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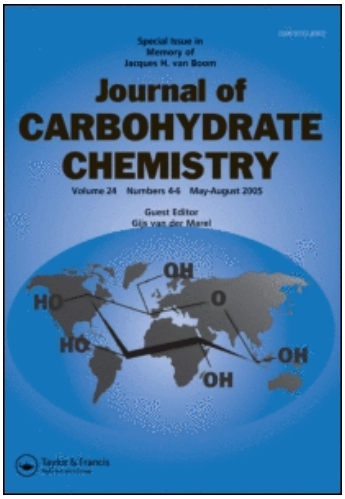

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Synthetic Studies on Sialoglycoconjugates 81: Synthesis of Positional Isomers of Sialyl Lewis X Epitope Containing 1-Deoxy-d Glucose in Place of *N*-Acetylglucosamine, and Their Inhibitory Activity to Selectin-Mediated Adhesion

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SYNTHETIC STUDIES ON SIALOGLYCOCONJUGATES 81: SYNTHESIS OF POSITIONAL ISOMERS OF SIALYL LEWIS X EPITOPE CONTAINING 1-DEOXY-D-GLUCOSE IN PLACE OF *N*-ACETYLGLUCOSAMINE, AND THEIR INHIBITORY ACTIVITY TO SELECTIN-MEDIATED ADHESION

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ABSTRACT

Three sialyl-Le^x epitope analogs, which carry fucose and α-sialyl-(2→3)-galactose residues at *O*-2 and *O*-3, *O*-3 and *O*-2, and *O*-4 and *O*-6 positions of 1-deoxy-D-glucose backbone, respectively, have been synthesized. Glycosylation of 1,5-anhydro-4,6-*O*-benzylidene-D-glucitol (**1**) or 1,5-anhydro-6-*O*-benzoyl-2,3-di-*O*-benzyl-D-glucitol (**4**) prepared from 1,5-anhydro-D-glucitol, with methyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-fucopyranoside (**5**) using dimethyl(methylthio)sulfonium triflate (DMTST) as a promoter, afforded the corresponding fucosyl 1,5-anhydro-D-glucitol derivatives **7**, **8** and **9**. Glycosylation of **7**, **8** or **10** derived from **9**, with methyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-2,4,6-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside (**11**) in the presence of DMTST gave the expected tetrasaccharide derivatives **12**, **16** and **20**. Hydrolysis of the benzylidene group in **12** and **16** gave compounds **13** and **17**. Finally **13**, **17** and **20** were transformed, by reductive removal of the benzyl groups, *O*-deacylation and subsequent hydrolysis of the methyl ester, into the sialyl-Le^x epitope analogs **15**, **19** and **22**, respectively.

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INTRODUCTION

The Selectins[1-4] (E–, P– and L–selectin), a family of cell–cell adhesion molecules, recognize 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 the terminal carbohydrate structure in both glycolipids and glycoproteins.

Previously, we reported the synthesis of a variety of sialyl-Le^x ganglioside analogs containing the modified sialic acid,[5] galactose[6] and fucose,[7,8] and sialyl-Le^x epitope analogs in which the terminal *N*-acetylglucosamine was replaced by 1-deoxynojirimycin,[9] 1-deoxy-*N*-acetylglucosamine,[10] 1-deoxy-D-glucose[11] or 1,2-dideoxy-D-glucose,[11] and examined their competitive inhibition as well as binding activity to selectin-mediated adhesion. The data clearly showed[12,13] that the configuration of galactose and fucose moieties was critically required for the selectin recognition, and the side-chain structure of the sialic acid residue however was not important for the binding activity. In addition, sialyl-Le^x epitope analogs containing other carbohydrate residues described above, in place of *N*-acetylglucosamine, inhibited the binding between the Selectins and sialyl-Le^x ganglioside, in a competitive manner. In view of these facts, we describe herein the synthesis of sialyl-Le^x epitope analogs in which fucose and sialyl-α(2→3)-galactose moieties are linked at the different positions of 1-deoxy-D-glucose backbone, to clarify the confomational requirement of sialyl-Le^x epitope for the selectin recognition, by changing the linkage positions of their indispensable carbohydrate units to the 1-deoxy-D-glucose residue.

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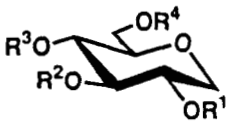
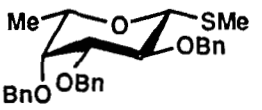
RESULTS AND DISCUSSION

For the synthesis of the desired sialyl-Le^x epitope analogs which carry fucose and α-sialyl-(2→3)-galactose residue at a variety of positions of 1-deoxy-D-glucose, we selected 1,5-anhydro-4,6-*O*-benzylidene-D-glucitol[14] (**1**) and 1,5-anhydro-6-*O*-benzoyl-2,3-di-*O*-benzyl-D-glucitol (**4**) as the key glycosyl acceptors, and methyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-fucopyranoside[15] (**5**) and methyl thioglycoside derivative[16] (**11**) of α-sialyl-(2→3)-galactose as the glycosyl donors.



