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SYNTHESIS OF A PRECURSOR OF 3-*O*-(2-ACETAMIDO-2-DEOXY-3-*O*-METHYL-α-D-GALACTOPYRANOSYL)-4-*O*-(4-*O*-METHYL-β-D-GLUCOPYRANOSYLURONIC ACID)-L-FUCOSE*

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ABSTRACT

The glycosphingolipids isolated from spermatozoa of a fresh-water bivalve, *Hyriopsis schlegelii,* have a unique structure containing one or two mannosyl residues, novel linkages including an internal fucopyranosyl residue, as well as terminal xylosyl and 4-*O*-methyl-D-glucopyranosyluronic acid groups. The trisaccharide derivatives that constitute the partial structure of lipid IV were synthesized as follows. Condensation of 4,6-di-*O*-acetyl-2-azido-2-deoxy-3-*O*-methyl-α-D-galactopyranosyl bromide with 2-(trimethylsilyl)ethyl 4-*O*-acetyl-2-*O*-benzyl-β-L-fucopyranoside, in the presence of mercuric cyanide and mercuric bromide, gave the corresponding disaccharide in 87% yield. Condensation of methyl (2,3-di-*O*-acetyl-4-*O*-methyl-α-D-glucopyranosyl bromide)uronate with the appropriate OH-4-free disaccharide derivative afforded the corresponding precursor of 4-*O*-Me-β-D-Glc*p*A-(1→4)-[3-*O*-Me-α-D-Gal*p*NAc-(1→3)]-L-Fuc, namely 2-(trimethylsilyl)ethyl 2-*O*-benzyl-3-*O*-(4,6-di-*O*-acetyl-2-azido-2-deoxy-3-*O*-methyl-α-D-galactopyranosyl]-4-*O*-[methyl (2,3-di-*O*-acetyl-4-*O*-methyl-β-D-glucopyranosyl)uronate]-β-L-fucopyranoside.

INTRODUCTION

In the course of a systematic study on the spermatozoa glycosphingolipids of the fresh-water bivalve, *Hyriopsis schlegelii,* T. Hori *et al.*[2] have isolated and characterized seven glycolipids. These neutral glycolipids differ from mammalian glycolipids in having mannosyl residues. Recently, they also have isolated[3] a novel acidic glycolipid (Lipid IV) containing 4-*O*-methylglucuronic acid, and elucidated the structure as **1**. In our previous paper[1], we reported the synthesis of the trisaccharide derivatives which constitute the partial structure of Lipids I and II, namely β-D-Glc*p*NAc-(1→2)-α-D-Man*p*-(1→3)-D-Man. We chose a nonreducing-end trisaccharide corresponding to the partial structure derived from Lipid IV as a target for our synthetic studies on oligosaccharides of biological interest.

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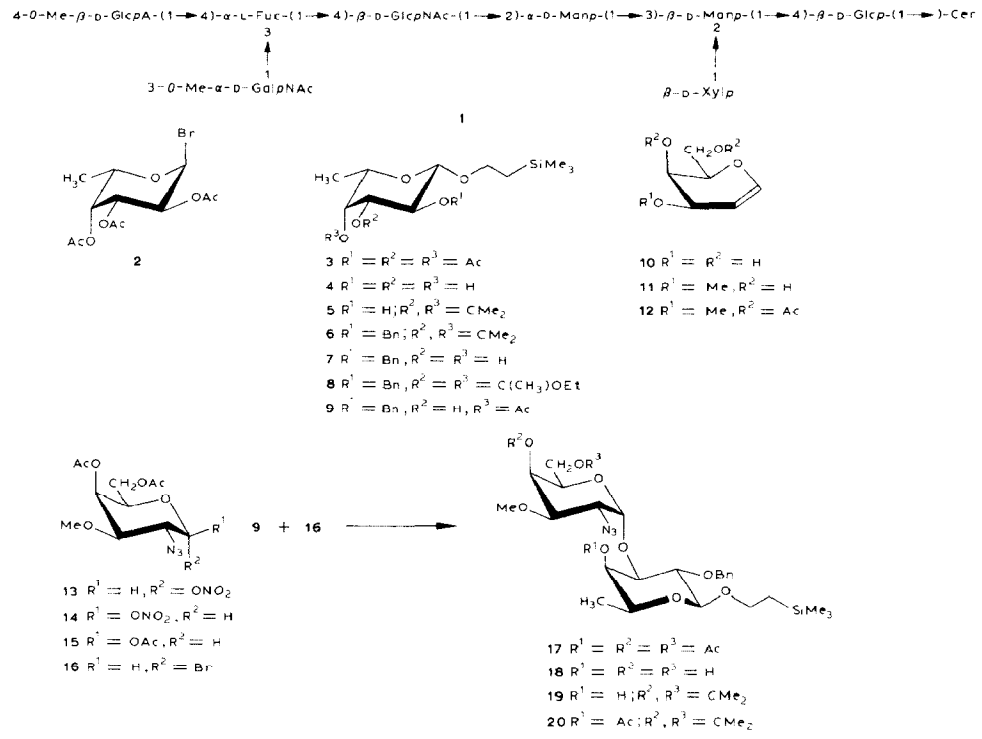
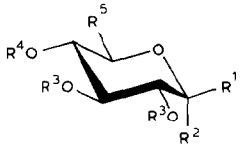
RESULTS AND DISCUSSION

In this work, the derivative **32**, a precursor of 3-*O*-(2-acetamido-2-deoxy-3-*O*-methyl-α-D-galactopyranosyl)-4-*O*-(4-*O*-methyl-β-D-glucopyranosyluronic acid)-L-fucose, was synthesized, by stepwise condensation of suitably protected monosaccharide units, an L-fucose derivative being used as glycosyl acceptor, and bromide derivatives of D-galactose and D-glucuronic acid as donors. 2-(Trimethylsilyl)ethyl β-L-fucopyranoside (**4**), prepared from 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide (**2**), according to Lipshutz *et al.*[4], was isopropylidenated and benzylated, and then deisopropylidenated with 80% acetic acid to afford 2-(trimethylsilyl)ethyl 2-*O*-benzyl-β-L-fucopyranoside (**7**) in 89% yield as reported earlier[5]. Compound **7** was added to a mixture of dry toluene, triethyl orthoacetate, and 4-toluenesulfonic acid to give 2-(trimehylsilyl)ethyl 2-*O*-benzyl-3,4-*O*-(ethyl orthoacetyl)-β-L-fucopyranoside (**8**), and 2-(trimethylsilyl)ethyl 4-*O*-acetyl-2-*O*-benzyl-β-L-fucopyranoside (**9**) was readily prepared in high yield by controlled acid hydrolysis[6] of **8**. The ^{1}H-n.m.r. data for **9** established the configuration at C-1 to be β-L since the signal for H-1 of **9** at δ 4.38 was a doublet with *J* 7.7 Hz. The signal for H-4 of **9** had the largest downfield shift (~1.6 p.p.m.) at δ 5.16 as a double doublet ($J_{3,4}$ 3.7, $J_{4,5}$ 0.9 Hz) on transformation from **7** to **9**, which indicated substitution of OH-4 with an acetyl group.

