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SYNTHESIS OF SOME OLIGOSACCHARIDES CONTAINING THE *O*-α-L-FUCOPYRANOSYL-(1→2)-D-GALACTOPYRANOSYL UNIT*

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ABSTRACT

A practical approach for the synthesis of oligosaccharides containing the *O*-α-L-fucopyranosyl-(1→2)-D-galactopyranosyl unit has been developed by utilizing the readily accessible 3,4,6-tri-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-α-D-galactopyranosyl bromide (**1**). Thus, condensation of bromide **1** with 8-(methoxycarbonyl)octanol in benzene, in the presence of mercuric cyanide, afforded, after column-chromatographic separation, the anomers (**3** and **4**) of 8-(methoxycarbonyl)octyl 3,4,6-tri-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-D-galactopyranoside in the ratio of 13:4. On the basis of their specific rotations, compounds **3** and **4** were tentatively assigned the α and β configuration, respectively. Similarly, bromide **1** was allowed to react with some other, appropriately protected sugars having a free alcohol group, to afford the corresponding α and β anomers of a galactopyranosyl residue having an α-L-fucopyranosyl substituent at O-2. Column-chromatographic separation of the anomeric mixtures, followed by systematic removal of the protecting groups, then provided the final oligosaccharides desired. In this manner, the synthesis of the following oligosaccharides has been accomplished: α-L-Fuc-(1→2)-α-D-Gal-1→O$(CH_2)_8CO_2$Me (**5**), α-L-Fuc-(1→2)-β-D-Gal-1→O$(CH_2)_8CO_2$Me (**6**), α-L-Fuc-(1→2)-α-D-Gal-(1→3)-β-D-GlcNAc-1→O$C_6H_4NO_2$-*p* (**11**), α-L-Fuc-(1→2)-β-D-Gal-(1→3)-β-D-GlcNAc-1→O$C_6H_4NO_2$-*p* (**13**), α-L-Fuc-(1→2)-α-D-Gal-(1→3)-α-D-GalNAc-1→O$C_6H_4NO_2$-*o*, and α-L-Fuc-(1→2)-β-D-Gal-(1→3)-α-D-GalNAc-1→O$C_6H_4NO_2$-*o* (**18**). The structures assigned to compounds **5**, **6**, **11**, **13**, and **18** were all supported by their respective ^{13}C-n.m.r. spectra.

INTRODUCTION

The disaccharide unit α-L-Fuc-(1→2)-β-D-Gal has been found to occur as part of the carbohydrate moiety of various glycoconjugates, particularly the blood-

*Synthetic Studies in Carbohydrates, Part XXXVII. For Part XXXVI, see ref. 1.

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TABLE I

STRUCTURE OF SOME HUMAN BLOOD-GROUP DETERMINANTS[a]

Antigenic determinant	*Structure*[b]
Lewis-d (H type 1)	α-Fuc-(1→2)-β-Gal-(1→3)-β-GlcNAc-
Lewis-b	α-Fuc-(1→2)-β-Gal-(1→3)-[α-Fuc-(1→4)]-β-GlcNAc-
H type 2	α-Fuc-(1→2)-β-Gal-(1→4)-β-GlcNAc-
Y	α-Fuc-(1→2)-β-Gal-(1→4)-[α-Fuc-(1→3)]-β-GlcNAc-
AH type 2	β-GalNAc-(1→3)-α-Fuc-(1→2)]-β-Gal-(1→4)]-β-GlcNAc-

[a]Taken from ref. 2. [b]Except for L-fucose, all of the sugars are members of the D series.

group-specific glycoproteins and glycolipids[2]. The structures of some human, blood-group determinants containing this disaccharide unit are given in Table I.

Recent progress in the field of carbohydrate chemistry provided various approaches for the chemical synthesis of the carbohydrate units of such blood-group antigens[3,4]. However, it is always tempting, and often desirable, to improve on the existing methods with the aim of rendering them simpler and more amenable. With this in mind, we now describe an alternative approach for the synthesis of some oligosaccharides containing the α-L-Fuc-(1→2)-D-Gal unit.

