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Synthesis of the methyl thioglycosides of 2-, 3-, and 4-deoxy-L-fucose†

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Abstract

Methyl thioglycoside derivatives of 2-, 3-, and 4-deoxy-L-fucopyranose have been prepared as glycosyl donors for the synthesis of sialyl Le^x ganglioside analogues containing modified α-L-fucopyranose residues. Reductive dethioacylation of 2-(trimethylsilyl)ethyl 3,4-di-*O*-benzoyl-2-*O*-(phenoxy)thiocarbonyl-β-L-fucopyranoside, prepared from L-fucose in eight steps, gave the 2-deoxy compound, which was transformed via selective removal of the 2-(trimethylsilyl)ethyl group, subsequent acetylation, and displacement of the 1-acetoxy group by a methylthio group, into methyl 3,4-di-*O*-benzoyl-2,6-dideoxy-1-thio-α,β-L-*lyxo*-hexopyranoside (**11**). 2-(Trimethylsilyl)ethyl 2,4-di-*O*-benzoyl-3-*O*-(phenoxy)thiocarbonyl-β-L-fucopyranoside, prepared from the unsubstituted glycoside in four steps, and 2-(trimethylsilyl)ethyl 2,3-di-*O*-benzoyl-4-*O*-(phenoxy)thiocarbonyl-β-L-fucopyranoside, similarly prepared in two steps, were transformed via reduction of the (phenoxy)thiocarbonyloxy group, selective removal of the 2-(trimethylsilyl)ethyl group, *O*-acetylation, displacement of the 1-acetoxy group by a methylthio group as described for **11**, and finally replacement of the benzoyl groups by benzyl groups, into the analogous, protected methyl 3- and 4-deoxy-1-thio-β-L-fucopyranosides.

1. Introduction

Since the demonstration [2–4] that the selectin family of proteins recognizes the sialyl Le^x determinant, α-Neu5Ac-(2 → 3)-β-D-Gal-(1 → 4)-[α-L-Fuc-(1 → 3)]-β-D-GlcNAc, which is found as a terminal carbohydrate structure in both glycoproteins

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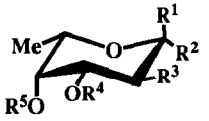
and glycolipids of cell membranes, the importance of this structure in leukocyte–endothelium adhesion and in tumor metastasis has focused attention on the general phenomenon of lectin-mediated cell adhesion. We have reported the synthesis of sialyl Le^x ganglioside (a hexasaccharide glycolipid [6]), a pentasaccharide analogue [7], and sialyl $\alpha(2 \rightarrow 6)$-Le^x ganglioside [8], and demonstrated an energy minimized conformation [9]. Based on this three-dimensional structure, various types of sialyl Le^x analogues [10] containing chemically modified sialic acids have been synthesized in order to clarify the structural features of the sialic acid moiety required for selectin recognition. As a part of our continuing studies on structure–activity correlations in the sialyl Le^x epitope, we describe here the synthesis of protected methyl 1-thioglycosides of 2-, 3-, and 4-deoxy-L-fucopyranose, to be used as glycosyl donors in the synthesis of deoxyfucose-containing sialyl Le^x oligosaccharides and ganglioside analogues.

2. Results and discussion

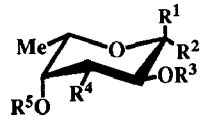
For the synthesis of the target 1-thioglycosides, which were to be appropriately derivatized for use in α-glycoside synthesis, we set out to prepare 2-(trimethylsilyl)ethyl 3,4-di-*O*-benzoyl-2-*O*-(phenoxy)thiocarbonyl-β-L-fucopyranoside (**8**), 2-(trimethylsilyl)ethyl 2,4-di-*O*-benzoyl-3-*O*-(phenoxy)thiocarbonyl-β-L-fucopyranoside (**15**), and 2-(trimethylsilyl)ethyl 2,3-di-*O*-benzoyl-4-*O*-(phenoxy)thiocarbonyl-β-L-fucopyranoside (**21**). We then planned to undertake reductive cleavage of these (phenoxy)thiocarbonyloxy derivatives to afford the corresponding deoxy compounds, and convert the latter by thiomethylation and appropriate protecting-group manipulation into the end products **11**, **19**, and **25**.

Compound **2** was prepared from the easily obtainable acetobromofucose by coupling with 2-(trimethylsilyl)ethanol under Königs–Knorr conditions, and on Zemplen *O*-deacetylation it gave 2-(trimethylsilyl)ethyl β-L-fucopyranoside (**3**) in high overall yield. Treatment of **3** with 2,2-dimethoxypropane in *N*,*N*-dimethylformamide (DMF) in the presence of *p*-toluenesulfonic acid monohydrate gave the 3,4-*O*-isopropylidene derivative (**4**) in 95% yield, and this on *O*-benzylation and subsequent hydrolysis of the isopropylidene group with aqueous 80% acetic acid, followed by *O*-benzoylation, was converted into 2-(trimethylsilyl)ethyl 3,4-di-*O*-benzoyl-2-*O*-benzyl-β-L-fucopyranoside (**6**) in good yield. Treatment of 2-(trimethylsilyl)ethyl 3,4-di-*O*-β-L-fucopyranoside (**7**), derived by catalytic hydrogenolysis (10% Pd–C) of the benzyl group of **6**, with phenyl chlorothionoformate [11] in pyridine–dichloromethane gave the 2-*O*-(phenoxy)thiocarbonyl derivative (**8**) in 83% yield, and this was reduced with tributyltin hydride in the presence of α,α'-azobisisobutyronitrile (AIBN) to give the 2-deoxy compound (**9**) quantitatively. Significant signals in the ^{1}H NMR spectrum of **9** were a one-proton doublet of doublets at δ 4.63 ($J_{1,2ax}$ 8.9, $J_{1,2eq}$ 2.8 Hz, H-1) and a multiplet at δ 2.11 (2 H-2), indicating the structure assigned. Treatment [12] of **9** with boron trifluoride etherate in toluene in the presence of acetic anhydride at −50°C gave the 1-*O*-acetyl derivative (**10**) in 50% yield. When this reaction was performed at 0°C