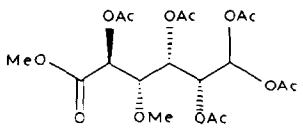


The utility of the azido group as a nonparticipating substituent at C-2 of glycosyl halides engaged in Koenigs–Knorr glycosidation reactions was established by Paulsen *et al.*[7], and 4,6-di-*O*-acetyl-2-azido-2-deoxy-3-*O*-methyl-α-D-galactopyranosyl bromide (**16**) was obtained in five steps from 1,5-anhydro-2-deoxy-D-*lyxo*-hex-1-enitol (**10**). Its dibutylstannylene derivative was immediately methylated according to Nashed[8], and then acetylated to give 4,6-di-*O*-acetyl-1,5-anhydro-2-deoxy-3-*O*-methyl-D-*lyxo*-hex-1-enitol (**12**) in 60% yield from **10**. Treatment of **12** with sodium azide and ceric(IV) ammonium nitrate in acetonitrile according to Lemieux and Ratcliffe[9] gave 4,6-di-*O*-acetyl-2-azido-2-deoxy-3-*O*-methyl-α-D-galactopyranosyl nitrate (**13**) in 62% yield, and acetolysis provided crystalline 1,4,6-tri-*O*-acetyl-2-azido-2-deoxy-3-*O*-methyl-β-D-galactopyranose (**15**). The α-bromide **16** was readily prepared by replacement of the acetate group of **15** by treatment with titanium tetrabromide.

Compound **9** was condensed with **16** in dichloromethane for 10 h at room temperature, in the presence of mercuric cyanide–mercuric bromide and molecular sieves. Purification of the crude product by column chromatography afforded in 87% yield the disaccharide derivative **17**, the ^{1}H-n.m.r. spectrum of which



	R^1	R^2	R^3	R^4	R^5
21	OMe	H	Bn	H	CH_2OTr
22	OMe	H	Bn	Me	CH_2OH
23	OMe	H	Bn	Me	CO_2Me
24	OMe	H	H	Me	CO_2Me
25	OMe	H	Ac	Me	CO_2Me
26	H,OH		H	Me	CO_2Me
27	H,OAc		Ac	Me	CO_2Me
28	H	Br	Ac	Me	CO_2Me



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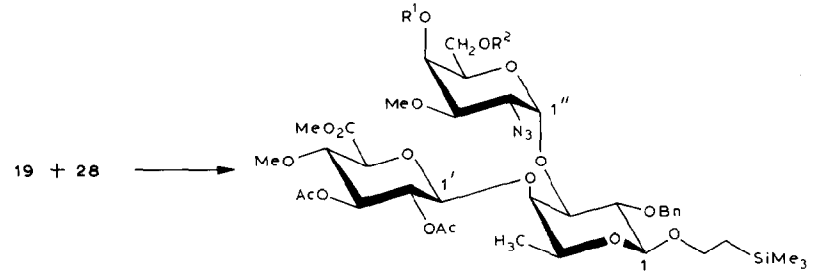

30 R^1, R^2 = CMe_2
31 R^1 = R^2 = H
32 R^1 = R^2 = Ac

supported the presence of the α-D-(1→3) linkage (doublets at δ 5.44 with J 3.7 Hz). The ^{13}C-n.m.r. data showed two anomeric C atom signals at δ 103.3 ($J_{C,H}$ 159.17 Hz, C-1) and 99.3 ($J_{C,H}$ 177.72 Hz, C-1′) and an α-D-configuration of the disaccharide bond. Deacetylation of **17** with sodium methoxide provided the triol **18**, which was isopropylidenated (**19**) with 2,2-dimethoxypropane and 4-toluenesulfonic acid in *N,N*-dimethylformamide. Treatment of **19** with acetic anhydride–pyridine gave **20** in quantitative yield.

Methyl (methyl 4-*O*-methyl-β-D-glucopyranosid)uronate (**24**) was synthesized from methyl β-D-glucopyranoside by a modification of the method of Kováč and Palovčík[10], which involved isopropylidenation, benzylation, deisopropylidenation, tritylation (**21**), methylation, and detritylation to give methyl 2,3-di-*O*-benzyl-4-*O*-methyl-β-D-glucopyranoside (**22**). This was oxidized with potassium bichromate and dilute sulfuric acid in acetone to afford the corresponding uronic acid derivative which upon esterification yielded methyl (methyl 2,3-di-*O*-benzyl-4-*O*-methyl-β-D-glucopyranosid)uronate (**23**). Treatment with palladium on charcoal gave the methyl ester **24**, and acetolysis provided the acyclic compound **29** and a small proportion of methyl 1,2,3-tri-*O*-acetyl-4-*O*-methyl-α-D-glucopyranos-

