Synthesis of Blood-group Substances. Part 8.[1] A Synthesis of the Branched Trisaccharide 2-Acetamido-2-deoxy-4-*O*-(α-L-fucopyranosyl)-3-*O*-(β-D-galactopyranosyl)-D-glucopyranose

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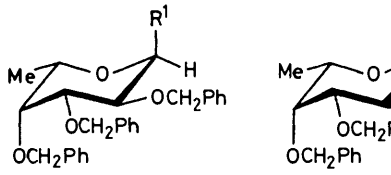
Reaction of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide with benzyl 2-acetamido-4-*O*-allyl-6-*O*-benzyl-2-deoxy-α-D-glucopyranoside provided crystalline benzyl 2-acetamido-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-4-*O*-allyl-6-*O*-benzyl-2-deoxy-α-D-glucopyranoside in 87% yield. Deallylation followed by condensation with 1-*O*-(*N*-methyl)acetimidyl-2,3,4-tri-*O*-benzyl-β-L-fucopyranose provided the crystalline derivative (13). The title trisaccharide was obtained after *O*-deacetylation followed by catalytic hydrogenolysis. Preparations of 2-acetamido-2-deoxy-3-*O*-(β-D-galactopyranosyl)-D-glucopyranose and 2-acetamido-2-deoxy-4-*O*-(α-L-fucopyranosyl)-D-glucopyranose are reported.

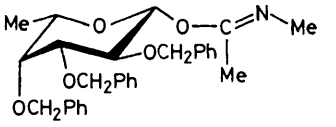
LEMIEUX and DRIGUEZ [2] in 1975 reported an efficient stereochemically controlled synthesis of the title trisaccharide, which is the serologically active compound in the Le^a system. The discovery [3] in our laboratory of a novel method of selective activation of the anomeric centre of carbohydrates designed to produce α-glycosides prompted us to use it for an independent approach to the Lewis^a blood-group antigenic determinant.

Previous publications in this series [1,4] have stressed the usefulness of benzyl 2-acetamido-3-*O*-allyl-6-*O*-benzyl-2-deoxy-α-D-glucopyranoside (4) for the synthesis of branched oligosaccharides involving the secondary hydroxy-groups of 2-acetamido-2-deoxy-D-glucopyranosides. This alcohol (4) was, therefore, initially selected as the starting material for the construction of the title trisaccharide.

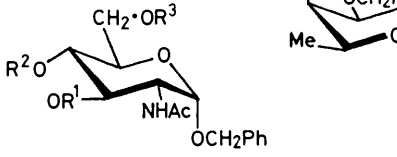
Our studies in recent years towards the development of the imidate procedure to produce α-glycosides [3,5] were recently summarized in a preliminary communication.[6] Although the halide ion-catalysed reaction [7] is remarkably effective in the case of α-fucosylations,[2,7,8] this imidate procedure was tentatively applied for the same purpose. 2,3,4-Tri-*O*-benzyl-α-L-fucopyranose [9] (1) was conveniently and quantitatively transformed into crystalline 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl chloride (2) under the agency of dimethylchloroformadinium chloride, prepared from dimethylformamide and phosphorus pentachloride.[10] The chloride (2) reacts smoothly with *N*-methylacetamide in the presence of silver oxide, di-isopropylethylamine, and powdered 4 Å molecular sieves to give crystalline 1-*O*-(*N*-methyl)acetimidyl-2,3,4-tri-*O*-benzyl-β-L-fucopyranose (3) in excellent yield.



