Parasite glycoconjugates. Part 4.[1] Chemical synthesis of disaccharide and phosphorylated oligosaccharide fragments of *Leishmania donovani* antigenic lipophosphoglycan

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The disaccharide **1**, tetraglycosyl monophosphate **2**, hexaglycosyl diphosphate **3** and octaglycosyl triphosphate **4**, which are fragments of the phosphoglycan portion of *Leishmania donovani* lipophosphoglycan, have been synthesized. Elongation of the chain was performed using the suitably protected glycobiosyl hydrogenphosphonate derivatives **5** and **6** for the successive introduction of glycobiosyl phosphate units.

Introduction

The *Leishmania* are trypanosomatid protozoan parasites that cause a variety of diseases in the tropics and sub-tropics. The geographical distribution and pathology of leishmaniasis varies according to the species of the *Leishmania* parasite. For example, *Leishmania donovani* causes visceral leishmaniasis (known as kalazar), characterised by an enlarged liver and spleen, that is often fatal, whereas *L. major* generally causes a self-limiting skin lesion (known as oriental sore). The parasites undergo a complex life-cycle between their insect vectors and their mammalian hosts. In the sand-fly, the parasites divide in the mid-gut as non-infectious procyclic promastigote forms and many of these parasites are found attached to the gut epithelium. After a few days, the parasites differentiate into non-dividing, infectious metacyclic promastigote forms that detach from the gut epithelium and migrate to the mouth parts. The metacyclic promastigotes are transmitted to a mammalian host in the sand-fly saliva during a blood meal, where they bind to and invade host macrophages to initiate the infection. They then rapidly differentiate into round amastigote forms of the parasite that undergo division inside the macrophage phagolysosome. Heavily parasitised macrophages eventually lyse and the released amastigotes invade adjacent macrophages to propagate the infection. Amastigotes in infected macrophages that are ingested by a sand-fly differentiate into procyclic promastigotes in the sand-fly mid-gut, thus completing the cycle.

The most abundant macromolecule on the surface of promastigote forms of all *Leishmania* species is a complex glycoconjugate called lipophosphoglycan (LPG). The general structure of LPG[2] is:

(R→3)
|
α-D-Man*p*-(1→2)-α-D-Man*p*-(1-PO_3H-[-6)-β-D-Gal*p*-(1→4)-
α-D-Man*p*-(1-PO_3H-]$_n$ – glycosyl phosphatidylinositol anchor,

where n = 14–30. The nature of the R group substituting the 3-position of the β-D-Gal*p* residue of the common β-D-galactopyranosyl-(1→4)-α-D-mannopyranosyl phosphate repeat unit varies according to the species of *Leishmania*. For example, in *L. donovani* the R group is simply H, whereas in *L. major* R is mostly monosaccharide, disaccharide or trisaccharide (made up of β-D-Gal*p* and β-D-Ara*p* residues).[2] The LPG changes in structure, principally in the doubling of phosphosaccharide repeats, when the procyclic promastigote forms differentiate into metacyclic promastigote forms.[3,4] LPG has been shown to be required for procyclic promastigote adhesion to the insect gut epithelium[5,6] and for the successful invasion of macrophages.[7] Biological, biochemical and biophysical experiments designed to probe the function, immunology, biosynthesis and conformation of LPG require the chemical synthesis of sub-structures of the LPG molecule. We now report the synthesis of the di-, tetra-, hexa- and octa-saccharide fragments **1**–**4** of the phosphoglycan portion of *L. donovani* LPG. All the synthetic oligomers contain a dec-9-enyl aglycone moiety and are designed to be used for both biosynthetic studies and the preparation of artificial antigens.

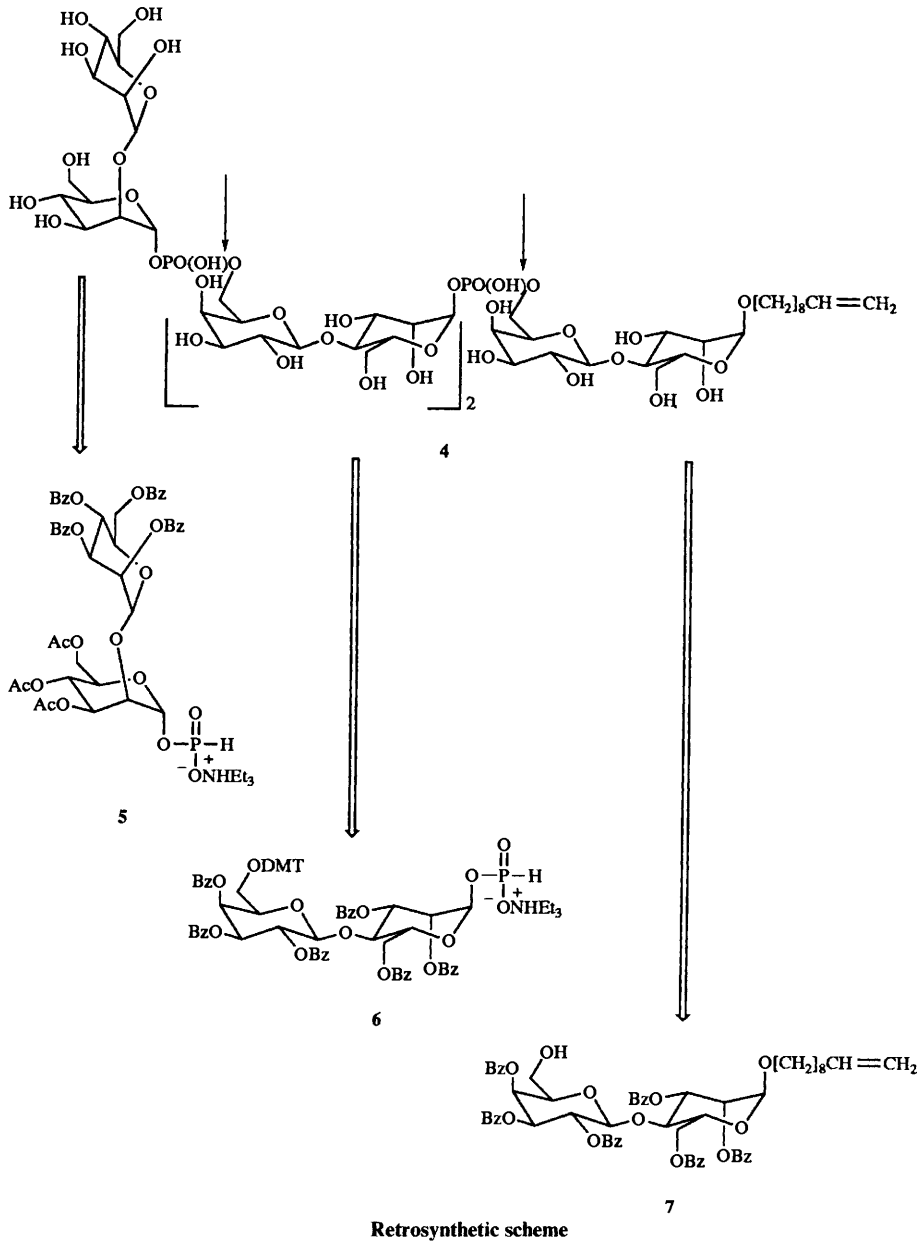
β-D-Gal*p*-(1→4)-α-D-Man*p*-(1-[-PO_3H-6)-β-D-Gal*p*-(1→4)-α-D-Man*p*-(1-]$_n$-O[CH_2]$_8$CH=CH_2
1 n = 0; **2** n = 1; **3** n = 2

α-D-Man*p*-(1→2)-α-D-Man*p*-(1-[-PO_3H-6)-β-D-Gal*p*-(1→4)-α-D-Man*p*-(1-]$_3$-O[CH_2]$_8$CH=CH_2
4

Results and discussion

A retrosynthetic analysis of the most complicated oligomer, octaglycosyl triphosphate **4**, shows that it can be prepared from the glycobiosyl H-phosphonate synthons **5** and **6** (for the consecutive introduction of the mannobiosyl phosphate and galactosylmannosyl phosphate fragments) and the monohydroxylic disaccharide synthon **7**. The synthons **6** and **7** can also be used to synthesize the shorter oligomers **1**–**3**. The general approach for the preparation of the phosphorylated oligosaccharides **2**–**4** is based on the use of the glycosyl hydrogenphosphonate method[8] for construction of the phosphodiester linkages and for stepwise elongation of the oligomeric chain.

The key galactosylmannosyl H-phosphonate block **6**, containing a temporary dimethoxytrityl protecting group at the 6′-position, was prepared using acetobromogalactose **8** and 1,2,3,6-tetra-*O*-benzoyl-α-D-mannopyranose **9** as the starting materials (Scheme 1). Compound **9** was synthesized in 64% yield (in addition to a small proportion of 1,2,3,6-tetra-*O*-benzoyl-β-D-mannopyranose **10**) by selective benzoylation of D-mannose with benzoyl chloride (4 mol equiv.; −40 °C) in pyridine. Base-deficient glycosylation[9] of the acceptor **9** with the galactopyranosyl bromide **8** in the presence of silver triflate and 2,4,6-trimethylpyridine (2,4,6-collidine) gave, after 20–30 min, the β-linked disaccharide **11** (74%), a small proportion



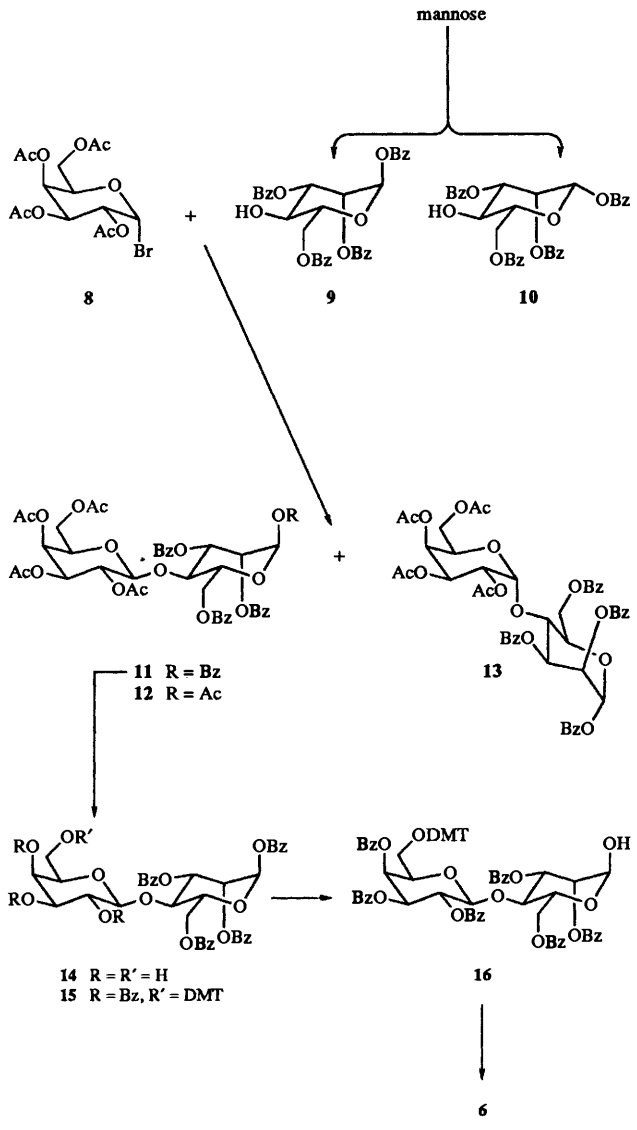
Retrosynthetic scheme

(4%) of the α-linked isomer **13**, and recovered acceptor **9** (9.5%). If the glycosylation reaction was prolonged for 24 h, the disaccharide **12** (19%), presumably formed from the disaccharide **11**, was isolated in addition to the disaccharides **11** (47%) and **13** (7%). Condensation of the tetrabenzoate **9** and acetobromogalactose **8** in the presence of $Hg(CN)_2$–$HgBr_2$ in acetonitrile[10] produced the disaccharides **11** and **13** in 54 and 32% yield, respectively.