TABLE I

^{13}C-N.M.R. CHEMICAL SHIFT DATA (δ) FOR COMPOUNDS **9**, **15**, **17–19**, **27α**, AND **30–32**

Atom	*Compound*								
	9	**15**	**17**	**18**	**19**	**27α**	**30**	**31**	**32**
C-1	103.13		103.34	103.32	103.37		103.48	103.48	103.47
C-2	79.20		77.69	81.68	81.15		79.44	79.59	79.73
C-3	72.28		74.93[a]	78.37	78.66		75.40	76.48	75.44
C-4	69.20		72.40	67.65	67.60		74.17	74.10	73.88[a]
C-5	71.98		68.93	71.51	72.18		72.01	72.07	71.74
C-6	16.38		16.22	16.38	16.33		17.26	17.16	17.06
C-1′		92.70	99.26	99.67	98.93		99.12	99.49	99.76
C-2′		61.16	58.56	59.26	58.92		58.85	59.05	59.46
C-3′		80.50	74.91[a]	77.83	75.98		74.17	74.20	74.03[a]
C-4′		64.55	66.18	70.08[a]	75.98		69.96	69.56	66.52
C-5′		71.95	67.46	70.37[a]	63.06		62.94	67.16	66.91
C-6′		61.56	62.30	62.87	69.98		65.46	63.20	63.26
C-1″						89.19	101.20	101.24	101.37
C-2″						71.94[a]	78.39[a]	77.39[a]	77.93[a]
C-3″						71.11[a]	76.81[a]	77.28[a]	77.49[a]
C-4″						78.81	79.15	79.35	78.81
C-5″						69.30	69.96	70.11	70.03
C-6″						169.80	170.24	170.34	170.58
OCH_2CH_2Si	67.60		67.84	66.43	64.96		67.10	67.04	66.91
OCH_2CH_2Si	18.57		18.65	18.67	18.62		18.72	18.67	18.62
OCH_2Ph	74.71		74.97	75.05	74.96		74.58	74.81	74.86
OCH_3		58.10	57.53	57.22	56.48		56.86	57.38	57.56
						60.43	60.49	60.52	60.43
CO_2CH_3						52.88	52.65	52.83	53.02

[a]These assignments may be exchanged.

uronate (**27α**). Kováč *et al.*[11] reported that sulfuric acid-catalyzed acetolysis of methyl (methyl 4-*O*-methyl-α-D-glucopyranosid)uronate gave, in addition to methyl (methyl 2,3-di-*O*-acetyl-4-*O*-methyl-α-D-glucopyranosid)uronate, the crystalline acyclic compound **29**. By varying the acetolysis reaction conditions, we were able to regulate the formation of several acetolysis products. The structure of **24** was identified by comparison of its ^{1}H-n.m.r. spectrum with the spectrum reported earlier[11]. Deacetylation of **29** gave the pyranosyl compound **26**, which was acetylated in the usual manner to afford a mixture of the anomers of **27** in 90% yield.

Methyl (2,3-di-*O*-acetyl-4-*O*-methyl-α-D-glucopyranosyl bromide)uronate (**28**), obtained from **27** by treatment with hydrogen bromide in acetic acid, was condensed without purification, in the presence of mercuric cyanide–mercuric bromide, with **19** to give the trisaccharide **30** in 50% yield. The ^{1}H-n.m.r. spectrum showed a isopropylidene methyl group signal at δ 1.45 and 1.41, two acetyl group signals at δ 2.04 and 2.02, two methoxy group signals at δ 3.54 and 3.35, and a methyl ester group signal at δ 3.80. The ^{13}C-n.m.r. data showed three signals for anomeric carbon atoms at δ 103.5 ($J_{C,H}$ 158.26 Hz, C-1), 99.1 ($J_{C,H}$ 174.37 Hz, C-1′), and 101.2 ($J_{C,H}$ 162.65 Hz, C-1″). The ^{13}C shifts of the related compounds are listed in Table I. The β-D-configuration of the newly formed glycoside bond was indicated by the $J_{C,H}$ value of 162.7 Hz in the ^{13}C-n.m.r. spectrum and the coupling constant of 6.3 Hz for H-1″ in the ^{1}H-n.m.r. spectrum. Deisopropylidenation of **30** with 80% acetic acid, followed by acetylation with acetic anhydride–pyridine, gave the amorphous derivative **32**.

EXPERIMENTAL

General methods. — Melting points were determined with a Yanagimoto microapparatus and are uncorrected. Optical rotations were measured with a Jasco DIP-4 digital polarimeter. ^{1}H-N.m.r. and ^{13}C-n.m.r. spectra were recorded with JEOL FX-100 and JEOL GSX-400 MHz spectrometers. T.l.c. was conducted on precoated silica gel plates (Merck 60F-254), and the detection of compounds was achieved by quenching of u.v. fluorescence and with 10% H_2SO_4 solution. Column chromatography was carried out on silica gel (Merck Kieselgel 60).

Materials. — 1,5-Anhydro-2-deoxy-D-*lyxo*-hex-1-enitol (D-galactal) was obtained by the procedure of Shafizadeh[12]. Methyl 2,3-di-*O*-benzyl-β-D-glucopyranoside[13] was obtained by a modification of the procedure of Kováč and Palovčík[10].

2-(Trimethylsilyl)ethyl β-L-fucopyranoside (**4**). — Treatment of 2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl bromide[4] (**2**), synthesized from L-fucose (7.6 g, 46.3 mmol), with 2-(trimethylsilyl)ethanol (13 mL, 90.7 mmol) in dichloromethane (50 mL) containing Ag_2CO_3 (7.8 g), $AgClO_4$(0.7 g), and molecular sieves (4A, 15 g) for 20 h at room temperature gave **3** which was deacetylated with 0.4% sodium methoxide in methanol at room temperature to afford **4** (9.0 g, 74% yield from L-fucose), $[\alpha]_D^{17}$ +14.8° (*c* 0.4, chloroform), t.l.c. (5:1 chloroform–methanol) R_F

0.46; ^{1}H-n.m.r. ($CDCl_3$): δ 4.30 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 1.09 (d, 3 H, J 6.6 Hz, H_3-6), and 1.00 (m, 2 H, OCH_2CH_2Si).

Anal. Calc. for $C_{11}H_{24}O_5Si$: C, 49.97; H, 9.14. Found: C, 49.75; H, 9.14.

*2-(Trimethylsilyl)ethyl 3,4-O-isopropylidene-β-*L*-fucopyranoside* (**5**). — A mixture of **4** (2.34 g, 8.35 mmol), 2,2-dimethoxypropane (4 mL), and 4-toluenesulfonic acid (120 mg) in *N,N*-dimethylformamide (20 mL) in the presence of Drierite (500 mg) was stirred for 1 h at room temperature. The mixture was made neutral with Amberlite IR-410 (OH^-) anion-exchange resin, and then evaporated *in vacuo*. The syrup was chromatographed on silica gel with 8:1 hexane–ethyl acetate as eluent to give **5** (2.56 g, 95%), syrup, $[\alpha]_D^{17}$ −19.4° (*c* 0.5, chloroform), t.l.c. (15:1 chloroform–methanol) R_F 0.83; ^{1}H-n.m.r. ($CDCl_3$): δ 4.12 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 1.45, 1.34 (each s, 3 H, CMe_2), 1.39 (d, 3 H, H_3-6), and 0.95 (bt, 2 H, OCH_2CH_2Si).