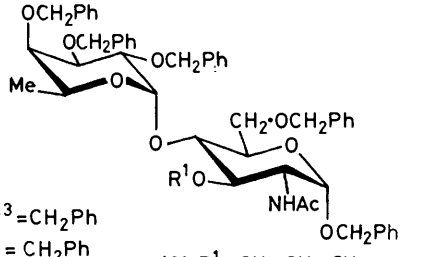
(1) R^1 = OH
(2) R^1 = Cl



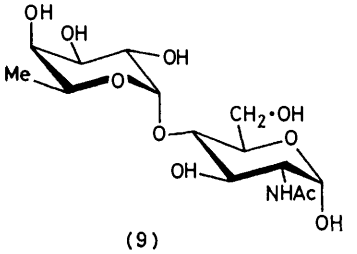
(3)



(4) R^1 = CH_2·CH=CH_2, R^2 = H, R^3 = CH_2Ph
(5) R^1 = H, R^2 = CH_2·CH=CH_2, R^3 = CH_2Ph



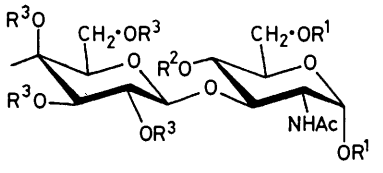
(6) R^1 = CH_2·CH=CH_2
(7) R^1 = H
(8) R^1 = Ac



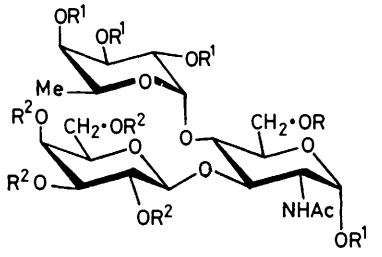
(9)

Condensation of the imidate (3) with benzyl 2-acetamido-3-*O*-allyl-6-*O*-benzyl-2-deoxy-α-D-glucopyranoside (4) in nitromethane in the presence of anhydrous toluene-*p*-sulphonic acid and powdered molecular sieves (4 Å) (16 h at room temperature) gave the protected disaccharide (6) in high yield (93%). The disaccharide (6) was *O*-deallylated with chloro[tris(triphenylphosphine)]-rhodium(I) [11] in benzene–ethanol–water at reflux temperature during 5 days to obtain the alcohol (7), which did not crystallise but was transformed into its crystalline acetate (8). The structure of the disaccharide (7) was ascertained after hydrogenolysis to the known disaccharide (9).[8b] Owing to its high degree of crystallinity, its stability on storage, and its ease of preparation, the imidate (3) is a useful α-L-fucosylating agent and use of the sensitive 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide is avoided. However, the alcohol (7) did not condense with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (or the corresponding orthoesters) under a wide range of conditions, for which steric factors are probably responsible.

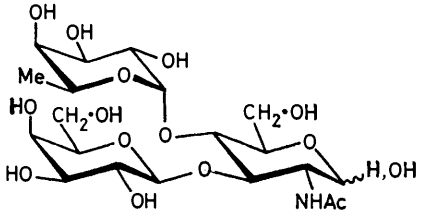
As a new approach, benzyl 2-acetamido-4-*O*-allyl-6-*O*-benzyl-2-deoxy-α-D-glucopyranoside (5) was next prepared. It was easily available from (4) by isomerisation of the allyl group, followed by allylation and acid hydrolysis of the prop-1-enyl group. Reaction of the alcohol (5) with 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide in 1,2-dichloroethane in the presence of mercuric bromide and molecular sieves (4 Å) [12] gave the β-linked product (10) in excellent yield. The disaccharide (10) was *O*-deallylated with chloro(tristriphenylphosphine)rhodium(I) as previously described to obtain the crystalline alcohol (11). *O*-Deacetylation of (11) followed by hydrogenolysis of the benzyl groups provided the known disaccharide (12).[2,13] Condensation of the imidate (3) with the disaccharide (11) gave the protected trisaccharide (13) in 85% yield. *O*-Deacetylation of (13) provided the crystalline trisaccharide (14) in high yield and this product was debenzylated to the title trisaccharide by hydrogenolysis in acetic acid in the presence of palladium on carbon. It formed a crystalline peracetate derivative (15).



