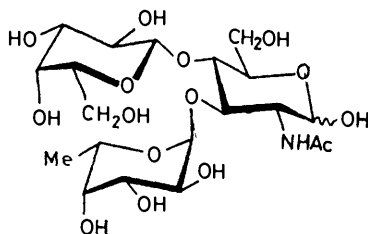


Synthesis of Blood-group Substances. Part 7.¹ Synthesis of the Branched Trisaccharide *O*- α -L-Fucopyranosyl-(1 \rightarrow 3)-[*O*- β -D-galactopyranosyl-(1 \rightarrow 4)]-2-acetamido-2-deoxy-D-glucopyranose²

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Reaction of 2,3,4,6-tetra-*O*-acetyl- α -D-galactopyranosyl bromide with benzyl 2-acetamido-3-*O*-allyl-6-*O*-benzyl-2-deoxy- α -D-glucopyranoside in 1,2-dichloroethane in the presence of mercuric bromide and molecular sieves (4 Å) provided crystalline benzyl 2-acetamido-4-*O*-(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-3-*O*-allyl-6-*O*-benzyl-2-deoxy- α -D-glucopyranoside in 77% yield. Deallylation with chloro(trisphenylphosphine)-rhodium(I) followed by condensation with 2,3,4-tri-*O*-benzyl- α -L-fucopyranosyl bromide provided the derivative (14). The title trisaccharide was obtained after *O*-deacetylation followed by catalytic hydrogenolysis.

α -3-L-FUCOSYLTRANSFERASE is a frequently occurring enzyme of human serum³ and numerous oligosaccharides or glycoconjugates of human origin have a structure



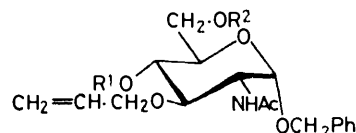
(1)

where the title trisaccharide (1) is located at the 'non-reducing end.' For instance, a tetrasaccharide of this type has been isolated from the products of alkaline degradation of Le^a blood-group specific glycoprotein obtained from an ovarian-cyst fluid.⁴ Later, Lloyd *et al.*⁵ isolated from the same material an oligosaccharide having this same characteristic structure. Blood-group active (A, B, H) difucosyl oligosaccharides of glycoprotein origin with a fucose residue linked to C-3 of *N*-acetylglucosamine have also been characterised by Lloyd *et al.*⁶⁻⁸ The pentasaccharide lacto-*N*-fucopentaose III,⁹ isolated from human milk, belongs to the same class, together with more complex oligosaccharides isolated from the same source.¹⁰ A sphingolipid having a carbohydrate moiety identical to lacto-*N*-fucopentaose III was first isolated from human adenocarcinomas by Yan and Hakomori,¹¹ a similar fucolipid (fucolipid B) being subsequently obtained from hog gastric mucosa.¹² The occurrence of this glycolipid in normal and adenocarcinoma tissue seemed independent of the known blood-group systems. It failed to inhibit either Le^a or Le^b hemagglutination. Kobata and Ginsburg⁹ similarly found that lacto-*N*-fucopentaose III failed to inhibit various blood-group systems. An antibody has nevertheless been detected in the serum of a female patient which reacts specifically with cell samples from Le (a-b-) individuals who are non-secretors of H substance.¹³ It has been decided to call the antibody anti-Le^c and the corresponding antigen Le^c. It was then suggested¹³ that the antigenic determinant Le^c might be identical with the trisaccharide *O*- α -L-fucopyranosyl-(1 \rightarrow 3)-

O- β -D-galactopyranosyl-(1 \rightarrow 4)-2-acetamido-2-deoxy-D-glucopyranose.

It thus appears that, besides the rather stimulating challenge associated with the efficient construction of the 'Le^c' trisaccharide, such an endeavour presents an interest for immunological studies.