Anal. Calc. for $C_{14}H_{28}O_5Si$: C, 55.23; H, 9.26. Found: C, 55.08; H, 8.97.

*2-(Trimethylsilyl)ethyl 2-O-benzyl-3,4-O-isopropylidene-β-*L*-fucopyranoside* (**6**). — Sodium hydride (60%, 0.5 g) was added portionwise to a solution of **5** (2.31 g, 7.59 mmol) in *N,N*-dimethylformamide (27 mL) at 5°, and the mixture was stirred for 90 min. To this mixture was added dropwise benzyl bromide (1.27 mL) at 0–5°, and the mixture was stirred for 5 h at 20°. Excess NaH was decomposed by adding methanol and the mixture was partitioned between water and ethyl acetate. The organic layer was washed with water, dried (Na_2SO_4), and evaporated *in vacuo*. The residual oil was chromatographed on silica gel with 8:1 hexane–ethyl acetate as eluent to give **6** (2.8 g, 93.5%), syrup, $[\alpha]_D^{17}$ −38.8° (*c* 0.5, chloroform), t.l.c. (3:1 hexane–ethyl acetate) R_F 0.56; ^{1}H-n.m.r. ($CDCl_3$): δ 7.42–7.18 (m, 5 H, Ph), 4.23 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 1.35 (d, 3 H, H_3-6), 1.34 (s, 6 H, CMe_2), and 1.01 (dd, 1 H, OCH_2CH_2Si).

Anal. Calc. for $C_{21}H_{34}O_5Si$: C, 63.92; H, 8.68. Found: C, 63.60; H, 8.52.

*2-(Trimethylsilyl)ethyl 2-O-benzyl-β-*L*-fucopyranoside* (**7**). — Compound **6** (2.75 g, 6.97 mmol) was treated with 80% acetic acid (70 mL) for 4 h at 45° to give **7** quantitatively, m.p. 81–83°, $[\alpha]_D^{17}$ −20.9° (*c* 3.6, chloroform), t.l.c. (2:1 hexane–ethyl acetate) R_F 0.24; ^{1}H-n.m.r. ($CDCl_3$): δ 7.43–7.26 (m, 5 H, Ph), 4.98, 4.66 (each d, 2 H, $PhCH_2$), 4.33 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 3.70–3.32 (m, 3 H, H-3,4,5), 1.34 (d, 3 H, J 7.0 Hz, H_3-6), and 1.02 (m, 2 H, OCH_2CH_2Si).

Anal. Calc. for $C_{18}H_{30}O_5Si$: C, 60.98; H, 8.52. Found: C, 60.64; H, 8.28.

*2-(Trimethylsilyl)ethyl 4-O-acetyl-2-O-benzyl-β-*L*-fucopyranoside* (**9**). — Compound **7** (1.3 g, 3.67 mmol) was added to a solution of triethyl orthoacetate (5.8 mL) and 4-toluenesulfonic acid (180 mg) in toluene (100 mL). After stirring for 2 h at room temperature, the reaction appeared complete as evidenced by t.l.c. in 2:1 hexane–ethyl acetate. After treatment with Amberlite IR-410 (OH^-) anion-exchange resin, the resulting solution was washed with water while back-extracting the aqueous layer with chloroform. The organic phases were combined and evaporated *in vacuo* to give a syrupy residue, 2-(trimethylsilyl)ethyl 2-*O*-benzyl-3,4-*O*-(ethyl orthoacetyl)-β-L-fucopyranoside (**8**) (t.l.c., 2:1 hexane–ethyl acetate,

R_F 0.82), which was treated with 80% aqueous acetic acid (30 mL) for 10 min at room temperature, after which time t.l.c. (2:1 hexane–ethyl acetate) showed no evidence for orthoacetate. The solution was taken to dryness *in vacuo* to give **9** (yield 82.5%, based on **7**), syrup, $[\alpha]_D^{17}$ −4.2° (*c* 0.44, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 7.38–7.27 (m, 5 H, Ph), 5.16 (dd, 1 H, $J_{3,4}$ 3.7, $J_{4,5}$ 0.9 Hz, H-4), 4.38 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 3.74 (dd, 1 H, $J_{2,3}$ 10.7 Hz, H-3), 2.14 (s, 3 H, OAc), 1.20 (d, 3 H, H_3-6), and 1.05 (m, 2 H, OCH_2CH_2Si).

Anal. Calc. for $C_{20}H_{32}O_6Si$: C, 60.57; H, 8.13. Found: C, 60.91; H, 8.36.

*1,5-Anhydro-2-deoxy-3-*O*-methyl-*D*-lyxo-hex-1-enitol* (**11**). — A suspension of 1,5-anhydro-2-deoxy-D-*lyxo*-hex-1-enitol[12] (**10**) (4.8 g, 32.8 mmol) and dibutyltin oxide (8.4 g, 33.7 mmol) in methanol (400 mL) was heated under reflux for 1.5 h, and then the solvent was removed under diminished pressure. The resulting 3,4-*O*-dibutylstannylene derivative was dried under vacuum, the residue taken up in *N,N*-dimethylformamide (120 mL), and treated with methyl iodide (15 mL, 0.24 mol). After the mixture had been heated for 5 h at 40°, t.l.c. (5:1 chloroform–methanol) showed complete disappearance of the starting material. The mixture was passed through a column of Amberlite IR-410 (OH^-) anion-exchange resin in 50% methanolic solution (60 mL), followed by evaporation of the solution under diminished pressure, and the syrup was chromatographed on silica gel. The effluent from 70:1 chloroform–methanol was evaporated and crystallized from ethyl acetate (3.38 g, 64.3%), m.p. 76–77°, $[\alpha]_D^{19}$ −2.1° (*c* 1.0, chloroform), t.l.c. (5:1 chloroform–methanol) R_F 0.60; ^{1}H-n.m.r. ($CDCl_3$): δ 6.33 (dd, 1 H, $J_{1,2}$ 6.4, $J_{1,3}$ 2.0 Hz, H-1), and 3.40 (s, 3 H, OMe).

Anal. Calc. for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.04; H, 7.48.