(10) $R^1 = CH_2Ph$, $R^2 = CH_2 \cdot CH{=}CH_2$, $R^3 = Ac$
(11) $R^1 = CH_2Ph$, $R^2 = H$, $R^3 = Ac$
(12) $R^1 = R^2 = R^3 = H$



(13) $R^1 = CH_2Ph$, $R^2 = Ac$
(14) $R^1 = CH_2Ph$, $R^2 = H$
(15) $R^1 = R^2 = Ac$



(16)

EXPERIMENTAL

See Part 7 [1] for general conditions.

2,3,4,-*Tri*-O-*benzyl*-α-L-*fucopyranosyl Chloride* (2).—A mixture of 2,3,4-tri-*O*-benzyl-α-L-fucopyranose [9] (1) (434 mg, 1 mmol) and freshly prepared dimethylchloroformadinium chloride [10] (2.5 mmol) in dichloromethane was stirred for 30 min under dry nitrogen. The reaction mixture was diluted with dichloromethane (20 ml), washed with water, aqueous sodium hydrogen carbonate, and water again, dried ($CaCl_2$), and evaporated. Crystallisation of the residue occurred after azeotroping several times with benzene to yield the *chloride* (2) (435 mg, 96%) which was used without further purification for the synthesis of the imidate (3). A portion was recrystallised (ether–hexane) for analysis, m.p. 72—73°, $[\alpha]_D$ −169° (*c* 1 in CH_2Cl_2), δ 1.13 (3 H, d, *J* 7 Hz, Me), 3.65 (1 H, br s, H-4), 3.95 (1 H, dd, $J_{2,3}$ 9 Hz, $J_{3,4}$ 2.5 Hz, H-3), 6.15 (1 H, d, $J_{1,2}$ 4 Hz, H-1), and 7.32 (15 H, Ph) (Found: C, 71.35; H, 6.4; O, 14.2. $C_{27}H_{29}ClO_4$ requires C, 71.6; H, 6.45; O, 14.15%).

1-O-(N-*Methyl*)*acetimidyl*-2,3,4-*tri*-O-*benzyl*-β-L-*fucopyranose* (3).—A solution of 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl chloride (2) (434 mg) in benzene was stirred for 20 h at room temperature under dry nitrogen in the presence of *N*-methylacetamide (81 mg), freshly prepared silver oxide (580 mg), di-isopropylethylamine (190 mg), and molecular sieves (4 Å) (250 mg). In order to remove insoluble salts and the excess of *N*-methylacetamide, the solution was run through a bed of neutral alumina, which was then washed with triethylamine in ether (0.1% solution). The filtrate was evaporated; crystallisation of the residue from hexane gave the *imidate* (3) (431 mg, 90%), m.p. 89–90°, $[\alpha]_D$ −67° (*c* 1 in C_6H_6), δ 1.20 (3 H, d, *J* 7

Hz, CH–*Me*), 1.34 (3 H, s, C–Me), 2.97 (3 H, s, N–Me), 3.97 (1 H, t, $J_{1,2} = J_{2,3} = 8$ Hz, H-2), 5.82 (1 H, d, $J_{1,2}$ 8 Hz, H-1), and 7.30 and 7.32 (15 H, Ph) (Found: C, 73.7; H, 7.3; N 2.9; O 16.2. $C_{30}H_{35}NO_5$ requires C 73.6; H 7.2; N 2.85; O 16.35%).