	R^1	R^2	R^3	R^4
1	H	H	benzylidene	
2	Bn	Bn	benzylidene	
3	Bn	Bn	H	H
4	Bn	Bn	H	Bz



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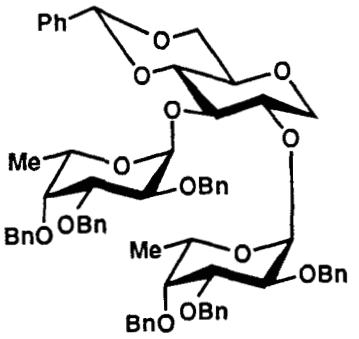

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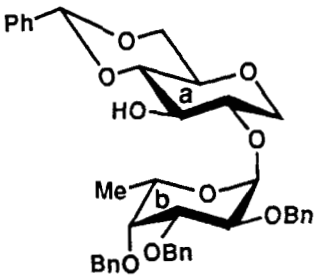

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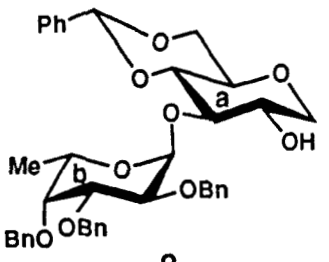

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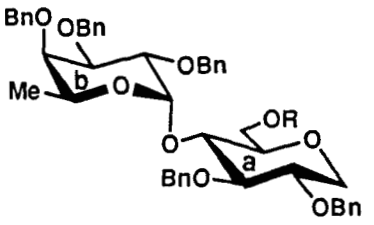
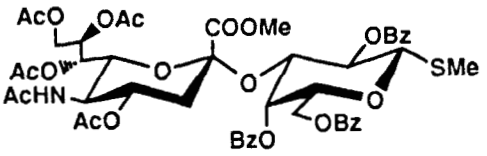


9 R = Bz
10 R = H



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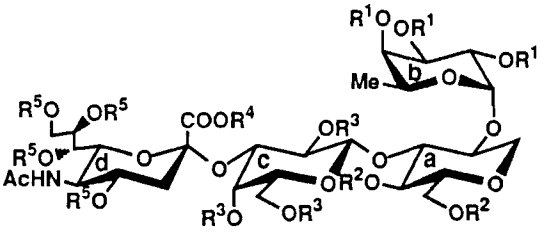
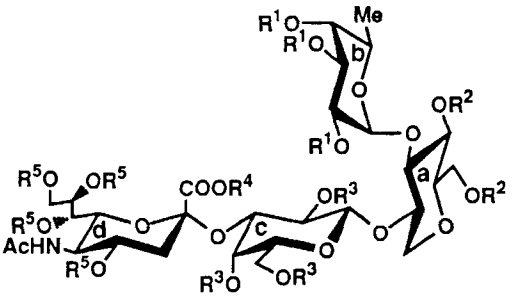
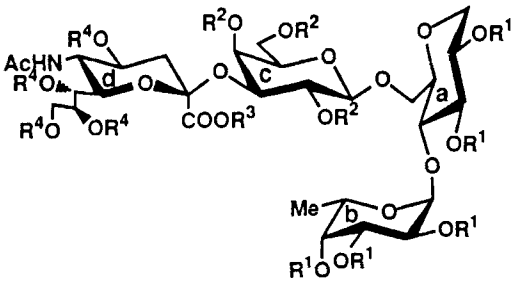


	R^1	R^2	R^3	R^4	R^5
12	Bn	benzylidene	Bz	Me	Ac
13	Bn	H	Bz	Me	Ac
14	H	H	Bz	Me	Ac
15	H	H	H	H	H



	R^1	R^2	R^3	R^4	R^5
16	Bn	benzylidene	Bz	Me	Ac
17	Bn	H	Bz	Me	Ac
18	H	H	Bz	Me	Ac
19	H	H	H	H	H



	R^1	R^2	R^3	R^4
20	Bn	Bz	Me	Ac
21	H	Bz	Me	Ac
22	H	H	H	H

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Treatment of **1** with benzyl bromide in *N,N*-dimethylformamide (DMF) in the presence of sodium hydride gave 1,5-anhydro-3,4-di-*O*-benzyl-4,6-*O*-benzylidene-D-glucitol (**2**; 99%). Hydrolysis of the benzylidene group in **2** with aqueous 80% acetic acid gave the 2,3-di-*O*-benzyl derivative **3** in 93% yield. Selective 6-*O*-benzoylation of **3** with benzoyl chloride in pyridine-dichloromethane for 1 h at -50 °C gave the another glycosyl acceptor **4** in good yield.

The glycosylation[15] of **1** with the fucose donor **5** (1.2 equiv with respect to the acceptor) in dichloromethane for 12 h at room temperature in the presence of dimethyl(methylthio)sulfonium triflate[17,18] (DMTST) gave the 2,3-di-*O*-α-L-fucosyl- (**6**), 2-*O*-α-L-fucosyl- (**7**), and 3-*O*-α-L-fucosyl-1-deoxy-D-glucose derivatives (**8**) in 26%, 28% and 42% yields, respectively. Significant signals in the ^{1}H NMR spectrum of the acetyl derivative of **7** were at δ 4.93 ($J_{1,2}$ = 3.7 Hz, H-1 of Fuc) and 5.34 ($J_{2,3}$ = $J_{3,4}$ = 9.3 Hz, H-3 of Glc), and of **8** was at δ 5.12 ($J_{2,3}$ = 10.4 Hz, $J_{3,4}$ = 9.3 Hz, H-2 of Glc) and 5.31 ($J_{1,2}$ = 3.7 Hz, H-1 of Fuc), indicating the structure asigned. In the same way, reaction of **4** with **5** afforded the desired disaccharide **9** in 97% yield, and subsequent *O*-deacylation gave **10** in high yield. H-1 proton of the fucose residue in the ^{1}H NMR spectrum of **10** appeared at δ 5.18 ($J_{1,2}$ = 3.5 Hz), indicating the newly formed glycosidic linkage to be α.

The glycosylation[15,19] of **7** or **8** with the sialyl galactose donor **11** in dichloromethane in the presence of DMTST for 72 h at 7 °C gave the tetrasaccharide **12** (70%) and **16** (82%) which, on hydrolysis of the benzylidene group with aqueous 80% acetic acid at 45 °C, gave **13** and **17** in good yields, respectively. In essentially the same way, glycosylation of **10** with **11** furnished the corresponding tetrasaccharide **20** in 64% yield.