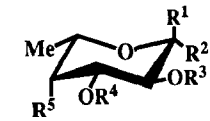
compound **10** was not formed, but several other products arose, which were not further investigated. The replacement [13] of the anomeric acetoxy group in **10** with methylthio by stirring for 2 h at 0°C with trimethyl(methylthio)silane in dry dichloromethane in the presence of boron trifluoride etherate gave the methyl 1-thioglycoside derivative **11** of 2,6-dideoxy-L-*lyxo*-hexopyranose in 95% yield as a ~ 1 : 1 anomeric mixture.



	R^1	R^2	R^3	R^4	R^5
1	H,OH		OH	H	H
2	H	OSE	OAc	Ac	Ac
3	H	OSE	OH	H	H
4	H	OSE	OH	⌊—Ipd—⌋	
5	H	OSE	OBn	⌊—Ipd—⌋	
6	H	OSE	OBn	Bz	Bz
7	H	OSE	OH	Bz	Bz
8	H	OSE	OC(S)OPh	Bz	Bz
9	H	OSE	H	Bz	Bz
10	H,OAc		H	Bz	Bz
11	H,SMe		H	Bz	Bz



	R^1	R^2	R^3	R^4	R^5
12	H	OSE	H	OBn	H
13	H	OSE	Bz	OBn	Bz
14	H	OSE	Bz	OH	Bz
15	H	OSE	Bz	OC(S)OPh	Bz
16	H	OSE	Bz	H	Bz
17	H,OAc		Bz	H	Bz
18	H	SMe	Bz	H	Bz
19	H	SMe	Bn	H	Bn



	R^1	R^2	R^3	R^4	R^5
20	H	OSE	Bz	Bz	OH
21	H	OSE	Bz	Bz	OC(S)OPh
22	H	OSE	Bz	Bz	H
23	H,OAc		Bz	Bz	H
24	H	SMe	Bz	Bz	H
25	H	SMe	Bn	Bn	H

SE = 2-(trimethylsilyl)ethyl
Ipd = isopropylidene
Bn = benzyl
Bz = benzoyl

Dibutyltin oxide-mediated, selective etherification [14] of **3**, using benzyl bromide and tetrabutylammonium bromide, gave 2-(trimethylsilyl)ethyl 3-*O*-benzyl-β-D-fucopyranoside (**12**) in 67% yield, and this was converted by *O*-benzoylation followed by hydrogenolysis of the 3-*O*-benzyl group into 2-(trimethylsilyl)ethyl 2,4-di-*O*-benzoyl-β-L-fucopyranoside (**14**) in 90% yield. In a similar way as described for **7**, when treated with phenyl chlorothionoformate in pyridine for 1.5 h at 45°C, **14** afforded the 3-*O*-(phenoxy)thiocarbonyl derivative (**15**) in 96% yield. Reductive cleavage of the (phenoxy)thiocarbonyloxy group as described for **8** gave

the 3-deoxyfucose derivative (**16**), and this was converted via treatment with boron trifluoride etherate in the presence of acetic anhydride, replacement of the 1-acetoxy group with methylthio in essentially the same way as described for **10**, and finally *O*-debenzoylation followed by benzylation, into methyl 2,4-di-*O*-benzyl-3,6-dideoxy-1-thio-β-L-*xylo*-hexopyranoside (**19**).

In a similar way, treatment of 2-(trimethylsilyl)ethyl 2,3-di-*O*-benzoyl-β-L-fucopyranoside (**20**), derived from **3** by selective 2,3-di-*O*-benzoylation, with phenyl chlorothionoformate afforded the 4-*O*-(phenoxy)thiocarbonyl derivative (**21**) in good yield. Essentially as described for **15**, compound **21** was transformed via reductive cleavage of the (phenoxy)thiocarbonyloxy group, replacement of the 2-(trimethylsilyl)ethyl group by the acetyl (to give **23**), introduction of the methylthio group with trimethyl(methylthio)silane, and finally *O*-debenzoylation followed by *O*-benzylation, into methyl 2,3-di-*O*-benzyl-4,6-dideoxy-1-thio-β-L-*xylo*-hexopyranoside (**25**). The methyl 1-thioglycosides **11**, **19**, and **25** proved to be excellent α-fucosyl donors for oligosaccharide synthesis, as described in the immediately following paper [15].

3. Experimental

General methods.—Optical rotations were determined with a Union PM-201 polarimeter at 25°C and IR spectra were recorded with a Jasco IRA-100 spectrophotometer. ^{1}H NMR spectra were recorded at 270 MHz with a Jeol JNM-GX 270 spectrometer. Preparative chromatography was performed on silica gel (Wako Chemical Co., 200 mesh) with the solvent systems specified. Concentrations were conducted in vacuo.