*4,6-Di-*O*-acetyl-1,5-anhydro-2-deoxy-3-*O*-methyl-*D*-lyxo-hex-1-enitol* (**12**). — Compound **11** (3.25g, 20.3 mmol) was acetylated with 3:2 pyridine–acetic anhydride (25 mL). After the usual work-up, the material was chromatographed on a column of silica gel with 5:1 hexane–ethyl acetate as eluent to afford **12** (4.8 g, 96.9% yield), $[\alpha]_D^{19}$ −18.5° (*c* 0.9, chloroform); t.l.c. (2:1 hexane–ethyl acetate) R_F 0.43; ^{1}H-n.m.r. ($CDCl_3$): δ 6.38 (dd, 1 H, $J_{1,2}$ 6.4, $J_{1,3}$ 1.8 Hz, H-1), 3.38 (s, 3 H, OMe), and 2.15, 2.10 (each s, 3 H, 2 OAc).

Anal. Calc. for $C_{11}H_{16}O_6$: C, 54.09; H, 6.60. Found: C, 53.70; H, 6.31.

*4,6-Di-*O*-acetyl-2-azido-2-deoxy-3-*O*-methyl-α-* (**13**) *and -β-*D*-galactopyranosyl nitrate* (**14**). — To a solution of compound **12** (233.5 mg, 0.96 mmol) in acetonitrile (4.5 mL) was added a mixture of NaN_3 (93.1 mg, 1.43 mmol) and $Ce(NH_4)_2(NO_3)_6$ (1.56 g, 3.47 mmol), and the suspension was vigorously stirred at <−20°. After 8–10 h, cold ether and water were added, the organic layer was separated and washed with ice-cold water, and then dried (Na_2SO_4). Evaporation of the solvent gave a pale-yellow syrup that was chromatographed on silica gel. Elution with 80:1 benzene–acetone provided the α-D anomer (**13**), which crystallized from ether (209.3 mg, 62.4%), and with 60:1 benzene–acetone the β-D anomer (**14**) (13.0 mg, 3.9%).

Compound **13**. M.p. 93°, $[\alpha]_D^{20}$ +84.5° (*c* 0.4, chloroform); t.l.c. (2:1 hexane–

ethyl acetate) R_F 0.63; ^{1}H-n.m.r. ($CDCl_3$): δ 6.27 (d, 1 H, $J_{1,2}$ 4.2 Hz, H-1), 3.98 (dd, 1 H, $J_{2,3}$ 10.8 Hz, H-2), 3.66 (dd, 1 H, $J_{3,4}$ 3.4 Hz, H-3), 3.47 (s, 3 H, OMe), and 2.16, 2.06 (each s, 3 H, 2 OAc).

Anal. Calc. for $C_{11}H_{16}N_4O_9$: C, 37.93; H, 4.63; N, 16.09. Found: C, 38.05; H, 4.50; N, 16.38.

Compound **14**. T.l.c. (2:1 hexane–ethyl acetate) R_F 0.48; ^{1}H-n.m.r. ($CDCl_3$): δ 5.43 (d, 1 H, $J_{1,2}$ 9.0 Hz, H-1), 3.64 (dd, 1 H, $J_{2,3}$ 10.2 Hz, H-2), 3.45 (s, 3 H, OMe), and 2.16, 2.04 (each s, 3 H, 2 OAc).

1,4,6-Tri-O-acetyl-2-azido-2-deoxy-3-O-methyl-β-D-galactopyranose (**15**). — (*a*). A suspension of **13** (0.52 g, 1.5 mmol) and anhydrous potassium acetate (300 mg) in acetic anhydride (4 mL) was heated to 100° for 1.5 h. The mixture was diluted with dichloromethane, and this mixture was susccessively treated with ice-cold water, saturated aqueous $NaHCO_3$, and water. Drying and evaporation of the organic layer left a solid which crystallized from ether to provide **15** (480 mg, 88.5%), m.p. 111–113°, $[\alpha]_D^{20}$ +54.5° (*c* 0.2, chloroform); t.l.c. (2:1 hexane–ethyl acetate) R_F 0.43; ^{1}H-n.m.r. ($CDCl_3$): δ 5.45 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1), 3.46 (s, 3 H, OMe), and 2.19, 2.16, 2.06 (each s, 3 H, 3 OAc).

Anal. Calc. for $C_{13}H_{19}N_3O_8$: C, 45.21; H, 5.54; N, 12.16. Found: C, 44.86; H, 5.35; N, 11.69.

(*b*). Treatment of **13** (100 mg, 0.27 mmol) with 0.272M $TiBr_4$ in 10:1 dichloromethane–ethyl acetate (4.7 mL) and acetyl chloride (0.6 mL) at room temperature for 30 min gave **15** and its α-D anomer in 85% yield in the ratio of β to α of 5:2.

4,6-Di-O-acetyl-2-azido-2-deoxy-3-O-methyl-α-D-galactopyranosyl bromide (**16**). — Compound **15** (372 mg, 1.08 mmol) was treated with 0.272M $TiBr_4$ in 10:1 dichloromethane–ethyl acetate (8 mL) for 8 h at 30°. The solution was extracted with chloroform, washed with $NaHCO_3$ and water, dried, and evaporated to give **16**, t.l.c. (2:1 hexane–ethyl acetate) R_F 0.55.

2-(Trimethylsilyl)ethyl 4-O-acetyl-2-O-benzyl-3-O-(4,6-di-O-acetyl-2-azido-2-deoxy-3-O-methyl-α-D-galactopyranosyl)-β-L-fucopyranoside (**17**). — A solution of **16** (394 mg, 1.08 mmol) in dichloromethane (4 mL) was added to a mixture of **9** (395 mg, 0.9 mmol), $Hg(CN)_2$ (500 mg), $HgBr_2$ (35 mg), and molecular sieves 4A (1 g) in the same solvent (5 mL), and stirred for 10 h at room temperature. The suspension was filtered and the filtrate extracted with chloroform. The extract was washed with water and evaporated to give a syrup which was chromatographed on silica gel with 50:1 benzene–acetone as eluent. The eluate containing the disaccharide fraction was evaporated to dryness to give pure **17** (536 mg, 87%), $[\alpha]_D^{19}$ +86° (*c* 0.4, chloroform); t.l.c. (5:1 benzene–acetone) R_F 0.65; ^{1}H-n.m.r. ($CDCl_3$): δ 7.40–7.28 (m, 5 H, Ph), 5.44 (d, 1 H, $J_{1',2'}$ 3.7 Hz, H-1'), 4.40 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 3.45 (s, 3 H, OMe), 2.19, 2.11, 2.05 (each s, 3 H, 3 OAc), 1.24 (d, 3 H, H_3-6), and 1.06 (m, 2 H, OCH_2CH_2Si).