RESULTS AND DISCUSSION

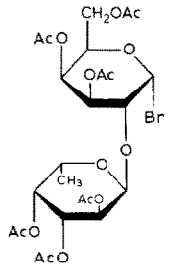
Since it was first announced, almost two decades ago[5], halide-ion-catalyzed glycosylation has been one of the most extensively utilized methods for the synthesis of α-linked fucopyranosides. However, the preparation of the fucosylating agent (*i.e.*, 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide) from the commercially available L-fucose involves a lengthy, multistep procedure. An alternative method, advocated by Flowers and Dejter-Juszynski[6] also suffers from a similar shortcoming, as it utilizes 2-*O*-benzyl-3,4-di-*O*-(*p*-nitrobenzoyl)-α-L-fucopyranosyl bromide, the preparation of which is far from simple.

In their first synthesis of the disaccharide α-L-Fuc-(1→2)-Gal, Levy and coworkers[7] condensed 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide with benzyl 6-*O*-benzoyl-3,4-*O*-isopropylidene-β-D-galactopyranoside. This method appears to be attractive, in so far as the preparation of the glycosylating agent (*i.e.*, the acetylated fucosyl bromide) from L-fucose requires only two, relatively good-yielding, steps. In our own experience[8], however, use of the readily accessible 1,3,4,6-tetra-*O*-acetyl-α-D-galactopyranose[9], instead of benzyl 6-*O*-benzoyl-3,4-*O*-isopropylidene-β-D-galactopyranoside, under otherwise similar reaction-conditions, provided a yet even simpler (and straightforward) synthesis of the same disaccharide.

Also, we previously described the synthesis of 3,4,6-tri-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-α-D-galactopyranosyl bromide[10] (**1**), and, by syn-

thesis of *p*-nitrophenyl 2-*O*-α-L-fucopyranosyl-β-D-galactopyranoside, demonstrated that it can be utilized as a glycosyl donor. We have now extended the use of bromide **1** for the synthesis of a variety of other oligosaccharides containing the α-L-Fuc-(1→2)-Gal unit.

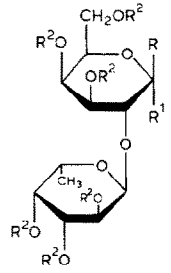
On condensation of bromide **1** with 8-(methoxycarbonyl)octanol (**2**) in benzene, in the presence of mercuric cyanide, examination of the reaction mixture by thin-layer chromatography (t.l.c.) revealed the presence of a major, slower-migrating, and a minor, faster-migrating product. Column-chromatographic separation of the mixture afforded compounds **3** and **4** in the ratio of 13:4. On the basis of their specific rotations, compounds **3** and **4** were tentatively designated as the α and β anomer, respectively; this was supported by the ^{13}C-n.m.r. spectra of their *O*-deacetylated derivatives. Thus, *O*-deacetylation of **3** in methanol with Amberlyst A-26 (OH^-) anion-exchange resin[11] furnished, quantitatively, 8-(methoxycarbonyl)octyl 2-*O*-α-L-fucopyranosyl-α-D-galactopyranoside (**5**), the ^{13}C-n.m.r. spectrum of which was in accord with the structure assigned; the signals for C-1 (98.86 p.p.m.) and C-1′ (102.59 p.p.m.) were in agreement with an α and a β configuration, respectively, at the two glycosidic linkages. Similarly, *O*-deacetylation of **4** afforded 8-(methoxycarbonyl)octyl 2-*O*-α-L-fucopyranosyl-β-D-galactopyranoside (**6**), the ^{13}C-n.m.r. spectrum of which was, also, in agreement with the structure assigned; see Table II. It is noteworthy that such compounds as **6** are complete hap-



1

$HO(CH_2)_8CO_2Me$

2



3 R = H, R^1 = $O(CH_2)_8CO_2Me$, R^2 = Ac
4 R = $O(CH_2)_8CO_2Me$, R^1 = H, R^2 = Ac
5 R = R^2 = H, R^1 = $O(CH_2)_8CO_2Me$
6 R = $O(CH_2)_8CO_2Me$, R^1 = R^2 = H

tens, as they possess the functional group (CO_2Me) that had been successfully employed by Lemieux *et al.*[12] for the preparation of artificial oligosaccharide antigens having a nine-carbon-atom linking-arm.