*2-(Trimethylsilyl)ethyl 2,3,4-tri-*O*-acetyl-β-L-fucopyranoside* (**2**).—Acetylation of L-fucose (19 g, 0.12 mol) with Ac_2O (100 mL) in pyridine (150 mL) overnight at room temperature gave the 1,2,3,4-tetraacetate. To a solution of this peracetate (38 g, 0.11 mol) in CH_2Cl_2 (120 mL) was added a 25% (w/w) solution of HBr in acetic acid (100 mL) at 0°C, and this was stirred for 5 h at 0°C and extracted with CH_2Cl_2. The extract was washed with water and M Na_2CO_3, dried (Na_2SO_4), then concentrated. A mixture of the residue and powdered 4A molecular sieves (MS-4A, 18 g) in dry CH_2Cl_2 (120 mL) was stirred for 6 h at room temperature and then added with stirring to a mixture (stirred for 6 h in the dark) of 2-(trimethylsilyl)ethanol (36 mL, 0.26 mol), silver carbonate (15 g, 0.05 mol), silver perchlorate (11 g, 0.05 mol), and powdered MS-4A (18 g) in dry CH_2Cl_2 (100 mL), and the stirring was continued overnight at 25°C in the dark. The precipitate was then collected and washed with CH_2Cl_2. The combined filtrate and washings were concentrated. Column chromatography (1:6 EtOAc–hexane) of the residue on silica gel (500 g) afforded **2** (36 g, 80%) as a colorless glass; $[\alpha]_D$ + 8.7° (*c* 1.0, $CHCl_3$); ν 1760 and 1230 (ester), and 870 and 850 cm^{-1} (Me_3Si); ^{1}H NMR ($CDCl_3$): δ 0.94 (m, 2 H, $Me_3SiCH_2CH_2$), 1.22 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.97, 2.04, 2.16 (3 s, 9 H, 3 AcO), 3.79 (m, 1 H, $J_{4,5}$ 1.0 Hz, H-5), 4.44 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 5.00 (dd, 1 H, $J_{2,3}$ 10.4, $J_{3,4}$ 3.5 Hz, H-3), 5.17 (dd, 1 H, H-2), and 5.22

(dd, 1 H, H-4). Anal. Calcd for $C_{17}H_{30}O_8Si$ (390.5): C, 52.29; H, 7.74. Found: C, 52.07; H, 7.85.

2-(Trimethylsilyl)ethyl β-L-fucopyranoside (**3**).—Compound **2** (36 g, 0.09 mol) in abs MeOH (160 mL) was deacetylated by Zémplen's method ($NaOCH_3$, 1.0 g) to give **3** (quantitative); $[\alpha]_D$ +20.5° (*c* 2.2, MeOH); ν 3600 (OH), and 860 and 840 cm^{-1} (Me_3Si). Anal. Calcd for $C_{11}H_{24}O_5Si$ (264.4): C, 49.97; H, 9.15. Found: C, 49.95; H, 9.36.

2-(Trimethylsilyl)ethyl 3,4-O-isopropylidene-β-L-fucopyranoside (**4**).—To a solution of **3** (2.9 g, 11.0 mmol) in DMF (20 mL) was added Drierite (3 g), and the mixture was stirred for 2 h at room temperature. 2,2-Dimethoxypropane (2.8 mL, 22 mmol) and *p*-toluenesulfonic acid monohydrate (10 mg) were added, and the mixture was stirred for 12 h at 60°C, then neutralized with Amberlite IR-410 (OH^-) resin and concentrated. Column chromatography (1:2 EtOAc–hexane) of the residue on silica gel (100 g) afforded **4** (3.2 g, 95%) as a syrup; $[\alpha]_D$ −11.0° (*c* 1.0, $CHCl_3$); ν 3500 (OH), and 860 and 840 cm^{-1} (Me_3Si, Me_2C); ^1H NMR ($CDCl_3$): δ 0.98 (m, 2 H, $Me_3SiCH_2CH_2$), 1.33, 1.51 (2 s, 6 H, Me_2C), 1.40 (d, 3 H, $J_{5,6}$ 6.6 Hz, H-6), and 4.13 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1). Anal. Calcd for $C_{14}H_{28}O_5Si$ (304.5): C, 55.23; H, 9.27. Found: C, 55.09; H, 9.44.

2-(Trimethylsilyl)ethyl 2-O-benzyl-3,4-O-isopropylidene-β-L-fucopyranoside (**5**).—To a solution of **4** (3.2 g, 10.5 mmol) in DMF (30 mL) was added a suspension of NaH in oil (0.4 g, 60% NaH by weight), and the mixture was stirred for 30 min at 0°C. Benzyl bromide (1.9 mL, 16 mmol) was added dropwise and stirring was continued for 3 h at room temperature. After completion of the reaction MeOH (1 mL) was added, and the mixture was concentrated then extracted with CH_2Cl_2. The extract was washed with water, dried (Na_2SO_4), and concentrated. Column chromatography (1:5 EtOAc–hexane) of the residue on silica gel (100 g) gave **5** (3.9 g, 93%) as a syrup; $[\alpha]_D$ −37.6° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.01 (m, 2 H, $Me_3SiCH_2CH_2$), 1.29, 1.32 (2 s, 6 H, Me_2C), 1.35 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 3.33 (t, 1 H, $J_{1,2} = J_{2,3} = 7.2$ Hz, H-2), 3.76 (m, 1 H, $J_{4,5}$ 1.9 Hz, H-5), 4.07 (dd, 1 H, $J_{3,4}$ 5.3 Hz, H-3), 4.24 (d, 1 H, H-1), and 7.21–7.38 (m, 5 H, Ph). Anal. Calcd for $C_{21}H_{34}O_5Si$ (394.6): C, 63.92; H, 8.69. Found: C, 63.89; H, 8.39.