The disaccharide **11** was converted into the 6′-*O*-dimethoxytrityl derivative **15** (72%) by O-deacetylation[11] with HCl in MeOH, followed by treatment of the resulting tetraol **14** first with dimethoxytrityl chloride in pyridine and then with benzoyl chloride in pyridine. The disaccharide **15** was selectively 1-*O*-debenzoylated with dimethylamine in acetonitrile[8,12] to give the α-hydroxy derivative **16** (77%), which on phosphitylation[8,12] with tri-imidazolylphosphine (prepared from PCl_3, imidazole and Et_3N) and mild hydrolysis gave the H-phosphonate synthon **6** in 92% yield. Signals characteristic of the H-phosphonate group [δ_P 1.57; δ_H 5.71 (dd, $J_{1,2}$ 1.8, $J_{1,P}$ 8.85 Hz, 1-H), 7.17 (d, $^1J_{H,P}$ 636 Hz, HP)] were present in the ^{31}P and ^1H NMR spectra of the disaccharide **6**. The α-configuration followed from the characteristic value (171 Hz) of $^1J_{C,H}$ for the signal of C-1 (δ_C 92.61).

The monohydroxylic dec-9-enyl bioside **7** was prepared from acetobromogalactose **8** and dec-9-enyl 2,3,6-tri-*O*-benzoyl-α-D-mannopyranoside **20**, as shown in Scheme 2. The mannoside **20** resulted from the glycosylation of dec-9-en-1-ol with acetobromomannose **17** in the presence of $Hg(CN)_2$–$HgBr_2$ in acetonitrile[10] (⟶ **18**), followed by O-deacetylation and selective benzoylation[13] of dec-9-enyl α-D-mannopyranoside **19**. Base-deficient galactosylation of the acceptor **20** with acetobromogalactose **8** (as above) gave the β-linked disaccharide **21** (67%) and some of the α-linked isomer **22** (15%). The bioside **7** was prepared from the disaccharide **21** in an overall yield of 71% by O-deacetylation[11] with HCl–MeOH (⟶ **23**), dimethoxytritylation of the 6′-position and benzoylation (⟶ **24**), followed by detritylation (⟶ **7**) under mildly acidic conditions. Compound **21** also served as the direct precursor of the disaccharide **1** (see below).

To prepare the mannobiosyl H-phosphonate synthon **5** (Scheme 3), 1,3,4,6-tetra-*O*-acetyl-β-D-mannopyranose **26** was first glycosylated with benzobromomannose **25** under base-



Scheme 1

deficient conditions (as above) to give quantitatively the disaccharide **27**, which was transformed into the H-phosphonate **5** (92%) by selective 1-O-deacetylation with Me_2NH in MeCN (⟶ **28**), followed by H-phosphonylation. The structure of compound **5** was confirmed by fast-atom bombardment mass spectrometric [FAB-MS(+)] (*m/z* 1050.84, $[M + H]^+$) and the ^{31}P and ^1H NMR data [δ_P 1.88; δ_H 5.87 ($J_{1,2}$ 1.5 Hz, $J_{1,P}$ 8.85 Hz, 1-H), 7.01 ($^1J_{H,P}$ 632.6 Hz, HP)]. The α-configuration of the reducing D-mannose residues in disaccharides **28** and **5** was evident from the characteristic values (171 and 170 Hz, respectively) of $^1J_{C,H}$ for the signals of C-1 (see Experimental section).

The chain-elongation cycle for synthesis of the oligo(glycobiosyl phosphates) **2–4** involved the coupling of a glycobiosyl H-phosphonate derivative with a hydroxylic acceptor, followed by oxidation of the resulting H-phosphonic diester to the phosphoric diester prior to removal of the temporary dimethoxytrityl protecting group. Oxidation of the H-phosphonic diester to the phosphoric diester during each elongation cycle is essential, since the higher stability of glycosyl phosphoric diesters permits selective deprotection and chromatographic isolation of the products, whereas the same operations with the glycosyl H-phosphonic diesters led to significant degradation.[14,15]

Condensation of the H-phosphonate **6** with the disaccharide **7** (Scheme 4) in pyridine in the presence of adamantane-1-carbonyl chloride, followed by *in situ* oxidation with iodine in aq. pyridine and subsequent dedimethoxytritylation with 1% CF_3CO_2H (TFA) in CH_2Cl_2 (1 min; 0 °C), gave the tetrasaccharide phosphoric diester **29** in 81% overall yield. A similar sequence of reactions using either trimethylacetyl chloride or bis(2-oxooxazolidin-3-yl)phosphinic chloride[16] as the condensing reagent resulted in the compound **29** in 79 and 70% yield, respectively. The hexasaccharide diphosphate derivative **30** was prepared in 75% yield from the H-phosphonate **6** and the tetrasaccharide monophosphate **29** by using the prescribed route involving condensation (with adamantane-1-carbonyl chloride), oxidation and detritylation. In similar fashion, the octasaccharide triphosphate derivative **31** was obtained in 89% yield following the coupling between the mannobiosyl H-phosphonate **5** and the hexasaccharide derivative **30** and *in situ* oxidation.

The deprotected disaccharide **1** and oligo(glycobiosyl phosphates) **2–4** were prepared from the derivatives **21**, **29**, **30** and **31**, respectively, by O-deacylation with 0.05 mol dm^{-3} methanolic sodium methoxide.

The structures of the compounds **1–4** and **29–31** were confirmed by NMR and mass spectrometry data. The ^{31}P NMR data (see Experimental section) are characteristic of glycoside-linked phosphoric diesters.[8,12,14,15] For the deprotected mono-, di- and tri-phosphates **2–4** in D_2O, the ^{31}P NMR spectra exhibited single signals at δ_P −1.28, −1.29 and −1.27, respectively. However, the spectra of the protected di- and triphosphates **30** and **31** in $CDCl_3$ consisted of two and three signals, respectively: δ_P −2.99 (P), −3.08 (P′) for diphosphate **30**, and −2.55 (P″), −2.95 (P) and −3.02 (P′) for triphosphate **31**, indicating the non-equivalence of the phosphate groups in these oligomers (*cf.* ref. 8).

The presence of the (1→6)-phosphodiester linkages was confirmed by the C-1 and C-2 signals of the corresponding D-mannose units and the C-5 and C-6 signals of the corresponding D-galactose units in the ^{13}C NMR spectra of compounds **2–4** (see Table 1). The signals were shifted as a result of the α- and β-effects of phosphorylation and were coupled with phosphorus. The α-configuration of the D-mannosyl phosphate fragments followed from the positions of the C-3 and C-5 resonances of Man′, Man″ and Man‴. The chemical shifts of these signals were close to those of C-3 and C-5 of α-D-mannopyranosyl phosphate,[17] taking into account the influence of the glycosyl substituents at position-4 (of Man′ and Man″) and position-2 (of Man‴).

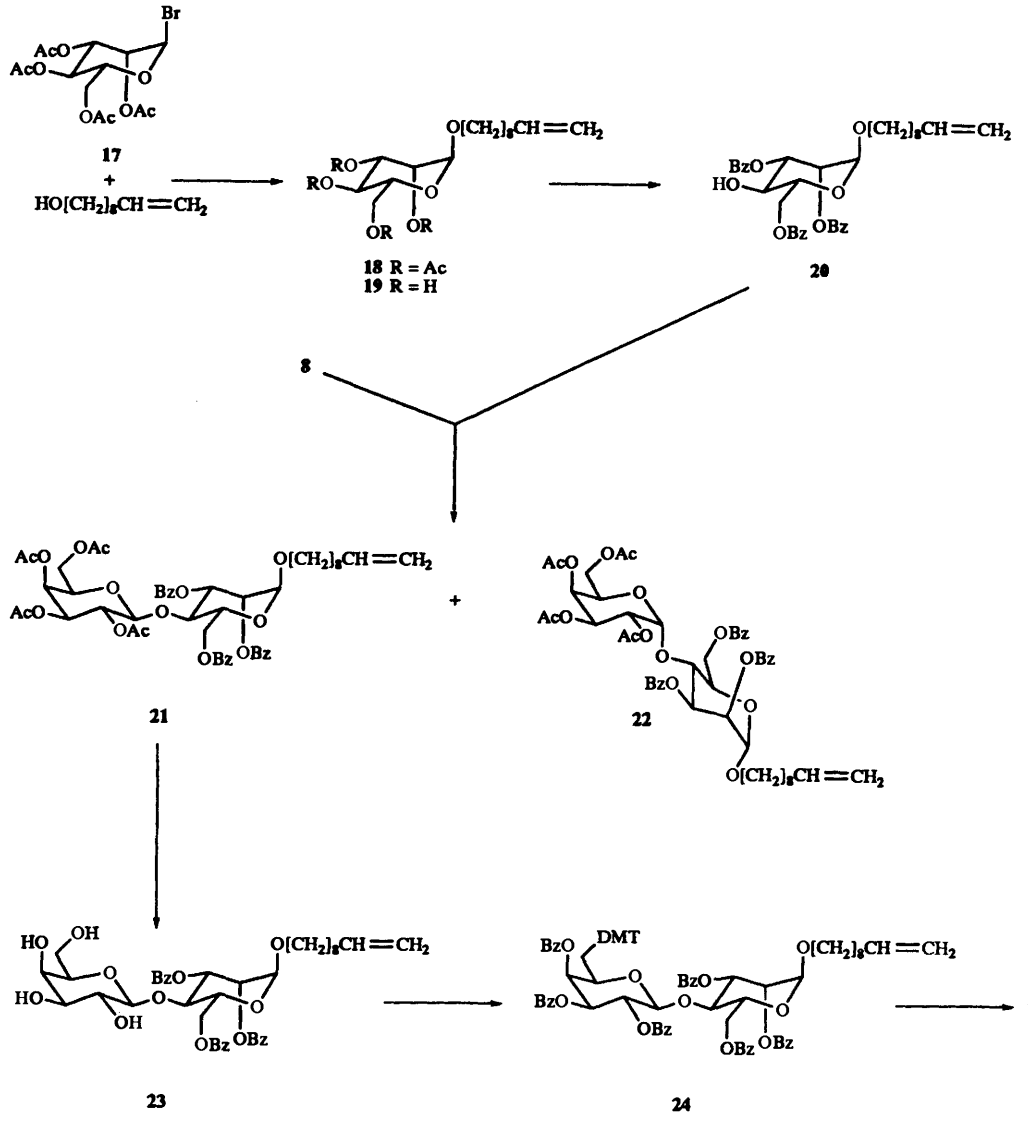
The molecular masses of the oligomers **1–4** and **29–31** were confirmed by electrospray [ES(−)] and FAB(+) mass spectrometry. The main signals in the spectra corresponded to the pseudo-molecular ions for the disaccharide **1** (*m/z* 479.4, $[M - H]^-$), the monophosphates **2** (*m/z* 883.4, $[M - Et_3N - H]^-$) and **29** (*m/z* 2236.22, $[M + H]^+$), the diphosphates **3** (*m/z* 643.3, $[M - 2\,Et_3N - 2\,H]^{2-}$) and **30** (*m/z* 1580.1, $[M - 2\,Et_3N - 2\,H]^{2-}$), and the triphosphates **4** (*m/z* 563.3, $[M - 3\,Et_3N - 3\,H]^{3-}$) and **31** (*m/z* 1368.5, $[M - 3\,Et_3N - 3\,H]^{3-}$).

To summarise, the first chemical syntheses of fragments (up to octasaccharide) of a natural antigenic phosphoglycan consisting of glycobiosyl phosphate units have been achieved using the glycosyl hydrogenphosphonate method.

