Carbohydrate Research, 112 (1983) 213–220
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

SYNTHESIS OF *p*-NITROPHENYL 2-*O*-α- AND -β-L-FUCOPYRANOSYL-β-D-FUCOPYRANOSIDE*

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(Received July 16th, 1982; accepted for publication, August 19th, 1982)

ABSTRACT

Reaction of 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide with *p*-nitrophenyl 3,4-*O*-isopropylidene-β-D-fucopyranoside in the presence of mercuric cyanide in acetonitrile, followed by removal of the isopropylidene group under mild conditions, gave a mixture of *p*-nitrophenyl 2-*O*-(2,3,4-tri-*O*-acetyl-α- and -β-L-fucopyranosyl)-β-D-fucopyranoside. These compounds were conveniently separated by preparative, thin-layer chromatography, and, on deacetylation, gave the title disaccharides, whose structures were established by ^{1}H- and ^{13}C-n.m.r. spectroscopy.

INTRODUCTION

Highly specific (1→2)-α-L-fucosidases have been found to occur in various biological sources[2–5]. These specific fucosidases do not act on simple aryl or alkyl α-L-fucopyranosides, but specifically cleave an α-L-fucopyranosyl group linked at O-2 of galactose in saccharides, glycolipids, and glycoproteins. Availability of chemically synthesized *p*-nitrophenyl 2-*O*-α-L-fucopyranosyl-β-D-galactopyranoside in our laboratory led us to develop a rapid assay-procedure for the enzyme[6]. For further specificity studies on (1→2)-α-L-fucosidase, we here describe the preparation of the title disaccharides.

RESULTS AND DISCUSSION

Reaction of 2,3,4-tri-*O*-acetyl-α-D-fucopyranosyl bromide (**1**) with *p*-nitrophenol in aqueous acetone in the presence of alkali is known to give *p*-nitrophenyl 2,3,4-tri-*O*-acetyl-β-D-fucopyranoside (**2**) as a gummy material, as reported by Levvy and McAllan[7]. Recently, we reported[8] that, when it reacts with sodium *p*-nitrophenoxide in anhydrous *N*,*N*-dimethylformamide, 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide gives *p*-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside which, when submitted to *O*-deacetylation, gives pure *p*-nitrophenyl β-D-galacto-

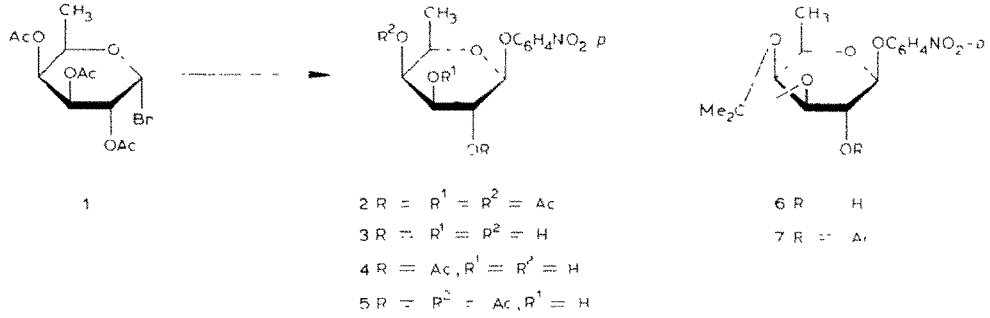
*Synthetic Studies in Carbohydrates, Part XXVI. For Part XXV, see ref. 1.