Benzyl 2-*Acetamido*-3-O-*allyl*-6-O-*benzyl*-4-O-(2 3 4-*tri*-O-*benzyl*-α-L-*fucopyranosyl*)-2-*deoxy*-α-D-*glucopyranoside* (6).—A solution of benzyl 2-acetamido-3-*O*-allyl-6-*O*-benzyl-2-deoxy-α-D-glucopyranoside (4) (883 mg) in anhydrous nitromethane (40 ml) was stirred for 5 h at room temperature in the presence of powdered molecular sieves (4 Å) (1g) under an atmosphere of dry nitrogen. Freshly prepared imidate (3) (1.96 g) and anhydrous toluene-*p*-sulphonic acid (344 mg) were added and the mixture was stirred at room temperature for 16 h under dry nitrogen. After addition of triethylamine (5 ml) insoluble material was filtered off and the filtrate was washed with saturated aqueous sodium hydrogen carbonate and water, dried ($CaCl_2$), and evaporated. The residue was chromatographed on silica gel (200 g); elution with ethyl acetate–hexane (4 : 3) gave the *disaccharide* (6), which was crystallised from ether–hexane (1.592 g, 93%), m.p. 87—88°, $[\alpha]_D$ +2° (*c* 1 in chloroform), δ 1.10 (3 H, d, *J* 7 Hz, Me), 1.90 (3 H, s, Ac), 4.86 (1 H, d, $J_{1,2}$ 4.5 Hz, H-1), 5.13 (1 H, d, $J_{1',2'}$ 3 Hz, H-1'), 5.60 (1 H, d, 9 Hz, NH), and 7.30 and 7.33 (25 H, Ph) (Found: C, 72.75; H, 7.05; N, 1.55; O, 18.75. $C_{52}H_{59}NO_{10}$ requires C, 72.8; H, 6.95; N, 1.65; O, 18.65%).

Benzyl 2-*Acetamido*-6-O-*benzyl*-4-O-(2,3,4-*tri*-O-*benzyl*-α-L-*fucopyranosyl*)-2-*deoxy*-α-D-*glucopyranoside* (7).—Compound (6) (1.5 g), ethanol (22 ml), benzene (10 ml), water (3 ml), and chloro[tris(triphenylphosphine)]rhodium(I) (577 mg) were mixed and the solution was then heated under reflux for 5 days. The reaction mixture was cooled, concentrated to 10 ml diluted with ether (200 ml) and washed with saturated aqueous potassium chloride (acidified to *ca.* pH 2 with HCl), aqueous sodium hydrogen carbonate, and water, and dried (Na_2SO_4) and evaporated. The residue was chromatographed on silica gel (70 g); elution with ethyl acetate–hexane (9 : 1) gave the disaccharide (7) (1.241 g, 87%), $[\alpha]_D$ +4.5° (*c* 1 in chloroform), δ 1.13 (3 H, d, *J* 7 Hz, Me), 1.93 (3 H, s, Ac), 5.72 (1 H d, *J* 9 Hz, NH), and 7.30 and 7.33 (25 H, Ph) (Found: C, 71.15; H, 6.75; N, 1.7; O, 20.7. $C_{49}H_{55}NO_{10}\cdot 0.5H_2O$ requires C, 71.15; H, 6.8; N, 1.7; O, 20.3%).

Benzyl 2-*Acetamido*-3-O-*acetyl*-6-O-*benzyl*-4-O-(2,3,4-*tri*-O-*benzyl*-α-L-*fucopyranosyl*)-2-*deoxy*-α-D-*glucopyranoside* (8).—The disaccharide (7) (100 mg) was acetylated for 72 h with acetic anhydride (0.5 ml) in dichloromethane (10 ml) containing pyridine (0.5 ml). After usual work-up, the product was crystallised from ether–hexane to give the *disaccharide* (8) (96 mg, 91%), m.p. 80—82° (with evolution of a gas at 45° and softening at 60—61°), $[\alpha]_D$ +2° (*c* 1 in chloroform), δ 1.05 (3 H, d, 7 Hz, Me), 1.86 and 2.00 (6 H, 2s Ac), 4.91 (1 H, d, $J_{1,2}$ 3.5 Hz, H-1), 4.96 (1 H, d, $J_{1',2'}$ 3 Hz, H-1'), 5.70 (1 H, d, *J* 9 Hz, NH), and 7.30 and 7.32 (25 H, Ph) (Found: C, 70.75; H, 6.6; N, 1.55; O, 20.55. $C_{51}H_{57}NO_{10}$ requires C, 71.2; H, 6.55; N, 1.65; O, 20.45%).