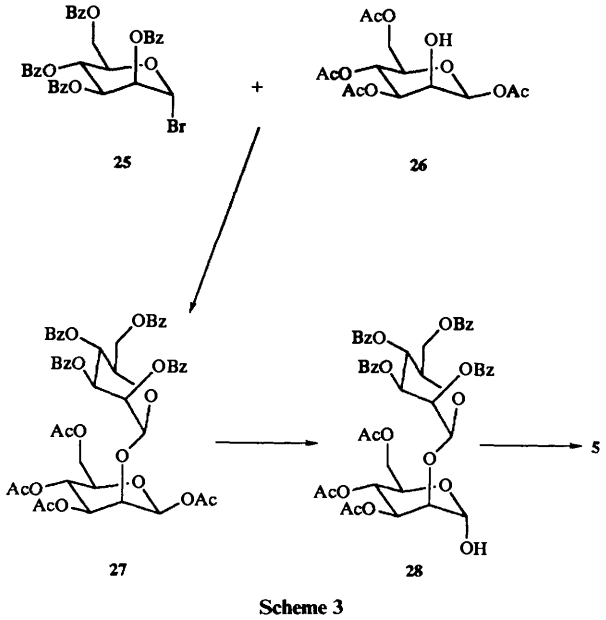
Experimental

General procedures

Mps were determined on a Reichert hot-plate apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 141 polarimeter; $[\alpha]_D$-values are given in units of 10^{-1} deg cm^2 g^{-1}. NMR spectra (^1H at 200 and 500 MHz, ^{13}C at 50.3

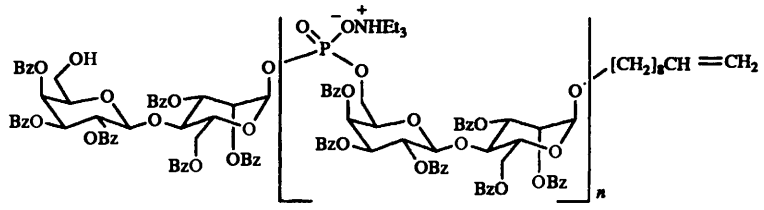


Scheme 2

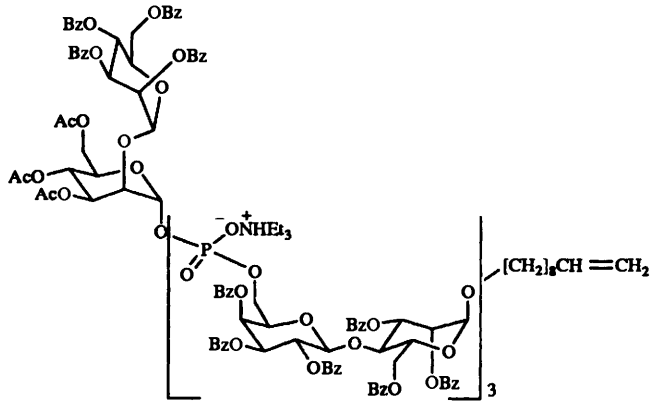


Scheme 3

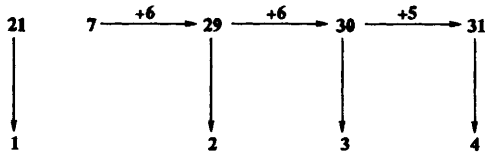
and 125 MHz, and ^{31}P at 81 and 202.5 MHz) were recorded with Bruker AM-200 and AM-500 spectrometers for solutions in $CDCl_3$, unless otherwise indicated. Chemical shifts (δ in ppm) are given relative to those for Me_4Si (for ^1H and ^{13}C) and external aq. 85% H_3PO_4 (for ^{31}P); J values are given in Hz. FAB mass spectra were recorded with a VG 70-250 SE mass spectrometer using an Ion-tech xenon gun. ES mass spectra were recorded with a VG Quattro system (VG Biotech, UK). TLC was performed on Polygram Sil G/UV_{254} (Macherey-Nagel, Germany) with *A*, toluene–ethyl acetate (9:1); *B*, toluene–ethyl acetate (8:2); *C*, toluene–ethyl acetate (7:3); *D*, ethyl acetate–methanol (9:1); *E*, chloroform–methanol (95:5); *F*, chloroform–methanol (9:1); *G*, chloroform–methanol–water (93:7:0.35); *H*, chloroform–methanol–water (10:10:3); and *I*, propan-2-ol–water (85:15) as developers and detection by charring with sulfuric acid–water–ethanol (15:85:5). Column chromatography was performed on Kieselgel 60 (0.040–0.063 mm) (Merck). 1,3,4,6-Tetra-*O*-acetyl-β-D-mannopyranose, dec-9-en-1-ol, silver triflate, *p,p'*-dimethoxytriphenylmethylchloride, adamantane-1-carbonyl chloride, and bis(2-oxooxazolidin-3-yl)phosphinic chloride were purchased from Aldrich. Solutions worked up were concentrated under reduced pressure at < 40 °C.



29 $n = 1$
30 $n = 2$



31



Scheme 4

1,2,3,6-Tetra-*O*-benzoyl-α-D-mannopyranose 9

Benzoyl chloride (9.27 cm^3, 80 mmol) was added dropwise to a stirred, cooled (−40 °C) solution of D-mannose (3.6 g, 20 mmol) in pyridine (40 cm^3) during *ca.* 1 h. The temperature was increased to 20 °C for 3–4 h, and the mixture then was stirred overnight. Most of the pyridine was evaporated off under reduced pressure, and a solution of the residue in chloroform was washed successively with saturated aq. $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated. Crystallisation of the residue from ethanol, and recrystallisation subsequently from ethyl acetate–hexane, gave the *α-tetrabenzoate* **9** (6.14 g). Column chromatography (solvent *A*) of the mother liquor gave an additional quantity of compound **9** (1.5 g; total yield 7.64 g, 64%); mp 183–184 °C; $[\alpha]_D^{22}$ +41 (*c* 1, $CHCl_3$); R_f 0.64 (solvent *B*) (Found: C, 68.6; H, 4.5. $C_{34}H_{28}O_{10}$ requires C, 68.45; H, 4.7%); δ_H 3.20 (1 H, d, $J_{OH,4}$ 4.3, OH), 4.25 (1 H, ddd, $J_{5,6a}$ 1.7, 5-H), 4.39 (1 H, dt, $J_{3,4} = J_{4,5}$ = 10.0, 4-H), 4.55 (1 H, dd, $J_{6a,6b}$ 12.5, 6-H^a), 4.97 (1 H, dd, $J_{5,6b}$ 3.4, 6-H^b), 5.80 (2 H, m, 2- and 3-H), 6.56 (1 H, d, $J_{1,2}$ 1.7, 1-H) and 7.25–8.16 (20 H, m, 4 × Ph). Continued elution gave 1,2,3,6-*tetra*-O-*benzoyl*-β-D-*mannopyranose* **10** (0.8 g, 7%) as an amorphous solid; $[\alpha]_D^{22}$ −42.5 (*c* 1, $CHCl_3$); R_f 0.53 (solvent *B*) (Found: C, 68.2; H, 4.8%); δ_H 3.18 (1 H, d, $J_{OH,4}$ 4.5, OH), 4.00 (1 H, ddd, $J_{5,6a}$ 2.1, 5-H), 4.32 (1 H, dt, $J_{3,4} = J_{4,5}$ = 9.8, 4-H), 4.67 (1 H, dd, $J_{6a,6b}$ 12.1, 6-H^a), 4.96 (1 H, dd, $J_{5,6b}$ 3.6, 6-H^b), 5.52 (1 H, dd, 3-H), 5.99 (1 H, dd, $J_{2,3}$ 3.3, 2-H), 6.31 (1 H, d, $J_{1,2}$ 1.0, 1-H) and 7.30–8.25 (20 H, m, 4 × Ph). The benzoylation reaction at 0 °C (instead of at −40 °C) resulted in the compounds **9** and **10** in 27 and 26% yield, respectively.

1,2,3,6-Tetra-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-mannopyranose 11

Silver triflate (1.566 g, 6.092 mmol) was dried by evaporation of anhydrous toluene (2 × 20 cm^3) therefrom. A solution of acetobromogalactose **8** (2.17 g, 5.28 mmol), the tetrabenzoate **9** (2.1 g, 3.52 mmol) and 2,4,6-collidine (0.606 cm^3, 4.576 mmol) in CH_2Cl_2 (30 cm^3) was added dropwise to a stirred suspension of silver triflate in CH_2Cl_2 (10 cm^3) at −20 °C. Cooling was discontinued after the addition was complete, and, after 20 min, the mixture became slightly acidic; TLC (solvent *C*) then showed the formation of one major product (R_f 0.42). The mixture was neutralised with pyridine (1 cm^3), filtered through a Celite pad, and the filtrate was concentrated. Column chromatography [toluene–ethyl acetate, (95:5)→(80:20)] of the residue gave the *disaccharide derivative* **11** (2.4 g, 74%); mp 107–109 °C (from ethanol); $[\alpha]_D^{23}$ +26 (*c* 1, $CHCl_3$); R_f 0.42 (solvent *C*) (Found: C, 61.9; H, 4.85. $C_{48}H_{46}O_{19}$ requires C, 62.2; H, 5.0%); δ_H 1.78 and 1.92 (6 H, 2 × s, 2 × Ac), 2.02 (6 H, s, 2 × Ac), 3.51 (2 H, m, 5′-H and 6′-H^a), 3.76 (1 H, dd, $J_{5',6b'}$ 5.8, $J_{6a',6b'}$ 9.5, 6′-H^b), 4.34 (1 H, ddd, $J_{5,6a}$ 3.0, 5-H), 4.52 (1 H, dd, $J_{6a,6b}$ 12.0, 6-H^a), 4.62 (1 H, t, $J_{3,4} = J_{4,5}$ = 9.5, 4-H), 4.74 (1 H, d, $J_{1',2'}$ 7.8, 1′-H), 4.80 (1 H, dd, $J_{5,6b}$ 1.9, 6-H^b), 4.90 (1 H, dd, $J_{3',4'}$ 3.5, 3′-H), 5.17 (1 H, dd, $J_{2',3'}$ 10.5, 2′-H), 5.18 (1 H, br d, 4′-H), 5.86 (1 H, dd, $J_{2,3}$ 3.5, 2-H), 5.96 (1 H, dd, 3-H), 6.54 (1 H, d, $J_{1,2}$ 1.9, 1-H) and 7.33-8.15 (20 H, m, 4 × Ph); δ_C 20.36, 20.58 and 20.73 (*Me*CO), 60.44 (C-6′), 62.29 (C-6), 66.53 (C-4′), 69.41 (C-2′), 69.42 (C-2), 70.39 (C-3), 70.75 (C-5′), 71.05 (C-3′), 71.68 (C-5), 73.51 (C-4), 91.40 (C-1), 101.25 (C-1′), 128.60–130.25 and 133.47–134.15 (Ph), 164.07, 165.03

Table 1 ^{13}C NMR data (D_2O, δ_C in ppm, J in Hz) for oligosaccharides **1–4** ($J_{C,P}$-values in parentheses)

Residue	Atom	1	2[a]	3[a]	4[a]
Man	C-1	100.94	100.76	100.54	100.51
	C-2	71.22	70.84	70.65	70.67
	C-3	70.89	70.84	70.65	70.67
	C-4	77.45	78.14	78.64	78.66
	C-5	72.46	72.34	72.33	72.33
	C-6	61.38	61.37	61.45	61.45
Gal	C-1	104.33	104.42	104.46	104.49
	C-2	72.10	72.13	72.00	71.97
	C-3	74.02	73.69	73.64	73.51
	C-4	69.85	69.28	69.30	69.25
	C-5	76.51	74.89d (7.3)	74.93d (7.5)	74.84d (8.1)
	C-6	62.32	65.53d (4.0)	65.64d (5.5)	65.43d (5.2)
Man′	C-1		97.12d (5.4)	97.03d (5.5)	96.99d (4.6)
	C-2		71.08d (8.3)	71.07d (7.4)	71.05d (7.4)
	C-3		69.83	69.84	69.94
	C-4		77.05	78.17	78.22
	C-5		73.69	73.64	73.51
	C-6		61.37	61.45	61.45
Gal′	C-1		104.20	104.46	104.49
	C-2		72.13	72.00	71.97
	C-3		73.69	73.64	73.51
	C-4		69.83	69.30	69.25
	C-5		76.52	74.93d (7.5)	74.84d (8.1)
	C-6		62.30	65.64d (5.5)	65.43d (5.2)
Man″	C-1			97.03d (5.5)	96.99d (4.6)
	C-2			71.07d (7.4)	71.05d (7.4)
	C-3			69.84	69.94
	C-4			77.04	78.22
	C-5			73.64	73.51
	C-6			61.45	61.45
Gal″	C-1			104.20	104.49
	C-2			72.00	71.97
	C-3			73.64	73.51
	C-4			69.84	69.25
	C-5			76.52	74.84d (8.1)
	C-6			62.27	65.43d (5.2)
Man‴	C-1				95.85d (4.6)
	C-2				80.15d (7.4)
	C-3				70.67
	C-4				67.83
	C-5				75.03
	C-6				62.03
Man⁗	C-1				103.35
	C-2				71.13
	C-3				71.47
	C-4				67.83
	C-5				74.40
	C-6				62.03
Dec-9-en-1-yl	$=CH_2$	115.29	115.29	115.17	115.13
	$-CH=$	140.11	140.56	140.64	141.46
	OCH_2	68.91	69.11	69.30	69.25
	CCH_2C	27.24, 29.91–30.68, 34.89	26.90, 29.74–30.21, 34.65	26.51, 29.20–29.62, 34.27	26.51, 29.29–29.63, 34.30