2-(Trimethylsilyl)ethyl 3,4-di-O-benzoyl-2-O-benzyl-β-L-fucopyranoside (**6**).—A solution of **5** (3.9 g, 9.9 mmol) in aq 80% AcOH (80 mL) was stirred for 3 h at 50°C and concentrated. The residue was benzoylated with benzoyl chloride (3.4 mL, 29.7 mmol) in 2:1 CH_2Cl_2–pyridine (75 mL) for 4 h at room temperature. The product was purified by chromatography on a column of silica gel (100 g) with 1:4 EtOAc–hexane to give **6** (5.3 g, 96%) as a syrup; $[\alpha]_D$ −134.5° (*c* 2.2, $CHCl_3$); ν 1740 and 1280 (ester), 860 and 840 (Me_3Si), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 1.06 (m, 2 H, $Me_3SiCH_2CH_2$), 1.22 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 3.78 (dd, 1 H, $J_{1,2}$ 7.8, $J_{2,3}$ 10.2 Hz, H-2), 3.89 (m, 1 H, H-5), 4.53 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), 5.30 (dd, 1 H, $J_{3,4}$ 3.6 Hz, H-3), 5.51 (d, 1 H, $J_{4,5}$ 3.5 Hz, H-4), and 7.05–7.96 (m, 15 H, 3 Ph). Anal. Calcd for $C_{32}H_{38}O_7Si$ (562.7); C, 68.30; H, 6.81. Found: C, 68.05; H, 6.77.

2-(Trimethylsilyl)ethyl 3,4-di-O-benzoyl-β-L-fucopyranoside (**7**).—A solution of **6** (5.3 g, 9.4 mmol) in EtOH (130 mL) and AcOH (20 mL) was hydrogenolyzed in the

presence of 10% Pd–C (5 g) for 24 h at 40°C, then filtered and concentrated. Column chromatography (1:3 EtOAc–hexane) of the residue on silica gel (200 g) gave **7** (3.7 g, 83%) as an amorphous mass. Crystallization from EtOAc–hexane gave needles; mp 133–135°C; $[\alpha]_D$ −80.2° (*c* 0.5, $CHCl_3$); ν 3500 (OH), 1730 and 1280 (ester), 860 and 840 (Me_3Si), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 1.02 (m, 2 H, $Me_3SiCH_2CH_2$), 1.25 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 3.98 (dd, 1 H, $J_{1,2}$ 7.7, $J_{2,3}$ 10.3 Hz, H-2), 4.42 (d, 1 H, H-1), 5.28 (dd, 1 H, $J_{3,4}$ 3.5 Hz, H-3), 5.56 (br d, 1 H, H-4), and 7.20–8.03 (m, 10 H, 2 Ph). Anal. Calcd for $C_{25}H_{32}O_7Si$ (472.6): C, 63.54; H, 6.83. Found: C, 63.34; H, 6.55.

2-(Trimethylsilyl)ethyl 3,4-di-O-benzoyl-2-O-(phenoxy)thiocarbonyl-β-L-fucopyranoside (**8**).—To a solution of **7** (1.9 g, 4.0 mmol) in 1:1 CH_2Cl_2–pyridine (40 mL) was added phenyl chlorothionoformate (2.8 mL, 20 mmol), and the mixture was heated for 4 h at 45°C. After completion of the reaction, MeOH (1 mL) was added to the solution and it was concentrated, then extracted with CH_2Cl_2. The extract was successively washed with 2 M HCl and water, dried (Na_2SO_4), and concentrated. Column chromatography (1:5 EtOAc–hexane) of the residue on silica gel (150 g) gave **8** (quantitative) as an amorphous mass. Crystallization from EtOAc–hexane gave needles; mp 83–85°C; $[\alpha]_D$ −110.5°C (*c* 1.4, $CHCl_3$); ν 1730 and 1260 (ester), 860 and 840 (Me_3Si), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 1.00 (m, 2 H, $Me_3SiCH_2CH_2$), 1.26 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 4.73 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 5.45 (dd, 1 H, $J_{2,3}$ 10.4, $J_{3,4}$ 3.4 Hz, H-3), 5.65 (br d, 1 H, H-4), 6.08 (dd, 1 H, H-2), and 6.75–8.04 (m, 15 H, 3 Ph). Anal. Calcd for $C_{32}H_{36}O_8SSi$ (608.8): C, 63.13; H, 5.96. Found: C, 63.22; H, 5.83.

2-(Trimethylsilyl)ethyl 3,4-di-O-benzoyl-2,6-dideoxy-β-L-lyxo-hexopyranoside (**9**).—To a solution of **8** (2.5 g, 4.1 mmol) in toluene (140 mL) were added tributyltin hydride (10.8 mL) and α,α′-azobisisobutyronitrile (AIBN, 300 mg), and the mixture was stirred for 2 h at 100°C then concentrated. Column chromatography of the residue on silica gel (150 g) with 1:6 EtOAc–hexane gave **9** (quantitative) as an amorphous mass; $[\alpha]_D$ −41.2° (*c* 1.0, $CHCl_3$); ν 1730 and 1270 (ester), 860 and 840 (Me_3Si) and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 0.98 (m, 2 H, $Me_3SiCH_2CH_2$), 1.27 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 2.11 (m, 2 H, H-2*ax*, 2*eq*), 4.63 (dd, 1 H, $J_{1,2ax}$ 8.9, $J_{1,2eq}$ 2.8 Hz, H-1), 5.30 (m, 1 H, H-3), 5.44 (d, 1 H, $J_{3,4}$ 2.9 Hz, H-4), and 7.21–8.10 (m, 10 H, 2 Ph). Anal. Calcd for $C_{25}H_{32}O_6Si$ (456.6): C, 65.76; H, 7.06. Found: C, 65.64; H, 7.19.

