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SYNTHESIS OF PHENYL 2-ACETAMIDO-2-DEOXY-4-*O*-α-L-FUCOPYRANOSYL-β-D-GLUCOPYRANOSIDE AND *p*-NITROPHENYL 2-ACETAMIDO-2-DEOXY-6-*O*-α-L-FUCOPYRANOSYL-β-D-GLUCOPYRANOSIDE*

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ABSTRACT

The reaction of phenyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside with 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide (catalyzed by bromide ion) proceeded readily, to give the protected, 4-*O*-substituted α-L-fucopyranosyl derivative which, on *O*-deacetylation, followed by hydrogenolysis, gave phenyl 2-acetamido-2-deoxy-4-*O*-α-L-fucopyranosyl-β-D-glucopyranoside. The reaction of 2-acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-β-D-glucopyranose with the same glycosyl bromide under similar conditions gave the protected disaccharide derivative which, on hydrogenolysis, furnished 2-acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-6-*O*-α-L-fucopyranosyl-β-D-glucopyranose (**9**). Treatment of compound **9** with acetyl chloride provided the corresponding glycosyl halide which, on reaction with sodium *p*-nitrophenoxide in *N*,*N*-dimethylformamide, gave compound **12**. *O*-Deacetylation of **12** gave *p*-nitrophenyl 2-acetamido-2-deoxy-6-*O*-α-L-fucopyranosyl-β-D-glucopyranoside. The synthesis of *p*-nitrophenyl 2-acetamido-2-deoxy-6-*O*-β-L-fucopyranosyl-β-D-glucopyranoside is also described. The structures of the final disaccharides were established by ^{1}H- and ^{13}C-n.m.r. spectroscopy.

INTRODUCTION

Recently, we reported the synthesis of phenyl 2-acetamido-2-deoxy-3-*O*-α-L-fucopyranosyl-β-D-glucopyranoside[2] (**2**) from **1**. Our continued interest in the synthesis of such aryl saccharides for rapid detection of highly specific α-L-fucosidases has led us to the synthesis of the title disaccharides.

RESULTS AND DISCUSSION

Condensation of phenyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-D-glucopyrano-

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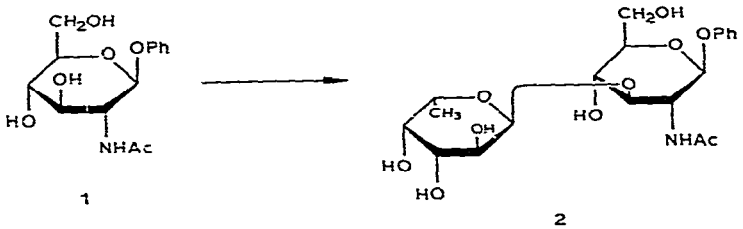
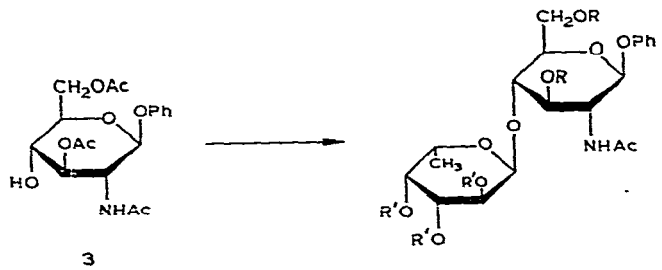
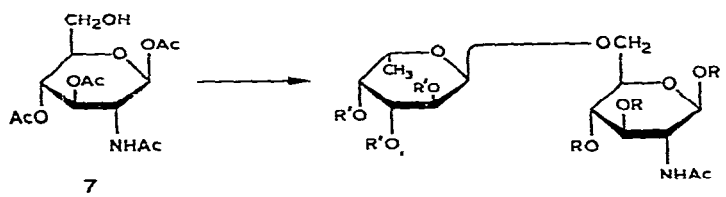
side[3] (3) with 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide under bromide ion-catalyzed reaction-conditions[4] gave crystalline compound **4** in 81% yield. The ^{1}H-n.m.r. spectrum of the disaccharide derivative **4** exhibited a clear doublet at δ 4.72 (J 3.5 Hz), supporting the presence of an α-linked L-fucosyl group in **4**. On treatment with a catalytic amount of sodium methoxide in chloroform–methanol, compound **4** gave **5**, which was isolated in 67% yield. Catalytic hydrogenolysis of **5** produced the title disaccharide phenyl 2-acetamido-2-deoxy-4-*O*-α-L-fucopyranosyl-β-D-glucopyranoside (**6**) as an amorphous material.