Anal. Calc. for $C_{31}H_{47}N_3O_{12}Si$: C, 54.61; H, 6.94; N, 6.16. Found: C, 54.23; H, 7.21; N, 5.97.

2-(Trimethylsilyl)ethyl 3-O-(2-azido-2-deoxy-3-O-methyl-α-D-galactopyrano-

*syl)-2-O-benzyl-β-*L*-fucopyranoside* (**18**). — Compound **17** (500 mg, 0.73 mmol) was treated with methanolic sodium methoxide (5 mg/20 mL) for 4 h at 50°. The mixture was passed through a column of cation-exchange resin [Amberlite IR-120 (H^+)] with methanol as a solvent to yield 365 mg (yield 90%) of **18**, syrup, $[\alpha]_D^{21}$ +39.5° (*c* 1.2, chloroform), t.l.c. (5:1 benzene–acetone) R_F 0.22; ^{1}H-n.m.r. ($CDCl_3$): δ 7.42–7.18 (m, 5 H, Ph), 5.23 (bs, 1 H, H-1′), 4.32 (d, 1 H, $J_{1,2}$ 6.2 Hz, H-1), 3.28 (s, 3 H, OMe), 1.30 (d, 3 H, H_3-6), 1.02 (t, 2 H, OCH_2CH_2Si).

Anal. Calc. for $C_{25}H_{41}N_3O_9Si$: C, 54.03; H, 7.43; N, 7.56. Found: C, 53.67; H, 7.50; N, 7.88.

*2-(Trimethylsilyl)ethyl 3-O-(2-azido-2-deoxy-4,6-O-isopropylidene-3-O-methyl-α-*D*-galactopyranosyl)-2-O-benzyl-β-*L*-fucopyranoside* (**19**). — Compound **18** (582 mg, 1.05 mmol) was treated with 2,2-dimethoxypropane (5 mL) in *N,N*-dimethylformamide (12 mL) in the presence of 4-toluenesulfonic acid (300 mg) at 0° for 3 h. The reaction was made neutral with Amberlite IR-410 (OH^-) anion-exchange resin. Filtration, evaporation of the solvent, and purification by silica gel column chromatography using 30:1 benzene-acetone as eluent gave **19** (575 mg, 92%), $[\alpha]_D^{19}$ +57° (*c* 1.0, chloroform); t.l.c. (15:1 chloroform–methanol) R_F 0.7; ^{1}H-n.m.r. ($CDCl_3$): δ 7.39–7.27 (m, 5 H, Ph), 5.32 (d, 1 H, $J_{1',2'}$ 3.2 Hz, H-1′), 4.33 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1), 3.48 (s, 3 H, OMe), 1.47, 1.45 (each s, 3 H, CMe_2), 1.30 (d, 3 H, H_3-6), and 1.02–0.96 (m, 2 H, OCH_2CH_2Si).

Anal. Calc. for $C_{28}H_{45}N_3O_9Si$: C, 56.45; H, 7.61; N, 7.05. Found: C, 56.59; H, 7.82; N, 6.92.

*2-(Trimethylsilyl)ethyl4-O-acetyl-3-O-(2-azido-2-deoxy-4,6-O-isopropylidene-3-O-methyl-α-*D*-galactopyranosyl)-2-O-benzyl-β-*L*-fucopyranoside* (**20**) — Acetylation of **19** (10 mg) with acetic anhydride (0.3 mL) in pyridine (0.5 mL) gave **20**, a monoacetate which confirmed the presence of a free hydroxyl group in **19**; ^{1}H-n.m.r. ($CDCl_3$): δ 7.33–7.20 (m, 5 H, Ph), 5.46 (bs, 1 H, H-1′), 5.01 (bd, 1 H, $J_{3,4}$ 3.5 Hz, H-4), 4.33 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 3.42 (s, 3 H, OMe), 2.13 (s, 3 H, OAc), 1.43, 1.40 (each s, 3 H, CMe_2), 1.17 (d, 3 H, H_3-6), and 1.02–0.96 (m, 2 H, OCH_2CH_2Si).

Anal. Calc. for $C_{30}H_{47}N_3O_{10}Si$: C, 56.49; H, 7.42; N, 6.58. Found: C, 56.04; H, 7.49; N, 6.28.

*Methyl 2,3-di-O-benzyl-6-O-trityl-β-*D*-glucopyranoside* (**21**). — Chlorotriphenylmethane (1.69 g, 6.02 mmol) was added with stirring to a solution of methyl 2,3-di-*O*-benzyl-β-D-glucopyranoside[13] (2.05 g, 5.48 mmol) in pyridine (50 mL), and the solution was heated with the exclusion of moisture at 60° until t.l.c. showed almost complete conversion of the starting material into **21**. The mixture was processed in the usual manner; $[\alpha]_D^{19}$ −33° (*c* 2.3, chloroform).

*Methyl 2,3-di-O-benzyl-4-O-methyl-β-*D*-glucopyranoside* (**22**). — To a solution of **21** (2.59 g, 4.2 mmol) in *N,N*-dimethylformamide (20 mL) was added NaH (0.52 g), followed by methyl iodide (0.52 mL). The mixture was stirred under gentle reflux. After 0.5 h, the excess of the methylation reagent was destroyed by careful addition of methanol, and the organic solvents were concentrated. Water (2 mL) was added at 80° to a solution of the residue in 8:3 acetic acid–1,4-dioxane (22 mL),

and the solution was kept at the same temperature for 15 h, after which time t.l.c. showed that the detritylation was complete. The mixture was cooled to room temperature, the separated triphenylmethanol was filtered off and washed with ethanol, the filtrate was concentrated, and the residual acetic acid was co-evaporated with water. The residue was chromatographed on silica gel, and **22** was eluted with 20:1 benzene–ethanol in 73% yield, m.p. 84–86°, $[\alpha]_D^{19}$ +40.5° (*c* 1.2, chloroform); lit.[13] m.p. 87.5–88.5°, $[\alpha]_D^{19}$ +42.9° (chloroform).

