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SYNTHESIS OF A TRI- AND A HEPTA-SACCHARIDE WHICH CONTAIN α-L-FUCOPYRANOSYL GROUPS AND ARE PART OF THE COMPLEX TYPE OF CARBOHYDRATE MOIETY OF GLYCOPROTEINS

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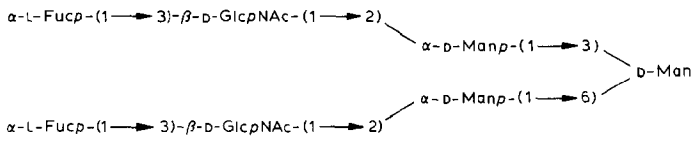
ABSTRACT

Reaction of a thioglycoside with methyl trifluoromethanesulfonate (methyl triflate) in the presence of a hydroxyl compound is an efficient glycosylation method. Thus, methyl triflate-promoted condensation of ethyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-glucopyranoside with benzyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside and with benzyl 2,4-di-*O*-benzyl-3,6-di-*O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-α-D-mannopyranoside gave a trisaccharide and a heptasaccharide derivative, respectively. The trisaccharide **1** and the heptasaccharide **2**, which are parts of the complex type of glycoproteins, were obtained by removal of the protecting groups and *N*-acetylation.

α-L-Fuc*p*-(1→3)-β-D-Glc*p*NAc-(1→2)-D-Man

1



2

INTRODUCTION

As part of our programme on the synthesis of oligosaccharides which form part of the carbohydrate portion of the complex (*N*-acetyl-D-lactosaminic) type of glycoproteins[1], and investigation of their biological activity[2,3], we now report the

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synthesis of oligosaccharides **1** and **2**. These oligosaccharides, which contain terminal α-L-fucopyranosyl groups, are structural elements of glycopeptides isolated from urine of patients with fucosidosis[4].

As in previous studies, the oligosaccharides were prepared by block synthesis. A new and efficient method, using thioglycosides as glycosylating agents and methyl triflate as promoter, has been developed.

RESULTS AND DISCUSSION

Trisaccharide **1** and heptasaccharide **2** contain the common disaccharide residue **3**. A suitable protected derivative of **3**, namely **8**, was therefore prepared and used in the subsequent synthesis.

Ethyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**5**) was prepared by conventional methods. 2,3,4-Tri-*O*-benzyl-α-L-fucopyranosyl bromide[5] (**7**) was prepared by treating the corresponding ethyl 1-thio-β-L-glycoside **6** with bromine[6]. Reaction of **5** with **7** in dichloromethane–*N*,*N*-dimethylformamide, in the presence of 4 Å molecular sieves and promoted by tetraethylammonium bromide, gave 81% of **8**.

The use of thioglycosides as glycosidation agents is well known[7–11] but, in our hands, none of the reported methods was successful for reacting **8** with benzyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside[12] (**9**). Methyl triflate, however, proved to be an efficient promoter for these reactions. One problem was concurrent elimination, giving the glycal derivative **11**, but this side-reaction was minimised by performing the reaction in ether at room temperature and in the presence of 4 Å molecular sieves as an acid acceptor. Under these conditions and with chromatography of the product mixture, 72% of the trisaccharide derivative **10** and 9% of the glycal **11** were obtained. The function of the methyl triflate is to *S*-methylate the thioglycoside and generate a sulfonium salt, thereby producing an efficient glycosylating agent. *O*-Methylated products, which might also be formed concurrently, could not be detected by t.l.c.