2-*Acetamido*-2-*deoxy*-4-O-α-L-*fucopyranosyl*-α-D-*glucopyranose* (9).—Compound (7) (580 mg) in acetic acid (15 ml) was hydrogenolysed over Pd–C (10%; 500 mg) for 8 days. The reaction mixture was filtered and evaporated to give the disaccharide (9) which was crystallised from methanol–acetone (218 mg, 84%), m.p. 193—195°, $[\alpha]_D$ −77→−98° (after 4 h) (*c* 0.9 in methanol–water, 1 : 1 v/v) [lit.,[8b] m.p. 194—196°, $[\alpha]_D$ −79°→−99° (after 5 h) (*c* 0.8 in methanol–water, 1 : 1 v/v).

Benzyl 2-*Acetamido*-4-O-*allyl*-6-O-*benzyl*-α-D-*glucopyranoside* (5).—Compound (4) (1 g) was isomerised with potassium t-butoxide (1 g) in anhydrous dimethyl sulphoxide (20 ml) (1 h at 100° under dry nitrogen); t.l.c. (ethyl acetate–ether, 3 : 2) showed complete conversion of the allyl group into the prop-1-enyl group. The reaction mixture was cooled, diluted with ice-cold water (100 ml), and extracted with dichloromethane. The extracts were washed with water, dried (Na_2SO_4), and evaporated. The solid residue (1 g) was dissolved in *NN*-dimethylformamide and stirred at room temperature for 1 h with allyl bromide (0.5 ml), barium oxide (2 g), and barium hydroxide octahydrate (0.6 g). The mixture was diluted with dichloromethane (100 ml), washed with acetic acid (60%) and water, and evaporated. The residue was refluxed for 30 min in a mixture of acetone (20 ml) and M-hydrochloric acid (5 ml). After cooling, the solution was concentrated to half volume, diluted with ice-cold water and extracted with dichloromethane. The extracts were washed with aqueous sodium hydrogen carbonate and water, dried ($CaCl_2$), and evaporated. The residue was crystallised from ethyl acetate–ether to give *compound* (5) (816 mg, 81.5%), m.p. 148—149°, $[\alpha]_D$ +94° (*c* 1 in chloroform), δ 1.93 (3 H, s, Ac), 4.91 (1 H, d, $J_{1,2}$ 4 Hz, H-1), 5.95 (1 H, d, *J* 9 Hz, NH), and 7.33 (10 H, Ph) (Found: C, 68.1; H, 6.9; N, 3.15; O, 21.75. $C_{25}H_{31}NO_6$ requires C, 68.0; H, 7.1; N, 3.15; O, 21.75%).

Benzyl 2-*Acetamido*-3-O-(2,3,4,6-*tetra*-O-*acetyl*-β-D-*galactopyranosyl*)-4-O-*allyl*-6-O-*benzyl*-2-*deoxy*-α-D-*glucopyranoside* (10).—A solution of benzyl 2-acetamido-4-*O*-allyl-6-*O*-benzyl-2-deoxy-α-D-glucopyranoside (5) (1.104 g) in anhydrous 1,2-dichloroethane (20 ml) containing anhydrous powdered mercuric bromide (360 mg) and powdered molecular sieves (4 Å) (1.5 g) was heated under dry nitrogen. After solvent (5 ml) had been distilled off a freshly prepared solution of 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide (1.545 g) in anhydrous 1,2-dichloroethane (8 ml) was added and more solvent (8 ml) was distilled off. The reaction mixture was heated at 90° during 1.5 h. After cooling, it was filtered, washed with aqueous potassium iodide, aqueous sodium hydrogen carbonate, and water, dried ($CaCl_2$), and evaporated. The residue was chromatographed on silica gel (170 g); elution with ethyl acetate–hexane (3 : 1) gave the *disaccharide* (10), which was crystallised from ether (1.681 g, 87%), m.p. 138—139°, $[\alpha]_D$ +56° (*c* 1 in chloroform), δ 1.92, 1.96, 2.04, and 2.09 (15 H, 4s, Ac), 4.62 (1 H, d, $J_{1',2'}$ 7.5 Hz, H-1'), 4.83 (1 H, d, $J_{1,2}$ 4 Hz, H-1), 5.60 (1 H, d, *J* 9 Hz, NH), 7.33 (10 H, s, Ph) (Found: C, 60.75; H, 6.45; N, 1.8; O, 31.3. $C_{39}H_{49}NO_{15}$ requires C, 60.7; H, 6.4; N, 1.8; O, 31.1%).