[a] Additional signals of Et_3NH^+ (δ_C 9.40–9.45 and δ_C 47.82–47.85) were present.

and 165.92 ($PhCO_2$), 169.43, 169.97 and 170.15 ($MeCO_2$). Also isolated were the acceptor **9** (0.2 g, 9.5% recovery) and 1,2,3,6-*tetra*-O-*benzoyl*-4-O-(2,3,4,6-*tetra*-O-*acetyl*-α-D-*galacto*-*pyranosyl*)-α-D-*mannopyranose* **13** (0.13 g, 4%); amorphous solid; $[\alpha]_D^{23}$ +74 (*c* 1.23, $CHCl_3$); R_f 0.49 (solvent *C*) (Found: C, 61.9; H, 4.7%); δ_H 1.80, 1.94, 1.95 and 2.07 (12 H, 4 × s, 4 × Ac), 3.90 (1 H, dd, $J_{5',6a'}$ 5.8, 6′-H[a]), 4.04 (1 H, dd, $J_{6a',6b'}$ 11.0, 6′-H[b]), 4.36 (1 H, dd, $J_{5',6b'}$ 7.4, 5′-H), 4.44 (1 H, ddd, $J_{5,6a}$ 3.6, 5-H), 4.61 (1 H, dd, $J_{6a,6b}$ 13.0, 6-H[a]), 4.68 (1 H, t, $J_{3,4} = J_{4,5}$ = 9.0, 4-H), 4.86 (1 H, dd, $J_{5,6b}$ 2.0, 6-H[b]), 5.21 (1 H, dd, $J_{2',3'}$ 11.0, 2′-H), 5.34 (1 H, dd, $J_{3',4'}$ 3.0, 3′-H), 5.45 (1 H, br d, 4′-H), 5.59 (1 H, d, $J_{1',2'}$ 3.8, 1′-H), 5.86 (2 H, m, $J_{2,3}$ 3.0, 2- and 3-H), 6.57 (1 H, d, $J_{1,2}$ 1.5, 1-H) and 7.32–8.21 (20 H, m, 4 × Ph); δ_C 20.40 and 20.63 (*Me*CO), 61.21 (C-6′), 63.23 (C-6), 66.82 (C-2′), 67.37 (C-3′), 67.71 (C-5′), 67.76 (C-4′), 69.20 (C-2), 71.63 (2 C, C-4 + -5), 72.70 (C-3), 91.46 (C-1), 97.66 (C-1′), 128.31–130.24 and 133.45–134.11 (Ph), 164.18, 165.03, 165.50 and 165.98 ($PhCO_2$), 169.63, 169.86, 170.08 and 170.30 ($MeCO_2$); ES-MS(+) data: *m*/*z* 949.3 (100%, $[M + Na]^+$) ($C_{48}H_{46}O_{19}$ requires M, 926.26).

1,2,3,6-Tetra-*O*-benzoyl-4-*O*-[2,3,4-tri-*O*-benzoyl-6-*O*-(*p*,*p*′-dimethoxytrityl)-β-D-galactopyranosyl]-α-D-mannopyranose 15 A solution of HCl in MeOH [prepared at 0 °C from acetyl chloride (0.4 cm^3) and methanol (10 cm^3)] was added to a solution of compound **11** (1.41 g, 1.52 mmol) in $CHCl_3$ (3 cm^3), and the resulting solution was kept at 20 °C for 40–43 h; TLC (solvent *F*) then showed the formation of one major product (R_f 0.48; presumably the O-deacetylated derivative **14**). Ethanol (10 cm^3) was added to the reaction mixture, which was neutralised with anhydrous Na_2CO_3 and filtered, and the solids were washed with ethanol. The filtrate and washings were

concentrated, and pyridine (3 × 15 cm^3) was evaporated from the residue. The residue was dissolved in pyridine (15 cm^3), *p,p'*-dimethoxytriphenylmethyl chloride (0.7 g, 2.07 mmol) was added, and the solution was kept for 48 h at 20 °C before benzoyl chloride (1 cm^3, 8.6 mmol) was also added to the stirred mixture at −10 °C. After 16 h at 20 °C, the reaction mixture was diluted with $CHCl_3$ and washed successively with saturated aq. $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated. Column chromatography [hexane–ethyl acetate, (3:2)] gave the *dimethoxytrityl derivative* **15** (1.5 g, 72%) as an amorphous solid; $[\alpha]_D^{22}$ +62.7 (*c* 1, $CHCl_3$); R_f 0.5 (solvent *A*), 0.74 (solvent *B*) (Found: C, 72.0; H, 5.2. $C_{82}H_{68}O_{20}$ requires C, 71.7; H, 5.0%); δ_H 3.13 (1 H, t, $J_{5',6a'} = J_{6a',6b'}$ = 8.6, 6'-H^a), 3.28 (1 H, dd, $J_{5',6b'}$ 5.4, 6'-H^b), 3.63 and 3.64 (6 H, 2 × s, 2 × MeO), 3.86 (1 H, br dd, 5'-H), 4.20 (1 H, br d, 5-H), 4.59 (2 H, m, 6-H_2), 4.68 (1 H, t, $J_{3,4} = J_{4,5}$ = 9.5, 4-H), 5.0 (1 H, d, $J_{1',2'}$ 7.8, 1'-H), 5.52 (1 H, dd, $J_{3',4'}$ 3.0, 3'-H), 5.69 (1 H, dd, $J_{2',3'}$ 10.4, 2'-H), 5.85 (1 H, dd, $J_{2,3}$ 3.2, 2-H), 5.91 (1 H, dd, 3-H), 6.04 (1 H, dd, $J_{4',5'}$ ~0.5, 4'-H), 6.49 (1 H, d, $J_{1,2}$ 1.9, 1-H) and 6.59 (2 H, d) and 6.90–8.15 (46 H, m) (2 × C_6H_4, 8 × Ph); δ_C 55.18 (MeO), 59.64 (C-6'), 62.22 (C-6), 67.66 (C-4'), 69.71 (C-2), 70.28 (C-3), 70.38 (C-2'), 72.10 (C-5), 72.26 (C-3'), 72.71 (C-5'), 72.80 (C-4), 86.40 (Ar_3C), 91.34 (C-1), 101.55 (C-1'), 113.14, 125.44–130.27, 133.21–135.77, 144.12, 158.42 and 158.52 (C_6H_4 and Ph) and 164.12–165.82 (PhCO_2).

2,3,6-Tri-*O*-benzoyl-4-*O*-[2,3,4-tri-*O*-benzoyl-6-*O*-(*p,p'*-dimethoxytrityl)-β-D-galactopyranosyl]-α-D-mannopyranose 16

Anhydrous dimethylamine (0.2 cm^3, 3.0 mmol) was added to a solution of compound **15** (0.686 g, 0.5 mmol) in MeCN (5 cm^3) at −20 °C, and the mixture was kept at 20 °C with monitoring by TLC (solvent *B*). After 27 h (note: compound **15** was not allowed to be consumed completely), the mixture was concentrated to dryness, and acetonitrile was evaporated off from the residue. Column chromatography [toluene–ethyl acetate, (95:5)→(80:20)] gave unchanged **15** (0.081 g, 12% recovery) and 1-*hydroxy derivative* **16** (0.489 g, 77%); amorphous solid; $[\alpha]_D^{22}$ +31.5 (*c* 1, $CHCl_3$); R_f 0.44 (solvent *B*) (Found: C, 70.7; H, 5.15. $C_{75}H_{64}O_{19}$ requires C, 71.0; H, 5.1%); δ_H 3.15 (1 H, t, $J_{5',6a'} = J_{6a',6b'}$ = 8.8, 6'-H^a), 3.28 (1 H, dd, $J_{5',6b'}$ 4.6, 6'-H^b), 3.64 and 3.65 (6 H, 2 × s, 2 × MeO), 3.76 (1 H, br dd, 5'-H), 3.89 (1 H, d, $J_{OH,1}$ 3.6, OH), 4.29 (1 H, br d, 5-H), 4.52 (2 H, m, 6-H_2), 4.61 (1 H, t, $J_{3,4} = J_{4,5}$ = 9.7, 4-H), 4.95 (1 H, d, $J_{1',2'}$ 7.7, 1'-H), 5.32 (1 H, dd, $J_{1,2}$ 1.5, 1-H), 5.49 (1 H, dd, $J_{3',4'}$ 3.0, 3'-H), 5.64 (1 H, dd, 2-H), 5.65 (1 H, dd, $J_{2',3'}$ 10.6, 2'-H), 5.84 (1 H, dd, $J_{2,3}$ 2.7, 3-H), 5.98 (1 H, br d, 4'-H) and 6.55 (2 H, d) and 7.10–8.01 (41 H, m) (2 × C_6H_4, 7 × Ph); δ_C 55.0 (MeO), 59.65 (C-6'), 62.56 (C-6), 67.57 (C-4'), 69.49 (C-5), 69.68 (C-3), 70.26 (C-2'), 71.04 (C-2), 71.95 (C-3'), 72.44 (C-5'), 72.94 (C-4), 86.26 (Ar_3C), 91.99 (C-1), 100.88 (C-1'), 112.99, 125.44–130.26, 133.23–135.77, 144.20, 158.41 and 158.51 (C_6H_4 and Ph) and 165.09–166.17 (PhCO_2).

Triethylammonium 2,3,6-tri-*O*-benzoyl-4-*O*-[2,3,4-tri-*O*-benzoyl-6-*O*-(*p,p'*-dimethoxytrityl)-β-D-galactopyranosyl]-α-D-mannopyranosyl hydrogenphosphonate 6

To a stirred solution of imidazole (0.456 g, 6.72 mmol) in MeCN (12 cm^3) at 0 °C was added phosphorus trichloride (0.178 cm^3, 2.02 mmol) and then triethylamine (0.98 cm^3, 7.06 mmol). The mixture was stirred for 15 min, after which a solution of compound **16** (0.585 g, 0.461 mmol) in MeCN (12 cm^3) was added dropwise during 30 min at 0 °C. The mixture was stirred at 20 °C for 10–15 min and quenched with 1 mol dm^{-3} triethylammonium (TEA) hydrogen carbonate (pH 7; 2.8 cm^3). The clear solution was stirred for 15 min, $CHCl_3$ (150 cm^3) was added, and the organic layer was washed in turn with ice–water (2 × 80 cm^3) and cold 0.5 mol dm^{-3} TEA hydrogen carbonate (2 × 80 cm^3), dried by filtration through cotton wool, and concentrated. Column chromatography [CH_2Cl_2–MeOH–Et_3N, (98:1:1)→(93:6:1)] gave the biosyl H-phosphonate **6** (0.607 g, 92%) as an amorphous solid; $[\alpha]_D^{22}$ +24 (*c* 1, $CHCl_3$); R_f 0.44 (solvent *F*); δ_H 1.30 (9 H, t, 3 × *Me*CH_2), 3.00 (6 H, q, 3 × MeCH_2), 3.10 (1 H, t, $J_{5',6a'} = J_{6a',6b'}$ = 8.6, 6'-H^a), 3.22 (1 H, dd, $J_{5',6b'}$ 5.0, 6'-H^b), 3.64 and 3.65 (6 H, 2 s, 2 × MeO), 3.76 (1 H, br dd, 5'-H), 4.30 (1 H, dt, $J_{5,6}$ 2.2, 5-H), 4.49 (1 H, t, $J_{3,4} = J_{4,5}$ = 9.6, 4-H), 4.55 (2 H, d, 6-H_2), 4.89 (1 H, d, $J_{1',2'}$ 7.6, 1'-H), 5.46 (1 H, dd, $J_{3',4'}$ 3.8, 3'-H), 5.59 (1 H, dd, $J_{2',3'}$ 10.2, 2'-H), 5.66 (1 H, dd, $J_{2,3}$ 3.2, 2-H), 5.71 (1 H, dd, $J_{1,2}$ 1.8, $J_{1,P}$ 8.9, 1-H), 5.76 (1 H, dd, 3-H), 5.97 (1 H, dd, $J_{4',5'}$ ~0.5, 4'-H), 7.17 (1 H, d, $J_{H,P}$ 636.0, HP) and 6.54 (2 H, d) and 6.90–8.00 (41 H, m) (2 × C_6H_4, 7 × Ph); δ_C 8.50 and 45.58 (Et), 54.98 (MeO), 59.42 (C-6'), 62.52 (C-6), 67.48 (C-4'), 70.12 (C-3), 70.15 (C-5), 70.40 (C-2'), 70.87 (d, $J_{C,P}$ 6.9, C-2), 71.93 (C-3'), 72.35 (C-5'), 72.58 (C-4), 86.17 (Ar_3C), 92.61 (d, $J_{C,P}$ 3.6, $^1J_{C,H}$ 171, C-1), 100.99 (C-1'), 112.95, 126.65–130.06, 132.68–135.62, 143.95, 158.22 and 158.32 (C_6H_4 and Ph) and 164.79–165.42 (PhCO_2); δ_P 1.57.