Condensation of bromide **1** with *p*-nitrophenyl 2-acetamido-2-deoxy-4,6-*O*-(*p*-methoxybenzylidene)-α-D-glucopyranoside (**7**) in 1:1 benzene–nitromethane, in the presence of mercuric cyanide, also provided an anomeric mixture that was separated by repeated column-chromatography on silica gel, to afford compounds **8** and **9**. Cleavage of the acetal group of **8** and **9** in warm, 70% aqueous acetic acid gave compounds **10** and **12**, respectively; these were separately purified by silica gel

TABLE II

^{13}C-N.M.R. CHEMICAL SHIFTS[a]

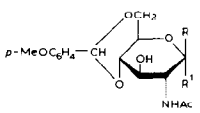
Atoms	*Compound*		
	6	**13**	**18**
C-1	102.45	98.83	96.39
C-2	77.72	53.53	96.39
C-3	74.82	79.51	75.37
C-4	70.59	68.03	67.42
C-5	75.89	76.39	72.46
C-6	61.81	60.15	60.10
$NHCOCH_3$	—	22.79	22.17
C=O	—	168.88	169.81
OCH_3	53.03	—	—
C-1′	100.39	99.66	101.60
C-2′	69.35	76.91	79.64
C-3′	71.38	71.31	71.28
C-4′	72.92	67.79	67.42
C-5′	67.70	75.45	74.92
C-6′	16.57	60.15	60.10
C-1″		100.49	100.74
C-2″		68.60	68.96
C-3″		69.46	69.64
C-4″		73.74	72.88
C-5″		65.87	66.07
C-6″		16.29	16.20

[a]Solvent was Me_2SO-d_6, except for D_2O for **6**. The reference standard (Me_4Si) was internal for solutions in Me_2SO-d_6, and external for solutions in D_2O.

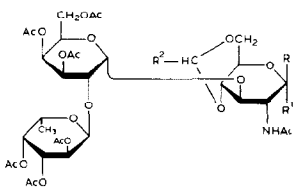
chromatography and then deacetylated, to afford, respectively, crystalline trisaccharide α-L-fuc-(1→2)-α-D-Gal-(1→3)-β-D-GlcNAc-1→$OC_6H_4NO_2$-*p* (**11**) and amorphous α-L-fuc-(1→2)-β-D-Gal-(1→3)-β-D-GlcNAc-1→$OC_6H_4NO_2$-*p* (**13**).

Condensation of bromide **1** with *o*-nitrophenyl 2-acetamido-2-deoxy-4,6-*O*-(*p*-methoxybenzylidene)-α-D-galactopyranoside (**14**) under conditions similar to those already described also gave a mixture of anomers that was separated, and analogously processed, to furnish the final oligosaccharides **16** and **18**.

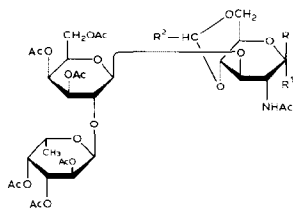
It is noteworthy that our synthetic disaccharide β-Gal-(1→3)-α-GalNAc-1→$OC_6H_4NO_2$-*p* acted as a chromogenic substrate for an endo-α-*N*-acetylgalactosaminidase[13]. It would thus be reasonable to expect compound **18** to act, also, as