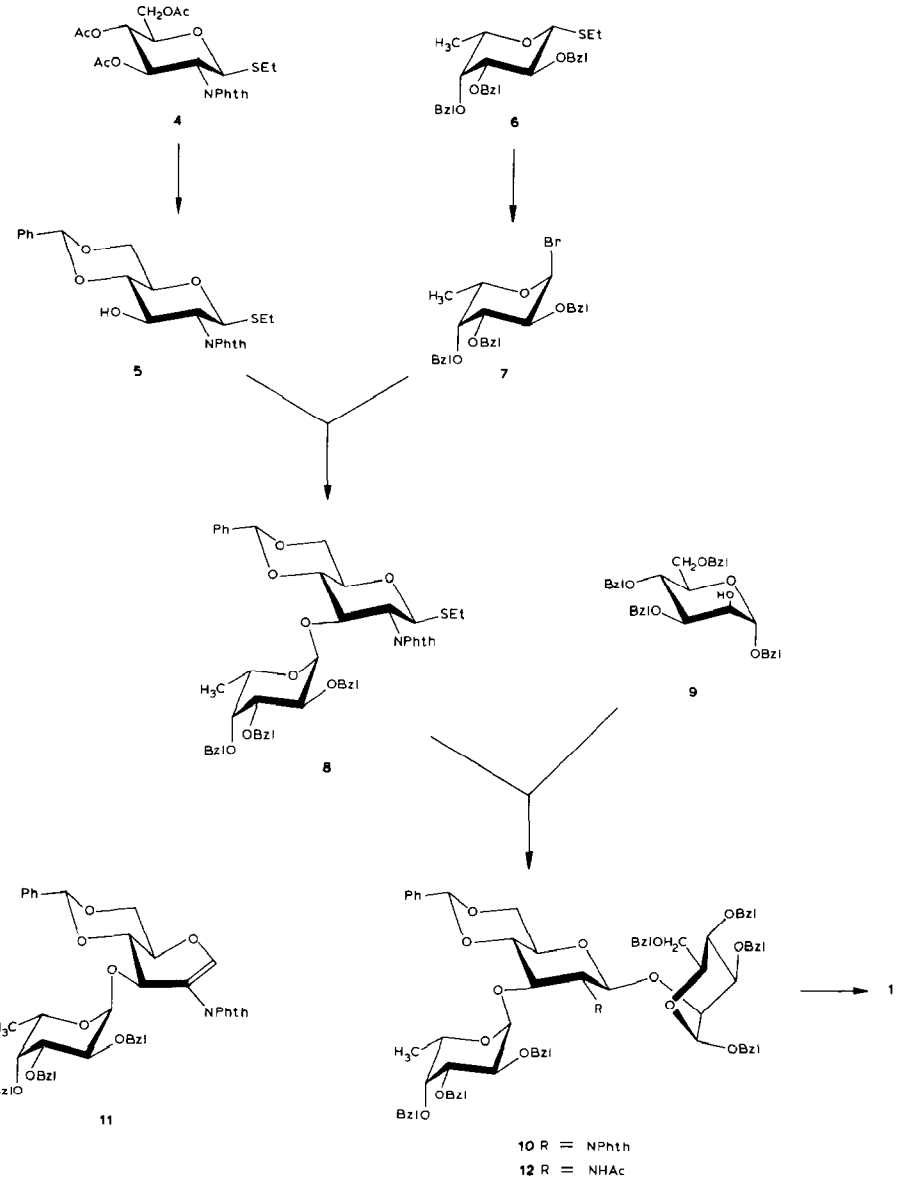
Treatment of **10** first with hydrazine hydrate in boiling ethanol and then with acetic anhydride–pyridine, followed by chromatography of the product, yielded **12** (86%). Hydrogenolysis of **12** and chromatography of the product on Biogel P-2 then yielded **1** (85%).

For the synthesis of heptasaccharide derivative **14**, the mannotrioside **13** was used. This substance, which had been prepared by Arnarp and Lönngren[13], was synthesised by a slightly modified procedure, using silver triflate instead of mercury(II) cyanide–mercury(II) bromide as promoter in the glycosidation step. With silver triflate, the yield of **13** was increased from 49 to 67%.

Reaction of **13** with the thioglycoside **8**, promoted by methyl triflate as described above, gave 63% of the heptasaccharide derivative **14**. The heptasaccharide **2** (59%) was prepared from **14** as described above for the corresponding tetrasaccharide, followed by gel filtration of the product.