Methyl (methyl 2,3-di-O-benzyl-4-O-methyl-β-D-glucopyranosid)uronate (**23**). — A solution of $K_2Cr_2O_7$ (4.4 g) in 3.5M H_2SO_4 (17 mL) was added with stirring to a solution of **22** (4.3 g, 11.1 mmol) in acetone (80 mL). The solution was stirred for 5 min and then heated at 50° for 1 h. After being cooled to room temperature, the solid settled and the supernatant solution was slowely poured into water. The chromium salts were washed with acetone. The washings, combined with the product, were extracted with chloroform, and the chloroform solution was washed with water, dried, and evaporated. The residue (4.5 g) was treated with 10% HCl in methanol (45 mL) for 3 h. After concentration and chromatography on silica gel, **23** was obtained in 74.4% yield (4.43 g), $[\alpha]_D^{19}$ +22.2° (*c* 1.1, ethanol); lit.[14] $[\alpha]_D^{18}$ +19 ±1° (*c* 1.1, ethanol).

Methyl (methyl 4-O-methyl-β-D-glucopyranosid)uronate (**24**). — A mixture of **23** (3.43 g, 8.24 mmol) and 5% Pd–C (2.6 g) in 5:1 methanol–acetic acid (24 mL) was stirred at room temperature in an H_2 atmosphere until the reaction was complete. The product was isolated in the usual manner, $[\alpha]_D^{19}$ −37.5° (*c* 0.8, chloroform); lit.[14] $[\alpha]_D^{18}$ −45 ±1° (*c* 1.1, water).

Methyl 2,3,5-tri-O-acetyl-1-deoxy-4-O-methyl-aldehydo-D-*glucuronate 1,1-diacetate* (**29**). — Compound **24** (300 mg, 0.94 mmol) was added to a solution of BF_3·etherate (2 mL) in acetic anhydride (20 mL) at room temperature for 4 h. The solution was then poured into a large excess of ice-cold water and stirred. The product was extracted with chloroform, and the extract was washed successively with an aqueous $NaHCO_3$ solution and water. The dried extract was evaporated to dryness under reduced pressure, and the syrupy residue was chromatographed on silica gel using 3:1 hexane–ethyl acetate as eluent to give **29** (260 mg, 61.5%), $[\alpha]_D^{21}$ −1.3° (*c* 1.0, chloroform), t.l.c. (3:2 hexane–ethyl acetate) R_F 0.38; ^{1}H-n.m.r. ($CDCl_3$): δ 6.96–6.92 (m, 1 H, H-1), 5.52–5.48 (m, 2 H, H-2,3), 5.33 (d, 1 H, $J_{4,5}$ 4.2 Hz, H-5), 3.79 (s, 3 H, CO_2Me and 1 H, H-4), 3.46 (s, 3 H, OMe), and 2.17, 2.12, 2.11, 2.09, 2.07 (each s, 3 H, 5 OAc).

Anal. Calc. for $C_{18}H_{26}O_{13}$: C, 48.00; H, 5.81. Found: C, 48.32; H, 5.91.

Methyl 4-O-methyl-D-glucopyranuronate (**26**). — Compound **29** (260 mg, 0.58 mmol) was treated with sodium methoxide (40 mg) in methanol (15 mL) at room temperature for 3 h, and the base was neutralized with Amberlite IR-120 (H^+ cation-exchange resin. Filtration, evaporation of the solvent, and purification by silica gel column chromatography using chloroform–methanol as eluent gave **26** (122 mg, 94%), $[\alpha]_D^{21}$ +47.5° (equil., *c* 0.6, 1:1 water–ethanol), t.l.c. (5:1 chloroform–methanol) R_F 0.38; ^{1}H-n.m.r. ($CDCl_3$): δ 5.09 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1α), 4.48 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1β), 3.77 (s, 3 H, CO_2Me), and 3.47 (s, 3 H, OMe).

Anal. Calc. for $C_{18}H_{14}O_7$: C, 43.24; H, 6.35. Found: C, 43.00; H, 6.52.

Methyl 1,2,3-tri-O-acetyl-4-O-methyl-α,β-D-glucopyranuronate (**27**). — Compound **26** (122 mg, 0.55 mmol) was acetylated with 5:8 acetic anhydride–pyridine (13 mL) to give **27** (189 mg, 90%), t.l.c. (3:2 hexane–ethyl acetate) R_F 0.44.

27-α. $[\alpha]_D^{21}$ +57° (*c* 0.52, chloroform); ^{1}H-n.m.r. ($CDCl_3$): δ 6.29 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 5.44 (dd, 1 H, $J_{2,3}$ 10.0, $J_{3,4}$ 9.4 Hz, H-3), 5.03 (dd, 1 H, H-2), 4.28 (d, 1 H, $J_{4,5}$ 9.8 Hz, H-5), 3.83 (s, 3 H, CO_2Me), 3.66 (t, 1 H, H-4), 3.44 (s, 3 H, OMe), and 2.18, 2.10, 2.01 (each s, 3 H, 3 OAc).

Anal. Calc. for $C_{14}H_{20}O_{13}$: C, 48.27; H, 5.78. Found: C, 48.33; H, 5.80.

27-β. ^{1}H-N.m.r. data were identical with reference data[11].

Methyl (2,3-di-O-acetyl-4-O-methyl-α-D-glucopyranosyl bromide)uronate (**28**). — (*a*). Compound **27** (189 mg, 0.54 mmol) was treated with 25% HBr–acetic acid (2 mL) in dichloromethane (2 mL) for 20 h at room temperature. The solution was poured into ice–water, extracted with chloroform, and the extract washed with $NaHCO_3$ and water. The dried solution was evaporated to give **28** (199 mg, 98%), t.l.c. (2:1 hexane–ethyl acetate) R_F 0.43; ^{1}H-n.m.r. ($CDCl_3$): δ 6.55 (d, 1 H, $J_{1,2}$ 3.9 Hz, H-1), 5.55 (t, 1 H, $J_{2,3} = J_{3,4}$ 9.2 Hz, H-3), 4.77 (d, 1 H, H-2), 4.47 (d, 1 H, $J_{4,5}$ 9.0 Hz, H-5), 3.84 (s, 3 H, CO_2Me), 3.68 (t, 1 H, H-4), 3.44 (s, 3 H, OMe), and 2.11, 2.08 (each s, 3 H, 2 OAc).

(*b*). Treatment of **27** (51.7 mg, 0.15 mmol) with 0.272M $TiBr_4$ in 1:10 ethyl acetate–dichloromethane (1.2 mL) for 10 h at 30° gave, after silica gel column chromatography in 5:1 hexane–ethyl acetate, **28** (30.3 mg, 55%) and the starting material **27α** (22.1 mg, 43%).