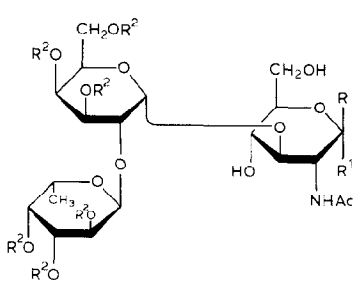
7 R = $OC_6H_4NO_2$-*p*, R′ = H



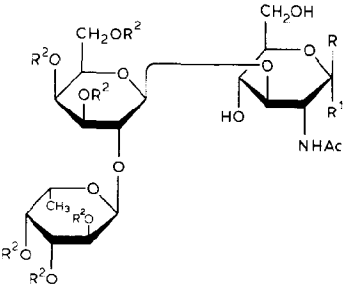
8 R = $OC_6H_4NO_2$-*p*, R′ = H, R″ = C_6H_4OMe-*p*



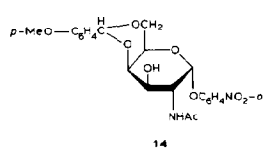
9 R = $OC_6H_4NO_2$-*p*, R′ = H, R″ = C_6H_4OMe-*p*



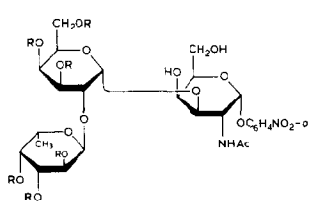
10 R = $OC_6H_4NO_2$-*p*, R^1 = H, R^2 = Ac
11 R = $OC_6H_4NO_2$-*p*, R^1 = R^2 = H



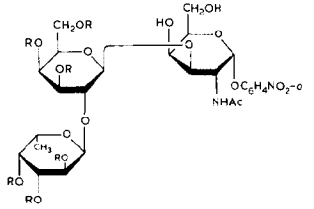
12 R = $OC_6H_4NO_2$-*p*, R^1 = H, R^2 = Ac
13 R = $OC_6H_4NO_2$-*p*, R^1 = R^2 = H



14



15 R = Ac
16 R = H



17 R = Ac
18 R = H

a chromogenic substrate for such endoenzymes. Moreover, compound **18** may also serve as a reference compound for the modification of an assay procedure for α-(1→2)-L-fucosyltransferase, when the disaccharide β-Gal-(1→3)-α-GalNAc-1→$OC_6H_4NO_2$-*o* is used as the acceptor[14].

After reduction of the nitro group, and subsequent attachment to a solid support, oligosaccharides *O*-glycosylically linked to *p*-nitrophenol have frequently been utilized for the purification of lectins[15], and also as synthetic antigens[16,17]. It would seem plausible to designate compound **13** "a potential blood-group Lewis-d antigen", as the carbohydrate sequence α-Fuc-(1→2)-β-Gal-(1→3)-β-GlcNAc-1→ (see Table I) occurs as part of the blood-group Lewis-d (H type 1) antigen.

EXPERIMENTAL

General methods. — These were the same as those already described[1], except that the following solvent systems (v/v) were used for chromatography: *A*, 1:1 ethyl acetate–hexane; *B*, 3:1 chloroform–methanol; *C*, 2:1 chloroform–acetone; *D*, 4:1 chloroform–acetone; *E*, 6:1 chloroform–acetone; *F*, 9:1 chloroform–acetone; *G*, 15:1 chloroform–acetone; and *H*, 19:1 chloroform–acetone.

*Condensation of 3,4,6-tri-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-acetyl-α-*L*-fucopyranosyl)-α-*D*-galactopyranosyl bromide* (**1**) *with 8-(methoxycarbonyl)octanol* (**2**). — A mixture of bromide **1** (1.1 g), mercuric cyanide (0.7 g), and 8-(methoxycar-

bonyl)octanol (**2**; 0.37 g) in dry benzene (50 mL) was stirred for two days at room temperature. T.l.c. (solvent *A*) then revealed the presence of a major, slower-migrating, and a minor, faster-migrating product. The solution was successively washed with aqueous sodium hydrogencarbonate and water, dried, and evaporated to a thick syrup which was dissolved in a small volume of ethyl acetate, and the solution applied to a column of silica gel. On elution with solvent *A*, evaporation of the fractions corresponding to the minor product afforded syrupy 8-(methoxycarbonyl)octyl 3,4,6-tri-*O*-acetyl-2-*O*-(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-β-D-galactopyranoside* (**4**) (0.2 g, 13%); $[\alpha]_D$ −88.8° (*c* 2.6, chloroform).