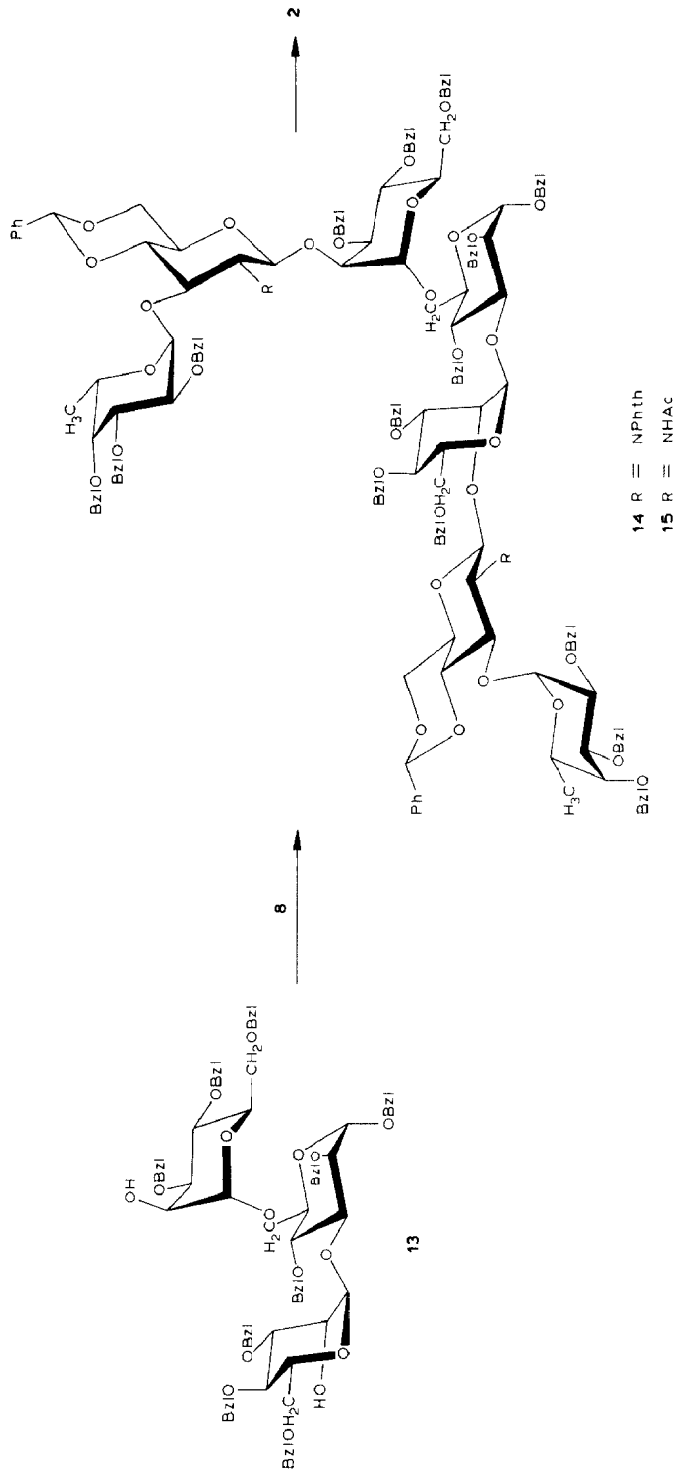
α-L-Fucp-(1→3)-β-D-GlcpNAc

3



10 R = NPhth

12 R = NHAc


2
8
13
14 R = NPhth
15 R = NHAc

All the above synthesis intermediates and also **1** and **2** gave ^{1}H- and ^{13}C-n.m.r. spectra in agreement with the postulated structures. The purity of **1** and **2** was also determined by chromatography.