4 R = Ac, R′ = Bn
5 R = H, R′ = Bn
6 R = R′ = H

Bn = CH_2Ph



8 R = Ac, R′ = Bn
9 R = Ac, R′ = H

For the synthesis of disaccharide derivative **8**, we treated 2-acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-β-D-glucopyranose[5,6] (**7**) with 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide under similar conditions. Compound **8** was isolated from the reaction mixture as an amorphous material after chromatography in a column of silica gel. Hydrogenolysis of **8** in glacial acetic acid in the presence of 10% Pd–C gave **9** as an

TABLE I

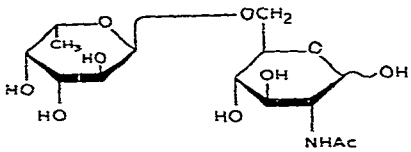
^{13}C-N.M.R. CHEMICAL SHIFTS[a] (25.2 MHz)

Compound	*GlcNAc residue*								L-*Fucosyl group*					
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C=O*	*CH*$_3$	*C-1′*	*C-2′*	*C-3′*	*C-4′*	*C-5′*	*C-6′*
1	99.07	55.42	73.96	70.21	77.08	60.65	169.11	22.94						
2	99.74	54.55	81.21	69.63	76.75	60.43	169.88	22.90	98.49	71.54	68.07	68.62	66.41	16.33
6	99.04	55.73	72.10	77.11	75.42	59.69	168.98	22.85	98.59	71.56	67.90	69.34	66.14	16.39
14	98.28	55.16	73.71	69.93	77.24	60.42	169.21	22.95						
13	98.19	55.12	73.45	69.92	76.27	67.93	169.07	22.87	99.12	71.41	66.21	69.59	65.70	16.24
17	98.45	55.04	73.61	69.87	75.02	67.69	169.13	22.89	102.56	70.91[b]	70.43[b]	70.08[b]	69.87	16.51
10α	91.85	55.13	71.66	71.01	74.83	68.38	175.38	23.06	100.13					16.38
										72.90	69.30	70.57	67.80	
10β	96.01	57.77	71.92	71.26	76.03	68.78	175.63	23.29	100.44					16.44

[a]In p.p.m. downfield from Me_4Si. The solvent was Me_2SO-d_6, except for D_2O for **10**. The reference (Me_4Si) was internal for solutions in Me_2SO-d_6, and external for that in D_2O. [b]Indistinguishable; may be interchanged.

amorphous material; its ^{1}H-n.m.r. spectrum clearly showed the presence of one NAc and three acetyl groups, and a doublet at δ 5.85 (J 8.5 Hz, H-1), suggesting that the anomeric *O*-acetyl group had remained intact during the hydrogenolysis in glacial acetic acid. An anomeric *O*-acetyl group in such compounds has been observed to be labile in acidic media[6]. Exposure of **9** to acetyl chloride overnight resulted in the formation of the acetylated glycosyl halide **11** which, without purification, was treated with sodium *p*-nitrophenoxide in *N*,*N*-dimethylformamide to afford **12** in 64% yield. *O*-Deacetylation of **12** under the usual conditions gave the disaccharide **13**; its ^{1}H- and ^{13}C-n.m.r. spectra confirmed the structure assigned.