Continued elution with the same solvent-system, and evaporation of the fractions corresponding to the major product, afforded the α-D-galactopyranosyl* anomer **3** (0.65 g, 43%) as a syrup; $[\alpha]_D$ −11.4° (*c* 1.0, chloroform).

8-(Methoxycarbonyl)octyl 2-O-α-L-fucopyranosyl-α-D-galactopyranoside (**5**). — A solution of **3** (0.5 g) in methanol (20 mL), containing a catalytic amount of Amberlyst A-26 (OH^-) anion-exchange resin[11], was stirred overnight at room temperature. The resin was then filtered off and washed with methanol, and the filtrate and washings were combined and evaporated, to furnish compound **5** (0.3 g, 90%), amorphous; $[\alpha]_D$ +1.1° (*c* 1.3, methanol); t.l.c. (solvent *B*): R_F 0.62; ^{1}H-n.m.r. data (D_2O): δ 1.60–2.20 [15 H, $(CH_2)_6$ + CMe], 2.84 (t, 2 H, *J* 7 Hz, CH_2CO), 4.16 (s, 3 H, OMe), and 5.52 (2 H, H-1,1′); ^{13}C-n.m.r. data (D_2O): δ 16.67 (C-6′), 53.03 (OCH_3), 62.01 (C-6), 79.08 (C-2), 98.86 (C-1), and 102.59 (C-1′).

Anal. Calc. for $C_{22}H_{40}O_{12}$: C, 53.21; H, 8.12. Found: C, 52.93; H, 8.31.

8-(Methoxycarbonyl)octyl 2-O-α-L-fucopyranosyl-β-D-galactopyranoside (**6**). — *O*-Deacetylation of **4** (90 mg), as described for **3**, to give **5**, furnished amorphous **6** (30 mg, 50%); $[\alpha]_D$ −81.5° (*c* 0.8, methanol); t.l.c. (solvent *B*): R_F 0.48; ^{1}H-n.m.r. data (D_2O): δ 1.60–2.20 [m, 15 H, $(CH_2)_6$ + CMe], 2.84 (t, 2 H, *J* 6.5 Hz, CH_2CO), 4.16 (s, 3 H, OMe), 4.93 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), and 5.72 (1 H, H-1′); for ^{13}C-n.m.r. data, see Table II.

Anal. Calc. for $C_{22}H_{40}O_{12}$: C, 53.21; H, 8.12. Found: C, 53.45; H, 8.38.

p-*Nitrophenyl 2-acetamido-2-deoxy-4,6-O-(p-methoxybenzylidene)-3-O-[3,4,6-tri-O-acetyl-2-O-(2,3,4-tri-O-acetyl-α-L-fucopyranosyl)-α-D-galactopyranosyl]-β-D-glucopyranoside* (**8**) *and* p-*nitrophenyl 2-acetamido-2-deoxy-4,6-O-(p-methoxybenzylidene)-3-O-[3,4,6-tri-O-acetyl-2-O-(2,3,4-tri-O-acetyl-α-L-fucopyranosyl)-β-D-galactopyranosyl]-β-D-glucopyranoside* (**9**). — A solution of compound **7** (0.92 g, 2 mmol) in 1:1 (v/v) benzene–nitromethane (100 mL) was boiled until 20 mL of the solvent had distilled off. The temperature was then adjusted to ~55° (bath), mercuric cyanide (0.76 g, 3 mmol) and a solution of bromide **1** (1.92 g, 3 mmol) in 1:1 nitromethane–benzene (20 mL) were added, and the mixture was stirred for 2 days, allowed to cool to room temperature, diluted with benzene (50 mL), successively washed with aqueous sodium hydrogencarbonate, and water, dried, and evaporated; the crude mixture was subjected to column chromatog-