In Part 6,¹ we showed that benzyl 2-acetamido-3-*O*-allyl-6-*O*-benzyl-2-deoxy- α -D-glucopyranoside (4) is an attractive aglycone for the synthesis of branched oligosaccharides. The reactivity of this alcohol with 2,3,4,6-tetra-*O*-acetyl- α -D-galactopyranosyl bromide was therefore investigated. The Koenigs-Knorr reaction¹⁴ was not considered, in view of expected side reactions involving the acetamido group.¹⁵ Condensation of glycosyl halides with alcohols in benzene and in the presence of mercuric cyanide was introduced by Zemplén and Gerecs.¹⁶ Helferich and associates have used nitromethane¹⁷ as a solvent, Jeanloz *et al.* using a mixture of



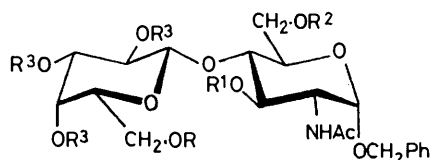
- (2) R¹ = R² = H
- (3) R¹ = H, R² = Ac
- (4) R¹ = H, R² = CH₂Ph
- (5) R¹ = Ac, R² = CH₂Ph

benzene and nitromethane.¹⁸ Such conditions present a double disadvantage: mercuric cyanide is reactive in nitromethane with 2,3,4,6-tetra-*O*-acetyl- α -D-galactopyranosyl bromide¹⁹ and the reaction is stereochemically capricious.²⁰ A large number of disaccharides have nevertheless been prepared through this route.

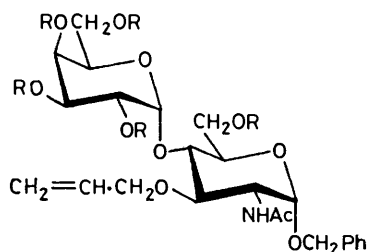
The alcohol (4) was condensed with 2,3,4,6-tetra-*O*-acetyl- α -D-galactopyranosyl bromide in nitromethane-benzene and in the presence of mercuric cyanide and the product was chromatographed on silica gel to obtain benzyl 2-acetamido-4-*O*-acetyl-3-*O*-allyl-6-*O*-benzyl- α -D-glucopyranoside (5) (7%) and a more complex fraction. The latter was *O*-deacetylated and chromatographed on silica gel to obtain the starting material (4) (11%) and the pure β -linked protected disaccharide (7) (65% after crystallisation). Compound (5) results from trans-

acetylation of the starting alcohol (4) with 2,3,4,6-tetra-*O*-acetyl- α -D-galactopyranosyl bromide. Such a side reaction is well documented in this field.²¹ Very similar results were obtained when dry benzene was used as solvent. Acetylation of the disaccharide (7) gave crystalline benzyl 2-acetamido-6-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-3-*O*-allyl-2-deoxy- α -D-glucopyranoside (6).

A cleaner reaction was achieved when the alcohol (4) was condensed 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).²² In this case the pure protected disaccharide (6) was obtained directly (77%) from the reaction mixture after chromatography on silica gel. The disaccharide (6) was *O*-deallylated with chloro(trisphenylphosphine)rhodium(I)²³ in benzene-ethanol-water at reflux temperature during 72 h to obtain directly the alcohol (10) in crystalline form. Condensation of 2,3,4-tri-*O*-benzyl- α -L-fucopyranosyl bromide²⁴ with benzyl 2-acetamido-4-*O*-(2,3,4,6-tetra-*O*-acetyl- β -D-galactopyranosyl)-6-*O*-benzyl-2-deoxy- α -D-glucopyranoside (10) in 1,2-dichloroethane-*NN*-dimethylformamide in the presence of tetraethylammonium bromide and molecular sieves (4 Å) (halide ion-catalysed reaction²⁵) gave the protected trisaccharide (14) in crystalline form in 85% yield. *O*-Deacetylation followed by hydrogenolysis of the benzyl groups gave the title trisaccharide (1) which was converted into its crystalline peracetate derivative (17).



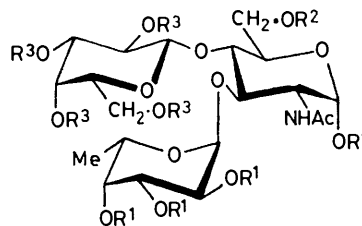
- (6) $R^1 = \text{CH}_2\cdot\text{CH}=\text{CH}_2$, $R^2 = \text{CH}_2\text{Ph}$, $R^3 = \text{Ac}$
 (7) $R^1 = \text{CH}_2\cdot\text{CH}=\text{CH}_2$, $R^2 = \text{CH}_2\text{Ph}$, $R^3 = \text{H}$
 (8) $R^1 = \text{CH}_2\cdot\text{CH}=\text{CH}_2$, $R^2 = R^3 = \text{Ac}$
 (9) $R^1 = \text{CH}_2\cdot\text{CH}=\text{CH}_2$, $R^2 = R^3 = \text{H}$
 (10) $R^1 = \text{H}$, $R^2 = \text{CH}_2\text{Ph}$, $R^3 = \text{Ac}$
 (11) $R^1 = \text{H}$, $R^2 = R^3 = \text{Ac}$