Catalytic hydrogenolysis (10% Pd-C) in methanol-acetic acid at 40 °C of the benzyl groups in **13**, **17** or **20**, and subsequent *O*-deacylation with sodium methoxide in methanol followed by saponification of the methyl ester group yielded the end products **15**, **19** and **22** in almost quantitative yields after chromatography on a column of Sephadex LH-20.

The synthesized sialyl-Le^x epitope analogs (**15**, **19** and **22**) did not show any competitive inhibition activity between the Selectins (E–, P– and L–selectin) and sialyl-

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Le^x ganglioside, indicating that the Selectins can recognize a certain, restricted conformation of the tetrasaccharides consisting of fucose, sialic acid, galactose and another sugar. In short, fucose and α-sialyl-(2→3)-galactose residues are able to switch at *O*-3 and *O*-4, or *O*-4 and *O*-3, but not able to switch at other positions, i.e., at *O*-2 and *O*-3, *O*-3 and *O*-2, or *O*-4 and *O*-6, of the *gluco*-structure.

EXPERIMENTAL

General Procedures. Melting points were determined with a Yanagimoto micro melting point apparatus and uncorrected. Specific rotations were determined with a Union PM-201 polarimeter at 25 °C and IR spectra were recorded with a Jasco A-100 spectrophotometer. ^1H NMR spectra were recorded with a JEOL JNM-GX 270 spectrometer. Preparative chromatography was performed on silica gel (Fuji Silysia Co., 127 mesh) with the solvent systems specified. Concentrations were conducted *in vacuo*.

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1,5-Anhydro-2,3-di-*O*-benzyl-4,6-*O*-benzylidene-D-glucitol (2). To a solution of 1,5-anhydro-4,6-*O*-benzylidene-D-glucitol[14] (**1**; 300 mg, 1.2 mmol) in *N*,*N*-dimethylformamide (DMF; 3 mL) was added a suspension of sodium hydride in oil (140 mg, 60% of sodium hydride by weight), and the mixture was stirred for 1 h at 0 °C. Benzyl bromide (0.42 mL, 3.5 mmol) was added dropwise with stirring, at 0 °C and the stirring was continued for 3 h at room temperature. MeOH (1 mL) was added to the mixture, and concentrated then extracted with AcOEt. The extract was washed with water, dried (Na_2SO_4) and concentrated. Column chromatography (1:5 AcOEt-hexane) of the residue on silica gel (80 g) gave **2** (510 mg, 99%) as an amorphous mass: $[\alpha]_D$ -51.3° (*c* 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 3.32 (dd, 1H, J_{gem} = 11.2 Hz, $J_{1ax,2}$ = 10.3 Hz, H-1*ax*), 3.35 (m, 1H, H-5), 3.60 (t, 1H, $J_{2,3}$ = $J_{3,4}$ = 8.9 Hz, H-3), 3.65 (m, 1H, H-2), 3.66 (t, 1H, J_{gem} = $J_{5,6ax}$ = 10.3 Hz, H-6*ax*), 3.75 (t, 1H, H-4), 4.01 (dd, 1H, $J_{1eq,2}$ = 5.7 Hz, H-1*eq*), 4.31 (dd, 1H, $J_{5,6eq}$ = 4.9 Hz, H-6*eq*), 5.55 (s, 1H, PhC*H*), and 7.26-7.51 (m, 15H, 3Ph).

Anal. Calcd for $C_{27}H_{28}O_5$ (432.5): C, 74.98; H, 6.53. Found: C, 74.87; H, 6.32.

1,5-Anhydro-2,3-di-*O*-benzyl-D-glucitol (3). A solution of **2** (510 mg, 1.2 mmol) in aqueous 80% AcOH (25 mL) was heated for 3 h at 45 °C and concentrated to give a crystalline mass. Recrystallization from hexane gave needles: mp 121-124°; $[\alpha]_D$ -13.7° (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 3.21 (t, 1H, J_{gem} = $J_{1ax,2}$ = 11.1 Hz, H-1*ax*), 3.22 (m, 1H, H-5), 3.67 (dd, 1H, J_{gem} = 11.8 Hz, $J_{5,6a}$ = 4.9 Hz, H-6a), 3.80 (dd, 1H, $J_{5,6b}$ = 3.2 Hz, H-6b), 4.00 (dd, 1H, $J_{1eq,2}$ = 5.1 Hz, H-1*eq*), and 7.28-7.40 (m, 10H, 2Ph).

Anal. Calcd for $C_{20}H_{24}O_5$ (344.4): C, 69.75; H, 7.02. Found: C, 69.58; H, 6.96.

1,5-Anhydro-6-*O*-benzoyl-2,3-di-*O*-benzyl-D-glucitol (4). To a solution of **3** (100 mg, 0.29 mmol) in pyridine (1 mL) and CH_2Cl_2 (0.5 mL), cooled to -50 °C, was added dropwise, with stirring, a solution of benzoyl chloride (57 μL, 0.49 mmol) in CH_2Cl_2 (0.1 mL), and the stirring was continued for 1 h at -50 °C. MeOH (1 mL) was added to the mixture, and this was concentrated and extracted with CH_2Cl_2. The extract was successively washed with 2M HCl and water, dried (Na_2SO_4) and concentrated. Column chromatography (1:3 AcOEt-hexane) of the residue on silica gel (50 g) gave **4** (83 mg, 64%) as an amorphous mass: $[\alpha]_D$ +5.3° (*c* 1.7, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 3.24 (t, 1H, J_{gem} = $J_{1ax,2}$ = 11.0 Hz, H-1*ax*), 4.05 (dd, 1H, $J_{1eq,2}$ = 5.0 Hz, H-1*eq*), 4.57 (m, 1H, H-6a), 4.58 (m, 1H, H-6b), and 7.31-8.04 (m, 15H, 3Ph).