*The assignments of these configurations are only tentative; but, see later.

raphy on silica gel. Elution with solvent *H*, and evaporation of the fractions corresponding to the major product gave the α anomer **8** (1.1 g). Further elution, with solvent *G*, afforded the minor, slower-migrating β anomer **9** (0.3 g). Both **8** and **9** were characterized after cleavage of their *p*-methoxybenzylidene group; see later.

p-*Nitrophenyl 2-acetamido-2-deoxy-3*-O-[*3,4,6-tri*-O-*acetyl-2*-O-*(2,3,4-tri*-O-*acetyl-α*-L-*fucopyranosyl)-α*-D-*galactopyranosyl*]-*β*-D-*glucopyranoside* (**10**). — Compound **8** (1.1 g) in 70% aqueous acetic acid (50 mL) was heated for 1 h at 55°. The acetic acid was evaporated under diminished pressure, the last traces being removed by co-evaporation with several portions of water, and then of toluene. The solid residue so obtained was applied to a column of silica gel and sequentially eluted with chloroform, with solvent *F*, and with solvent *D*. Evaporation of the fractions corresponding to the product gave **10** (0.8 g, 44% overall yield, based on **7**); amorphous; $[\alpha]_D$ −4.7° (*c* 0.9, methanol); t.l.c. (solvent *C*): R_F 0.49; ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.05 (d, 1 H, *J* 6.5 Hz, CMe), 1.83–2.16 (cluster of singlets, 21 H, 6 OAc and NAc), 5.17 (d, 1 H, $J_{1'',2''}$ 3.5 Hz, H-1''), 5.65 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1'), and 7.25 and 8.27 (2 m, 2 × 2 H, aromatic); ^{13}C-n.m.r. data (Me_2SO-d_6): δ 15.42 (C-''), 20.28 (OAc), 22.55 (NAc), 53.62 (C-2), 60.15 (C-6), 60.59 (C-6'), 77.00 (C-2'), 78.21 (C-3), 95.88 (C-1''), 96.95 (C-1'), 97.85 (C-1), and 169.03–169.98 (C=O).

Anal. Calc. for $C_{38}H_{50}N_2O_{23}$: C, 50.55; H, 5.58; N, 3.10. Found: C, 50.09; H, 5.63; N, 2.75.

p-*Nitrophenyl 2-acetamido-2-deoxy-3*-O-[*3,4,6-tri*-O-*acetyl-2*-O-*(2,3,4-tri*-O-*acetyl-α*-L-*fucopyranosyl)-β*-D-*galactopyranosyl*]-*β*-D-*glucopyranoside* (**12**). — Cleavage of the acetal group of compound **9** (0.3 g), exactly as described for **8** (to give **10**), afforded compound **12** (0.2 g, 11% overall yield, based on **7**); amorphous; $[\alpha]_D$ −42.6° (*c* 1.2, methanol); t.l.c. (solvent *C*): R_F 0.54; ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.05 (d, 3 H, *J* 6 Hz, CMe), 1.90–2.13 (cluster of singlets, 21 H, 6 OAc and NAc), 5.10 (d, 1 H, $J_{1'',2''}$ 4 Hz, H-1''), 7.11 and 8.25 (2 m, 2 × 2 H, aromatic), and 8.09 (d, 1 H, *J* 9 Hz, NH); ^{13}C-n.m.r. data (Me_2SO-d_6): δ 15.21 (C-6''), 20.28 (OAc), 22.50 (NAc), 53.37 (C-2), 60.23 (C-6), 60.81 (C-6'), 76.83 (C-2'), 79.56 (C-3), 95.96 (C-1), 98.60 (C-1''), 99.19 (C-1'), and 168.54–169.77 (C=O).