- (12) $R = \text{H}$
 (13) $R = \text{Ac}$

As the synthesis of benzyl 2-acetamido-3-*O*-allyl-6-*O*-benzyl-2-deoxy- α -D-glucopyranoside (4) is not straightforward,¹ a more readily accessible alcohol was sought. Selective acetylation of benzyl 2-acetamido-3-*O*-allyl-

2-deoxy- α -D-glucopyranoside (2) with *N*-acetylimidazole gave the corresponding 6-*O*-acetate (3) in good yield (85%). This alcohol (3) was condensed without difficulty with 2,3,4,6-tetra-*O*-acetyl- α -D-galactopyranosyl bromide



- (14) $R^1 = R^2 = \text{CH}_2\text{Ph}$, $R^3 = \text{Ac}$
 (15) $R^1 = \text{CH}_2\text{Ph}$, $R^2 = R^3 = \text{Ac}$
 (16) $R^1 = R^2 = \text{CH}_2\text{Ph}$, $R^3 = \text{H}$
 (17) $R^1 = R^2 = R^3 = \text{Ac}$

in 1,2-dichloroethane and in the presence of mercuric bromide and molecular sieves (4 Å)²² and the product was chromatographed on silica gel to give the pure β -linked protected disaccharide (8) as an amorphous solid (78%). The other fractions were *O*-deacetylated to give after chromatography (silica gel) the crystalline α -linked disaccharide (12) in moderate yield (7%). Therefore, the reactivity of the 4-hydroxy group is not appreciably affected by the presence of an acetoxymethyl group on C-5, a result which introduces a further simplification in the practical synthesis of 1 \rightarrow 4 disaccharides. A study of some factors affecting such a reactivity will be reported elsewhere.²⁶

After *O*-deacetylation, the amorphous disaccharide (8) was transformed into the crystalline disaccharide (9). Using chloro(trisphenylphosphine)rhodium(I)²³ as previously described, this disaccharide (8) was *O*-deallylated to obtain the alcohol (11), which was condensed with 2,3,4-tri-*O*-benzyl- α -L-fucopyranosyl bromide as reported for the preparation of compound (14). The crystalline trisaccharide (15) was obtained in good yield (85%). Deprotection in the usual manner gave the title trisaccharide.

EXPERIMENTAL

Melting points were determined on a Büchi apparatus. Specific optical rotations were measured at 22–24 °C with a Perkin-Elmer model 141 polarimeter. I.r. spectra were recorded with a Jouan-Jasco IRA-1 spectrometer. ¹H N.m.r. spectra were obtained for solutions in deuteriochloroform (tetramethylsilane as internal standard) unless otherwise stated; indices refer respectively to: primary, glucosamine; secondary, galactose; tertiary, fucose. Gas-liquid chromatography (g.l.c.) of the per-*O*-(trimethylsilyl)-derivatives was performed with a Girdel 3000 apparatus provided with a flame ionization detector and a 3.40 m Pyrex column (4% OV 17 on Gas-Chrom Q, 80–100 mesh), programmed for a rise of 10 °C min⁻¹ from 150 to 300 °C; *t*_R is given relative to that of per-*O*-(trimethylsilyl)-*myo*-inositol. Purity of products was determined by thin layer chromatography [t.l.c. on silica gel 60 F 254 (E. Merck)]. Components were located by spraying with sulphuric acid in ethanol (50% solution) and charring. Column chromato-

graphy was performed on silica gel Merck 60 (powder, 0.063–0.200 mm) which was used without pretreatment. Elemental analyses were obtained from the Service Central de Microanalyse du Centre National de la Recherche Scientifique.