Anal. Calcd for $C_{27}H_{28}O_6$ (448.5): C, 72.30; H, 6.29. Found: C, 72.19; H, 6.28.

***O*-(2,3,4-Tri-*O*-benzyl-α-L-fucopyranosyl)-(1→2)-*O*-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)]-1,5-anhydro-4,6-*O*-benzylidene-D-glucitol (6), *O*-(2,3,4-Tri-*O*-benzyl-α-L-fucopyranosyl)-(1→2)-1,5-anhydro-4,6-*O*-benzylidene-D-glucitol (7) and *O*-(2,3,4-Tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)-1,5-anhydro-4,6-*O*-benzylidene-D-glucitol (8).** To a solution of **1** (500 mg, 2.0 mmol) and methyl 2,3,4-tri-*O*-benzyl-1-thio-β-L-fucopyranoside (**5**; 1.1 g, 2.4 mmol) in CH_2Cl_2 (16 mL) were added powdered molecular sieves 4Å (3.3 g), and the mixture was stirred for 7 h at room temperature,

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then cooled to 7 °C. A mixture of dimethyl(methylthio)sulfonium triflate (DMTST) and molecular sieves 4Å (3.3 g; 46% DMTST by weight) was added to the mixture, and the resultant mixture was stirred for 12 h at room temperature. The precipitate was filtered off and washed with CH_2Cl_2. The filtrate and washings were combined, and the solution was successively washed with M Na_2CO_3 and water, dried (Na_2SO_4) and concentrated. Column chromatography (1:5 AcOEt-hexane) of the residue on silica gel (150 g) gave **6** (559 mg, 26%), **7** (371 mg, 28%) and **8** (557 mg, 42%) as an amorphous mass, respectively. Compound **6** had $[\alpha]_D$ -76.4° (*c* 1.1, $CHCl_3$), ^1H NMR ($CDCl_3$) δ 1.03 (d, 1H, $J_{5,6}$ = 6.6 Hz, H-6 of Fuc), 1.13 (d, 1H, $J_{5,6}$ = 6.4 Hz, H-6 of fuc), 3.36 (t, 1H, $J_{gem} = J_{1ax,2}$ = 10.7 Hz, H-1*ax* of 1-deoxy-Glc), 4.92 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1 of Fuc), 5.13 (m, 1H, H-1 of Fuc), 5.49 (s, 1H, PhC*H*), and 7.12-7.72 (m, 35H, 7Ph); Compound **7** had $[\alpha]_D$ -46.2° (*c* 0.7, $CHCl_3$), ^1H NMR ($CDCl_3$), after *O*-acetylation, δ 1.09 (d, 1H, $J_{5,6}$ = 6.4 Hz, H-6b), 1.83 (s, 3H, AcO), 3.41 (t, 1H, $J_{gem} = J_{1ax,2}$ = 10.8 Hz, H-1a-*ax*), 3.44(m, 1H, H-5a), 3.55 (t, 1H, $J_{3,4} = J_{4,5}$ = 9.3 Hz, H-4a), 3.61 (d, 1H, $J_{3,4}$ = 2.7 Hz, H-4b), 3.68 (t, 1H, $J_{gem} = J_{5,6}$ = 10.7 Hz, H-6a), 3.89 (dd, 1H, $J_{2,3}$ = 10.1 Hz, H-3b), 4.00 (dd, 1H, $J_{1,2}$ = 3.7 Hz, H-2b), 4.17 (dd, 1H, $J_{5,6'}$ = 5.6 Hz, H-6'a), 4.31 (dd, 1H, $J_{1eq,2}$ = 4.9 Hz, H-1a-*eq*), 4.93 (d, 1H, H-1b), 5.34 (t, 1H, $J_{2,3}$ = 9.3 Hz, H-3a), 5.47 (s, 1H, PhC*H*), and 7.17-7.45 (m, 20H, 4Ph); Compound **8** had $[\alpha]_D$ -78.0° (*c* 1.0, $CHCl_3$), ^1H NMR ($CDCl_3$), after *O*-acetylation, δ 0.86 (δ, 1H, $J_{5,6}$ = 6.4 Hz, H-6b), 1.88 (s, 3H, AcO), 3.23 (t, 1H, $J_{gem} = J_{1ax,2}$ = 10.6 Hz, H-1a-*ax*), 3.41 (ddd, 1H, $J_{4,5} = J_{5,6}$ = 9.7 Hz, $J_{5,6'}$ = 5.0 Hz, H-5a), 3.52 (d, 1H, $J_{3,4}$ = 2.8 Hz, H-4b), 3.69 (t, 1H, J_{gem} = 9.7 Hz, H-6a), 3.69 (t, 1H, $J_{3,4}$ = 9.3 Hz, H-4a), 3.93 (dd, 1H, $J_{2,3}$ = 10.1 Hz, H-3b), 4.06 (dd, 1H, $J_{1,2}$ = 3.7 Hz, H-2b), 4.16 (m, 1H, H-6'a), 4.31 (dd, 1H, $J_{1eq,2}$ = 5.3 Hz, H-1a-*eq*), 5.12 (ddd, 1H, $J_{2,3}$ = 10.4 Hz, H-2a), 5.31 (d, 1H, H-1b), 5.49 (s, 1H, PhC*H*), and 7.17-7.68 (m, 20H, 4Ph).

Anal. Calcd for compound **6**; $C_{67}H_{72}O_{13}$ (1085.3): C, 74.15; H, 6.69. Found: C, 73.88; H, 6.64.

Anal. Calcd for compound **7** and **8**; $C_{40}H_{44}O_9$ (668.8): C, 71.84; H, 6.63. Found for **7**: C, 71.54; H, 6.55. Found for **8**: C, 71.62; H, 6.52.