TABLE I

^{13}C-N.M.R. CHEMICAL-SHIFTS[a] (25.2 MHz, Me_2SO-d_6)

Compound	D-*Fucose residue*						L-*Fucosyl group*					
	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C-1'*	*C-2'*	*C-3'*	*C-4'*	*C-5'*	*C-6'*
3	99.96	69.51	73.07	70.64	70.44	16.34						
12	98.16	77.47	71.42	70.56	70.33	16.34	100.78	68.52	69.55	73.54	66.21	16.34
14	99.08	77.85	71.34	70.79	70.31	16.33	102.80	73.13	70.10	70.01	69.81	16.33

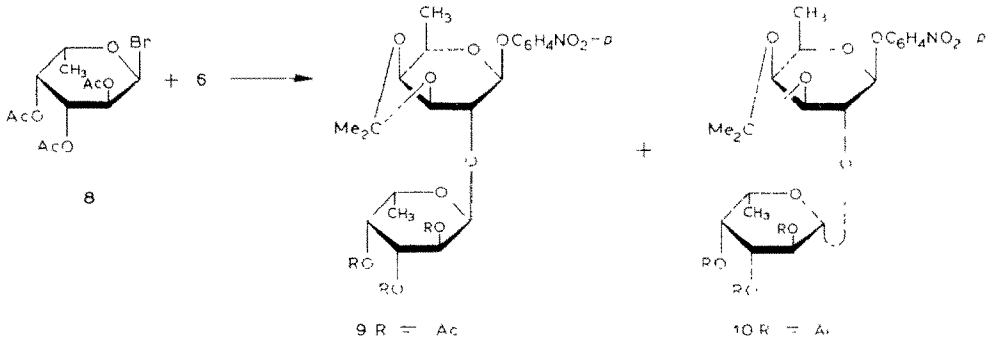
[a]In p.p.m. downfield from Me_4Si (internal).



1

2 R = R^1 = R^2 = Ac
3 R = R^1 = R^2 = H
4 R = Ac, R^1 = R^2 = H
5 R = R^2 = Ac, R^1 = H

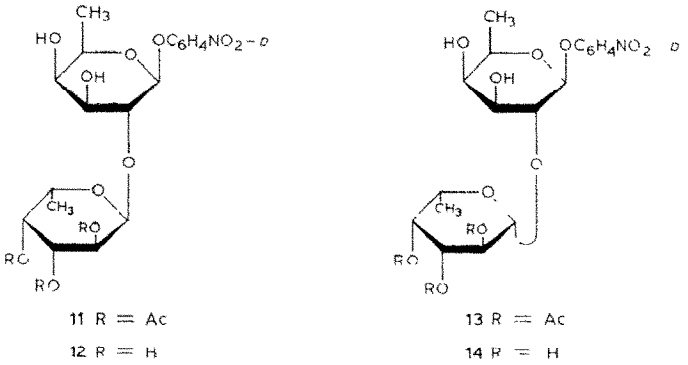
6 R = H
7 R = Ac



8

9 R = Ac

10 R = Ac



11 R = Ac
12 R = H

13 R = Ac
14 R = H

pyranoside[8]. In the present studies, sugar halide **1** gave, under the latter conditions, a semisolid material that readily crystallized from ethanol, to give pure **2**. We did not attempt to isolate any tri-*O*-acetyl-(hydroxyfucal) derivative, likely to be formed in minor yield under these reaction conditions, and in a previous investigation[8], during the preparation of *p*-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside, we did not try to isolate the tetra-*O*-acetyl-(hydroxy-D-galactal) derivative. It has been well documented that, when acetylated sugar halides react with phenoxide in the presence of an aprotic solvent (*e.g.*, $HCONMe_2$), the proportion of hydroxyglycal derivative is considerably increased[9,10]. The tendency to afford such derivatives seems to depend on the nature of the acetylated sugar halide employed[9,10]. Recently, the use of phase-transfer catalysis[11] has been recommended for the preparation of certain aryl glycopyranosides. The structure of our synthetic compound **2** was clearly supported by its n.m.r. spectrum (see Experimental section). Conventional *O*-deacetylation of compound **2** gave *p*-nitrophenyl β-D-fucopyranoside (**3**) as a crystalline compound.