EXPERIMENTAL

General methods. — Commercially available methyl triflate was used. Melting points are corrected. Concentrations were performed at <40° (bath). Optical rotations were measured with a Perkin–Elmer 241 polarimeter. ^{13}C-N.m.r. spectra (25 MHz) were recorded with a JEOL FX-100 spectrometer and ^{1}H-n.m.r. spectra (100 MHz, 400 MHz) with a JEOL FX-100 or JEOL GX-400 spectrometer for solutions in $CDCl_3$ (internal Me_4Si) or D_2O [external Me_4Si (^{13}C), internal HOD (^{1}H)]. Silica gel 60 F-254 (Merck) was used for t.l.c. with detection by u.v. fluorescence or by charring with sulfuric acid. Column chromatography was performed on silica gel 60 (Merck, 0.040–0.063). Elemental analyses were performed by Novo Microanalytical Laboratory (Bagsværd, Denmark). Satisfactory elemental analyses were not obtained for syrupy or amorphous products, but they were shown to be pure by chromatography and n.m.r. spectroscopy.

Ethyl 3,4,6-tri-O-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**4**). — Titanium tetrachloride (3.0 mL) was added to a stirred mixture of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-2-phthalimido-β-D-glucopyranose[14] (10.0 g), ethanethiol (4.0 mL), and ground molecular sieves (15 g, 4 Å) in dichloromethane (100 mL) at 0°. After 1 h at room temperature, the mixture was filtered through a layer of Celite, washed with ice-cold M sulfuric acid, aqueous sodium hydrogencarbonate, and water, dried (Na_2SO_4), and concentrated. The residue was crystallised from ethyl acetate–light petroleum to give **4** (7.21 g, 72%), m.p. 118–119°, $[\alpha]_{578}^{22}$ +44° (*c* 0.8, dichloromethane). N.m.r. data: ^{1}H (100 MHz), δ 5.48 (d, 1 H, 10 Hz, H-1); ^{13}C, δ 14.4 (CH_3CH_2), 20.6, 20.7, 20.8 (3 Ac), 24.6 (CH_3CH_2), 53.9 (C-2), 69.2, 71.8, 76.2 (C-3,4,5), 81.3 (C-1), 123.9, 131.6, 134.7 (aromatic), 166.8, 167.3 (Pht), 169.6, 170.1, 170.7 (OAc).

Anal. Calc. for $C_{22}H_{25}NO_9S$: C, 55.1; H, 5.3; N, 2.9; S, 6.7. Found: C, 54.7; H, 5.3; N, 2.9; S, 6.1.

Ethyl 4,6-O-benzylidene-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (**5**). — Sodium methoxide in methanol (25 mL, 0.3M) was added to a stirred solution of **4** (25.0 g) in dichloromethane–methanol (125 mL, 3:2) at room temperature. After 2 h, acetic acid (0.6 mL) was added and the solution was concentrated. Toluene (100 mL) was distilled from the residue, which was then dissolved in *N,N*-dimethylformamide (100 mL) containing α,α-dimethoxytoluene (15 mL) and toluene-*p*-sulfonic acid (1.72 g). The mixture was stirred at 50° for 1 h, cooled, and partitioned between aqueous sodium hydrogencarbonate and toluene. The organic layer was washed with water, dried (Na_2SO_4), treated with silica gel (5 g) for 5 min, filtered, and concentrated. Crystallisation of the product from iso-octane (500 mL) and ethyl acetate (25 mL) gave **5** (16.7 g, 73%), m.p. 168°, $[\alpha]_{578}^{22}$ −9° (*c* 0.9,

dichloromethane). ^{13}C-N.m.r. data: δ 14.8 (CH_3CH_2), 24.0 (CH_3CH_2), 55.9 (C-2), 68.5, 69.5, 70.4, 81.9, 82.0 (C-1,3,4,5,6), 101.7 (PhCH), 123.4, 126.3, 128.1, 129.1, 131.6, 134.0, 137.2 (aromatic), 167.9 (Pht).

Anal. Calc. for $C_{23}H_{23}NO_6S$: C, 62.6; H, 5.2; N, 3.2; S, 7.3. Found: C, 62.5; H, 5.4; N, 3.3; S, 7.2.