1-O-Acetyl-3,4-di-O-benzoyl-2,6-dideoxy-α,β-L-lyxo-hexopyranose (**10**).—To a solution of **9** (350 mg, 0.77 min toluene (6 mL) and Ac_2O (1.1 mL), cooled to −50°C, was added dropwise $BF_3 \cdot OEt_2$ (85 μL). The mixture was stirred for 48 h at −50°C, CH_2Cl_2 (50 mL) was added, and the solution was successively washed with M Na_2CO_3 and water, dried (Na_2SO_4), and concentrated. Column chromatography (1:5 EtOAc–hexane) of the residue on silica gel (50 g) gave **10** (150 mg, 49%) as an amorphous mass; ν 1730 and 1240 (ester), and 710 cm^{-1} (Ph). Anal. Calcd for $C_{22}H_{22}O_7$ (398.4): C, 66.32; H, 5.57. Found: C, 66.42; H, 5.51.

Methyl 3,4-di-O-benzoyl-2,6-dideoxy-1-thio-α,β-L-lyxo-hexopyranoside (**11**).—To a solution of **10** (374 mg, 0.94 mmol) in dry CH_2Cl_2 (10 mL), cooled to 0°C, were added Me_3SiSMe (0.3 mL, 2.35 mmol) and $BF_3 \cdot OEt_2$ (0.25 mL, 0.94 mmol), and

the mixture was stirred for 2 h at 0°C, then extracted with CH_2Cl_2. The extract was successively washed with M Na_2CO_3 and water, dried (Na_2SO_4), and concentrated. Column chromatography (1:6 EtOAc–hexane) of the residue on silica gel (50 g) gave **11** (344 mg, 95%) as a syrup; ν 1730 and 1280 (ester), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 1.27 (d, $J_{5,6}$ 6.6 Hz, H-6α), 1.32 (d, $J_{5,6}$ 6.4 Hz, H-6β), 2.17, 2.32 (2 s, 3 H, MeS), 2.63 (ddd, J_{gem} 12.4, $J_{1,2ax}$ 5.9 Hz, H-2$ax\alpha$), 4.68 (dd, $J_{1,2ax}$ 8.2 Hz, H-1β), 5.36 (ddd, $J_{2ax,3}$ 7.2, $J_{2eq,3}$ 2.8 Hz, H-3β), and 5.53 (d, $J_{3,4}$ 2.9 Hz, H-4β). The anomeric ratio ($\alpha:\beta$) was estimated as ~1:1 from the ratio of intensities of the *S*-methyl signals. Anal. Calcd for $C_{21}H_{22}O_5S$ (386.5): C, 65.27; H, 5.74. Found: C, 65.36; H, 5.54.

2-(Trimethylsilyl)ethyl 3-O-benzyl-β-L-fucopyranoside (**12**).—A suspension of **3** (3.6 g, 13.7 mmol) and dibutyltin oxide (3.8 g) in MeOH (70 mL) was heated, with stirring, for 10 h at 70°C, then concentrated. To a solution of the residue in benzene (80 mL) were added benzyl bromide (2.4 mL) and tetrabutylammonium bromide (1.4 g), and the mixture was heated, with stirring, for 4 h at 60°C, then concentrated. Column chromatography (1:4 EtOAc–hexane) of the residue on silica gel (150 g) gave **12** (3.2 g, 67%) as crystals. Recrystallization from EtOAc–hexane gave needles; mp 99–101°C; $[\alpha]_D$ +0.1° (*c* 0.5, $CHCl_3$); ν 3470 (OH), 860 and 840 (Me_3Si), and 700 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 0.99 (m, 2 H, $Me_3SiCH_2CH_2$), 1.34 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6), 3.41 (dd, 1 H, $J_{2,3}$ 9.7, $J_{3,4}$ 3.1 Hz, H-3), 3.71 (dd, 1 H, $J_{1,2}$ 7.9 Hz, H-2), 3.74 (br d, 1 H, H-4), 4.19 (d, 1 H, H-1), and 7.25–7.39 (m, 5 H, Ph). Anal. Calcd for $C_{18}H_{30}O_5Si$ (354.5): C, 60.98; H, 8.53. Found: C, 60.92; H, 8.55.

2-(Trimethylsilyl)ethyl 2,4-di-O-benzoyl-3-O-benzyl-β-L-fucopyranoside (**13**).—To a solution of **12** (3.2 g, 9.0 mmol) in pyridine (50 mL) was added benzoyl chloride (3.1 mL, 27 mmol), and the mixture was stirred for 2 h at room temperature. A conventional workup gave the product, which was purified by column chromatography (1:5 EtOAc–hexane) on silica gel (150 g). Crystallization from ether–hexane gave needles (5.0 g, 98%); mp 73–74°C; $[\alpha]_D$ −115.5° (*c* 1.1, $CHCl_3$); ν 1720 and 1240 (ester), 850 and 830 (Me_3Si), and 700 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 0.97 (m, 2 H, $Me_3SiCH_2CH_2$), 1.41 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 3.85 (dd, 1 H, $J_{2,3}$ 9.7, $J_{3,4}$ 3.3 Hz, H-3), 3.91 (q, 1 H, H-5), 4.65 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 5.58 (dd, 1 H, H-2), 5.73 (br d, 1 H, H-4), and 7.14–8.23 (m, 15 H, 3 Ph). Anal. Calcd for $C_{32}H_{38}O_7Si$ (562.7): C, 68.30; H, 6.81. Found: C, 68.35; H, 6.22.