Benzyl 2-*Acetamido*-3-O-(2,3,4,6-*tetra*-O-*acetyl*-β-D-*galactopyranosyl*)-6-O-*benzyl*-2-*deoxy*-α-D-*glucopyranoside* (11).—Compound (10) (1 g), ethanol (16 ml), benzene (7 ml), water (2 ml), and chloro[tris(triphenylphosphine)]rhodium(I) (370 mg) were mixed and the solution was heated under reflux for 4 days. The mixture was cooled and filtered, the filtrate was evaporated, and the residue was dissolved in chloroform (80 ml). The solution was washed with saturated aqueous potassium iodide (adjusted to pH 2 by addition of HCl) and water, dried ($CaCl_2$), and evaporated. The residue was chromatographed on silica gel (50 g); elution with ethyl acetate–hexane (2 : 1) gave *compound* (11), which was crystallised from ethyl acetate–ether (699 mg,

74%), m.p. 172—173°, $[\alpha]_D$ +63° (*c* 1 in chloroform), δ 1.92, 1.93, 1.98, 2.05, and 2.12 (15 H, 5s, Ac), 4.58 (1 H, d, $H_{1',2'}$ 8 Hz, H-1'), and 7.33 (10 H, s, Ph) (Found: C, 58.9; H, 6.1; N, 2.0; O, 32.95. $C_{36}H_{45}NO_{15}$ requires C, 59.1; H, 6.2; N, 1.9; O, 32.8%).

2-*Acetamido*-2-*deoxy*-3-O-β-D-*galactopyranosyl*-α-D-*glucopyranose* (12).—Compound (11) (120 mg) was *O*-deacetylated using sodium methoxide in methanol. After usual work-up, the residue was dissolved in acetic acid (10 ml) and hydrogenolysed with Pd–C (10%) (100 mg) for 24 h. The mixture was filtered and evaporated to give the disaccharide (12) (49 mg), m.p. 193—195° (softening at 184—185°), $[\alpha]_D$ +33°→+14.5° (after 10 h) (*c* 1 in water–methanol 19 : 1), lit.,[2,13,14] m.p. 197°, $[\alpha]_D$ +22°→+7°; m.p. 193—194° (decomp.), $[\alpha]_D$ +32°→+14.5° (*c* 1.58 in water); m.p. 193—194° (softening at 184°), $[\alpha]_D$ +32°→+14° (*c* 1 in water). After reduction with sodium borohydride and per-*O*-(trimethylsilyl)ation, the product was homogeneous on g.l.c. (t_R 2.09).