Dec-9-enyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside 18

A solution of acetobromomannose **17**[10] (4.11 g, 10 mmol) in MeCN (15 cm^3) was added dropwise to a stirred mixture of dec-9-en-1-ol (1.04 g, 6.67 mmol), $Hg(CN)_2$ (2.53 g, 10.0 mmol) and $HgBr_2$ (0.5 g) in MeCN (30 cm^3). The mixture was stirred at 20 °C overnight, then was concentrated under reduced pressure, and the residue was dissolved in $CHCl_3$. The suspension was filtered to remove mercury salts, and the filtrate was washed successively with 1 mol dm^{-3} KBr and water, dried ($MgSO_4$), and concentrated. Column chromatography [toluene–ethyl acetate, (97:3)→(90:10)] of the residue gave the *decenyl glycoside* **18** (2.3 g, 71%) as a syrup; $[\alpha]_D^{22}$ +40 (*c* 1, $CHCl_3$); R_f 0.67 (solvent *C*) (Found: C, 59.55; H, 8.0. $C_{24}H_{38}O_{10}$ requires C, 59.25; H, 7.9%); δ_H 1.32 (10 H, m, 5 × CH_2), 1.60 (2 H, m, CH_2), 1.97, 2.09 and 2.15 (9 H, 3 × s, 3 × Ac), 2.03 (5 H, m, Ac and CH_2), 3.45 and 3.67 (2 H, 2 × dt, $^2J_{H,H}$ 10.0, $^3J_{H,H}$ 7.0, OCH_2CH_2), 3.98 (1 H, ddd, $J_{5,6a}$ 2.5, 5-H), 4.11 (1 H, dd, $J_{6a,6b}$ 12.5, 6-H^a), 4.28 (1 H, dd, $J_{5,6b}$ 5.5, 6-H^b), 4.60 (1 H, d, $J_{1,2}$ 1.5, 1-H), 4.93 (1 H, dd, $^2J_{H,H}$ 1.8, $^3J_{H,H}$ 10.0, CH=CH_2), 4.99 (1 H, dd, $^3J_{H,H}$ 17.5, CH=CH_2), 5.23 (1 H, dd, $J_{2,3}$ 3.6, 2-H), 5.27 (1 H, t, $J_{3,4} = J_{4,5}$ = 10.0, 4-H), 5.35 (1 H, dd, 3-H) and 5.81 [1 H, ddt, $J_{(H,CH_2)}$ 6.5, CH_2CH=CH_2].

Dec-9-enyl α-D-mannopyranoside 19

A solution of the tetraacetate **18** (3.26 g, 6.71 mmol) in MeOH (30 cm^3) and tetrahydrofuran (8 cm^3) was treated with 4.6 mol dm^{-3} NaOMe in MeOH (1 cm^3) overnight at 20 °C, and was then deionised with Dowex 50W-X4 (H^+) resin, and concentrated to give the *decenyl mannoside* **19** (2.13 g, 99.7%) as an amorphous solid; $[\alpha]_D^{22}$ +56 (*c* 0.5, MeOH); R_f 0.5 (solvent *D*) (Found: C, 60.1; H, 9.5. $C_{16}H_{30}O_6$ requires C, 60.4; H, 9.5%); δ_C(CD_3OD + $CDCl_3$) 26.30, 29.05, 29.11, 29.50, 29.62 and 33.81 (CH_2), 61.75 (C-6), 67.45 (C-4), 67.72 ($^1J_{C,H}$ 140.0, OCH_2CH_2), 71.22 (C-2), 71.73 (C-3), 73.15 (C-5), 100.41 ($^1J_{C,H}$ 168.5, C-1), 113.91 (CH=CH_2) and 139.09 (CH=CH_2).

Dec-9-enyl 2,3,6-tri-*O*-benzoyl-α-D-mannopyranoside 20

Benzoyl chloride (2.57 cm^3, 22.14 mmol) was added dropwise over a period of 30 min to a cooled (−40 °C) and stirred solution of the mannoside **19** (2.13 g, 6.69 mmol) in pyridine (20 cm^3). The temperature was increased to 20 °C for 3 h, and stirring was continued overnight. Most of the pyridine was evaporated off under reduced pressure. A solution of the residue in $CHCl_3$ was washed in turn with saturated aq. $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated. Column chromatography [toluene–ethyl acetate, (100:0)→(95:5)] of the residue gave the *tribenzoate* **20** (2.16 g, 51%); mp 85–87 °C; $[\alpha]_D^{22}$ +12.5 (*c* 1, $CHCl_3$); R_f 0.62 (solvent

A), 0.74 (solvent *B*) (Found: C, 70.2; H, 6.75. $C_{37}H_{42}O_9$ requires C, 70.5; H, 6.7%); δ_H 1.30 (10 H, m, 5 × CH_2), 1.66 (2 H, quintet, *J* 6.5, $OCH_2CH_2CH_2$), 2.05 (2 H, quartet, *J* 6.5, CH_2CH_2CH=), 3.15 (1 H, d, $J_{OH,4}$ 4.8, OH), 3.52 and 3.78 (2 H, 2 × dt, $^2J_{H,H}$ 9.5, $^3J_{H,H}$ 6.8, OCH_2CH_2), 4.12 (1 H, ddd, $J_{5,6a}$ 1.5, 5-H), 4.28 (1 H, dt, $J_{3,4} = J_{4,5}$ = 9.5, 4-H), 4.65 (1 H, dd, $J_{6a,6b}$ 11.8, 6-H^a), 4.87 (1 H, dd, $J_{5,6b}$ 3.9, 6-H^b), 4.93 (1 H, dd, $^2J_{H,H}$ 1.5, $^3J_{H,H}$ 10.2, CH=CH_2), 5.00 (1 H, dd, $^3J_{H,H}$ 16.5, CH=CH_2), 5.01 (1 H, d, $J_{1,2}$ 1.5, 1-H), 5.61 (1 H, dd, $J_{2,3}$ 3.1, 2-H), 5.65 (1 H, dd, 3-H), 5.82 [1 H, ddt, J(H,CH_2) 6.5, CH_2CH=CH_2] and 7.30–8.14 (15 H, m, 3 × Ph); δ_C 26.08, 28.86, 29.01, 29.28, 29.34 and 33.72 (CH_2), 63.47 (C-6), 66.44 (C-4), 68.45 (OCH_2CH_2), 70.70 (C-2), 71.22 (C-5), 72.83 (C-3), 97.60 ($^1J_{C,H}$ 171, C-1), 114.09 (CH=CH_2), 128.29–129.87, 133.12–133.28 (Ph), 139.13 (CH=CH_2), 165.34, 166.69 and 166.81 (PhCO_2).

Dec-9-enyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-mannopyranoside 21

The reaction of compounds **8** (0.822 g, 2.0 mmol) and **20** (0.63 g, 1.0 mmol) in CH_2Cl_2 (15 cm^3) in the presence of AgO_3SCF_3 (0.6 g, 2.33 mmol) and 2,4,6-collidine (0.229 cm^3, 1.73 mmol) was accomplished at −20→+20 °C, as described for the preparation of the disaccharide **11**. Column chromatography (solvent *A*) gave the *disaccharide derivative* **21** (0.638 g, 67%) as an amorphous solid; $[\alpha]_D^{22}$ −10 (*c* 1, $CHCl_3$); R_f 0.37 (solvent *B*) (Found: C, 63.8; H, 6.2. $C_{51}H_{60}O_{18}$ requires C, 63.7; H, 6.3%); δ_H 1.34 (10 H, m, 5 × CH_2), 1.65 (2 H, quintet, *J* 6.5, $OCH_2CH_2CH_2$), 1.79, 1.93, 2.00 and 2.01 (12 H, 4 × s, 4 × Ac), 2.05 (2 H, quartet, *J* 6.5, CH_2CH_2CH=), 3.35–3.57 (3 H, m, OCH_2CH_2, 5'-H and 6'-H^a), 3.73 (1 H, dd, $J_{5',6b'}$ 6.9, $J_{6a',6b'}$ 10.0, 6'-H^b), 3.78 (1 H, dt, $^2J_{H,H}$ 9.6, $^3J_{H,H}$ 6.7, OCH_2CH_2), 4.21 (1 H, ddd, $J_{5,6a}$ 4.3, 5-H), 4.45 (1 H, t, $J_{3,4} = J_{4,5}$ = 9.0, 4-H), 4.50 (1 H, dd, $J_{6a,6b}$ 12.0, 6-H^a), 4.70 (1 H, d, $J_{1',2'}$ 7.9, 1'-H), 4.82 (1 H, dd, $J_{5,6b}$ 2.0, 6-H^b), 4.85–5.05 (4 H, m, CH=CH_2, 1- and 3'-H), 5.15 (1 H, br d, $J_{3',4'}$ 2.5, 4'-H), 5.16 (1 H, dd, $J_{2',3'}$ 10.5, 2'-H), 5.64 (1 H, dd, $J_{1,2}$ 1.9, 2-H), 5.81 (1 H, dd, $J_{2,3}$ 3.5, 3-H), 5.82 [1 H, ddt, $J_{H,H}$ 10.1, $J_{H,H}$ 16.7, J(H,CH_2) 6.5, CH_2CH=CH_2] and 7.30–8.15 (15 H, m, 3 × Ph); δ_C 20.40, 20.58 and 20.72 (*Me*CO), 26.17, 29.00, 29.16, 29.44 and 33.88 (CH_2), 60.35 (C-6'), 62.84 (C-6), 66.50 (C-4'), 68.81 (OCH_2CH_2), 69.28 (C-5), 69.47 (C-2'), 70.64 (3 C, C-2, -3 and -5'), 71.05 (C-3'), 74.17 (C-4), 97.62 (C-1), 101.15 (C-1'), 114.23 (CH=CH_2), 128.49–130.03 and 133.43 (Ph), 139.30 (CH=CH_2), 164.80, 165.31 and 166.05 (PhCO_2), 169.36, 169.88 and 170.16 (MeCO_2). Also isolated was *dec-9-enyl* 2,3,6-*tri*-O-*benzoyl*-4-O-(2,3,4,6-*tetra*-O-*acetyl*-α-D-*galactopyranosyl*)-α-D-*mannopyranoside* **22** (0.14 g, 15%) as an amorphous solid; $[\alpha]_D^{22}$ +38 (*c* 1, $CHCl_3$); R_f 0.46 (solvent *B*) (Found: C, 63.4; H, 6.4%); δ_H 1.34 (10 H, m, 5 × CH_2), 1.67 (2 H, quintet, *J* 6.5, $OCH_2CH_2CH_2$), 1.79, 1.90, 1.95 and 2.06 (12 H, 4 × s, 4 × Ac), 2.05 (2 H, quartet, *J* 6.5, CH_2CH_2CH=), 3.53 and 3.79 (2 H, 2 × dt, $^2J_{H,H}$ 9.8, $^3J_{H,H}$ 6.6, OCH_2CH_2), 3.89 (1 H, dd, $J_{5',6a'}$ 6.0, 6'-H^a), 4.05 (1 H, dd, $J_{6a',6b'}$ 10.8, 6'-H^b), 4.26 (1 H, ddd, $J_{5,6a}$ 4.1, 5-H), 4.36 (1 H, ddd, $J_{5',6b'}$ 7.1, 5'-H), 4.54 (1 H, t, $J_{3,4} = J_{4,5}$ = 9.3, 4-H), 4.61 (1 H, dd, $J_{6a,6b}$ 11.8, 6-H^a), 4.86 (1 H, dd, $J_{5,6b}$ 1.7, 6-H^b), 4.90–5.06 (3 H, m, CH=CH_2 and 1-H), 5.16 (1 H, dd, $J_{2',3'}$ 10.9, 2'-H), 5.30 (1 H, dd, $J_{3',4'}$ 3.0, 3'-H), 5.44 (1 H, dd, $J_{4',5'}$ 0.9, 4'-H), 5.53 (1 H, d, $J_{1',2'}$ 3.8, 1'-H), 5.62 (1 H, dd, $J_{1,2}$ 1.9, 2-H), 5.74 (1 H, dd, $J_{2,3}$ 3.4, 3-H), 5.83 [1 H, ddt, $J_{H,H}$ 10.2, $J_{H,H}$ 16.9, J(H,CH_2) 6.5, CH_2CH=CH_2] and 7.31–8.15 (15 H, m, 3 × Ph); δ_C 20.41 and 20.62 (*Me*CO), 26.16, 29.01, 29.18, 29.45, 29.77 and 33.89 (CH_2), 61.30 (C-6'), 63.71 (C-6), 66.73 (C-2'), 67.48 (C-3'), 67.56 (C-5'), 67.84 (C-4'), 68.91 (OCH_2CH_2), 69.12 (C-5), 70.31 (C-2), 71.95 (C-4), 73.23 (C-3), 97.48 (2 C, C-1 and -1'), 114.23 (CH=CH_2), 128.61, 129.71, 129.78, 133.40 and 133.54 (Ph), 139.17 (CH=CH_2), 165.42 and 166.25 (PhCO_2) and 170.0 (MeCO_2).