*Ethyl 2,3,4-tri-*O*-benzyl-1-thio-β-*L*-fucopyranoside* (**6**). — α-L-Fucose (10.0 g) was treated with acetic anhydride–pyridine (300 mL, 2:1) at 100° for 1 h. The solution was concentrated and xylene (2 × 50 mL) was distilled from the residue. The product was dissolved in dichloromethane (250 mL), and ground molecular sieves (25 g, 4 Å), ethanethiol (4.5 mL), and zinc chloride (24.5 g) were added. The mixture was stirred for 3 h, filtered through a layer of Celite, washed with ice-cold M sulfuric acid, aqueous sodium hydrogencarbonate, and water, dried (Na_2SO_4), and concentrated. The residue was dissolved in methanol (250 mL) containing a catalytic amount of sodium methoxide and stirred until t.l.c. revealed one major component having R_F 0.14 (chloroform–acetone, 2:1). The solution was concentrated, and a solution of the residue in *N,N*-dimethylformamide (150 mL) containing benzyl bromide (32 mL) was added to sodium hydride (8.8 g) at 0° and under nitrogen. After 1 h, methanol (20 mL) was added, the mixture was partitioned between toluene and water, and the organic layer was washed with water and concentrated. The product was purified by column chromatography (light petroleum–ethyl acetate, 5:1) to yield **6** (16.4 g, 56%), m.p. 53° (from iso-octane), $[\alpha]_{578}^{22}$ −16° (*c* 1.5, dichloromethane). N.m.r. data: ^{1}H (400 MHz), δ 4.39 (d, 1 H, 9.3 Hz, H-1); ^{13}C, δ 15.0 (CH_3CH_2), 17.2 (C-6), 24.5 (CH_3CH_2), 72.7, 74.5 (2 C), 75.5, 76.5, 78.3, 84.4, 84.5 (C-1,2,3,4,5, and 3 PhCH$_2$), 127.4–128.3, 138.4 (2 C), 138.7 (aromatic).

Anal. Calc. for $C_{29}H_{34}O_4S$: C, 74.0; H, 7.3. Found: C, 73.1; H, 7.2.

*Ethyl 4,6-*O*-benzylidene-2-deoxy-2-phthalimido-1-thio-3-*O*-(2,3,4-tri-*O*-benzyl-α-*L*-fucopyranosyl)-β-*D*-glucopyranoside* (**8**). — Bromine (0.165 mL) was added to a solution of **6** (1.52 g) in dichloromethane (20 mL) at 0°. After 20 min, the solution was concentrated and toluene (2 × 25 mL) was distilled from the residue, a solution of which in dichloromethane (3 mL) was added to a stirred mixture of **5** (0.75 g), tetraethylammonium bromide (0.67 g), and ground molecular sieves (3 g, 4 Å) in *N,N*-dimethylformamide (4 mL). The mixture was stirred for 18 h, ethanol (1 mL) was then added, and, after 1 h, the mixture was filtered through a layer of Celite, diluted with toluene, washed with aqueous sodium hydrogencarbonate and water, and concentrated. The product was purified by column chromatography (toluene–ethyl acetate, 15:1), to give **8** as a syrup (1.18 g, 81%), $[\alpha]_{578}^{22}$ −36° (*c* 1, dichloromethane), R_F 0.45. ^{13}C-N.m.r. data: δ 14.0 (CH_3CH_2), 15.5 (C-6′), 23.1 (CH_3CH_2), 53.7 (C-2), 66.4, 67.7, 69.7, 71.8, 72.2, 73.8, 74.6, 75.5, 77.1, 78.7, 80.9, 81.1 (C-1,3,4,5, C-2′,3′,4′,5′ and 3 PhCH$_2$), 98.5 (C-1′, $J_{C\text{-}1',H\text{-}1'}$ 167 Hz), 100.2 (PhCH), 122.3, 125.1, 126.1–128.0, 131.0, 132.9, 136.2, 137.4, 137.6, 137.9 (aromatic), 166.8, 167.3 (Pht).