Anal. Calc. for $C_{38}H_{50}N_2O_{23} \cdot 0.5\ H_2O$: C, 50.05; H, 5.64; N, 3.07. Found: C, 49.94; H, 5.66; N, 2.79.

p-*Nitrophenyl 2-acetamido-2-deoxy-3*-O-*(2*-O-*α*-L-*fucopyranosyl-α*-D-*galactopyranosyl)-β*-D-*glucopyranoside* (**11**). — A solution of compound **10** (0.6 g) in a mixture of methanol (18 mL), triethylamine (6 mL), and water (5 mL) was kept overnight at ~4°, whereupon the deacetylation product crystallized out. The crystalline material was filtered off, thoroughly washed with ethanol, and dried, to afford compound **11** (0.23 g, 53%); m.p. 262–264°, $[\alpha]_D$ +14.3° (*c* 0.5, Me_2SO).

Anal. Calc. for $C_{26}H_{38}N_2O_{17}$: C, 48.00; H, 5.89; N, 4.31. Found: C, 48.01; H, 6.00; N, 4.13.

p-*Nitrophenyl 2-acetamido-2-deoxy-3*-O-*(2*-O-*α*-L-*fucopyranosyl-β*-D-*galactopyranosyl)-β*-D-*glucopyranoside* (**13**). — *O*-Deacetylation of **12** (0.15 g), as de-

scribed for **10** (to give **11**), furnished trisaccharide **13** (0.1 g, 92%); amorphous; $[\alpha]_D$ −52.5° (*c* 0.5, Me_2SO); ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.09 (d, 3 H, *J* 6.5 Hz, CMe), 1.90 (s, 3 H, NAc), 5.14 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), 7.18 and 8.25 (2 m, 2 × 2 H, aromatic), and 7.88 (d, 1 H, *J* 9 Hz, NH); for ^{13}C-n.m.r. data, see Table II.

Anal. Calc. for $C_{26}H_{38}N_2O_{17} \cdot 0.5\ H_2O$: C, 47.34; H, 5.96; N, 4.25. Found: C, 47.12; H, 6.27; N, 4.31.

o-*Nitrophenyl 2-acetamido-2-deoxy-3*-O-[*3,4,6-tri*-O-*acetyl-2*-O-*(2,3,4-tri*-O-*acetyl-α*-L-*fucopyranosyl)-α*-D-(**15**) *and -β*-D-(**17**)-*galactopyranosyl*]-*α*-D-*glucopyranoside.* — Bromide **1** (1.92 g, 3 mmol) was condensed with compound **14** (0.92 g, 2 mmol) in 1:1 benzene–nitromethane, in the presence of mercuric cyanide (0.72 g, 3 mmol), exactly as described for **7** (to give **8** and **9**). After processing in the usual manner, t.l.c. (solvent *D*) revealed the presence of two products, both faster-migrating than **14**; a little unchanged **14**; and some faster-migrating contaminants (possibly due to the decomposition of **1**). The crude product was applied to a column of silica gel, and sequentially eluted with solvents *H*, *G*, and *F*. Evaporation of the fractions containing the faster-migrating product yielded 1.15 g of material that was contaminated (t.l.c., solvent *D*) with some faster-migrating impurities. On evaporation, the fractions containing the slower-migrating product yielded 1.30 g of material that was contaminated (t.l.c., solvent *D*) with some unchanged **14**.