Treatment of **3** with acetone in the presence of anhydrous copper sulfate for 18 h provided *p*-nitrophenyl 3,4-*O*-isopropylidene-β-D-fucopyranoside (**6**) in 66% yield. However, compound **6** was conveniently obtained in higher yield when **3** reacted with 2,2-dimethoxypropane in the presence of *p*-toluenesulfonic acid as the catalyst[12]. Compound **6** was characterized by conventional acetylation, to give **7**, which on deacetonation, gave *p*-nitrophenyl 2-*O*-acetyl-β-D-fucopyranoside (**4**). On reaction with triethyl orthoacetate in the presence of *p*-toluenesulfonic acid[13], compound **4** gave a 3,4-*O*-(ethyl orthoacetyl) derivative (not isolated) which, on treatment with aqueous acetic acid, gave *p*-nitrophenyl 2,4-di-*O*-acetyl-β-D-fucopyranoside **5**. Conversion of **4** into a 3,4-orthoacetyl derivative clearly suggests that the *O*-acetyl group did not migrate during the deacetonation of **7**. It may further be mentioned that the n.m.r. spectrum of the 2-*O*-acetyl compound **4** showed the presence of an equatorial acetoxyl signal at δ 2.06, whereas the spectrum of 2,4-di-*O*-acetyl derivative **5** exhibited signals for acetoxyl groups at δ 2.04 (equatorial) and δ 2.16 (axial). The n.m.r. spectrum of **2** clearly showed the presence of an axial (δ 2.20) and two equatorial (δ 1.98 and 2.06) acetoxyl groups.

Use of *O*-acylated sugar halides having a participating substituent at C-2 has been widely applied for the synthesis of glycosides[14,15]. There is no doubt that such halides tend to give mainly 1,2-*trans* glycosides. Nevertheless, the formation of 1,2-*cis* glycosides under such conditions has also been observed. In fact, the anomeric configuration of the resulting glycosides seems to depend upon various factors: (*a*) the position of a hydroxyl group of an aglycon hydroxide, (*b*) the nature of the groups protecting the other hydroxyl groups in the sugar, (*c*) the solvent used for the reaction, and (*d*) the nature of the catalyst.

Reaction of 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide (**8**) with benzyl 2-acetamido-3,4-di-*O*-acetyl-2-deoxy-β-D-glucopyranoside gives benzyl 2-acetamido-3,4-di-*O*-acetyl-2-deoxy-6-*O*-(2,3,4-tri-*O*-acetyl-β-L-fucopyranosyl)-β-D-glucopyranoside[16], whereas the same halide (**8**) with benzyl 6-*O*-benzoyl-3,4-*O*-isopropylidene-

β-D-galactopyranoside in 1:1 nitromethane–benzene in the presence of mercuric cyanide gives the 2-*O*-α-L-fucopyranosyl derivative exclusively[17]. As reported earlier[18], reaction of **8** with 1,3,4,6-tetra-*O*-acetyl-α-D-galactopyranose in different solvents and with various catalysts gives a mixture of acetylated 2-*O*-α-L- and 2-*O*-β-L-fucopyranosyl disaccharides. We also reported that the use of mercuric bromide retards the formation of α anomer. Thus, in the present studies, glycosylation of *p*-nitrophenyl 3,4-*O*-isopropylidene-β-D-fucopyranoside (**6**) with **8** was conducted in anhydrous acetonitrile in the presence of mercuric cyanide as the catalyst. On treatment with trifluoroacetic acid in chloroform, the syrupy reaction-product gave material found to contain two main products, along with impurities (t.l.c.). Anomers **11** and **13** were separated by preparative, thin-layer chromatography, or by column chromatography. The optical rotations and n.m.r. spectra confirmed the structures assigned to compounds **11** and **13**. Zemplén deacetylation of **11** and **13** afforded the title disaccharides, **12** and **14**, respectively. The purity of **12** and **14** was established by t.l.c. and by ^{13}C-n.m.r. spectroscopy.