2-(Trimethylsilyl)ethyl 2,4-di-O-benzoyl-β-L-fucopyranoside (**14**).—A solution of **13** (5.0 g, 8.9 mmol) in EtOH (130 mL) and AcOH (20 mL) was hydrogenolyzed in the presence of 10% Pd–C (5 g) for 24 h at 40°C, then filtered and concentrated. Column chromatography (1:3 EtOAc–hexane) of the residue on silica gel (200 g) gave **14** (3.7 g, 91%) as a crystalline mass. Recrystallization from EtOAc–hexane gave needles; mp 138–139°C; $[\alpha]_D$ −54.8° (*c* 0.5, $CHCl_3$); ν 3500 (OH), 1750 and 1250 (ester), 860 and 840 (Me_3Si), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 0.99 (m, 2 H, $Me_3SiCH_2CH_2$), 1.36 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 3.95 (q, 1 H, H-5), 4.12 (dd, 1 H, $J_{2,3}$ 10.1, $J_{3,4}$ 3.7 Hz, H-3), 4.71 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 5.34 (dd, 1 H, H-2), 5.54 (br d, 1 H, H-4), and 7.31–8.23 (m, 10 H, 2 Ph). Anal. Calcd for $C_{25}H_{32}O_7Si$ (472.6): C, 63.54; H, 6.83. Found: C, 63.45; H, 6.93.

2-(Trimethylsilyl)ethyl 2,4-di-O-benzoyl-3-O-(phenoxy)thiocarbonyl-β-L-fucopyranoside (**15**).—To a solution of **14** (3.7 g, 7.9 mmol) in 1:1 CH_2Cl_2–pyridine (76 mL) was added phenyl chlorothionoformate (1.6 mL, 12 mmol), and the mixture was heated for 1.5 h at 45°C. A workup similar to that described for **8** gave **15** (4.6 g, 96%) as a crystalline mass. Recrystallization from EtOAc–hexane gave needles; mp 112–113°C; $[\alpha]_D$ −110.5° (*c* 1.4, $CHCl_3$); ν 1730 and 1220 (ester), 860 and 840 (Me_3Si), and 700 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 0.99 (m, 2 H, $Me_3SiCH_2CH_2$), 1.41 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 4.81 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 5.75 (dd, 1 H, $J_{2,3}$ 10.5 Hz, H-2), 5.88 (br d, 1 H, $J_{3,4}$ 3.5 Hz, H-4), 5.96 (dd, 1 H, H-3), and 6.88–8.23 (m, 15 H, 3 Ph). Anal. Calcd for $C_{32}H_{36}O_8SSi$ (608.8): C, 63.13; H, 5.96. Found: C, 63.23; H, 6.03.

2-(Trimethylsilyl)ethyl 2,4-di-O-benzoyl-3,6-dideoxy-β-L-xylo-hexopyranoside (**16**).—To a solution of **15** (1.6 g, 2.6 mmol) in toluene (90 mL) were added tributyltin hydride (5.8 mL) and AIBN (0.2 g), and the mixture was stirred for 2 h at 100°C, then concentrated. Column chromatography of the residue on silica gel (100 g) with 1:6 EtOAc–hexane gave **16** (996 mg, 83%) as a syrup; $[\alpha]_D$ −23.6° (*c* 0.7, $CHCl_3$); ν 1730 and 1230 (ester), 860 and 840 (Me_3Si), and 700 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 1.00 (m, 2 H, $Me_3SiCH_2CH_2$), 1.34 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 2.01 (ddd, 1 H, J_{gem} 14.1, $J_{2,3ax}$ 11.2, $J_{3ax,4}$ 2.9 Hz, H-3*ax*), 2.64 (ddd, 1 H, H-3*eq*), 4.00 (br q, 1 H, H-5), 4.74 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), and 7.43–8.20 (m, 10 H, 2 Ph). Anal. Calcd for $C_{25}H_{32}O_6Si$ (456.6): C, 65.76; H, 7.06. Found: C, 65.62; H, 7.23.

1-O-Acetyl-2,4-di-O-benzoyl-3,6-dideoxy-α,β-L-xylo-hexopyranose (**17**).—To a solution of **16** (700 mg, 1.53mmol) in toluene (12 mL) and Ac_2O (2.2 mL), cooled to −25°C, was added dropwise $BF_3 \cdot OEt_2$ (170 μL), and the mixture was stirred for 24 h at −25°C. Processing as described for **10** gave **17** (320 mg, 52%) as an amorphous mass; $[\alpha]_D$ −118.0° (*c* 1.7, $CHCl_3$); ν 1740 and 1240 (ester), and 710 cm^{-1} (Ph). Anal. Calcd for $C_{22}H_{22}O_7$ (398.4): C, 66.32; H, 5.57. Found: C, 66.29; H, 5.37.