The slower-migrating, crude product (1.3 g) in 70% aqueous acetic acid (50 mL) was heated for 1 h at ~55°. After processing in the usual manner, the product was purified in a column of silica gel by sequential elution with solvents *E*, *D*, and *C*, to afford **15** (0.63 g; 51.4% yield based on **14**); amorphous; $[\alpha]_D$ +95.9° (*c* 2.3, methanol); ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.13 (d, 3 H, *J* 6 Hz, CMe), 1.90–2.14 (cluster of singlets, 21 H, 6 AcO and NAc), 5.92 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), and 7.17–7.98 (m, 5 H, NH and aromatic); ^{13}C-n.m.r. data (Me_2SO-d_6): δ 15.72 (C-6″), 20.31 (OAc), 22.52 (NAc), 47.26 (C-2), 60.44 (C-6′), 60.82 (C-6), 72.75 (C-2′), 74.70 (C-3), 95.34 (C-1″), 95.83 (C-1′), 97.10 (C-1), and 168.95–169.87 (C=O).

Anal. Calc. for $C_{38}H_{50}N_2O_{23}$: C, 50.55; H, 5.58; N, 3.10. Found: C, 50.28; H, 5.79; N, 2.95.

Cleavage of the acetal group of the faster-migrating compound afforded, after processing and column-chromatographic purification by using solvents *E*, *D*, and *C* as the eluants (as described for the slower-migrating compound to give **15**), the *β* anomer **17** (0.23 g; 19% yield, based on **14**); $[\alpha]_D$ +55.4° (*c* 1.5, methanol); ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.09 (d, 3 H, *J* 6 Hz, CMe), 1.92–2.14 (cluster of singlets, 21 H, 6 AcO and NAc), 5.66 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 7.20–8.00 (m, 4 H, aromatic, *J* 9 Hz, NH); ^{13}C-n.m.r. data (Me_2SO-d_6): δ 15.23 (C-6″), 20.27 (OAc), 22.67 (NAc), 47.61 (C-2), 60.02 (C-6), 61.32 (C-6′), 73.56 (C-2′), 73.85 (C-3), 95.78 (C-1), 97.82 (C-1″), 100.69 (C-1′), and 168.80–169.75 (C=O).

Anal. Calc. for $C_{38}H_{50}N_2O_{23}$: C, 50.55; H, 5.58; N, 3.10. Found: C, 50.36; H, 5.74; N, 3.17.

o-*Nitrophenyl 2-acetamido-2-deoxy-3*-O-*(2*-O-*α*-L-*fucopyranosyl-α*-D-*galactopyranosyl)-α*-D-*galactopyranoside* (**16**). — A solution of compound **15** (0.48 g) in

methanol (20 mL) containing 0.5M sodium methoxide in methanol (1 mL) was refrigerated overnight, whereupon crystallization occurred. The crystalline material was filtered off, thoroughly washed with cold methanol, and dried, to give compound **16** (0.3 g, 87%); m.p. 290–291° (from methanol), $[\alpha]_D$ +161.9° (*c* 0.5, Me_2SO).

Anal. Calc. for $C_{26}H_{38}N_2O_{17}$: C, 48.00; H, 5.89; N, 4.31. Found: C, 47.55; H, 6.04; N, 4.26.

o-*Nitrophenyl 2-acetamido-2-deoxy-3-*O-*(2-*O-*α-*L*-fucopyranosyl-β-*D*-galactopyranosyl)-α-*D*-galactopyranoside* (**18**). — *O*-Deacetylation of compound **17** (0.17 g), as described for **15** (to give **16**), afforded the trisaccharide **18** (90 mg, 74%); $[\alpha]_D$ +116.1° (*c* 0.5, Me_2SO); ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.09 (d, 3 H, *J* 6 Hz, CMe), 1.82 (s, 3 H, NAc), 4.64 (1 H, H-1′), 4.92 (1 H, H-1″), 5.85 (d, 1 H, *J* 3.5 Hz, H-1), and 7.16–7.96 (m, 5 H, NH and aromatic); for ^{13}C-n.m.r. data, see Table II.

Anal. Calc. for $C_{26}H_{38}N_2O_{17} \cdot 0.5\ H_2O$: C, 47.34; H, 5.96; N, 4.25. Found: C, 47.42; H, 6.06; N, 3.91.

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