O-Deacetylation of **9** provided the known disaccharide 2-acetamido-2-deoxy-6-*O*-α-L-fucopyranosyl-D-glucopyranose[7] (**10**), identical with an authentic sample in paper chromatography; its structure was confirmed by ^{1}H- and ^{13}C-n.m.r. spectroscopy.



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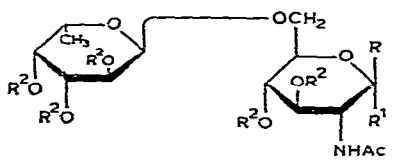
Treatment of *p*-nitrophenyl 2-acetamido-3,4-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside[8] (**15**) with 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide in anhydrous acetonitrile in the presence of mercuric cyanide gave a mixture of products that, on fractionation in a column of silica gel provided the crystalline disaccharide derivative **16** in 58% yield. *O*-Deacetylation of **16** gave *p*-nitrophenyl 2-acetamido-2-deoxy-6-*O*-β-L-fucopyranosyl-β-D-glucopyranoside (**17**) as an amorphous material in 70% yield.



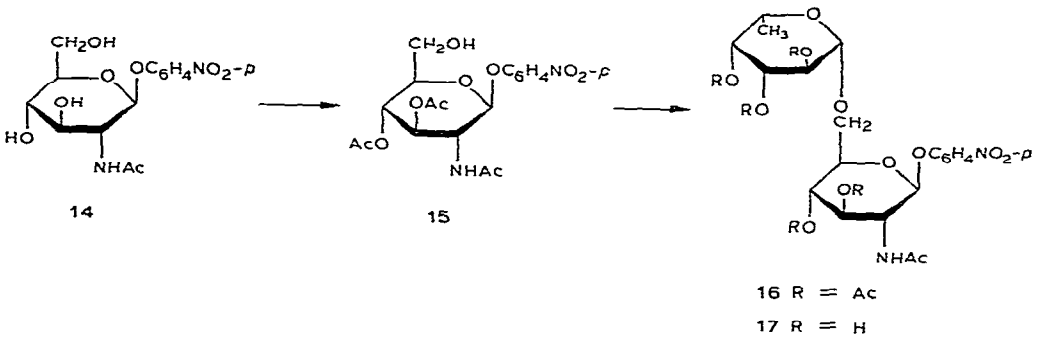
11 R = H, R^1 = Cl, R^2 = Ac
12 R = $OC_6H_4NO_2$-*p*, R^1 = H, R^2 = Ac
13 R = $OC_6H_4NO_2$-*p*, R^1 = R^2 = H

In some of the glycoconjugates, an L-fucosyl residue is α-L-linked at O-3, O-4, or O-6 of a 2-acetamido-2-deoxy-D-glucose residue. Availability of the synthetic disaccharides **2**, **6**, and **13** led us to examine their ^{13}C-n.m.r. spectra in detail, as it is obvious that such studies of these reference compounds will further aid in understanding the structures in which an α-L-fucosyl residue is linked to a 2-acetamido-2-deoxy-D-glucose residue in naturally occurring glycoconjugates; our results concerning

TABLE II

EFFECTS OF FUCOSYLATION ON CHEMICAL SHIFT

Compound	*L-Fucopyranosyl group*	*Position on β-D-GlcNAc residue*	*Shielding effects at position of substitution (p.p.m.)*	*Shielding effects at carbon atoms adjacent to position of substitution (p.p.m.)*
2	α-	3	C-3 (+7.25)	C-2 (−0.87) C-4 (−0.58)
6	α-	4	C-4 (+6.90)	C-3 (−1.86) C-5 (−1.66)
13	α-	6	C-6 (+7.51)	C-5 (−0.97)
17	β-	6	C-6 (+7.27)	C-5 (−2.22)