Dec-9-enyl 2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl)-α-D-mannopyranoside 7

A solution of HCl in MeOH [prepared at 0 °C from acetyl chloride (0.2 cm^3) and methanol (5 cm^3)] was added to a solution of compound **21** (0.524 g, 0.546 mmol) in $CHCl_3$ (1 cm^3), and the mixture was kept at 24 °C for 20 h; TLC (solvent *F*) then showed the formation of one major product (R_f 0.55; presumed to be the deacetylated compound **23**). The mixture was diluted with $CHCl_3$ (200–250 cm^3) and the solution was washed successively with saturated aq. $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated. The residue was dissolved in pyridine (10 cm^3), *p*,*p*'-dimethoxytriphenylmethyl chloride (0.222 g, 0.655 mmol) was added, and the solution was kept at room temperature for 16 h, whereafter a second portion of the reagent (0.2 g, 0.59 mmol) was added. After a further 20 h, benzoyl chloride (0.4 cm^3, 3.44 mmol) was added at −10 °C and the mixture was stirred overnight at 24 °C. Work-up as described above gave the crude product **24** (R_f 0.64, solvent *A*), which was dissolved in CH_2Cl_2 (30 cm^3), and 3% TFA in CH_2Cl_2 (30 cm^3) was added at 0 °C. After 2 min, the solution was washed in turn with saturated aq. $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated. Column chromatography [hexane–ethyl acetate, (2:1)] gave the *benzoylated disaccharide* **7** (0.426 g, 71%) as an amorphous solid; $[\alpha]_D^{24}$ +91.2 (*c* 1, $CHCl_3$); R_f 0.15 (solvent *A*), 0.40 (solvent *B*) (Found: C, 69.6; H, 6.0. $C_{64}H_{64}O_{17}$ requires C, 69.6; H, 5.8%); δ_H 1.30 (10 H, m, 5 × CH_2), 1.63 (2 H, quintet, *J* 6.5, $OCH_2CH_2CH_2$), 2.05 (2 H, quartet, *J* 6.5, CH_2CH_2CH=), 3.07 (1 H, dd, $J_{5',6a'}$ 7.2, 6'-H^a), 3.17 (1 H, dd, $J_{6a',6b'}$ 12.0, 6'-H^b), 3.21 (1 H, m, OH), 3.46 and 3.72 (2 H, 2 × dt, $^2J_{H,H}$ 9.5, $^3J_{H,H}$ 6.5, OCH_2CH_2), 3.61 (1 H, dd, $J_{5',6b'}$ 6.0, 5'-H), 4.16 (1 H, ddd, $J_{5,6a}$ 3.3, 5-H), 4.50 (1 H, dd, $J_{6a,6b}$ 12.0, 6-H^a), 4.55 (1 H, t, $J_{3,4} = J_{4,5}$ = 9.2, 4-H), 4.70 (1 H, dd, $J_{5,6b}$ 1.5, 6-H^b), 4.89–5.06 (2 H, m, CH=CH_2), 4.96 (1 H, d, $J_{1,2}$ 1.5, 1-H), 5.00 (1 H, d, $J_{1',2'}$ 7.9, 1'-H), 5.44 (1 H, dd, $J_{3',4'}$ 3.3, 3'-H), 5.62 (2 H, m, 2- and 4'-H), 5.80 (1 H, dd, $J_{2',3'}$ 10.1, 2'-H), 5.82 [1 H, ddt, $J_{H,H}$ 10.2, $J_{H,H}$ 16.5, J(H,CH_2) 6.5, CH_2CH=CH_2], 5.89 (1 H, dd, $J_{2,3}$ 3.6, 3-H) and 7.10–8.11 (30 H, m, 6 × Ph); δ_C 25.87, 28.74, 28.89, 29.16 and 33.63 (CH_2), 59.53 (C-6'), 62.38 (C-6), 68.30 (C-4'), 68.51 (OCH_2CH_2), 69.17 (C-5), 70.21 (C-2'), 70.30 (C-3), 70.72 (C-2), 71.79 (C-3'), 73.84 (2 C, C-4 and -5'), 97.33 (C-1), 101.14 (C-1'), 113.99 (CH=CH_2), 128.16–129.91 and 132.87–133.63 (Ph), 139.05 (CH=CH_2) and 164.94–166.43 (PhCO_2).

1,3,4,6-Tetra-*O*-acetyl-2-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-β-D-mannopyranose 27

Benzobromomannose **25** {$[\alpha]_D^{25}$ +12.8 (*c* 1, $CHCl_3$); δ_H 4.50 (1 H, dd, $J_{5,6a}$ 3.5, 6-H^a), 4.65 (1 H, ddd, $J_{5,6b}$ 2.0, 5-H), 4.74 (1 H, dd, $J_{6a,6b}$ 12.2, 6-H^b), 5.91 (1 H, dd, $J_{2,3}$ 3.0, 2-H), 6.19–6.35 (2 H, m, 3- and 4-H), 6.59 (1 H, d, $J_{1,2}$ 1.3, 1-H) and 7.21–8.18 (20 H, m, 4 × Ph)} was prepared from 1,2,3,4,6-penta-*O*-benzoyl-α,β-D-mannopyranose as described in ref. 10. The reaction of compounds **25** (0.604 g, 0.92 mmol) and **26** (0.21 g, 0.603 mmol) in CH_2Cl_2 in the presence of AgO_3SCF_3 (0.273 g, 1.06 mmol) and 2,4,6-collidine (0.105 cm^3, 0.8 mmol) was accomplished at −20→+20 °C, as described for the preparation of the disaccharide **11**. Column chromatography (solvent *C*) gave the *mannobiose derivative* **27** (0.559 g, 99.9%) as an amorphous solid; $[\alpha]_D^{22}$ −44 (*c* 1, $CHCl_3$); R_f 0.40 (solvent *C*) (Found: C, 62.5; H, 5.0. $C_{48}H_{46}O_{19}$ requires C, 62.2; H, 5.0%); δ_H 2.05, 2.19, 2.20 and 2.22 (12 H, 4 × s, 4 × Ac), 3.88 (1 H, ddd, $J_{5,6a}$ 2.3, 5-H), 4.24 (1 H, dd, $J_{6a,6b}$ 12.1, 6-H^a), 4.30 (1 H, dd, $J_{2,3}$ 2.6, 2-H), 4.38 (1 H, dd, $J_{5,6b}$ 4.7, 6-H^b), 4.44 (1 H, dd, $J_{5',6a'}$ 3.0, 6'-H^a), 4.71 (1 H, dd, $J_{6a',6b'}$ 12.0, 6'-H^b), 4.86 (1 H, ddd, $J_{5',6b'}$ 2.7, 5'-H), 5.23 (1 H, dd, 3-H), 5.32 (1 H, d, $J_{1',2'}$ 1.7, 1'-H), 5.50 (1 H, t, $J_{3,4} = J_{4,5}$ = 9.6, 4-H), 5.79 (1 H, dd, $J_{2',3'}$ 2.9, 2'-H), 5.90 (1 H, d, $J_{1,2}$ 0.9, 1-H), 6.07 (1 H, dd, 3'-H), 6.28 (1 H, t, $J_{3',4'} = J_{4',5'}$ = 10.0, 4'-H) and 7.22–8.10 (20 H, m, 4 × Ph);

δ_C 20.75, 20.83 and 21.10 (*Me*CO), 61.81 (C-6), 62.43 (C-6'), 65.85 (C-4), 66.69 (C-4'), 69.27 (2 C, C-3' and -5'), 70.71 (C-2'), 72.08 (C-3), 73.25 (C-5), 74.85 (C-2), 91.03 (C-1), 98.49 (C-1'), 128.40–129.89, 133.24 and 133.60 (Ph), 165.21, 165.31, 165.64 and 166.23 (Ph*C*O_2), 168.52, 169.44, 170.50 and 171.12 (Me*C*O_2).

3,4,6-Tri-*O*-acetyl-2-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-α-D-mannopyranose 28

Anhydrous dimethylamine (0.2 cm^3, 3.0 mmol) was added to a solution of compound **27** (0.508 g, 0.549 mmol) in MeCN (5 cm^3) at −20 °C, and the mixture was then kept at 20 °C for 5 h, with monitoring by TLC (solvent *C*). The mixture was concentrated and MeCN was evaporated off from the residue. The residue was then dissolved in $CHCl_3$ (200 cm^3); the solution was washed with water (3 × 70 cm^3), dried ($MgSO_4$), and concentrated to give the *α-hydroxy derivative* **28** (0.485 g, 99.8%) as an amorphous solid; $[\alpha]_D^{22}$ −55 (*c* 1, $CHCl_3$); R_f 0.28 (solvent *C*) (Found: C, 62.6; H, 4.9. $C_{46}H_{44}O_{18}$ requires C, 62.4; H, 5.0%); δ_H 2.05, 2.14 and 2.19 (9 H, 3 × s, 3 × Ac), 4.16 (2 H, m, 5- and 6-H), 4.24 (1 H, dd, $J_{2,3}$ 3.6, 2-H), 4.31 (1 H, dd, $J_{5,6b}$ 3.2, $J_{6a,6b}$ 11.5, 6-H^b), 4.43 (1 H, dd, $J_{5',6a'}$ 4.0, 6'-H^a), 4.57 (1 H, ddd, $J_{5',6b'}$ 2.0, 5'-H), 4.67 (1 H, dd, $J_{6a',6b'}$ 12.0, 6'-H^b), 5.25 (1 H, d, $J_{1',2'}$ 1.7, 1'-H), 5.48 (3 H, m, $J_{1,2}$ 1.9, 1-, 3- and 4-H), 5.75 (1 H, dd, $J_{2',3'}$ 3.3, 2'-H), 5.99 (1 H, dd, 3'-H), 6.14 (1 H, t, $J_{3',4'} = J_{4',5'}$ = 9.9, 4'-H) and 7.21–8.10 (20 H, m, 4 × Ph); δ_C 20.83, 20.92 and 21.58 (*Me*CO), 62.43 (C-6), 62.76 (C-6'), 66.50 (C-4'), 67.04 (C-4), 68.48 (C-5), 69.36 (C-3'), 69.51 (C-5'), 70.05 (C-3), 70.68 (C-2'), 77.45 (C-2), 92.96 ($^1J_{C,H}$ 171, C-1), 99.24 (C-1'), 128.38–129.93, 133.23 and 133.60 (Ph), 165.17, 165.34, 165.72 and 166.21 (Ph*C*O_2) and 169.62, 170.68 and 171.24 (Me*C*O_2).