Benzyl 2-*Acetamido*-3-O-(2,3,4,6-*tetra*-O-*acetyl*-β-D-*galactopyranosyl*)-6-O-*benzyl*-4-O-(2,3,4-*tri*-O-*benzyl*-α-L-*fucopyranosyl*)-2-*deoxy*-α-D-*glucopyranoside* (13).—A solution of compound (11) (100 mg) and the imidate (3) (70 mg) in anhydrous nitromethane (5 ml) was stirred for 3 h at room temperature in the presence of powdered molecular sieves (4 Å) (150 mg) under dry nitrogen. Anhydrous toluene-*p*-sulphonic acid (24 mg) was added and the mixture was stirred at room temperature for 24 h. Further imidate (3) (70 mg) and anhydrous toluene-*p*-sulphonic acid (24 mg) was added and reaction continued for a further 2 days. After addition of triethylamine (0.1 ml), the insoluble compounds were filtered off and the filtrate was washed with saturated aqueous sodium hydrogen carbonate and water, dried ($CaCl_2$), and evaporated. The residue was chromatographed on silica gel (20 g); elution with ethyl acetate–hexane (3 : 1) gave two compounds. First eluted was the *trisaccharide* (13) (133 mg, 85%), $[\alpha]_D$ +15.5° (*c* 1 in chloroform), δ 1.32 (3 H, d, *J* 7 Hz, Me), 1.80 (3 H, s, NAc), 1.91, 1.99, and 2.06 (12 H, 3s, OAc), 5.11 (1 H, d, $J_{1'',2''}$ 3 Hz, H-1''), 5.56 (1 H, d, 10 Hz, NH), and 7.31 and 7.35 (25 H, 2s, Ph) (Found: C, 65.8; H, 6.55; N, 1.3; O, 26.75. $C_{63}H_{73}NO_{19}$ requires C, 65.9; H, 6.4; N, 1.2; O, 26.45%). The second compound eluted was unchanged starting material (11) (6 mg, 6%), m.p. 171—174°.

Benzyl 2-*Acetamido*-6-O-*benzyl*-4-O-(2,3,4-*tri*-O-*benzyl*-α-L-*fucopyranosyl*)-2-*deoxy*-3-O-β-D-*galactopyranosyl*-α-D-*glucopyranoside* (14).—The trisaccharide (13) (200 mg) was *O*-deacetylated (sodium methoxide in methanol). After usual work-up, the residue was crystallised from ethyl acetate–ether to give *compound* (14) (154 mg, 91%), m.p. 180—181° $[\alpha]_D$ −15° (*c* 1 in chloroform), δ 1.15 (3 H, d, *J* 7 Hz, Me), 1.97 (3 H, s, Ac), 4.92 (1 H, d, $J_{1,2}$ 4.5 Hz, H-1), 5.10 (1 H, d, $J_{1'',2''}$ 3.5 Hz, H-1''), and 7.30 and 7.32 (25 H, 2s, Ph) (Found: C, 67.4; H, 6.65; N, 1.45; O, 24.4. $C_{55}H_{65}NO_{15}$ requires C, 67.4; H, 6.7; N, 1.45; O, 24.5%).

2-*Acetamido*-2-*deoxy*-4-O-α-L-*fucopyranosyl*-3-O-(β-D-*galactopyranosyl*)-D-*glucopyranose* (16).—A solution of compound (14) (280 mg) in acetic acid (10 ml) was hydrogenolysed with Pd–C (10%) (300 mg) for 48 h. The reaction mixture was filtered and evaporated to give the pure *trisaccharide* (16) (140 mg, 93%) as an amorphous powder which did not crystallise, $[\alpha]_D$ −44.5° (*c* 1 in water–methanol, 19 : 1), δ(D_2O; Me_4Si as external reference) 1.18 and 1.21 (3 H, 2d, *J* 7 Hz, α- and β-Me), 1.92 and 2.05 (3 H, 2s, α- and β-Ac), 4.69 (1 H, d, $J_{1',2'}$ 7 Hz,H-1'), 5.54 (1 H, d, $J_{1'',2''}$ 3 Hz, H-1''), and 5.65 (1 H, d, $J_{1,2}$ 3 Hz, H-1α) (Found: C, 43.7; H, 6.7; N, 2.7; O, 46.65. $C_{20}H_{35}NO_{15}$ H_2O requires C, 44.1; H, 6.8; N, 2.55; O, 46.75%); {lit.,[2,15] $[\alpha]_D$ −44 ±3° (*c* 0.3 in water); −45.1° (*c* 1 in water)}. After reduction with sodium borohydride and per-*O*-(trimethylsilyl)ation, the product was homogeneous on g.l.c. (t_R 2.73). Paper chromatography of the products from acid hydrolysis indicated the presence of fucose, galactose, and glucosamine.