*Benzyl 3,4,6-tri-*O*-benzyl-2-*O*-[4,6-*O*-benzylidene-2-deoxy-2-phthalimido-3-*

O-*(2,3,4-tri*-O-*benzyl*-α-L-*fucopyranosyl)*-β-D-*glucopyranosyl]*-α-D-*mannopyranoside* (**10**) *and 1,5-anhydro-4,6*-O-*benzylidene-2-deoxy-2-phthalimido-3*-O-*(2,3,4-tri*-O-*benzyl*-α-L-*fucopyranosyl)*-D-arabino-*hex-1-enitol* (**11**). — Methyl triflate (78 μL) was added to a stirred mixture of benzyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside[12] (**9**, 77 mg), **8** (122 mg), ether (10 mL), and ground molecular sieves (1 g, 4 Å) at room temperature. Triethylamine (200 μL) was added after 24 h and the mixture was stirred for 10 min, filtered through a layer of Celite, concentrated, and purified by column chromatography (toluene–ethyl acetate, 15:1), to yield **10** as a syrup (138 mg, 72%), $[\alpha]_{578}^{22}$ −6° (*c* 0.7, chloroform), R_F 0.45. ^{13}C-N.m.r. data: δ 16.4 (C-6″), 55.6 (C-2′), 66.4–81.9 (ring C, Ph*C*H$_2$), 96.6 (C-1′), 97.5 (C-1), 99.5 (C-1″), 101.1 (Ph*C*H), 122.6–138.8 (aromatic), 168.1 (Pht).

Eluted second was **11**, obtained as a syrup (10 mg, 9%), $[\alpha]_{578}^{22}$ −14° (*c* 1, chloroform), R_F 0.37. ^{13}C-N.m.r. data: δ 16.5 (C-6′), 67.3–79.7 (ring C, Ph*C*H$_2$), 99.6 (C-1′), 101.2 (Ph*C*H), 108.8, 123.3, 126.1–128.9, 132.3, 133.7, 136.9, 138.6, 138.9, 147.3 (C-1,2, aromatic), 168.0 (Pht).

Benzyl 2-O-*[2-acetamido-4,6*-O-*benzylidene-2-deoxy-3*-O-*(2,3,4-tri*-O-*benzyl*-α-L-*fucopyranosyl)*-β-D-*glucopyranosyl]-3,4,6-tri*-O-*benzyl*-α-D-*mannopyranoside* (**12**). — A solution of **10** (405 mg) and hydrazine hydrate (8 mL) in aqueous 90% ethanol (80 mL) was boiled under reflux overnight, cooled, and concentrated to dryness. The residue was acetylated with acetic anhydride–pyridine (15 mL, 1:2) at room temperature overnight. The solution was concentrated, and the product was purified by column chromatography (toluene–ethyl acetate, 3:1) to yield **12** as a syrup (322 mg, 86%), $[\alpha]_{578}^{22}$ −32° (*c* 1.1, chloroform), R_F 0.31. ^{13}C-N.m.r. data: δ 16.2 (C-6″), 23.2 (NAc), 59.2 (C-2′), 66.2–80.7 (ring C, Ph*C*H$_2$), 97.2, 97.8, 98.6 (C-1,1′,1″), 101.7 (Ph*C*H), 120.9–138.8 (aromatic), 171.2 (NAc).