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***O*-(2,3,4-Tri-*O*-benzyl-α-L-fucopyranosyl)-(1→4)-1,5-anhydro-6-*O*-benzoyl-2,3-di-*O*-benzyl-D-glucitol (9).** To a solution of **4** (83 mg, 0.19 mmol) and **5** (103 mg, 0.22 mmol) in benzene (1.7 mL), were added powdered molecular sieves 4Å (310 mg), and the mixture was stirred for 8 h at room temperature. DMTST (143 mg) and molecular sieves 4Å (127 mg) were added to the stirred mixture at 7 °C, and the stirring was continued for 15 h at 7 °C. The precipitate was filtered off and washed with CH_2Cl_2. The filtrate and washings were combined, and the solution was washed with M Na_2CO_3 and water, dried (Na_2SO_4) and concentrated. Column chromatography (1:5 AcOEt-hexane) of the residue on silica gel (50g) gave **9** (155 mg, 97%) as an amorphous mass: $[\alpha]_D$ -22.4° (*c* 2.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.76 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6b), 3.22 (t, 1H, $J_{gem} = J_{1ax,2}$ = 10.4 Hz, H-1a-*ax*), 3.42 (m, 1H, H-4b), 3.92 (dd, 1H, $J_{2,3}$ = 2.4 Hz, $J_{3,4}$ = 10.3 Hz, H-3b), 4.40 (dd, 1H, J_{gem} = 12.2 Hz, $J_{5,6}$ = 4.1 Hz, H-6a), 5.07 (d, 1H, $J_{1,2}$ = 4.3 Hz, H-1b), 7.17-8.06 (m, 30H, 6Ph).

Anal. Calcd for $C_{54}H_{56}O_{10}$ (865.0): C, 74.98; H, 6.53. Found: C, 74.71; H, 6.48.

***O*-(2,3,4-Tri-*O*-benzyl-α-L-fucopyranosyl)-(1→4)-1,5-anhydro-2,3-di-*O*-benzyl-D-glucitol (10).** To a solution of **9** (155 mg, 0.18 mmol) in MeOH (10 mL) was added sodium methoxide (150 mg), and the mixture was stirred for 15 h at room temperature, neutralized with Amberlite IR-120 (H^+) resin and filtered. The resin was washed with MeOH, and the combined filtrate and washings were concentrated. Column chromatography (1:3 AcOEt-hexane) of the residue on silica gel (50 g) gave **10** (126 mg, 93%) as an amorphous mass: $[\alpha]_D$ -33.5° (*c* 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.94 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6b), 3.19 (t, 1H, $J_{gem} = J_{1ax,2}$ = 10.8 Hz, H-1a-*ax*), 3.20 (m, 1H, H-5a), 3.89 (dd, 1H, $J_{2,3}$ = 2.7 Hz, $J_{3,4}$ = 10.4 Hz, H-3b), 3.97 (dd, 1H, $J_{1eq,2}$ = 4.9 Hz, H-1a-*eq*), 5.18 (d, 1H, $J_{1,2}$ = 3.5 Hz, H-1b), and 7.23-7.43 (m, 25H, 5Ph).

Anal. Calcd for $C_{47}H_{52}O_9$ (760.9): C, 74.19; H, 6.89. Found: C, 73.95; H, 6.70.

***O*-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-*O*-(2,4,6-tri-*O*-**

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benzoyl-β-D-galactopyranosyl)-(1→3)-*O*-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→2)]-1,5-anhydro-4,6-*O*-benzylidene-D-glucitol (12). To a solution of **7** (86 mg, 0.13 mmol) and methyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-2,4,6-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside[16] (**11**; 270 mg, 0.27 mmol) in CH_2Cl_2 (2 mL) were added molecular sieves 4Å (300 mg), and the mixture was stirred for 7 h at room temperature. DMTST (492 mg) and molecular sieves 4Å (308 mg) were added to the stirred mixture at 7 °C, and the stirring was continued for 72 h at 7 °C. The precipitate was filtered off and washed with CH_2Cl_2. The filtrate and washings were combined, and the solution was washed with M Na_2CO_3 and water, dried (Na_2SO_4) and concentrated. Column chromatography (3:2 AcOEt-hexane) of the residue on silica gel (80 g) gave **12** (146 mg, 70%) as an amorphous mass: $[\alpha]_D$ -3.3° (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.01 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6b), 1.36 (s, 3H, AcN), 1.62 (t, 1H, J_{gem} = $J_{3ax,4}$ = 12.5 Hz, H-3d-*ax*), 1.75, 1.90, 1.95, 2.16 (4s, 12H, 4AcO), 2.48 (d, 1H, $J_{3eq,4}$ = 4.5 Hz, H-3d-*eq*), 3.32 (t, 1H, J_{gem} = $J_{1ax,2}$ = 10.9 Hz, H-1a-*ax*), 3.42 (m, 1H, H-5a), 3.52 (d, 1H, $J_{3,4}$ = 2.8 Hz, H-4b), 3.87 (s, 3H, MeO), 4.26 (m, 1H, H-1a-*eq*), 4.26 (m, 1H, H-6a), 4.85 (m, 1H, H-4d), 5.19, (dd, 1H, $J_{6,7}$ = 2.8 Hz, $J_{7,8}$ = 9.5 Hz, H-7d), 5.34 (m, 1H, H-8d), 5.36 (d, 1H, $J_{3,4}$ = 3.3 Hz, H-4c), 5.65 (s, 1H, PhC*H*), and 7.04-8.19 (m, 35H, 7Ph).

Anal. Calcd for $C_{87}H_{93}NO_{29}$ (1616.7): C, 64.64; H, 5.80; N, 0.87. Found: C, 64.50; H, 5.52; N, 0.85.