the ^{13}C-n.m.r. spectra are summarized in Tables I and II. It was observed that the chemical shifts of all of the carbon atoms of the α-L-fucopyranosyl residue remain almost constant for disaccharides **2**, **6**, and **13**. In the case of the free disaccharide **10**, C-1′ showed a downfield shift compared to C-1′ of **13**. As expected, C-1 (102.56 p.p.m.) of the β-L-fucosyl group in **17** showed a shift more downfield than that of C-1 of the α-L-fucosyl group in **13**. It is well established[9] that alkylation of a hydroxyl group causes a 7–10-p.p.m. downfield shift in the resonance of a carbon atom originally bearing a hydroxyl group, and inspection of Tables I and II shows that this is the case. Thus, C-3 of **2** and C-4 of **6** showed downfield shifts of 7.25 and 6.9 p.p.m., respectively, relative to that of the parent glycoside **1**. Similarly, C-6 of the (1→6)-linked disaccharide **13** showed a downfield shift of 7.51 p.p.m. relative to that of the parent glycoside **14**.

EXPERIMENTAL

General methods. — Melting points were determined with a Fisher–Johns apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 polarimeter at room temperature. Ascending t.l.c. was conducted on

plates coated with a 0.25-mm layer of silica gel 60 PF-254 (E. Merck, Darmstadt, Germany); the components were located by exposure to u.v. light, or by spraying the plate with 5% sulfuric acid in ethanol and heating. Elemental analyses were performed by Robertson Laboratory, Florham Park, New Jersey, U.S.A. N.m.r. spectra were recorded with a Varian XL-100 instrument; ^{1}H-n.m.r. spectra (100 MHz) and ^{13}C-n.m.r. spectra (25.2 MHz) were determined by the Fourier-transform (F.t.) mode: the positions of the peaks are expressed in δ from the tetramethylsilane signal.

*Phenyl 2-acetamido-3,6-di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4-tri-*O*-benzyl-α-*L*-fucopyranosyl)-β-*D*-glucopyranoside* (**4**). — Compound **3** (0.925 g, 2.65 mmol) was dissolved in a mixture of dichloromethane (30 mL), *N*,*N*-dimethylformamide (6 mL), tetraethylammonium bromide (1.11 g, 5.30 mmol), and diisopropylethylamine (1 mL, 5.78 mmol). A solution of freshly prepared 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide (2.64 g, 5.31 mmol) in dichloromethane (10 mL) and dry $HCONMe_2$ (2 mL) was added, and the mixture was stirred for 4 days at room temperature. Dichloromethane (300 mL) was added, and the solution was washed with water (3 × 50 mL), dried, and evaporated. The residue was purified by chromatography on a column of silica gel, eluting first with chloroform, then with 19:1 (v/v) chloroform–acetone (to remove the 2,3,4-tri-*O*-benzyl-L-fucose), and finally with 9:1 (v/v) chloroform–acetone, giving **4** in a yield of 81%; m.p. 183–184° (from acetone–hexane), $[\alpha]_D$ −59.2° (*c* 1.2, chloroform); n.m.r. data ($CDCl_3$): δ 1.05 (d, 3 H, *J* 6.5 Hz, CMe), 1.87 (s, 3 H, NAc), 1.98 and 2.07 (s each, 2 × 3 H, 2 Ac), 4.72 (d, 1 H, *J* 3.5 Hz, H-1′), 5.09 (d, 1 H, *J* 7.5 Hz, H-1), and 6.96–7.50 (m, 20 H, aromatic).

Anal. Calc. for $C_{45}H_{51}NO_{12}$: C, 67.74; H, 6.44; N, 1.76. Found: C, 67.44; H, 6.43; N, 1.59.