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 at 100 MHz, and ^{13}C-n.m.r. spectra at 25.2 MHz, in the Fourier-transform mode; the positions of the peaks are expressed as δ values from the signal of tetramethylsilane.

p-*Nitrophenyl 2,3,4-tri*-O-*acetyl-β-*D-*fucopyranoside* (**2**). — A solution of 2,3,4-tri-*O*-acetyl-α-D-fucopyranosyl bromide (**1**, 20.1 g, 57 mmol) in anhydrous *N*,*N*-dimethylformamide (150 mL) containing sodium *p*-nitrophenoxide (14.33 g, 89 mmol) was stirred overnight at room temperature. The resulting, yellow solution was carefully poured into ice–water, and the solution was extracted with chloroform (3 × 200 mL). The extracts were combined, washed with cold water (3 × 100 mL), dried (anhydrous sodium sulfate), and evaporated to a syrup (18 g). Dissolved in hot ethanol, the crude syrup produced crystalline compound **2** in 18% yield (4.21 g); m.p. 165°, $[\alpha]_D$ −10 (*c* 1, chloroform); ν_{max}^{KBr} 1745 (Ac), 1610, 1590 (aromatic), 1515, 1345 (NO_2), and 750 cm^{-1} (aromatic). ^{1}H-n.m.r. (Me_2SO-d_6): δ 1.18 (d, 3 H, *J* 6 Hz, CMe), 1.98, 2.06, 2.20 (s each, 3 × 3 H, 3 Ac), 4.38 (q, 1 H, *J* 6 Hz, H-5), 5.30 (3 H, H-2,3,4), 5.66 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), and 7.2 and 8.36 (2 m, 2 × 2 H, aromatic).

p-*Nitrophenyl* β-D-*fucopyranoside* (**3**). — A solution of compound **2** (3.8 g) in absolute methanol (25 mL) was treated with 0.5M sodium methoxide (1 mL).

When kept overnight at 4°, the clear solution thus obtained afforded a thick precipitate of **3**. The mixture was made neutral with acetic acid, filtered, and the solid recrystallized from absolute ethanol, to give chromatographically pure **3** (2.2 g, 83.5%); m.p. 186–189° (lit.[7] m.p. 186–188°); ν_{max}^{KBr} 3450 (OH), 1605, 1590 (aromatic), 1510, 1340 (NO_2), and 750 cm^{-1} (aromatic); ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.16 (d, 3 H, *J* 6 Hz, CMe), 3.86 (q, 1 H, *J* 6 Hz, H-5), 5.06 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), and 7.16 and 8.36 (2 m, 2 × 2 H, aromatic).

p-*Nitrophenyl 3,4-*O*-isopropylidene-β-*D*-fucopyranoside* (**6**). — *Method A.* A solution of **3** (6 g) in anhydrous acetone (420 mL) was stirred with anhydrous copper sulfate (70 g) for 18 h at room temperature. The mixture was filtered through a Celite pad, and the filtrate was evaporated to dryness. The residue was stirred with dichloromethane (200 mL), and the suspension filtered, to remove unreacted **3** (0.7 g). The filtrate was washed with water, dried (Na_2SO_4), evaporated, and the residue crystallized from benzene–petroleum ether to give **6** (4 g, 66%); m.p. 137–138°, $[\alpha]_D$ −36.7° (*c* 1, chloroform); ν_{max}^{KBr} 3450 (OH), 1605, 1590 (Ph), 1510, 1345 (NO_2), and 750 cm^{-1} (aromatic); ^{1}H-n.m.r. data ($CDCl_3$): δ 1.48 (d, 3 H, *J* 6 Hz, CMe), 1.40 and 1.58 (s each, 2 × 3 H, isopropylidene methyls), 2.88 (1 H, OH), 3.8–4.3 (4 H, H-2,3,4,5), 5.96 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), and 7.02 and 8.30 (2 m, 2 × 2 H, aromatic).

Anal. Calc. for $C_{15}H_{19}NO_7$: C, 55.38; H, 5.89; N, 4.31. Found: C, 55.68; H, 6.00; N, 4.26.

