1 dichloromethane–methanol). The mixture was neutralised with Dowex-50 (H^+) resin, filtered, and concentrated to yield **26**, isolated quantitatively as a syrup. A solution of **26** (45.3 mg, 50.8 μmol) in ethanol (10.0 mL) was hydrogenolysed in the presence of 10% Pd–C (350 mg) at 4 atm. overnight, filtered through Celite, and concentrated to yield **27**, isolated as a syrup (28 mg, 90%), $[\alpha]_D$ −25° (*c* 1, water). N.m.r. data (D_2O): ^1H, δ 5.081 (bs, 1 H, H-1'), 5.124 (d, 1 H, $J_{1'',2''}$ 3.7 Hz, H-1''), 5.390 (d, 1 H, $J_{1''',2'''}$ 3.6 Hz, H-1'''); ^{13}C, δ 18.0 (C-6'), 96.8 (C-1''), 100.6 (C-1'''), 101.0 (C-1').

Anal. Calc. for $C_{23}H_{42}O_{19}\cdot 3H_2O$: C, 40.83; H, 7.15. Found: C, 41.23; H, 7.24.

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