Triethylammonium 3,4,6-tri-*O*-acetyl-2-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-α-D-mannopyranosyl hydrogenphosphonate 5

This compound was prepared from compound **28** (0.221 g, 0.25 mmol) as described for the derivative **6**. Column chromatography [CH_2Cl_2–MeOH–Et_3N, (98:1:1)→(93:6:1)] gave the *hydrogenphosphonate* **5** (0.24 g, 92%) as an amorphous solid; $[\alpha]_D^{22}$ −22 (*c* 1, $CHCl_3$); R_f 0.43 (solvent *F*); δ_H 1.23 (9 H, t, 3 × *Me*CH_2), 2.08, 2.17 and 2.20 (9 H, 3 × s, 3 × Ac), 2.93 (6 H, q, 3 × MeCH_2), 4.17 (1 H, br d, $J_{4,5}$ 10.0, 5-H), 4.30 (3 H, m, 2-H and 6-H_2), 4.43 (1 H, dd, $J_{5',6a'}$ 3.0, 6'-H^a), 4.62 (1 H, ddd, $J_{5',6b'}$ 2.0, 5'-H), 4.76 (1 H, dd, $J_{6a',6b'}$ 12.2, 6'-H^b), 5.28 (1 H, d, $J_{1',2'}$ 1.3, 1'-H), 5.52 (2 H, m, 3- and 4-H), 5.76 (1 H, dd, $J_{2',3'}$ 2.9, 2'-H), 5.87 (1 H, dd, $J_{1,2}$ 1.5, $J_{1,P}$ 8.9, 1-H), 5.99 (1 H, dd, 3'-H), 6.23 (1 H, t, $J_{3',4'} = J_{4',5'}$ = 10.0, 4'-H), 7.01 (1 H, d, $J_{H,P}$ 632.6, HP) and 7.25–8.14 (20 H, m, 4 × Ph); δ_C 9.34 and 45.63 (Et), 20.54 and 20.63 (*Me*CO), 62.10 (C-6), 62.32 (C-6'), 66.19 (C-4), 66.50 (C-4'), 69.39 (C-3'), 69.51 (2 C, C-5 and -5'), 70.27 (C-3), 70.54 (C-2'), 77.12 (d, $J_{C,P}$ 5.4, C-2), 93.34 (d, $J_{C,P}$ 3.6, $^1J_{C,H}$ 170, C-1), 98.91 (C-1'), 128.11–129.82 and 132.81–133.30 (Ph), 164.93, 165.09, 165.37 and 165.96 (Ph*C*O_2) and 169.29, 170.25 and 170.87 (Me*C*O_2); δ_P 1.88; FAB-MS(+) data: *m/z* 1050.74 (100%, [M + H]$^+$) ($C_{52}H_{60}NO_{20}P$ requires M, 1049.35).

Dec-9-enyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranoside 6-[2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranosyl phosphate], triethylammonium salt 29

A mixture of compounds **6** (129 mg, 0.09 mmol) and **7** (99 mg, 0.09 mmol) was dried by evaporation of pyridine (3 × 1 cm^3) therefrom. The residue was dissolved in pyridine (1 cm^3), adamantane-1-carbonyl chloride (47.5 mg, 0.239 mmol) was added, and the mixture was stirred at 20 °C for 30 min, whereafter a freshly prepared solution of iodine (46 mg, 0.18 mmol) in 95% aq. pyridine (2 cm^3) was added. After 10 min, $CHCl_3$ was added, and the solution was washed successively with cold 1 mol dm^{-3} $Na_2S_2O_3$ and cold 0.5 mol dm^{-3} TEA hydrogen carbonate, dried by filtration through cotton wool, and concentrated. The residue was dissolved in CH_2Cl_2 (6 cm^3), and 2% TFA in CH_2Cl_2 (6 cm^3) was added at 0 °C. After 1 min, the solution was washed successively with ice-cold saturated aq. $NaHCO_3$ and 0.5 mol dm^{-3} TEA hydrogen carbonate, dried by filtration through cotton wool, and concentrated. Column chromatography [CH_2Cl_2–MeOH–Et_3N, (98.8:0.2:1)→(95:4:1)] of the residue gave the *tetrasaccharide monophosphate derivative* **29** (163 mg, 81%) as an amorphous solid; $[\alpha]_D^{22}$ +70.2 (*c* 1, $CHCl_3$); R_f 0.43 (solvent *E*); δ_H 1.13 (9 H, t, 3 × *Me*CH_2), 1.30 (10 H, m, 5 × CH_2), 1.62 (2 H, quintet, *J* 6.5, $OCH_2CH_2CH_2$), 2.05 (2 H, quartet, *J* 6.5, CH_2CH_2CH=), 2.79 (6 H, quartet, 3 × MeCH_2), 3.04 (1 H, dd, $J_{6a,6b}$ 11.3, 6-H^a, Gal'), 3.18 (1 H, dd, 6-H^b, Gal'), 3.21 (1 H, dt, $J_{5,6a}$ 9.0, $J_{6a,6b}$ = $J_{6a,P}$ = 10.5, 6-H^a, Gal), 3.42 and 3.66 (2 H, 2 × dt, $^2J_{H,H}$ 9.5, $^3J_{H,H}$ 6.5, OCH_2CH_2), 3.52 (1 H, t, $J_{5,6a} = J_{5,6b}$ = 6.3, 5-H, Gal'), 3.88 (1 H, ddd, $J_{6b,P}$ 7.5, 6-H^b, Gal), 4.02 (1 H, dt, $J_{5,6a}$ = $J_{5,6b}$ = 2.5, 5-H, Man), 4.13 (1 H, dd, $J_{5,6b}$ 5.5, 5-H, Gal), 4.33 (1 H, br d, 5-H, Man'), 4.37 (1 H, m, 6-H^a, Man), 4.46 (1 H, m, 6-H^b, Man), 4.48 (1 H, t, $J_{3,4} = J_{4,5}$ = 9.5, 4-H, Man), 4.53 (1 H, t, $J_{3,4} = J_{4,5}$ = 9.5, 4-H, Man'), 4.56 (2 H, m, 6-H_2, Man'), 4.88–5.40 (2 H, m, CH=CH_2), 4.89 (1 H, d, $J_{1,2}$ 7.7, 1-H, Gal'), 4.94 (1 H, d, $J_{1,2}$ 2.0, 1-H, Man), 4.97 (1 H, d, $J_{1,2}$ 7.5, 1-H, Gal), 5.34 (1 H, dd, $J_{3,4}$ 3.5, 3-H, Gal'), 5.39 (1 H, dd, $J_{3,4}$ 3.4, 3-H, Gal), 5.45 (1 H, dd, $J_{1,2}$ 1.9, $J_{1,P}$ 7.0, 1-H, Man'), 5.55 (1 H, dd, $J_{2,3}$ 3.5, 2-H, Man), 5.57 (1 H, d, 4-H, Gal'), 5.67 (1 H, m, 2-H, Man'), 5.70 (1 H, dd, $J_{2,3}$ 10.0, 2-H, Gal'), 5.71 (1 H, m, C*H*=CH_2), 5.77 (1 H, dd, $J_{2,3}$ 2.5, 3-H, Man'), 5.83 (2 H, dd and d, $J_{2,3}$ 10.5, 2- and 4-H, Gal), 5.89 (1 H, dd, 3-H, Man) and 7.10–8.09 (60 H, m, 12 × Ph); δ_C 9.49 and 45.68 (Et), 25.95, 28.82, 29.00, 29.24 and 33.72 (CH_2), 60.04 (C-6, Gal'), 61.49 (d, $J_{C,P}$ 5.1, C-6, Gal), 62.26 (C-6, Man), 62.51 (C-6, Man'), 67.16 (C-4, Gal), 68.44 (2 C, OCH_2CH_2 + C-4, Gal'), 69.50 (C-3, Man'), 69.77 (C-5, Man), 69.83 (C-3, Man), 69.86 (C-5, Man'), 70.20 (C-2, Gal'), 70.40 (C-2, Gal), 70.70 (d, $J_{C,P}$ 8.5, C-2, Man'), 71.17 (C-2, Man), 71.87 (C-3, Gal'), 72.0 (d, $J_{C,P}$ 7.3, C-5, Gal), 72.50 (C-3, Gal), 72.83 (C-4, Man'), 74.08 (C-4, Man), 74.14 (C-5, Gal'), 93.44 (d, $J_{C,P}$ 4.8, C-1, Man'), 97.28 (C-1, Man), 100.45 (C-1, Gal'), 101.46 (C-1, Gal), 114.04 (CH=*C*H_2), 128.20–129.60, 132.94 and 133.17 (Ph), 139.13 (*C*H=CH_2) and 164.93–166.45 (Ph*C*O_2); δ_P −2.95 (dt, $J_{P,H}$ 7.5 and 10.5); FAB-MS(+) data: *m/z* 2157.77 (70%, [M − Et_3N + Na]$^+$) and 2236.22 (100, [M + H]$^+$) ($C_{124}H_{124}NO_{36}P$ requires M, 2235.31).

The condensation of compounds **6** and **7** in pyridine in the presence of either trimethylacetyl chloride (2.5 mol equiv.) or bis-(2-oxooxazolidin-3-yl)phosphinic chloride (2.5 mol equiv.), followed by oxidation and detritylation as described above, gave the compound **29** in 79 or 70% yield, respectively.

Dec-9-enyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranoside 6-{2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranosyl phosphate 6-[2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranosyl phosphate]}, bistriethylammonium salt 30

This compound was prepared by condensation of the disaccharide synthon **6** (165 mg, 0.115 mmol) and the tetrasaccharide block **29** (183 mg, 0.082 mmol) in the presence of adamantane-1-carbonyl chloride (57 mg, 0.288 mmol), followed by oxidation with iodine (46 mg, 0.18 mmol) and treatment with 0.7% TFA in CH_2Cl_2 (1 min, 0 °C), as described in the preparation of the compound **29**. Column chromatography [CH_2Cl_2–MeOH–Et_3N, (98.7:0.3:1)→(96:3:1)] gave the *hexasaccharide bisphosphate derivative* **30** (207 mg, 75%) as an amorphous solid; $[\alpha]_D^{22}$ +64.5 (*c* 1, $CHCl_3$); R_f 0.32

(solvent *E*); δ_C 9.82 and 45.91 (Et), 26.10, 28.80–29.20 and 33.61 (CH_2), 59.98 (C-6, Gal″), 61.36 (2 C, d, $J_{C,P}$ 4.2, C-6, Gal + C-6, Gal′), 62.06, 62.26 and 62.39 (C-6, Man; C-6, Man′; C-6, Man″), 67.10 and 67.11 (C-4, Gal; C-4, Gal′), 68.38 (2 C, OCH_2CH_2 + C-4, Gal″), 69.43 (2 C, C-3, Man′ + C-3, Man″), 69.73 (2 C), 69.77 (C-3 and -5, Man; C-5, Man″), 70.13 (C-5, Man′), 70.18 and 70.20 (C-2, Gal′; C-2, Gal″), 70.39 (C-2, Gal), 70.57 and 70.76 (2 d, $J_{C,P}$ 7.4 and 6.3, C-2, Man′; C-2, Man″), 71.14 (C-2, Man), 71.83 (C-3, Gal″), 71.90 and 72.0 (2 d, $J_{C,P}$ 7.6 and 7.1, C-5, Gal; C-5, Gal′), 72.38 and 72.43 (C-3, Gal; C-3, Gal′), 72.76 (C-4, Man″), 73.39 (C-4, Man′), 73.99 (C-4, Man), 74.07 (C-5, Gal″), 93.33 (2 C, d, $J_{C,P}$ 4.2, C-1, Man′ + C-1, Man″), 97.23 (C-1, Man), 100.33 (C-1, Gal″), 101.19 (C-1, Gal′), 101.40 (C-1, Gal), 114.01 ($CH{=}CH_2$), 128.40–129.82 and 132.90–133.90 (Ph), 139.45 ($CH{=}CH_2$) and 164.65–166.09 ($PhCO_2$); δ_P −2.99 (dt, $J_{P,H}$ 7.5 and 10.5, P) and −3.08 (dt, $J_{P,H}$ 7.5 and 10.5, P′); ES-MS(−) data: *m/z* 1580.1 (100%, $[M - 2\ Et_3N - 2\ H]^{2-}$) ($C_{184}H_{184}N_2O_{55}P_2$ requires M, 3363.12).