Method B. A solution of **3** (2.85 g, 10 mmol) in anhydrous *N,N*-dimethylformamide (20 mL) and 2,2-dimethoxypropane (3 mL) was maintained at 80°. A catalytic amount (20 mg) of *p*-toluenesulfonic acid was introduced, and the solution was stirred for 40 min at the same temperature, and cooled; triethylamine (1 mL) was added, the mixture was evaporated *in vacuo*, and the residual syrup was stirred with dichloromethane (100 mL). The organic solution was successively washed with cold, aqueous sodium hydrogencarbonate and water, dried (Na_2SO_4), and filtered. The solid residue obtained on evaporation crystallized as before, to give **6** (3.1 g, 95.4%).

p-*Nitrophenyl 2-*O*-acetyl-3,4-*O*-isopropylidene-β-*D*-fucopyranoside* (**7**). — A solution of compound **6** (1 g) in anhydrous pyridine (10 mL) and acetic anhydride (6 mL) was stirred for 24 h at room temperature. Absolute ethanol (10 mL) was added, and the solution was evaporated under diminished pressure. Traces of acetic anhydride and acetic acid were removed by co-distillation with toluene, and the resulting solid was recrystallized from acetone–ether–hexane, to give **7** (1.1 g, 97%); m.p. 148°, $[\alpha]_D$ +5.8° (*c* 1, chloroform); ν_{max}^{KBr} 1750 (Ac), 1605, 1590 (aromatic), 1510, 1340 (NO_2), and 750 cm^{-1} (aromatic); ^{1}H-n.m.r. data ($CDCl_3$): δ 1.40 and 1.60 (2 s, 2 × 3 H, isopropylidene methyls), 1.50 (d, 3 H, *J* 6 Hz, CMe), 2.14 (s, 3 H, Ac), 4.28 (q, 1 H, *J* 6 Hz, H-5), 5.34 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), and 7.1 and 8.2 (2 m, 2 × 2 H, aromatic).

Anal. Calc. for $C_{17}H_{21}NO_8$: C, 55.58; H, 5.76; N, 3.81. Found: C, 55.53; H, 5.71; N, 3.69.

p-*Nitrophenyl 2-O-acetyl-β-D-fucopyranoside* (**4**). — A solution of **7** (1 g) in chloroform (90 mL) was diluted with trifluoroacetic acid (10 mL) containing water (0.1 mL), stirred for 1 h at room temperature, evaporated, and traces of trifluoroacetic acid removed by co-distillation with toluene. The resulting, white residue crystallized from ethyl acetate–hexane to give chromatographically pure **4** (0.73 g, 82%): m.p. 189–191 °, $[\alpha]_D$ 15.7° (*c* 1, methanol); ν_{max}^{KBr} 3450 (OH), 1735 (Ac), 1605, 1590 (aromatic), 1510, 1345 (NO_2), and 750 cm^{-1} (aromatic); ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.22 (d, 3 H, *J* 6 Hz, CMe), 2.06 (s, 3 H, Ac), 3.96 (q, 1 H, *J* 6 Hz, H-5), and 7.2 and 8.25 (2 m, 2 × 2 H, aromatic).

Anal. Calc. for $C_{14}H_{17}NO_8$: C, 51.37; H, 5.24; N, 4.28. Found: C, 51.57; H, 5.45; N, 4.50.

p-*Nitrophenyl 2,4-di-O-acetyl-β-D-fucopyranoside* (**5**). — A suspension of **4** (0.63 g) in triethyl orthoacetate (40 mL) containing *p*-toluenesulfonic acid (25 mg) was stirred at room temperature. After 3 h, t.l.c. of the clear solution indicated almost complete absence of **4**. Triethylamine (3 mL) was added, and the solution was poured into ice-water. Extraction with dichloromethane in the usual way, followed by evaporation, gave a syrupy product containing triethyl orthoacetate which, without characterization, was dissolved in 80% acetic acid (50 mL), and the solution kept for 30 min at room temperature. The solution was evaporated to dryness, giving a solid residue which was recrystallized from ethyl acetate–hexane, to afford **5** (0.62 g, 87%): m.p. 193–195 °, $[\alpha]_D$ −8.2° (*c* 0.5, chloroform); ν_{max}^{KBr} 3410 (OH), 1730 (Ac), 1600, 1595 (aromatic), 1512, 1350 (NO_2), and 750 cm^{-1} (aromatic); ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.08 (d, 3 H, *J* 6 Hz, CMe), 2.04 and 2.16 (s each, 2 × 3 H, 2 Ac), 4.20 (q, 1 H, *J* 6 Hz, H-5), 5.46 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), and 7.20 and 8.25 (2 m, 2 × 2 H, aromatic).