***O*-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-*O*-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-*O*-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→2)]-1,5-anhydro-D-glucitol (13).** A solution of **12** (350 mg, 0.22 mmol) in aqueous 80% AcOH was heated for 48 h at 45 °C and concentrated. Column chromatography (50:1 CH_2Cl_2-MeOH) of the residue on silica gel (80 g) gave **13** (170 mg, 51%) as an amorphous mass: $[\alpha]_D$ -33.8° (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.99 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6b), 1.57 (s, 3H, AcN), 1.61 (t, 1H, J_{gem} = $J_{3ax,4}$ = 12.6 Hz, H-3d-*ax*), 1.79, 1.90, 2.03, 2.14 (4s, 12H, 4AcO), 2.42 (dd,

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1H, $J_{3eq,4}$ = 4.7 Hz, H-3d-*eq*), 3.28 (m, 1H, H-1a-*ax*), 3.32 (m, 1H, H-5a), 3.50 (m, 1H, H-4b), 5.14 (d, 1H, $J_{5,NH}$ = 10.3 Hz, NH), 5.17 (d, 1H, $J_{1,2}$ = 3.7 Hz, H-1b), 5.23 (dd, 1H, $J_{6,7}$ = 2.4 Hz, $J_{7,8}$ = 9.2 Hz, H-7d), 5.42 (d, 1H, $J_{3,4}$ = 3.3 Hz, H-4c), 5.53 (m, 1H, H-8d), 5.57 (dd, 1H, $J_{2,3}$ = 10.0 Hz, H-2c), and 7.25-8.14 (m, 30H, 6Ph).

Anal. Calcd for $C_{80}H_{89}NO_{29}$ (1528.6): C, 62.86; H, 5.87; N, 0.92. Found: C, 62.63; H, 5.79; N, 0.66.

***O*-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-*O*-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→3)-*O*-[(α-L-fucopyranosyl)-(1→2)]-1,5-anhydro-D-glucitol (14).** A solution of **13** (190 mg, 0.12 mmol) in MeOH (30 mL) and AcOH (5.3 mL) was hydrogenolyzed in the presence of 10% Pd-C (220 mg) for 48 h at 40 °C, then filtered and concentrated. Column chromatography (AcOEt) of the residue on silica gel (70 g) gave **14** (112 mg, 72%) as an amorphous mass: $[\alpha]_D$ -6.5° (*c* 2.4, 1:1 $CHCl_3$-MeOH); ^1H NMR (CD_3OD) δ 1.14 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6b), 1.53 (t, 1H, J_{gem} = $J_{3ax,4}$ = 12.5Hz, H-3d-*ax*), 1.59 (s, 3H, AcN), 1.77, 1.88, 2.07, 2.18 (4s, 12H, 4AcO), 2.44 (dd, 1H, $J_{3eq,4}$ = 4.7 Hz, H-3d-*eq*), 3.84 (s, 3H, MeO), 4.79 (m, 1H, H-4d), 4.88 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1b), 4.93 (dd, 1H, $J_{2,3}$ = 10.1 Hz, $J_{3,4}$ = 3.2 Hz, H-3c), 5.26 (m, 1H, H-7d), 5.44 (dd, 1H, $J_{1,2}$ = 8.1 Hz, H-2c), 5.66 (m, 1H, H-8d), 5.87 (d, 1H, NH), and 7.29-8.31 (m, 15H, 3Ph).

Anal. Calcd for $C_{59}H_{71}NO_{29}$ (1258.2): C, 56.32; H, 5.69; N, 1.11. Found: C, 56.29; H, 5.61; N, 1.10.

***O*-(5-Acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2→3)-*O*-(β-D-galactopyranosyl)-(1→3)-*O*-[(α-L-fucopyranosyl)-(1→2)]-1,5-anhydro-D-glucitol (15).** To a solution of **14** (116 mg, 0.092 mmol) in MeOH (7.8 mL) was added sodium methoxide (80 mg), and the mixture was stirred for 48 h at 40 °C. Water (1.3 mL) was added to the mixture, and this was stirred for 24 h at 40 °C, neutralized with Amberlite IR-120 (H^+) resin and filtered. The resin was washed with MeOH, and the combined filtrate and washings

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were concentrated. Column chromatography (1:1 $CHCl_3$-MeOH) of the residue on Sephadex LH-20 (80 g) gave **15** (65 mg, 93%) as an amorphous mass: $[\alpha]_D$ -33.8° (*c* 1.3, 1:1 $CHCl_3$-MeOH); ^1H NMR (CD_3OD) δ 1.23 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6b), 1.91 (broad t, 1H, H-3d-*ax*), 2.03 (s, 3H, AcN), 2.81 (broad d, 1H, H-3d-*eq*), 4.67 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1c), and 5.08 (d, 1H, $J_{1,2}$ = 3.1 Hz, H-1b).

Anal. Calcd for $C_{29}H_{49}NO_{22}$ (763.7): C, 45.61; H, 6.47; N, 1.83. Found: C, 45.51; H, 6.21; N, 1.70.