Benzyl 2-Acetamido-6-O-acetyl-3-O-allyl-2-deoxy- α -D-glucopyranoside (3).—Acetyl chloride (800 mg) in dichloromethane (6 ml) was added to a solution of imidazole (1.3 g) in dichloromethane (10 ml). After 15 min at 5 °C, imidazole hydrochloride was removed by filtration. The filtrate was added to a solution of benzyl 2-acetamido-3-O-allyl-2-deoxy- α -D-glucopyranoside (2) (3 g) in dioxan (30 ml). The mixture was heated at 95 °C for 5 days and then evaporated to dryness. The residue was dissolved in chloroform (200 ml) and the organic phase washed successively with dilute aqueous sodium hydrogen carbonate and water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel (100 g); elution with chloroform-methanol (24 : 1) gave *compound (3)* (2.85 g, 85%), m.p. 127–128° (from ethyl acetate-ether), $[\alpha]_D^{20} + 104^\circ$ (*c* 1 in CHCl_3), δ 1.91 and 2.08 (6 H, 2s, Ac), 4.87 (1 H, d, $J_{1,2}$ 4 Hz, H-1), and 7.35 (5 H, s, Ph) (Found: 60.9; 7.0; N, 3.8. $\text{C}_{20}\text{H}_{27}\text{NO}_7$ requires C, 61.0; H, 6.9; N, 3.6%).

Benzyl 2-Acetamido-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-3-O-allyl-6-O-benzyl-2-deoxy- α -D-glucopyranoside (6).—A solution of benzyl 2-acetamido-3-O-allyl-6-O-benzyl-2-deoxy- α -D-glucopyranoside (4) (882 mg) in 1,2-dichloroethane containing anhydrous powdered mercuric bromide (145 mg) and powdered molecular sieves 4 Å (1 g) was heated under a dry atmosphere of nitrogen. After solvent (10 ml) had been distilled off a freshly prepared solution of 2,3,4,6-tetra-O-acetyl- α -D-galactopyranosyl bromide (822 mg) in anhydrous 1,2-dichloroethane (5 ml) was added and more solvent (5 ml) was distilled off. After refluxing for 6 h, a solution of 2,3,4,6-tetra-O-acetyl- α -D-galactopyranosyl bromide (411 mg) in 1,2-dichloroethane (5 ml) and mercuric bromide (72 mg) were added. After solvent (5 ml) had been distilled off, the mixture was heated at 90 °C during 24 h. After cooling, the reaction mixture was diluted with 1,2-dichloroethane (100 ml), filtered, washed with aqueous potassium iodide, aqueous sodium bicarbonate, and water, and then dried (Na_2SO_4) and evaporated. The residue was chromatographed on silica gel (180 g); elution with ethyl acetate-ether (1 : 1) gave two compounds. The first compound eluted was benzyl 2-acetamido-4-O-acetyl-3-O-allyl-6-O-benzyl- β -D-glucopyranoside (5) (8%) and the major product was the *disaccharide (6)* (1.2 g, 77%), m.p. 79–80° (from ether), $[\alpha]_D^{20} + 59^\circ$ (*c* 1 in CHCl_3), δ 1.93, 2.01, and 2.10 (15 H, 3s, Ac), 4.55 (1 H, d, $J_{1',2'}$ 7.5 Hz, H-1'), 5.53 (1 H, d, J 9 Hz, NH), and 7.33 and 7.38 (10 H, 2s, Ph) (Found: C, 60.9; H, 6.3; N, 2.0; O, 30.8. $\text{C}_{39}\text{H}_{49}\text{NO}_{15}$ requires C, 60.7; H, 6.4; N, 1.8; O, 31.1%). Elution with ethyl acetate-ethanol (1 : 1) gave a small amount of starting material (4) (12 mg, 1.3%).

Benzyl 2-Acetamido-3-O-allyl-6-O-benzyl-4-O- β -D-galactopyranosyl-2-deoxy- α -D-glucopyranoside (7).—A solution of benzyl 2-acetamido-3-O-allyl-6-O-benzyl-2-deoxy- α -D-glucopyranoside (4) (441 mg) and mercuric cyanide (505 mg) in 3 : 1 nitromethane-benzene (20 ml) was stirred in the presence of powdered molecular sieves (4 Å) (500 mg). A solution of 2,3,4,6-tetra-O-acetyl- α -D-galactopyranosyl bromide (806 mg) in anhydrous 1,2-dichloroethane (6 ml) was added, and the mixture was stirred for 20 h at room temperature. Further bromide (403 mg) in anhydrous 1,2-dichloroethane (6 ml) was then added and the mixture was