Anal. Calc. for $C_{16}H_{19}NO_9$: C, 52.03; H, 5.19; N, 3.79. Found: C, 52.25; H, 5.32; N, 3.72.

p-*Nitrophenyl 3,4-O-isopropylidene-2-O-(2,3,4-tri-O-acetyl-α-L-fucopyranosyl)-β-D-fucopyranoside* (**9**) *and* p-*nitrophenyl 3,4-O-isopropylidene-2-O-(2,3,4-tri-O-acetyl-β-L-fucopyranosyl)-β-D-fucopyranoside* (**10**). — A solution of **6** (2.925 g, 9 mmol) in freshly distilled, anhydrous acetonitrile (20 mL) containing mercuric cyanide (2.27 g) was stirred with 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide (6.4 g) for 3 h at room temperature, evaporated under diminished pressure, and the resulting syrup stirred with chloroform (150 mL). The suspension was filtered through glass wool, and the filtrate successively washed with M KBr (3 × 50 mL), water (100 mL), saturated $NaHCO_3$ solution (100 mL), and water (2 × 50 mL), dried (anhydrous Na_2SO_4), and evaporated to a syrup which was used as such for the next reaction (as we were unable to separate compounds **9** and **10**).

p-*Nitrophenyl 2-O-(2,3,4-tri-O-acetyl-α-L-fucopyranosyl)-β-D-fucopyranoside* (**11**) *and* p-*nitrophenyl 2-O-(2,3,4-tri-O-acetyl-β-L-fucopyranosyl)-β-D-fucopyranoside* (**13**). — A solution of the foregoing syrup (8 g) in chloroform (270 mL) was treated with trifluoroacetic acid (30 mL) containing water (0.3 mL), and the mixture was stirred for 1.5 h at room temperature, and then evaporated, traces of trifluoroacetic

acid being removed by co-evaporation with toluene. The resulting syrup was dissolved in warm benzene (30 mL), and the solution cooled, and diluted with hexane (100 mL), with vigorous stirring, to give a semi-solid material from which the liquid was decanted, and the residue treated twice with benzene–hexane, to give an amorphous material (5.23 g), a portion (0.45 g) of which in dichloromethane was applied to six preparative-t.l.c. plates. The plates were developed four times in 14:14:1 (v/v) benzene–ether–methanol; two separate bands were observed under u.v. light, and each was scraped off the plates. The silica gel containing the disaccharide fractions was separately stirred with 1:1 (v/v) chloroform–methanol (200 mL) for 6 h. The suspension was filtered through a Celite pad, and the filtrate was evaporated to dryness. The dry residue (containing some particles of silica gel) was stirred with dichloromethane (100 mL), the suspension filtered through a Celite pad, and the filtrate evaporated under diminished pressure. The slow-moving material (**11**; 150 mg) had $[\alpha]_D$ −135° (*c* 1, chloroform); ^{1}H-n.m.r. data ($CDCl_3$): δ 1.04 and 1.40 (d each, 2 × 3 H, *J* 6 Hz, 2 CMe), 2.0, 2.10, and 2.18 (s each, 3 × 3 H, 3 Ac), 5.08 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), 5.52 (d, 1 H, $J_{1',2'}$ 3.5 Hz, H-1′), and 7.10 and 8.26 (2 m, 2 × 2 H, aromatic).