2-*Acetamido*-1,6-*di*-O-*acetyl*-4-O-(2,3,4-*tri*-O-*acetyl*-α-L-*fucopyranosyl*)-3-O-(2,3,4,6-*tetra*-O-*acetyl*-β-D-*galactopyranosyl*)-2-*deoxy*-α-D-*glucopyranose* (15).—The trisaccharide (16) (50 mg) was acetylated (acetic anhydride–pyridine). After usual work-up, the residue was crystallised from carbon tetrachloride to give the *derivative* (15) (57 mg, 66%), m.p. 142—144°, $[\alpha]_D$ −52° (*c* 1 in chloroform), δ 1.20 (3 H, d, *J* 7 Hz, Me), 1.92—2.18 (30 H, Ac), 6.18 (1 H, d, $J_{1,2}$ 4 Hz, H-1) (Found: C, 50.3; H, 5.9; N, 1.55. $C_{38}H_{53}NO_{24}$ requires C, 50.5; H, 6.0; N, 1.5%).

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REFERENCES

[1] Part 7, J.-C. Jacquinet and P. Sinaÿ, preceding paper.
[2] R. U. Lemieux and H. Driguez, *J. Amer. Chem. Soc.*, 1975, **97**, 4063.
[3] J.-R. Pougny and P. Sinaÿ, *Actual. Chim.*, 1976, **42** [Meeting in Tours (France), November 7, 1975].
[4] J.-C. Jacquinet and P. Sinaÿ, *J. Org. Chem.*, 1977, **42**, 720.
[5] J.-R. Pougny and P. Sinaÿ, Abstracts of the 10th International Symposium on Chemical Natural Products, Dunedin, 1976, B15; J.-R. Pougny and P. Sinaÿ, Abstracts of the 26th International Congress of Pure Applied Chemistry, Tokyo, 1977, *IV*, 1106.
[6] J.R.- Pougny, J.-C. Jacquinet, M. Nassr, D. Duchet, M.-L. Milat, and P. Sinaÿ, *J. Amer. Chem. Soc.*, 1977, **99**, 6762.
[7] R. U. Lemieux, K. B. Hendriks, R. V. Stick, and K. James, *J. Amer. Chem. Soc.*, 1975, **97**, 4056.
[8] (*a*) R. U. Lemieux and H. Driguez, *J. Amer. Chem. Soc.*, 1975, **97**, 4069; (*b*) J.-C. Jacquinet and P. Sinaÿ, *Carbohydrate Res.*, 1975, **42**, 251.
[9] M. Dejter-Juszynski and H. M. Flowers, *Carbohydrate Res.*, 1971, **18**, 219.
[10] H. H. Bosshard, R. Mory, M. Schmid, and Hch. Zollinger, *Helv. Chim. Acta*, 1959, **42**, 1653.
[11] E. J. Corey and J. W. Suggs, *J. Org. Chem.*, 1973, **38**, 3224.
[12] J.-C. Jacquinet, J.-R. Pougny, D. Duchet, and P. Sinaÿ, Abstracts of the 2nd Joint Conference of the Chemical Institute of Canada and the American Chemical Society, 1977, CARB 44.
[13] H. M. Flowers and R. W. Jeanloz, *J. Org. Chem.*, 1963, **28**, 1377.
[14] R. Kuhn, H. H. Baer, and A. Gauhe, *Chem. Ber.*, 1954, **87**, 289.
[15] V. P. Rege, T. J. Painter, W. M. Watkins, and W. T. J. Morgan, *Nature*, 1964, **104**, 740.