2-O-*(2-Acetamido-2-deoxy-3*-O-α-L-*fucopyranosyl*-β-D-*glucopyranosyl)*-D-*mannose* (**1**). — A solution of **12** (270 mg) in acetic acid–ethyl acetate–water (30 mL, 9:5:1) was hydrogenolysed at 400 kPa over 10% Pd/C (300 mg) overnight. The mixture was filtered and concentrated, and the product was purified on a column (2.5 × 80 cm) of Biogel P-2 by elution with water. After freeze-drying, **1** was obtained as an amorphous powder (97 mg, 85%), $[\alpha]_{578}^{22}$ −100° (*c* 0.4, water), R_F 0.50 (ethyl acetate–methanol–acetic acid–water, 4:3:3:2). N.m.r. data: ^{1}H (100 MHz, 85°), δ 1.14 (d, 3 H, $J_{5,6}$ 6.8 Hz, H-6″), 2.03 (s, 3 H, HNAc), 4.26 (q, 1 H, $J_{5,6}$ 6.8 Hz, H-5″), 4.60 (d, 1 H, $J_{1,2}$ 7.8 Hz, H-1′), 4.89 (d, 0.15 H, $J_{1,2}$ 0.5 Hz, H-1β), 4.98 (d, 1 H, $J_{1,2}$ 2.9 Hz, H-1″), 5.14 (d, 0.85 H, $J_{1,2}$ 2.0 Hz, H-1α); ^{13}C, δ 16.4 (C-6″), 23.5 (0.85 C, NAc α), 23.7 (0.15 C, NAc β), 56.3 (0.85 C, C-2′α), 56.7 (0.15 C, C-2′β), 61.8, 62.7 (C-6,6′), 68.0, 68.6, 69.2, 69.6, 70.4, 70.7, 73.0, 73.7, 77.0, 78.4, 81.0 (ring C), 92.3 (0.85 C, C-1α), 95.2 (0.15 C, C-1β), 100.5 (0.85 C, C-1′α), 100.9 (C-1″), 102.4 (0.15 C, C-1′β), 175.9 (0.85 C, NAc α), 176.2 (0.15 C, NAc β).

Benzyl 2,4-di-O-*benzyl-3,6-di*-O-*(3,4,6-tri*-O-*benzyl*-α-D-*mannopyranosyl)*-α-D-*mannopyranoside* (**13**). — A solution of 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl chloride[13] (7.90 g) in toluene (25 mL) was added to a stirred mixture

of benzyl 2,4-di-*O*-benzyl-α-D-mannopyranoside[13] (2.35 g) and silver triflate (6.70 g) in toluene (40 mL) and molecular sieves (15 g, 4 Å) at 0°. Pyridine (4 mL) was added after 1 h, and the mixture was filtered through a layer of Celite, washed with aqueous 10% sodium thiosulfate and water, and concentrated. A solution of the residue in methanol (150 mL) containing a catalytic amount of sodium methoxide was kept at room temperature overnight, neutralised with acetic acid, and concentrated. The residue was purified by column chromatography (light petroleum–acetone, 2:1), to give **13** as a syrup (4.60 g, 67%), $[\alpha]_{578}^{22}$ +59° (*c* 1.8, dichloromethane); lit.[13] $[\alpha]_{589}^{22}$ +58°, R_F 0.51. ^{13}C-N.m.r. data: 66.1–80.0 (ring C, Ph*C*H$_2$), 96.1 (C-1, $J_{C\text{-}1,H\text{-}1}$ 169 Hz), 99.7 [C-1, Man-(1→6), $J_{C\text{-}1,H\text{-}1}$ 169 Hz], 101.5 [C-1, Man-(1→3), $J_{C\text{-}1,H\text{-}1}$ 175 Hz], 127.5–130.5 (aromatic).

*Benzyl 2,4-di-*O*-benzyl-3,6-di-*O*-{3,4,6-tri-*O*-benzyl-2-*O*-[4,6-*O*-benzylidene-2-deoxy-phthalimido-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-glucopyranosyl]-α-D-mannopyranosyl}-α-D-mannopyranoside* (**14**). — Compound **14** was prepared from mannotrioside **13** (60 mg) as for **10**, using thioglucoside **8** (118 mg), methyl triflate (75 μL), and molecular sieves (0.5 g, 4 Å). The product was purified by column chromatography (toluene–ethyl acetate, 8:1) to yield **14** as a syrup (89 mg, 63%), $[\alpha]_{578}^{22}$ −7° (*c* 1, chloroform), R_F 0.39. ^{13}C-N.m.r. data: δ 16.4 (2 C-6, Fuc), 55.6 (2 C-2, PhtGlc), 66.4–82.0 (ring C, Ph*C*H$_2$), 96.4 (C-1, Man), 97.2 [C-1, Man-(1→6)], 97.7 (2 C-1, PhtGlc), 99.2 [C-1, Man-(1→3)], 99.5 (2 C-1, Fuc), 101.2 (2 C, Ph*C*H), 123.0, 126.1–129.0, 132.2, 133.5, 137.3–138.9 (aromatic), 168.0, 168.2, (Pht).