Anal. Calc. for $C_{24}H_{31}NO_{14}$: C, 51.70; H, 5.61; N, 2.51. Found: C, 51.72; H, 5.60; N, 2.50.

The fast-moving material (**13**, 100 mg) was isolated crystalline; m.p. 218–220° (from ethyl acetate–ether), $[\alpha]_D$ −39.0° (*c* 1, chloroform); ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.1 and 1.17 (d each, 2 × 3 H, *J* 6 Hz, 2 CMe), 1.37, 1.87, and 2.1 (s each, 3 × 3 H, 3 Ac), 5.07 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), and 7.2 and 8.13 (2 m, 2 × 2 H, aromatic).

In another approach, amorphous material (4.23 g) was dissolved in ethyl acetate (5 mL). Addition of ether (95 mL) gave crystalline **13** (0.53 g). T.l.c. of the product supported the presumed purity of the material. The mother liquor (containing the α anomer along with the β anomer and impurities, as observed by t.l.c.) was dried, dissolved in the minimum volume of benzene, and chromatographed in a column (3 × 54 cm) of silica gel packed in benzene. Fast-moving impurities were eluted with 9:1 (v/v) benzene–ether (200 mL) and 1:1 (v/v) benzene–ether (400 mL). Elution with 14:14:1 (v/v) benzene–ether–methanol then gave four major fractions: the first was pure β anomer **13** (0.38 g); the second (0.2 g) was β anomer (**13**) along with a small amount of α anomer (**11**); the third (0.76 g) was α anomer **11**, with some β anomer (minor); and the fourth was pure α anomer **11** (1.1 g).

p-*Nitrophenyl 2*-O-α-L-*fucopyranosyl*-β-D-*fucopyranoside* (**12**). — A solution of **11** (0.3 g) in a mixture of methanol (9 mL), triethylamine (3 mL), and water (2.5 mL) was kept for 24 h at 4°, and then evaporated; this was followed by a few additions and evaporations of toluene. Addition of ether to a solution of the residue in methanol gave **12** as an amorphous material (151 mg, 65%); $[\alpha]_D$ −158.6° (*c* 0.5, methanol); t.l.c. in 4:1 (v/v) chloroform–methanol: R_F 0.52; ^{1}H-n.m.r. data (Me_2SO-d_6): δ 1.0 and 1.17 (d each, 2 × 3 H, *J* 6 Hz, 2 CMe), and 7.1 and 8.13 (2 m, 2 × 2 H, aromatic).

Anal. Calc. for $C_{18}H_{25}NO_{11}$: C, 50.11; H, 5.84; N, 3.25. Found: C, 50.37; H, 5.92; N, 3.07.

p-*Nitrophenyl* 2-O-β-L-*fucopyranosyl*-β-D-*fucopyranoside* (**14**). — *O*-Deacetylation of compound **13** (0.2 g) as described for **12** afforded **14** (0.1 g, 65%): m.p. 263–264° (from methanol–ether), $[\alpha]_D$ 135.6 (*c* 1, pyridine); t.l.c. in 4:1 chloroform–methanol: R_f 0.68; ^{1}H-n.m.r. data (Me_2SO-d_6) δ 1.13 and 1.2 (2 d, 2 × 3 H, *J* 6 Hz, 2 CMe), 5.2 (d, 1 H, $J_{1,2}$ 7 Hz, H-1), and 7.2 and 8.2 (2 m, 2 × 2 H, aromatic).

Anal. Calc. for $C_{18}H_{25}NO_{11}$: C, 50.11; H, 5.84; N, 3.25. Found: C, 50.26; H, 5.95; N, 3.21.

ACKNOWLEDGMENTS

We thank Mrs. Onda Simmons for recording the n.m.r. spectra, and Marie Fox for kindly typing the manuscript. The n.m.r. studies were supported by National Cancer Institute Core Grant CA-16056. This investigation was supported by Grant No. ROI-CA-24051, awarded by the National Institutes of Health.

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