Dec-9-enyl 2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranoside 6-[2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranosyl phosphate 6-{2,3,4-tri-*O*-benzoyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-benzoyl-α-D-mannopyranosyl phosphate 6-[2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl-(1→2)-3,4,6-tri-*O*-acetyl-α-D-mannopyranosyl phosphate]}], tristriethylammonium salt 31

This compound was prepared by condensation of the disaccharide synthon **5** (52.5 mg, 0.05 mmol) and the hexasaccharide block **30** (107 mg, 0.0318 mmol) in the presence of adamantane-1-carbonyl chloride (25 mg, 0.125 mmol), followed by oxidation with iodine (25 mg, 0.1 mmol), as described for the synthesis of compound **29**. Column chromatography [CH_2Cl_2–MeOH–water–Et_3N, (98.8:0.18:0.02:1)→(89:9:1:1)] gave the *protected octasaccharide trisphosphate* **31** (125 mg, 89%) as an amorphous solid; $[\alpha]_D^{22}$ +31.2 (*c* 1, $CHCl_3$); R_f 0.60 (solvent *G*); δ_C 8.44 and 45.51 (Et), 25.92, 28.84–29.52, 33.61 (CH_2), 61.38 (3 C, br, C-6, Gal + C-6, Gal′ + C-6, Gal″), 61.93, 62.07, 62.14, 62.32 and 62.43 (C-6, Man; C-6, Man′; C-6, Man″; C-6, Man‴; C-6, Man⁗), 65.92 (C-4, Man‴), 66.53 (C-4, Man⁗), 67.14 (3 C, C-4, Gal + C-4, Gal′ + C-4, Gal″), 68.42 (OCH_2CH_2), 69.07 (C-5, Man‴), 69.27 (C-3, Man⁗), 69.44 (2 C, C-3, Man′ + C-3, Man″), 69.72 (2 C), 69.81 (C-3 and -5, Man; C-5, Man⁗), 70.14 (2 C, C-5, Man′ + C-5, Man″), 70.20 and 70.24 (C-2, Gal′; C-2, Gal″), 70.31 (C-3, Man‴), 70.43 (C-2, Gal), 70.51 and 70.82 (2 d, $J_{C,P}$ 7.2, C-2, Man′; C-2, Man″), 70.61 (C-2, Man⁗), 71.19 (C-2, Man), 71.61 (d, $J_{C,P}$ 7.2, C-5, Gal″), 71.85 and 71.95 (2 d, $J_{C,P}$ 7.2, C-5, Gal; C-5, Gal′), 72.37, 72.40 and 72.49 (C-3, Gal; C-3, Gal′; C-3, Gal″), 73.36 and 73.44 (C-4, Man′; C-4, Man″), 74.05 (C-4, Man), 77.21 (d, $J_{C,P}$ 6.0, C-2, Man‴), 93.35 (2 C, br, C-1, Man′ + C-1, Man″), 94.20 (C-1, br, Man‴), 97.27 (C-1, Man), 98.91 (C-1, Man⁗), 101.16 (C-1, Gal″), 101.20 (C-1, Gal′), 101.44 (C-1, Gal), 114.02 ($CH{=}CH_2$), 127.82–130.0 and 132.38–133.27 (Ph), 139.12 ($CH{=}CH_2$), 164.76–166.12 ($PhCO_2$), and 169.05, 170.34 and 170.88 ($MeCO_2$); δ_P −2.55 (dt, $J_{P,H}$ 7.5 and 10.5, P⁗), −2.95 (dt, $J_{P,H}$ 7.5 and 10.5, P) and −3.02 (dt, $J_{P,H}$ 7.5 and 10.5, P′); ES-MS(−) data: *m/z* 1368.5 (100%, $[M - 3\ Et_3N - 3\ H]^{3-}$) and 2053.6 (35, $[M - 3\ Et_3N - 2\ H]^{2-}$) ($C_{236}H_{242}N_3O_{75}P_3$ requires M, 4410.44).

Dec-9-enyl β-D-galactopyranosyl-(1→4)-α-D-mannopyranoside 1

To a solution of compound **21** (102 mg) in MeOH (20 cm^3) was added 4.6 mol dm^{-3} NaOMe in MeOH (0.44 cm^3). The mixture was kept at room temp. for 2 h, deionised with Dowex 50W-X4 (H^+) resin, and concentrated to dryness. Water (5 × 10 cm^3) was evaporated off from the residue to remove methyl benzoate. The *disaccharide* **1** (51 mg, 99.99%) was thereby obtained as an amorphous solid; $[\alpha]_D^{22}$ +41.5 (*c* 1, MeOH); R_f 0.69 (solvent *I*); $\delta_H(D_2O)$ (*inter alia*) 1.32 (10 H, m, 5 × CH_2), 1.60 (2 H, quintet, *J* 6.5, $OCH_2CH_2CH_2$), 2.03 (2 H, quartet, *J* 6.5, $CH_2CH_2CH{=}$), 3.32 (1 H, dt, *J* 6.5, OCH_2CH_2), 3.61 (1 H, dd, 2′-H), 3.78 (3 H, m, OCH_2CH_2 and 3′- and 4-H), 3.89 (1 H, dd, 3-H), 3.95 (1 H, d, 4′-H), 3.99 (1 H, dd, 2-H), 4.48 (1 H, d, $J_{1',2'}$ 7.5, 1′-H), 4.82 (1 H, d, $J_{1,2}$ 1.5, 1-H), 4.91 (1 H, br d, *J* 10.0, $CH{=}CH_2$), 4.97 (1 H, br d, *J* 17.0, $CH{=}CH_2$) and 5.77 [1 H, ddt, $J_{(H,CH_2)}$ 6.5, $CH_2CH{=}CH_2$]; δ_C, see Table 1; ES-MS(+) data: *m/z* 503.3 (100%, $[M + Na]^+$) and 983.5 (22, $[2\ M + Na]^+$); ES-MS(−) data: *m/z* 479.4 (100%, $[M - H]^-$) and 959.5 (15, $[2\ M - H]^-$) ($C_{22}H_{40}O_{11}$ requires M, 480.26).

Dec-9-enyl β-D-galactopyranosyl-(1→4)-α-D-mannopyranoside 6^{Gal}-[β-D-galactopyranosyl-(1→4)-α-D-mannopyranosyl phosphate], triethylammonium salt 2

To a solution of compound **29** (70 mg) in MeOH (20 cm^3) was added 4.6 mol dm^{-3} NaOMe in MeOH (0.22 cm^3). The mixture was kept for 2 h at 24 °C and for 16 h at 1 °C, then was deionised with Dowex 50W-X4 (H^+) resin, filtered, and immediately neutralised with Et_3N. After concentration, water (5 × 10 cm^3) was evaporated off from the residue to remove methyl benzoate. The *tetrasaccharide monophosphate* **2** (30.5 mg, 98.8%) was thereby obtained as an amorphous solid; $[\alpha]_D^{22}$ +40.5 (*c* 1, MeOH); R_f 0.59 (solvent *H*), 0.24 (solvent *I*); $\delta_P(D_2O)$ −1.28; δ_C, see Table 1; ES-MS(−) data: *m/z* 883.4 (100%, $[M - Et_3N - H]^-$) and 1789.6 (2, $[2\ M - 2\ Et_3N - 2\ H + Na]^-$) ($C_{40}H_{76}NO_{24}P$ requires M, 985.45).

Dec-9-enyl β-D-galactopyranosyl-(1→4)-α-D-mannopyranoside 6^{Gal}-{β-D-galactopyranosyl-(1→4)-α-D-mannopyranosyl phosphate 6^{Gal}-[β-D-galactopyranosyl-(1→4)-α-D-mannopyranosyl phosphate]}, bistriethylammonium salt 3

O-Deacylation of compound **30** (55 mg) with 0.05 mol dm^{-3} NaOMe in MeOH, followed by work-up as in the preceding experiment, gave the *hexasaccharide diphosphate* **3** (24 mg, 98.5%) as an amorphous solid; $[\alpha]_D^{21}$ +20 (*c* 1, MeOH); R_f 0.48 (solvent *H*); $\delta_P(D_2O)$ −1.29; δ_C, see Table 1; ES-MS(−) data: *m/z* 643.3 (100%, $[M - 2\ Et_3N - 2\ H]^{2-}$), 693.4 (20, $[M - Et_3N - 2\ H]^{2-}$), 1287.5 (2, $[M - 2\ Et_3N - H]^-$) and 1309.4 (5, $[M - 2\ Et_3N - 2\ H + Na]^-$) ($C_{58}H_{112}N_2O_{37}P_2$ requires M, 1490.64).

Dec-9-enyl β-D-galactopyranosyl-(1→4)-α-D-mannopyranoside 6^{Gal}-[β-D-galactopyranosyl-(1→4)-α-D-mannopyranosyl phosphate 6^{Gal}-{β-D-galactopyranosyl-(1→4)-α-D-mannopyranosyl phosphate 6^{Gal}-[α-D-mannopyranosyl-(1→2)-α-D-mannopyranosyl phosphate]}], tristriethylammonium salt 4

O-Deacylation of compound **31** (100 mg) with 0.05 mol dm^{-3} NaOMe in MeOH, followed by work-up as described in the preparation of the tetrasaccharide **2**, gave the *octasaccharide trisphosphate* **4** (45 mg, 99.5%) as an amorphous solid; $[\alpha]_D^{21}$ +39.5 (*c* 1, MeOH); R_f 0.30 (solvent *H*); $\delta_H(D_2O)$ (*inter alia*) 1.27 (10 H, m, 5 × CH_2), 1.59 (2 H, quintet, *J* 6.5, $OCH_2CH_2CH_2$), 2.05 (2 H, quartet, *J* 6.5, $CH_2CH_2CH{=}$), 4.46 (3 H, d, $J_{1,2}$ 7.4, 1-H, Gal + 1-H, Gal′ + 1-H, Gal″), 4.87 (1 H, d, $J_{1,2}$ 1.2, 1-H, Man), 4.96 (1 H, br d, *J* 10.0, $CH{=}CH_2$), 5.04 (1 H, br d, *J* 17.0, $CH{=}CH_2$), 5.06 (1 H, d, $J_{1,2}$ 1.2, 1-H, Man⁗), 5.43 (2 H, dd, $J_{1,2}$ 1.2, $J_{1,P}$ 7.2, 1-H, Man′ + 1-H, Man″), 5.65 (1 H, dd, $J_{1,2}$ 1.2, $J_{1,P}$ 7.2, 1-H, Man‴) and 5.92 [1 H, ddt, $J_{(H,CH_2)}$ 6.5, $CH_2CH{=}CH_2$]; $\delta_P(D_2O)$ −1.27; δ_C, see Table 1; ES-MS(−) data: *m/z* 563.3 (100%, $[M - 3\ Et_3N - 3\ H]^{3-}$), 845.4 (13, $[M - 3\ Et_3N - 2\ H]^{2-}$), 856.2 (40, $[M - 3\ Et_3N - 3\ H + Na]^{2-}$), 864.3 (4, $[M - 3\ Et_3N - 3\ H + K]^{2-}$), 867.5 (4, $[M - 3\ Et_3N - 4\ H + 2\ Na]^{2-}$), 1729.5 (1, $[M - 3\ Et_3N - 2\ H + K]^-$) and 1735.5 (2, $[M - 3\ Et_3N - 3\ H + 2\ Na]^-$) ($C_{76}H_{148}N_3O_{50}P_3$ requires M, 1995.83).

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