***O*-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-*O*-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→2)-*O*-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)]-1,5-anhydro-4,6-*O*-benzylidene-D-glucitol (16).** To a solution of **8** (100 mg, 0.15 mmol) and **11** (270 mg, 0.27 mmol) in CH_2Cl_2 (2 mL) were added molecular sieves 4Å (370 mg), and the mixture was stirred for 7 h at room temperature. DMTST (492 mg) and molecular sieves 4Å (328 mg) were added to the stirred mixture at 7 °C, and the stirring was continued for 72 h at 7 °C. The precipitate was filtered off and washed with CH_2Cl_2. The filtrate and washings were combined, and the solution was washed with M Na_2CO_3 and water, dried (Na_2SO_4) and concentrated. Column chromatography (3:2 AcOEt-hexane) of the residue on silica gel (80 g) gave **16** (198 mg, 82%) as an amorphous mass: $[\alpha]_D$ -33.7° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.89 (d, 3H, $J_{5,6}$ = 6.2 Hz, H-6b), 1.59 (t, 1H, J_{gem} = $J_{3ax,4}$ = 12.5 Hz, H-3d-*ax*), 1.63 (s, 3H, AcN), 1.78, 1.87, 1.99, 2.09 (4s, 12H, 4AcO), 2.39 (dd, 1H, $J_{3eq,4}$ = 4.6 Hz, H-3d-*eq*), 3.31 (m, 1H, H-5a), 3.38 (m, 1H, H-4b), 3.73 (s, 3H, MeO), 4.80 (m, 1H, H-4d), 5.03 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1c), 5.05 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1b), 5.25 (dd, 1H, $J_{6,7}$ = 2.6 Hz, H-7d), 5.39 (d, 1H, $J_{3,4}$ = 3.5Hz, H-4c), 5.40 (m, 1H, H-8d), 5.43 (s, 1H, PhC*H*), 5.51 (dd, 1H, $J_{2,3}$ = 10.2 Hz, H-2c), and 7.16-8.07 (m, 35H, 7Ph).

Anal. Calcd for $C_{87}H_{93}NO_{29}$ (1616.7): C, 64.64; H, 6.47; N, 1.83. Found: C, 64.52; H, 5.52; N, 0.65.

***O*-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-*O*-(2,4,6-tri-*O*-**

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benzoyl-β-D-galactopyranosyl)-(1→2)-*O*-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→3)]-1,5-anhydro-D-glucitol (17). A solution of **16** (260 mg, 0.16 mmol) in aqueous 80% AcOH was heated for 24 h at 45 °C and concentrated. Column chromatography (80:1 CH_2Cl_2-MeOH) of the residue on silica gel (80 g) gave **17** (133 mg, 54%) as an amorphous mass: $[\alpha]_D$ +5.3° (*c* 1.3, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.12 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6b), 1.56 (t, 1H, J_{gem} = $J_{3ax,4}$ = 12.6 Hz, H-3d-*ax*), 1.66 (s, 3H, AcN), 1.78, 1.87, 2.01, 2.11 (4s, 12H, 4AcO), 2.43 (dd, 1H, $J_{3eq,4}$ = 4.4 Hz, H-3d-*eq*), 3.22 (m, 1H, H-5a), 3.31 (m, 1H, H-4b), 3.73 (s, 3H, MeO), 5.23 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1c), 5.28 (m, 1H, H-7d), 5.41 (d, 1H, $J_{3,4}$ = 3.1 Hz, H-4c), 5.48 (m, 1H, H-8d), 5.50 (dd, 1H, $J_{2,3}$ = 10.1 Hz, H-2c), and 7.26-8.11 (m, 30H, 6Ph).

Anal. Calcd for $C_{80}H_{89}NO_{29}$ (1528.6): C, 62.86; H, 5.87; N, 0.92. Found: C, 62.81; H, 5.80; N, 0.89.

***O*-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-*O*-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→2)-*O*-[(α-L-fucopyranosyl)-(1→3)]-1,5-anhydro-D-glucitol (18).** A solution of **17** (133 mg, 0.087 mmol) in MeOH (21 mL) and AcOH (3.7 mL) was hydrogenolyzed in the presence of 10% Pd-C (150 mg) for 48 h at 40 °C, then filtered and concentrated. Column chromatography (5:1 CH_2Cl_2-MeOH) of the residue on silica gel (65 g) gave **18** (90 mg, 83%) as an amorphous mass: $[\alpha]_D$ +1.2° (*c* 1.2, 1:1 $CHCl_3$-MeOH); ^1H NMR (CD_3OD) δ 1.18 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6b), 1.54 (s, 3H, AcN), 1.57 (t, 1H, J_{gem} = $J_{3ax,4}$ = 12.5 Hz, H-3d-*ax*), 1.76, 1.91, 2.09, 2.18 (4s, 12H, 4AcO), 2.44 (dd, 1H, $J_{3eq,4}$ = 4.6 Hz, H-3d-*eq*), 3.84 (s, 3H, MeO), 4.77 (m, 1H, H-4d), 4.85 (dd, 1H, $J_{2,3}$ = 9.9 Hz, $J_{3,4}$ = 3.3 Hz, H-3c), 4.97 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1b), 5.21 (dd, 1H, $J_{6,7}$ = 2.2 Hz, $J_{7,8}$ = 9.9 Hz, H-7d), 5.41 (d, 1H, H-4c), 5.62 (m, 1H, H-8d), and 7.41-8.28 (m, 15H, 3Ph).

Anal. Calcd for $C_{59}H_{71}NO_{29}$ (1258.2): C, 56.32; H, 5.69; N, 1.11. Found: C, 56.10; H, 5.59; N, 1.09.

***O*-(5-Acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2→3)-*O*-(β-D-galactopyranosyl)-(1→2)-*O*-[(α-L-**

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fucopyranosyl)-(1→3)]-1,5-anhydro-D-glucitol (19). To a solution of **18** (90 mg, 0.072 mmol) in MeOH (6 mL) was added sodium methoxide (70 mg), and the mixture was stirred for 24 h at 40 °C. Water (1 mL) was added to the mixture and this was stirred for 24 h at 40 °C, neutralized with Amberlite IR-120 (H^+) resin and filtered. The resin was washed with MeOH, and the combined filtrate and washings were concentrated. Column chromatography (1:1 $CHCl_3$-MeOH) of the residue on Sephadex LH-20 (80 g) gave **19** (54 mg, quantitative) as an amorphous mass: $[\alpha]_D$ -37.6° (*c* 1.2, 1:1 $CHCl_3$-MeOH); ^1H NMR (CD_3OD) δ 1.23 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6b), 1.87 (broad t, 1H, H-3d-*ax*), 2.03 (s, 3H, AcN), 2.81 (broad d, 1H, H-3d-*eq*), 4.52 (d, 1H, $J_{1,2}$ = 7.3 Hz, H-1c), and 5.24 (broad s, 1H, H-1b).