Methyl 2,4-di-O-benzoyl-3,6-dideoxy-1-thio-β-L-xylo-hexopyranoside (**18**).—To a solution of **17** (319 mg, 0.8 mmol) in dry CH_2Cl_2 (6 mL), cooled to 0°C, were added Me_3SiSMe (0.28 mL, 2.0 mmol) and $BF_3 \cdot OEt_2$ (0.21 mL, 0.8 mmol), and the mixture was stirred for 1 h at 0°C. Processing as described for **11** gave **18** (223 mg, 72%) as an amorphous mass; $[\alpha]_D$ −52.1° (*c* 0.1, $CHCl_3$); ν 1740 and 1220 (ester), and 700 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 1.31 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 2.06 (ddd, 1 H, J_{gem} 14.1, $J_{2,3ax}$ 11.2, $J_{3ax,4}$ 3.4 Hz, H-3*ax*), 2.27 (s, 3 H, MeS), 2.66 (ddd, 1 H, $J_{2,3eq}$ 5.1, $J_{3eq,4}$ 3.4 Hz, H-3*eq*), 3.96 (q, 1 H, H-5), 4.62 (d, 1 H, $J_{1,2}$ 9.7 Hz, H-1), 5.32 (m, 1 H, H-4), 5.41 (ddd, 1 H, H-2), and 7.42–8.14 (m, 10 H, 2 Ph). Anal. Calcd for $C_{21}H_{22}O_5S$ (386.5): C, 65.27; H, 5.74. Found: C, 65.01; H, 5.70.

Methyl 2,4-di-O-benzyl-3,6-dideoxy-1-thio-β-L-xylo-hexopyranoside (**19**).—To a solution of **18** (644 mg, 1.7 mmol) in MeOH (10 mL) was added NaOMe (20 mg), and the mixture was stirred for 8 h at room temperature then neutralized with Amberlite IR-120 (H^+) resin. The solution was concentrated, and the residue was dissolved in dry DMF (15 mL). To the stirred solution was added NaH in oil suspension (200 mg, 60% NaH by weight), and the mixture was stirred for 30 min at 0°C, and then benzyl bromide (0.6 mL, 5.1 mmol) was added. The stirring was

continued for 5 h, and MeOH (1 mL) was added. The mixture was concentrated to a syrup, which was chromatographed on a column of silica gel (50 g) with 1:10 EtOAc–hexane to give **19** (562 mg, 94%) as an amorphous mass; $[\alpha]_D$ +94.5° (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.25 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 1.46 (ddd, 1 H, J_{gem} 13.7, $J_{2,3ax}$ 11.1, $J_{3ax,4}$ 2.6 Hz, H-3*ax*), 2.20 (s, 3 H, MeS), 2.44 (ddd, 1 H, $J_{2,3eq}$ 4.4, $J_{3eq,4}$ 3.4 Hz, H-3*eq*), 3.40 (br s, 1 H, H-4), 4.37 (d, 1 H, $J_{1,2}$ 9.3 Hz, H-1), and 7.26–7.39 (m, 10 H, 2 Ph). Anal. Calcd for $C_{21}H_{26}O_3S$ (358.5): C, 70.36; H, 7.31. Found: C, 70.16; H, 7.23.

*2-(Trimethylsilyl)ethyl 2,3-di-*O*-benzoyl-β-*L*-fucopyranoside* (**20**).—To a solution of **3** (1.8 g, 4.6 mmol) in 2:1 CH_2Cl_2–pyridine (40 mL), cooled to −40°C, was added, with stirring, a cooled solution of benzoyl chloride (1.1 mL) in CH_2Cl_2 (11 mL), and the mixture was stirred for 30 min at −40°C. After completion of the reaction MeOH (1 mL) was added to the mixture, and it was concentrated then extracted with CH_2Cl_2. The extract was successively washed with 2 M HCl and water, dried (Na_2SO_4), and concentrated. Column chromatography (1:3 EtOAc–hexane) of the residue on silica gel (70 g) gave **20** (1.7 g, 76%) as an amorphous mass; $[\alpha]_D$ −91.5° (*c* 1.2, $CHCl_3$); ν 3450 (OH), 1720 and 1240 (ester), 860 and 840 (Me_3Si), and 700 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 0.97 (m, 2 H, $Me_3SiCH_2CH_2$), 1.48 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 3.95 (q, 1 H, H-5), 4.17 (br d, 1 H, $J_{3,4}$ 3.3 Hz, H-4), 4.77 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 5.36 (dd, 1 H, $J_{2,3}$ 10.3 Hz, H-3), 5.76 (dd, 1 H, H-2), and 7.34–8.15 (m, 10 H, 2 Ph). Anal. Calcd for $C_{25}H_{32}O_7Si$ (472.6): C, 63.54; H, 6.83. Found: C, 63.51; H, 6.73.

*2-(Trimethylsilyl)ethyl 2,3-di-*O*-benzoyl-4-*O*-(phenoxy)thiocarbonyl-β-*L*-fucopyranoside* (**21**).—To a solution of **20** (3.0 g, 6.3 mmol) in 1:1 CH_2Cl_2–pyridine (60 mL) was added phenyl chlorothionoformate (4.4 mL, 20 mmol), and the mixture was heated for 1.5 h at 45°C. A workup similar to that described for **8** gave **21** (2.8 g, 72%) as a syrup; $[\alpha]_D$ −108.8° (*c* 0.3, $CHCl_3$); ν 1740 and 1220 (ester), 860 and 840 (Me_3Si), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 0.98 (m, 2 H, $Me_3SiCH_2CH_2$), 1.58 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6), 4.82 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 5.61 (dd, 1 H, $J_{2,3}$ 10.3, $J_{3,4}$ 3.5 Hz, H-3), 5.79 (dd, 1 H, H-2), 6.18 (br d, 1 H, H-4), and 6.89–8.19 (m, 15 H, 3 Ph). Anal. Calcd for $C_{32}H_{36}O_8SSi$ (608.8): C, 63.13; H, 5.96. Found: C, 62.88; H, 5.92.