stirred for 15 h. The mixture was diluted with benzene (100 ml), washed with aqueous potassium iodide and water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on silica gel (100 g); elution with ethyl acetate-ether (1 : 1) gave first benzyl 2-acetamido-4-O-acetyl-3-O-allyl-6-O-benzyl- α -D-glucopyranoside (5) (34 mg, 7%), and a major fraction (580 mg) containing the disaccharide (6) and the starting material (4). This fraction was O-deacetylated (sodium methoxide in methanol). After usual work-up, the residue was chromatographed on silica gel (50g); elution with chloroform-methanol (7 : 1) gave two compounds. First eluted was starting material (4) (49 mg, 11%) and the major product was the disaccharide (7) (392 mg, 65%), m.p. 195–196° (from ethyl acetate-ethanol), $[\alpha]_D^{20} + 97.5^\circ$ (*c* 1 in MeOH), δ 1.83 (3 H, s, Ac) and 7.38 (10 H, s, Ph) (Found: C, 61.6; H, 6.8; N, 2.2; O, 29.1. $\text{C}_{31}\text{H}_{41}\text{NO}_{11}$ requires C, 61.7; H, 6.8; N, 2.3; O, 29.1%).

Similar results were obtained in benzene at reflux temperature. The disaccharide (7) (250 mg) was acetylated (acetic anhydride-pyridine) to give *compound (6)* (285 mg, 89%), m.p. 79.5–80.5°, $[\alpha]_D^{20} + 59^\circ$ (*c* 1 in CHCl_3), identical with the disaccharide previously prepared.

Benzyl 2-Acetamido-6-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- β -D-galactopyranosyl)-3-O-allyl-2-deoxy- α -D-glucopyranoside (8).—A solution of benzyl 2-acetamido-6-O-acetyl-3-O-allyl-2-deoxy- α -D-glucopyranoside (3) (983 mg) in 1,2-dichloroethane (25 ml) containing anhydrous and powdered mercuric bromide (180 mg) and powdered molecular sieves (4 Å) (1 g) was heated under dry nitrogen. After solvent (10 ml) had been distilled off, a freshly prepared solution of 2,3,4,6-tetra-O-acetyl- α -D-galactopyranosyl bromide (1.028 g) in anhydrous 1,2-dichloroethane (8 ml) was added and more solvent (8 ml) was distilled off. After refluxing for 1.5 h, a solution of 2,3,4,6-tetra-O-acetyl- α -D-galactopyranosyl bromide (411 mg) in 1,2-dichloroethane (5 ml) and mercuric bromide (72 mg) were added. After solvent (5 ml) had been distilled off, the mixture was heated at 90 °C for 2 h. After cooling, the mixture was diluted with chloroform (150 ml), filtered, washed successively with aqueous potassium iodide, aqueous sodium bicarbonate, and water, and then dried (CaCl_2) and evaporated. The residue was chromatographed on silica gel (200 g); elution with ether-ethyl acetate (1.5 : 1) gave two main fractions, A and B. Fraction B was evaporated to give the disaccharide (8) (1.525 g, 78%) as a glass, $[\alpha]_D^{20} + 62^\circ$ (*c* 1 in CHCl_3); δ 1.92, 1.94, 2.01, 2.06, 2.10, and 2.12 (18 H, 6s, Ac), 4.65 (1 H, d, $J_{1',2'}$ 7.5 Hz, H-1'), 4.85 (1 H, d, $J_{1,2}$ 4.5 Hz, H-1), 5.65 (1 H, d, J 9 Hz, NH), and 7.35 (5 H, s, Ph) (Found: C, 56.3; H, 6.1; N, 2.1; O, 35.0. $\text{C}_{34}\text{H}_{45}\text{NO}_{16}$ requires C, 56.4; H, 6.3; N, 1.9; O, 35.4%). Fraction A was evaporated and the residue was O-deacetylated (sodium methoxide in methanol). After usual work-up, the residue (180 mg) was chromatographed on silica gel (12 g); elution with chloroform-methanol (4 : 1) gave two compounds. First eluted was benzyl 2-acetamido-3-O-allyl-2-deoxy- α -D-glucopyranoside (2) (42 mg, 6%), m.p. 176–178°, $[\alpha]_D^{20} + 164^\circ$ (*c* 1 in MeOH), and the second compound was *benzyl 2-acetamido-3-O-allyl-2-deoxy-4-O- α -D-galactopyranosyl- α -D-glucopyranoside (12)* (74 mg, 7.2%), m.p. 181–182° (from ethanol), $[\alpha]_D^{20} + 162^\circ$ (*c* 1 in pyridine); δ (in CD_3OD) 1.91 (3 H, s, Ac), 5.11 (1 H, d, $J_{1,2}$ 3 Hz, H-1), 5.50 (1 H, d, $J_{1',2'}$ 4 Hz, H-1'), and 7.32 (5 H, s, Ph) (Found: C, 56.1; H, 6.8; N, 2.7; O, 34.3. $\text{C}_{24}\text{H}_{35}\text{NO}_{11}$ requires C, 56.1; H, 6.9; N, 2.7; O, 34.3%).