*Phenyl 2-acetamido-2-deoxy-4-*O*-(2,3,4-tri-*O*-benzyl-α-*L*-fucopyranosyl)-β-*D*-glucopyranoside* (**5**). — To a solution of compound **4** (300 mg) in 1:1 (v/v) chloroform–methanol (6 mL) was added a 0.1M solution of sodium methoxide (0.3 mL). The solution was kept for 6 h at room temperature and then overnight at 5°, made neutral with acetic acid, and evaporated, followed by a few additions and evaporations of dry toluene. The residue crystallized from acetone–hexane, to give **5** (180 mg) in 67% yield; m.p. 185–187°, $[\alpha]_D$ −101.6° (*c* 1, Me_2SO); the i.r. spectrum showed the presence of hydroxyl group and absence of ester group; ^{1}H-n.m.r. data ($CDCl_3$): δ 1.16 (d, 3 H, *J* 6.5 Hz, CMe), 1.98 (s, 3 H, NAc), 5.64 (d, 1 H, *J* 8 Hz, H-1), and 6.94–7.50 (m, 20 H, aromatic).

*Phenyl 2-acetamido-2-deoxy-4-*O*-α-*L*-fucopyranosyl-β-*D*-glucopyranoside* (**6**). — A solution of **5** (200 mg) in acetic acid (20 mL) was hydrogenolyzed in the presence of 10% Pd–C for 2 days, the suspension filtered, and the filtrate evaporated to dryness. The residue was purified by chromatography on a column of silica gel, with elution with 3:1 (v/v) chloroform–methanol, to afford amorphous **6** (100 mg) in 80% yield; $[\alpha]_D$ −112.4° (*c* 0.5, water); t.l.c. (3:1 chloroform-methanol): R_F 0.46; ^{1}H-n.m.r. data (D_2O): δ 1.62 (d, 3 H, *J* 6.5 Hz, CMe), 2.47 (s, 3 H, NAc), 5.63 (d, 1 H, *J* 8 Hz, H-1), and 7.5–7.98 (m, 5 H, phenyl).

Anal. Calc. for $C_{20}H_{29}NO_{10} \cdot H_2O$: C, 52.05; H, 6.77; N, 3.04. Found: C, 52.31; H, 6.87; N, 3.18.

*2-Acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-6-*O*-(2,3,4-tri-*O*-benzyl-α-*L*-fucopyranosyl)-β-*D*-glucopyranose* (**8**). — A suspension of compound **7** (1.776 g, 5.30 mmol) in dry dichloromethane (80 mL) was stirred for 2 h at room temperature in the presence of tetraethylammonium bromide (2.22 g, 10.6 mmol) and molecular sieve 4A (20 g). A solution of freshly prepared 2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl bromide (5.28 g, 10.62 mmol) in dichloromethane (100 mL) and dry $HCONMe_2$ (120 mL) was added, and the mixture was stirred for 5 days at room temperature. Methanol (30 mL) was added, the mixture was stirred for 3 h, the solids were removed by filtration, and the filtrate was evaporated. A solution of the solid residue in dichloromethane (200 mL) was successively washed with sodium hydrogencarbonate solution and water, dried (anhydrous magnesium sulfate), and evaporated. The residue was purified by chromatography on a column of silica gel, with elution with 4:1 (v/v) chloroform–actone, to give **8** in 64% yield (2.5 g), amorphous, $[\alpha]_D$ −28.7° (*c* 1.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 1.12 (d, 3 H, *J* 6.5 Hz, CMe), 1.93 (s, 3 H, NAc), 1.99, 2.05, 2.08 (s each, 3 × 3 H, 3 Ac), 5.67 (d, 1 H, *J* 8.5 Hz, H-1), and 7.3–7.5 (m, 15 H, aromatic).

Anal. Calc. for $C_{41}H_{49}NO_{13}$: C, 64.47; H, 6.47; N, 1.83. Found: C, 64.45; H, 6.72; N, 1.73.