Anal. Calcd for $C_{29}H_{49}NO_{22}$ (763.7): C, 45.61; H, 6.47; N, 1.83. Found: C, 45.46; H, 6.38; N, 1.82.

***O*-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-*O*-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→6)-*O*-[(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1→4)]-1,5-anhydro-2,3-di-*O*-benzyl-D-glucitol (20).** To a solution of **10** (126 mg, 0.17 mmol) and **11** (300 mg, 0.30 mmol) in CH_2Cl_2 (2.3 mL) were added molecular sieves 4Å (426 mg), and the mixture was stirred for 5 h at room temperature. DMTST (530 mg) and molecular sieves 4Å (470 mg) were added to the stirred mixture at 7 °C, and the stirring was continued for 84 h at 7 °C. The precipitate was filtered off and washed with CH_2Cl_2. The filtrate and washings were combined, and the solution was washed with M Na_2CO_3 and water, dried (Na_2SO_4) and concentrated. Column chromatography (5:4 AcOEt-hexane) of the residue on silica gel (80 g) gave **20** (180 mg, 64%) as an amorphous mass: $[\alpha]_D$ +3.0° (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.77 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6b), 1.44 (s, 3H, AcN), 1.68 (t, 1H, J_{gem} = $J_{3ax,4}$ = 12.5 Hz, H-3d-*ax*), 1.77, 1.91, 2.00, 2.17 (4s, 12H, 4AcO), 2.46 (dd, 1H, $J_{3eq,4}$ = 4.4 Hz, H-3d-*eq*), 3.82 (s, 3H, MeO), 4.94 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1c), 5.00 (d, 1H, $J_{5,NH}$ = 10.1 Hz, NH), 5.04 (d, 1H, $J_{1,2}$ = 5.9 Hz, H-1b), 5.22 (dd, 1H, $J_{6,7}$ = 2.7 Hz, $J_{7,8}$ = 9.5 Hz, H-7d), 5.39 (d, 1H, $J_{3,4}$ = 3.3 Hz, H-4c), 5.50 (dd, 1H, $J_{2,3}$ = 8.1 Hz, H-2c), 5.62 (m, 1H, H-8d), and 7.22-8.19 (m, 40H, 8Ph).

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Anal. Calcd for $C_{94}H_{101}NO_{29}$ (1708.8): C, 66.07; H, 5.96; N, 0.82. Found: C, 65.84; H, 5.89; N, 0.55.

***O*-(Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-*O*-(2,4,6-tri-*O*-benzoyl-β-D-galactopyranosyl)-(1→6)-*O*-[(α-L-fucopyranosyl)-(1→4)]-1,5-anhydro-D-glucitol (21).** A solution of **20** (180 mg, 0.11 mmol) in MeOH (29 mL) and AcOH (5 mL) was hydrogenolyzed in the presence of 10% Pd-C (230 mg) for 72 h at 40 °C, then filtered and concentrated. Column chromatography (10:1 CH_2Cl_2-MeOH) of the residue on silica gel (50 g) gave **21** (68 mg, 51%) as an amorphous mass: $[\alpha]_D$ +9.1° (*c* 1.4, 1:1 $CHCl_3$-MeOH); ^1H NMR (CD_3OD) δ 1.21 (d, 3H, $J_{5,6}$ = 6.4 Hz, H-6b), 1.75-2.26 (5s, 15H, AcN and 4AcO), 2.47 (dd, 1H, J_{gem} = 12.2 Hz, $J_{3eq,4}$ = 4.5 Hz, H-3d-*eq*), 3.84 (s, 3H, MeO), 4.94 (m, 1H, H-4d), 5.22 (d, 1H, $J_{5,NH}$ = 9.9 Hz, NH), 5.68 (m, 1H, H-8d), and 7.43-8.22 (m, 15H, 3Ph).

Anal. Calcd for $C_{59}H_{71}NO_{29}$ (1258.2): C, 56.32; H, 5.69; N, 1.11. Found: C, 56.14; H, 5.62; N, 1.11.

***O*-(5-Acetamido-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2→3)-*O*-(β-D-galactopyranosyl)-(1→6)-*O*-[(α-L-fucopyranosyl)-(1→4)]-1,5-anhydro-D-glucitol (22).** To a solution of **21** (68 mg, 0.054 mmol) in MeOH (5 mL) was added sodium methoxide (70 mg), and the mixture was stirred for 24 h at 40 °C. Water (1 mL) was added to the mixture and this was stirred for 23 h at 40 °C, neutralized with Amberlite IR-120 (H^+) resin and filtered. The resin was washed with MeOH, and the combined filtrate and washings were concentrated. Column chromatography (1:1 $CHCl_3$-MeOH) of the residue on Sephadex LH-20 (80 g) gave **22** (30 mg, 73%) as an amorphous mass: $[\alpha]_D$ -14.9° (*c* 1.1, 5:4:0.7 $CHCl_3$-MeOH-H_2O); ^1H NMR (CD_3OD) δ 1.22 (d, 3H, $J_{5,6}$ = 6.6 Hz, H-6b), 1.81 (broad t, 1H, H-3d-*ax*), 2.04 (s, 3H, AcN), 2.76 (broad d, 1H, H-3d-*eq*), 3.23 (t, 1H, J_{gem} = $J_{1ax,2}$ = 10.7 Hz, H-1a-*ax*), 4.41 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1c), and 5.03 (broad d, 1H, H-1b).

Anal. Calcd for $C_{29}H_{49}NO_{22}$ (763.7): C, 45.61; H, 6.47; N, 1.83. Found: C, 45.48; H, 6.47; N, 1.74.

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