*Benzyl3,6-di-*O*-{2-O-[2-acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-β-D-glucopyranosyl]-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl}-2,4-di-*O*-benzyl-α-D-mannopyranoside* (**15**). — Compound **14** (122 mg) was treated with hydrazine hydrate (3 mL) in aqueous 90% ethanol (30 mL), and acetic anhydride–pyridine (15 mL, 1:2), as described for **12**. The product was purified by column chromatography (toluene–ethyl acetate, 5:2) to yield **15** as a syrup (81 mg, 75%), $[\alpha]_{578}^{22}$ −26° (*c* 0.6, chloroform), R_F 0.38. ^{13}C-N.m.r. data: δ 16.2 (2 C-6, Fuc), 23.2 (2 C, NAc), 57.3, 59.2 (C-2, GlcNAc), 65.8–79.4 (ring C, Ph*C*H$_2$), 96.5 (C-1, Man), 97.6 (2 C-1, GlcNAc), 98.1 [C-1, Man-(1→6)], 98.7 [C-1, Man-(1→3)], 99.4 (2 C-1, Fuc), 101.5, 101.7 (Ph*C*H), 126.2–138.9 (aromatic), 170.6, 171.2 (NAc).

*3,6-Di-*O*-[2-O-(2-acetamido-2-deoxy-3-*O*-α-L-fucopyranosyl-β-D-glucopyranosyl)-α-D-mannopyranosyl]-D-mannose* (**2**). — Compound **15** (60 mg) was hydrogenolysed and purified as described for **1**, to give **2** as an amorphous powder (21 mg, 79%), $[\alpha]_{578}^{22}$ −44° (*c* 0.2, water), R_F 0.23 (ethyl acetate–methanol–acetic acid–water, 4:3:3:2). N.m.r. data: ^{1}H (400 MHz, 85°), δ 1.16 (d, 6 H, $J_{5,6}$ 6.4 Hz, H-6, Fuc), 2.01 (3 s, 1 H, 0.70 H, 0.30 H, HNAc), 4.61, 4.62, 4.63 (3 d, 1 H, 0.70 H, 0.30 H, $J_{1,2}$ 7.9 Hz, H-1, GlcNAc), 4.87 [d, 1 H, $J_{1,2}$ 2.2 Hz, H-1, Man-(1→6)], 4.88 (d, 0.30 H, $J_{1,2}$ 1.2 Hz, H-1β), 4.99 (d, 2 H, $J_{1,2}$ 3.9 Hz, H-1 Fuc), 5.12 (d, 0.70 H, $J_{1,2}$ 1.2 Hz, H-1α), 5.13 [d, 1 H, $J_{1,2}$ 1.9 Hz, H-1, Man-(1→3)]; ^{13}C, δ 16.4 (2 C-6, Fuc), 23.6 (2 C, NAc), 56.4 (2 C-2, GlcNAc), 61.9, 62.8 (2 C-6, 2 C-6, Man, GlcNAc),

66.9–81.0 (ring C), 94.9, 95.4 (0.3 C-1, 0.6 C-1, $\alpha\beta$-Man), 98.0 [C-1, Man-(1→6)], 100.5, 101.0 [3 C-1, 2 C-1, Man-(1→6), Fuc, GlcNAc], 175.8, and 175.9 (0.3 C, 1.7 C, NAc).

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