*2-Acetamido-1,3,4-tri-*O*-acetyl-2-deoxy-6-*O*-α-*L*-fucopyranosyl-β-*D*-glucopyranose* (**9**). — Compound **8** (500 mg) was hydrogenolyzed as described for **6**, to give compound **9** (290 mg) in 90% yield, amorphous; $[\alpha]_D$ −52.1° (*c* 1.3, chloroform); the i.r. spectrum showed the presence of hydroxyl group; ^{1}H-n.m.r. ($CDCl_3$): δ 1.27 (d, 3 H, *J* 6.5 Hz, CMe), 1.96 (s, 3 H, NAc), 2.06, 2.08, 2.13 (s each, 3 × 3 H, 3 Ac), 5.85 (d, 1 H, *J* 8.5 Hz, H-1), and 6.3 (d, 1 H, *J* 9.5 Hz, NH).

Anal. Calc. for $C_{20}H_{31}NO_{13}$: C, 48.68; H, 6.33; N, 2.84. Found: C, 48.61; H, 6.22; N, 2.70.

*2-Acetamido-2-deoxy-6-*O*-α-*L*-fucopyranosyl-*D*-glucopyranose* (**10**). — A molar solution of sodium methoxide in methanol (0.5 mL) was added to a solution of compound **9** (200 mg) in methanol (20 mL), and the mixture was kept overnight at room temperature, made neutral with acetic acid, and evaporated; this was followed by a few additions and evaporations of dry toluene. The residue was taken up in water, the suspension filtered, and the filtrate lyophilized, to afford amorphous **10** in 82% yield; $[\alpha]_D$ −61.2→−63.2° (*c* 1, water) {lit.[7] $[\alpha]_D$ −66° (*c* 1, water)}. The purity of disaccharide **10** was established by chromatography on Whatman No. 1 paper, using 4:4:1 (v/v) 1-butanol–ethanol–water: R_{Fuc} 0.54 (silver nitrate reagent); ^{1}H-n.m.r. (D_2O): δ 1.67 (d, 3 H, *J* 6.5 Hz, CMe) and 2.50 (s, 3 H, NAc); for ^{13}C-n.m.r. data, see Table I.

*2-Acetamido-3,4-di-*O*-acetyl-2-deoxy-6-*O*-(2,3,4-tri-*O*-acetyl-α-*L*-fucopyranosyl)-α-*D*-glucopyranosyl chloride* (**11**). — A solution of compound **9** (1.0 g) in acetyl chloride (5 mL) was stirred overnight at room temperature, diluted with dichloromethane, and evaporated, followed by a few additions and evaporations of dry

dichloromethane, to give syrupy chloride **11** in almost quantitative yield; $[\alpha]_D$ −10.2° (*c* 0.5, dichloromethane); this was used, as such, for the next reaction.

p-*Nitrophenyl 2-acetamido-3,4-di*-O-*acetyl-2-deoxy-6*-O-(*2,3,4-tri*-O-*acetyl*-α-L-*fucopyranosyl*)-β-D-*glucopyranoside* (**12**). — A suspension of chloride **11** (598 mg, 1 mmol) in *N,N*-dimethylformamide (5 mL) was stirred for 15 h at room temperature in the presence of sodium *p*-nitrophenoxide (324 mg, 2 mmol), and then poured into cold water with stirring. The solution was extracted with chloroform (3 × 50 mL), and the extract was washed with water (3 × 25 mL), dried, and evaporated to dryness. The solid residue was purified by chromatography on a column of silica gel, with elution with 4:1 (v/v) chloroform–acetone, to afford amorphous **12** (0.448 g, 64%); $[\alpha]_D$ −82.4° (*c* 0.5, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 1.09 (d, 3 H, *J* 6.5 Hz, CMe), 1.76 (s, 3 H, NAc), 2.0, 2.08, 2.10, 2.18 (s each, 15 H, 5 Ac), 5.42 (d, 1 H, *J* 8 Hz, H-1), 5.96 (d, 1 H, *J* 9 Hz, NH), and 7.14 and 8.16 (2 m, 2 × 2 H, aromatic).