*2-(Trimethylsilyl)ethyl 2,3-di-*O*-benzoyl-4,6-dideoxy-β-*L*-xylo-hexopyranoside* (**22**).—To a solution of **21** (2.9 g, 4.8 mmol) in toluene (160 mL) were added tributyltin hydride (10.8 mL) and AIBN (530 mg), and the mixture was stirred for 2 h at 100°C then concentrated. A workup similar to that described for **9** gave **22** (1.85 g, 85%) as an amorphous mass; $[\alpha]_D$ −79.8° (*c* 0.7, $CHCl_3$); ν 1730 and 1220 (ester), 860 and 840 (Me_3Si), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 0.98 (m, 2 H, $Me_3SiCH_2CH_2$), 1.42 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 1.75 (dt, 1 H, J_{gem} 12.5, $J_{3,4ax} = J_{4ax,5} = 8.1$ Hz, H-4*ax*), 2.42 (ddd, 1 H, $J_{3,4eq}$ 4.8, $J_{4eq,5}$ 1.9 Hz, H-4*eq*), 3.88 (m, 1 H, H-5), 4.72 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1), and 7.34–8.08 (m, 10 H, 2 Ph). Anal. Calcd for $C_{25}H_{32}O_6Si$ (456.6): C, 65.76; H, 7.06. Found: C, 65.98; H, 6.89.

*1-*O*-Acetyl-2,3-di-*O*-benzoyl-4,6-dideoxy-α,β-*L*-xylo-hexopyranose* (**23**).—To a solution of **22** (245 mg, 0.54mmol) in toluene (4 mL) and Ac_2O (0.76 mL), cooled to −35°C, was added dropwise $BF_3 \cdot OEt_2$ (126 μL). The mixture was stirred for 20 h

at −35°C. A workup similar to that described for **10** gave **23** (142 mg, 66%) as a syrup; $[\alpha]_D$ −72.5° (*c* 0.5, $CHCl_3$); ν 1730 and 1230 (ester), and 710 cm^{-1} (Ph). Anal. Calcd for $C_{22}H_{22}O_7$ (398.4): C, 66.32; H, 5.57. Found: C, 66.50; H, 5.78.

*Methyl 2,3-di-*O*-benzoyl-4,6-dideoxy-1-thio-β-*L*-xylo-hexopyranoside* (**24**).—To a solution of **23** (517 mg, 1.3 mmol) in dry CH_2Cl_2 (10 mL), cooled to 0°C, were added Me_3SiSMe (0.46 mL, 3.2 mmol) and $BF_3 \cdot OEt_2$ (0.34 mL, 1.3 mmol), and the mixture was stirred for 2 h at 0°C. A workup similar to that described for **11** gave **24** (350 mg, 70%) as an amorphous mass; $[\alpha]_D$ −24.7° (*c* 0.5, $CHCl_3$); ν 1730 and 1240 (ester), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 1.35 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 1.71 (dt, 1 H, J_{gem} 12.7, $J_{3,4ax} = J_{4ax,5} = 9.4$ Hz, H-4*ax*), 2.23 (s, 3 H, MeS), 2.40 (ddd, 1 H, $J_{3,4eq}$ 4.8, $J_{4eq,5}$ 2.2 Hz, H-4*eq*), 3.86 (m, 1 H, $J_{4ax,5}$ 9.4, $J_{4eq,5}$ 2.2 Hz, H-5), 4.55 (d, 1 H, $J_{1,2}$ 9.3 Hz, H-1), 5.37 (dt, 1 H, $J_{2,3}$ 9.3 Hz, H-3), 5.43 (t, 1 H, H-2), and 7.34–8.00 (m, 10 H, 2 Ph). Anal. Calcd for $C_{21}H_{22}O_5S$ (386.5): C, 65.27; H, 5.74. Found: C, 65.34; H, 6.00.

*Methyl 2,3-di-*O*-benzyl-4,6-dideoxy-1-thio-β-*L*-xylo-hexopyranoside* (**25**).—To a solution of **24** (744 mg, 1.9 mmol) in MeOH (10 mL) was added NaOMe (20 mg), and the mixture was stirred for 12 h at room temperature then treated with Amberlite IR-120 (H^+) resin to neutralize the base. The solution was concentrated, and the residue was dissolved in dry DMF (15 mL). To the stirred solution was added NaH in oil suspension (0.2 g, 60% of NaH by weight), the mixture was stirred for 30 min at 0°C, and then benzyl bromide (0.7 mL, 5.7 mmol) was added. The stirring was continued for 5 h, and MeOH (1 mL) was added. The mixture was concentrated to a syrup, which was chromatographed on a column of silica gel (50 g) with 1:10 EtOAc–hexane to give **25** (642 mg, 93%) as an amorphous mass; $[\alpha]_D$ +9.4° (*c* 0.3, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 1.26 (d, 3 H, $J_{5,6}$ 6.0 Hz, H-6), 1.45 (dt, 1 H, J_{gem} 12.8, $J_{3,4ax} = J_{4ax,5} = 11.5$ Hz, H-4*ax*), 2.11 (ddd, 1 H, $J_{3,4eq}$ 5.1, $J_{4eq,5}$ 1.8 Hz, H-4*eq*), 2.21 (s, 3 H, MeS), 3.33 (t, 1 H, $J_{1,2} = J_{2,3} = 9.3$ Hz, H-2), 4.30 (d, 1 H, H-1), and 7.25–7.42 (m, 10 H, 2 Ph). Anal. Calcd for $C_{21}H_{26}O_3S$ (358.5): C, 70.36; H, 7.31. Found: C, 70.39; H, 7.54.

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