2-(Trimethylsilyl)ethyl 3-O-(2-azido-2-deoxy-4,6-O-isopropylidene-3-O-methyl-α-D-galactopyranosyl)-2-O-benzyl-4-O-(methyl 2,3-di-O-acetyl-4-O-methyl-β-D-glucopyranosyluronate)-β-L-fucopyranoside (**30**). — To a solution of **19** (88 mg, 0.15 mmol) in dichloromethane (0.5 mL) were added $Hg(CN)_2$ (200 mg), $HgBr_2$ (40 mg), and molecular sieves 4A (300 mg), and then a solution of **28** (277 mg, 75 mmol) in dichloromethane (0.5 mL). The suspension was stirred for 26 h at 20°, and then diluted with chloroform, filtered, and the filtrate washed successively with M HCl, saturated aqueous $NaHCO_3$, and water. The colorless solution was dried, evaporated, and the crude product was acetylated in the usual manner with 2:3 acetic anhydride-pyridine (5 mL) in order to improve the separation on silica gel column chromatography. Elution with 10:1 benzene–acetone gave **30** which crystallized from ether as colorless needles (65.5 mg, 50%), m.p. 96–97°, $[\alpha]_D^{19}$ +14.4° (*c* 0.6, chloroform); t.l.c. (60:1 chloroform–methanol) R_F 0.50, (5:1 benzene–acetone) R_F 0.50; ^{1}H-n.m.r. ($CDCl_3$): δ 7.33–7.21 (m, 5 H, Ph), 5.35 (d, 1 H, $J_{1',2'}$ 2.8 Hz, H-1'), 5.13 (t, 1 H, $J_{2'',3''} = J_{3'',4''}$ 7.6 Hz, H-3''), 4.97 (dd, 1 H, $J_{1'',2''}$ 6.3 Hz, H-2''), 4.62 (d, 1 H, $J_{1'',2''}$ 6.3 Hz, H-1''), 4.34 (bd, 1 H, $J_{3',4'}$ 2.3 Hz, H-4'), 4.20 (d, 1 H, $J_{1,2}$ 5.8 Hz, H-1), 3.80 (s, 3 H, CO_2Me), 3.54, 3.35 (each s, 3 H, 2 OMe), 2.04, 2.02 (each s, 3 H, 2 OAc), 1.45, 1.41 (each s, 3 H, CMe_2), and 1.27 (d, 3 H, H_3-6).

Anal. Calc. for $C_{40}H_{61}N_3O_{17}Si$: C, 54.34; H, 6.95; N, 4.75. Found: C, 53.92; H, 6.74; N, 4.58.

2-(Trimethylsilyl)ethyl 3-O-(2-azido-2-deoxy-3-O-methyl-α-D-galactopyranosyl)-2-O-benzyl-4-O-(methyl 2,3-di-O-acetyl-4-O-methyl-β-D-glucopyranosyluronate)-β-L-fucopyranoside (**31**). — Compound **30** (60 mg, 68 μmol) was treated with 80% acetic acid (3 mL) for 8 h at room temperature to give **31** (48 mg, 85%), m.p. 123–125°, $[\alpha]_D^{21}$ +1.7° (*c* 0.7, chloroform), t.l.c. (5:1 benzene–acetone) R_F 0.36; ^{1}H-n.m.r. ($CDCl_3$): δ 7.50–7.28 (m, 5 H, Ph), 5.43 (d, 1 H, $J_{1',2'}$ 3.7 Hz, H-1'), 5.20 (t, 1 H, $J_{2'',3''} = J_{3'',4''}$ 9.2 Hz, H-3''), 5.06 (dd, 1 H, $J_{1'',2''}$ 7.7 Hz, H-2''), 4.27 (m, 1 H, H-4'), 4.14 (bd, 1 H, $J_{1,2}$ 2.6 Hz, H-1), 3.98 (bt, 1 H, H-5'), 3.82 (s, 3 H, CO_2Me), 3.66, 3.39 (each s, 3 H, 2 OMe), 2.10, 2.09 (each s, 3 H, 2 OAc), 1.33 (d, 3 H, H_3-6), and 1.03–0.90 (m, 2 H, OCH_2CH_2Si).

Anal. Calc. for $C_{37}H_{57}N_3O_{17}Si$: C, 52.65; H, 6.80; N, 4.97. Found: C, 52.31; H, 6.96; N, 4.54.

2-(Trimethylsilyl)ethyl 2-O-benzyl-3-O-(4,6-di-O-acetyl-2-azido-2-deoxy-3-O-methyl-α-D-galactopyranosyl)-4-O-(methyl 2,3-di-O-acetyl-4-O-methyl-β-D-glucopyranosyluronate)-β-L-fucopyranoside (**32**). — Compound **31** (48.7 mg, 57.7 μmol) was acetylated with 5:8 acetic anhydride–pyridine (13 mL) in the usual manner to give **32**, m.p. 92–94°, $[\alpha]_D^{21}$ −27.5° (*c* 0.2, chloroform), t.l.c. (5:1 benzene–acetone) R_F 0.58; ^{1}H-n.m.r. ($CDCl_3$): δ 7.37–7.23 (m, 5 H, Ph), 5.42 (bd, 1 H, $J_{3',4'}$ 2.8 Hz, H-4'), 5.24 (d, 1 H, $J_{1',2'}$ 3.8 Hz, H-1'), 5.17 (t, 1 H, $J_{2'',3''} = J_{3'',4''}$ 9.6 Hz, H-3''), 5.06 (dd, 1 H, $J_{1'',2''}$ 7.9 Hz, H-2''), 4.61 (d, 1 H, H-1''), 4.25 (d, 1 H, $J_{1,2}$ 7.4 Hz, H-1), 3.88 (s, 3 H, CO_2Me), 3.54, 3.36 (each s, 3 H, 2 OMe), 2.10, 2.07, 2.05, 2.01 (each s, 3 H, 4 OAc), 1.31 (d, 3 H, H_3-6), and 0.98–0.91 (m, 2 H, OCH_2CH_2Si).

Anal. Calc. for $C_{41}H_{61}N_3O_{19}Si$: C, 53.06; H, 6.62; N, 4.52. Found: C, 52.73; H, 6.41; N, 3.95.

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