Benzyl 2-Acetamido-3-O-allyl-2-deoxy-4-O-β-D-galactopyranosyl-α-D-glucopyranoside (9).—Compound (8) (160 mg) was O-deacetylated (sodium methoxide in methanol). After usual work-up, the residue was crystallised from ethanol-methanol to give compound (9) (93 mg, 82%), m.p. 237—238°, $[\alpha]_D +96^\circ$ (c 1 in pyridine); δ 1.97 (3 H, s, Ac), 5.13 (1 H, d, $J_{1,2}$ 4.5 Hz, H-1), 7.23 (5 H, s, Ph), and 8.53 (1 H, d, 9 Hz, NH) (Found C, 56.2; H, 7.0; N, 2.6; O, 34.3. $C_{24}H_{35}NO_{11}$ requires C, 56.1; H, 6.9; N, 2.7; O, 34.3%).

Benzyl 2-Acetamido-6-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-α-D-galactopyranosyl)-3-O-allyl-2-deoxy-α-D-glucopyranoside (13).—Compound (12) (50 mg) was acetylated (pyridine-acetic anhydride). After work-up, the residue (69 mg, 98%) did not crystallise, $[\alpha]_D +112^\circ$ (c 1 in $CHCl_3$), δ 1.92, 1.95, 2.02, 2.10, and 2.12 (18 H, 5s, Ac), 4.85 (1 H, d, $J_{1,2}$ 4.5 Hz, H-1), 5.55 (1 H, d, $J_{1,2}$ 3.5 Hz, H-1'), 5.62 (1 H, d, J 9 Hz, NH), and 7.37 (5 H, s, Ph) (Found: C, 55.9; H, 6.3; N, 1.9. $C_{34}H_{45}NO_{16}$ requires C, 56.4; H, 6.3; N, 1.9%).

Benzyl 2-Acetamido-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-6-O-benzyl-2-deoxy-α-D-glucopyranoside (10).—Compound (6) (1.77 g), ethanol (32 ml), benzene (14 ml), water (4.5 ml), and chloro(trisphenylphosphine)-

5.08 (1 H, d, $J_{1,2}$ 3 Hz, H-1), 5.26 (1 H, d, $J_{1,2}$ 3 Hz H-1''), 6.55 (1 H, d, J 8 Hz, NH), and 7.30 (25 H, m, Ph) (Found: C, 65.7; H, 6.4; N, 1.2; O, 26.7. $C_{63}H_{73}NO_{19}$ requires C, 65.9; H, 6.4; N, 1.2; O, 26.5%).

Benzyl 2-Acetamido-6-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-3-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-2-deoxy-α-D-glucopyranoside (15).—Compound (11) (500 mg) was fucosylated as previously described. Crystallisation of the residue from ethyl acetate-ether gave the trisaccharide (15) (417 mg, 52%), m.p. 132—133°, $[\alpha]_D +15^\circ$ (c 1 in $CHCl_3$); more crystalline material (270 mg) was obtained by chromatography the mother liquors on silica gel (50 g) (dichloromethane-ether, 4:3); total yield 85%; δ 1.21 (3 H, d, J 7 Hz, Me), 1.54 (3 H, s, Ac), 1.91, 1.99, 2.01, and 2.08 (15 H, 4s, Ac), 5.18 (1 H, d, $J_{1,2}$ 3 Hz, H-1''), 6.67 (1 H, d, 8 Hz, NH), and 7.30 (20 H, m, Ph) (Found: C, 62.3; H, 6.3; N, 1.3; O, 29.9. $C_{58}H_{69}NO_{11}$ requires C, 62.2; H, 6.4; N, 1.3; O, 30.1%).

Benzyl 2-Acetamido-6-O-benzyl-3-O-(2,3,4-tri-O-benzyl-α-L-fucopyranosyl)-4-O-(β-D-galactopyranosyl)-2-deoxy-α-D-glucopyranoside (16).—Compound (14) (700 mg) was O-deacetylated (sodium methoxide in methanol). After usual work-up, the residue was crystallised from ethyl

² Presented at the Chemical Society Carbohydrate Group Easter Meeting, Norwich, April 1977.

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