Anal. Calc. for $C_{30}H_{38}N_2O_{17}$: C, 51.57; H, 5.48; N, 4.01. Found: C, 51.62; H, 5.46; N, 3.76.

p-*Nitrophenyl 2-acetamido-2-deoxy-6*-O-α-L-*fucopyranosyl*-β-D-*glucopyranoside* (**13**). — A solution of **12** (0.3 g) in a mixture of methanol (9 mL), triethylamine (3 mL), and water (2.5 mL) was kept overnight at 4°, and then evaporated to dryness. Toluene was added to, and evaporated from, the residue, and the resulting material was purified by chromatography on a column of silica gel, with elution with 2:1 (v/v) chloroform–methanol, to afford amorphous **13** (182 mg) in 87% yield; $[\alpha]_D$ −90.2° (*c* 0.5, water); ^{1}H-n.m.r. (D_2O): δ 1.48 (d, 3 H, *J* 6.5 Hz, CMe), 2.50 (s, 3 H, NAc), 5.36 (d, 1 H, *J* 3.5 Hz, H-1′), 5.8 (d, 1 H, *J* 8 Hz, H-1), and 7.66 and 8.68 (2 m, 2 × 2 H, aromatic).

Anal. Calc. for $C_{20}H_{28}N_2O_{12} \cdot H_2O$: C, 47.43; H, 5.97; N, 5.53. Found: C, 47.50; H, 6.18; N, 5.61.

p-*Nitrophenyl 2-acetamido-3,4-di*-O-*acetyl-2-deoxy-6*-O-(*2,3,4-tri*-O-*acetyl*-β-L-*fucopyranosyl*)-β-D-*glucopyranoside* (**16**). — A mixture of compound **15** (0.852 g, 2 mmol), 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide (1.06 g, 3 mmol), mercuric cyanide (0.506 g, 2 mmol), and dry acetonitrile (25 mL) was stirred for 5 h at room temperature, and then evaporated to dryness. A solution of the solid residue in chloroform (100 mL) was successively washed with water, a saturated solution of potassium bromide, sodium hydrogencarbonate solution, and water, dried (anhydrous magnesium sulfate), and evaporated. The solid mass was purified by chromatography on a column of silica gel, with elution with 4:1 (v/v) chloroform–acetone, to give compound **16** (0.81 g) in 58% yield; m.p. 250–251° (from ethanol), $[\alpha]_D$ −4.2° (*c* 1.1, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 1.15 (d, 3 H, *J* 6.5 Hz, CMe), 1.96, 2.0, 2.06, 2.1, 2.14 (s each, 18 H, 5 Ac + 1 NAc), 4.51 (d, 1 H, *J* 7.5 Hz, H-1′), 5.89 (d, 1 H, *J* 8.5 Hz, NH), and 6.1–7.26 (2 m, 2 × 2 H, aromatic).

Anal. Calc. for $C_{30}H_{38}N_2O_{17}$: C, 51.57; H, 5.48; N, 4.01. Found: C, 51.53; H, 5.75; N, 3.95.

p-*Nitrophenyl 2-acetamido-2-deoxy-6*-O-β-L-*fucopyranosyl*-β-D-*glucopyranoside* (**17**). — Deacetylation of compound **16** (300 mg) as described for **13** gave amorphous

17 (0.147 g, 70%); $[\alpha]_D$ −22.2° (*c* 0.5, water); the i.r. spectrum showed the presence of hydroxyl group and complete absence of ester group; ^{1}H-n.m.r. (D_2O): δ 1.67 (d, 3 H, *J* 6.5 Hz, CMe), 2.49 (s, 3 H, NAc), 5.81 (d, 1 H, *J* 8 Hz, H-1), and 7.66 and 8.68 (2 m, 2 × 2 H, aromatic).

Anal. Calc. for $C_{20}H_{28}N_2O_{12} \cdot 2\ H_2O$: C, 45.80; H, 6.15; N, 5.34. Found: C, 45.99; H, 5.95; N, 5.14.

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