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Synthesis of KDN-lactotetraosylceramide, KDN-neolactotetraosylceramide, and KDN-Lewis X ganglioside [†]

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Abstract

Analogues of sialyl-lactotetraosylceramide, sialyl-neolactotetraosylceramide, and sialyl Lewis X ganglioside, in which the *N*-acetylneuraminic acid residue is replaced by a 3-deoxy-D-*glycero*-D-*galacto*-2-nonulopyranosonic acid (KDN) unit, have been synthesized. Methyl *O*-(methyl 4,5,7,8,9-penta-*O*-acetyl-3-deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-2,4,6-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside (**4**) was prepared from 2-(trimethylsilyl)ethyl *O*-(methyl 4,5,7,8,9-penta-*O*-acetyl-3-deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-6-*O*-benzoyl-β-D-galactopyranoside, via *O*-benzoylation, replacement of the 2-(trimethylsilyl)ethyl group by acetyl, and introduction of the methylthio group with trimethyl(methylthio)silane. Glycosylation of 2-(trimethylsilyl)ethyl *O*-(2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**5**) or of 2-(trimethylsilyl)ethyl *O*-(2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside, prepared from **5** via *O*-benzylation and reductive opening of the benzylidene acetal ring, with **4** as a donor gave the corresponding pentasaccharides **9** and **13** in good yields. In the same way, **4** was reacted with 2-(trimethylsilyl)ethyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 3)-*O*-(2-acetamido-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside to yield the hexasaccharide **17**. These three oligosaccharides **9**, **13**, and **17** were converted via reductive removal of the benzyl groups and benzylidene group, *O*-acetylation, removal of the 2-(trimethylsilyl)ethyl group, and subsequent reaction with trichloroacetonitrile, into the corresponding trichloroacetimidates **12**, **16**, and **20**, respectively. Glycosylation of (2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol with **12**, **16**, and **20** in the presence of boron trifluoride etherate

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[†] Synthetic Studies on Sialoglycoconjugates, Part 57. For Part 56, see ref 1.

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afforded the expected β-glycosides, which were transformed via selective reduction of the azido group, coupling with octadecanoic acid, *O*-deacylation, and de-esterification, into the target gangliosides in high yields.

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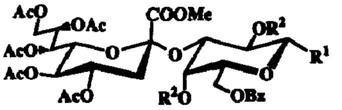
1. Introduction

Gangliosides are a kind of glycosphingolipid, and they are distinguished from other glycosphingolipids because of their containing sialic acid, mainly α-linked at C-3 or C-6 of galactose, C-6 of *N*-acetylgalactosamine, or C-8 of another sialic acid residue. More than 20 variant forms of sialic acid have been isolated from various gangliosides and glycoproteins, all derived, according to current knowledge, from two parent structures, namely *N*-acetyl- and *N*-glycolyl-neuraminic acid. These two compounds may have substitution on the hydroxyl groups at C-4, C-7, C-8, and C-9 by acetyl, glycolyl, lactoyl, methyl, sulfate, and phosphate, so that the number of possible derivatives becomes very large. In 1986, a novel type of sialic acid, 3-deoxy-D-*glycero*-D-*galacto*-2-nonulopyranosylonic acid (KDN), in which the acetamido group at C-5 of *N*-acetylneuraminic acid is replaced by a hydroxyl, was isolated by Inoue and co-workers [2,3] from the vitelline envelope of rainbow trout eggs. In 1991, KDN-ganglioside GM3 was isolated [4] from rainbow trout sperm, and this first finding of a KDN-ganglioside indicated the possible wide occurrence of this class of gangliosides in nature.

Recently, as various important biological functions of the gangliosides have been revealed [5–7], their chemical synthesis has become increasingly stimulating, and rewarding as an aid to the elucidation of their functions at the molecular level. The biological function of KDN-ganglioside has not been investigated in detail, because only a limited quantity has been available. We have developed [8,9] a systematic synthesis of gangliosides and their analogs, based on a facile α-glycosidation of sialic acids, achieved by activation of their thioglycosides with dimethyl(methylthio)sulfonium triflate [10,11] (DMTST) or *N*-iodosuccinimide–trifluoromethanesulfonic acid [12] (NIS-TfOH) in acetonitrile. Previously, we have reported the synthesis [13] of KDN-gangliosides GM3 and GM4 by our procedure. As a part of our continuing studies on preparation we now describe the total synthesis of KDN-lactotetraosylceramide, KDN-neolactotetraosylceramide, and KDN-Lewis X ganglioside. These compounds will be useful for elucidating biological functions of KDN-gangliosides, and also for clarifying the role of the C-5 hydroxyl group of KDN in biological systems.

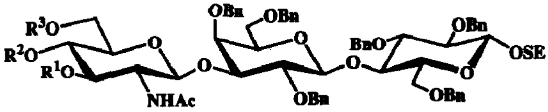
2. Results and discussion

Methyl *O*-(methyl 4,5,7,8,9-penta-*O*-acetyl-3-deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-2,4,6-tri-*O*-benzoyl-1-thio-β-D-galactopyranoside (**4**) was selected as the glycosyl donor, and 2-(trimethylsilyl)ethyl *O*-(2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-ga-

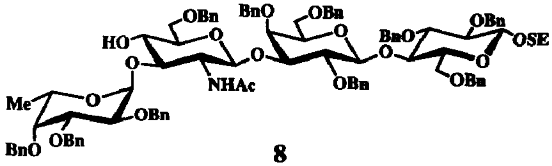


	R¹	R²
1	OSE	H
2	OSE	Bz
3	OAc	Bz
4	SMe	Bz

SE = 2-(trimethylsilyl)ethyl



	R¹	R²	R³
5	H	benzylidene	
6	Bn	benzylidene	
7	Bn	H	Bn



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lactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside [14] (**5**) and 2-(trimethylsilyl)ethyl *O*-(2-acetamido-3,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**7**) as acceptors for the synthesis of KDN-lactotetraosylceramide (**24**) and KDN-neolactotetraosylceramide (**27**), and 2-(trimethylsilyl)ethyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 3)-*O*-(2-acetamido-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside [15] (**8**) as the acceptor for the synthesis of KDN-Lewis X ganglioside (**30**).

Treatment of 2-(trimethylsilyl)ethyl *O*-(methyl 4,5,7,8,9-penta-*O*-acetyl-3-deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-6-*O*-benzoyl-β-D-galactopyranoside [13,16,17] (**1**) with benzoyl chloride in pyridine–dichloromethane gave compound **2**, which on treatment [18,19] with boron trifluoride etherate in toluene–acetic anhydride gave the β-1-acetate **3** in good yield. The ^{1}H NMR data for the galactose residue in **3** [δ 6.16 ($J_{1,2}$ 8.2 Hz, H-1), 5.56 ($J_{2,3}$ 9.8 Hz, H-2) and 5.45 ($J_{3,4}$ 3.0 Hz, H-4)] are characteristic of the structure assigned. Conversion of **3** into the methyl β-thioglycoside **4** (87%) was achieved by treatment [20] with trimethyl(methylthio)silane and boron trifluoride etherate in dichloromethane. Significant signals in the ^{1}H NMR spectrum of **4** were at δ 4.92 (d, $J_{1,2}$ 9.8 Hz, H-1), 5.54 (br d, $J_{3,4}$ 3.1 Hz, H-4) and 5.64 (t, $J_{2,3}$ 9.8 Hz, H-2). Other ^{1}H NMR data given in the Experimental section are also consistent with the structure **4**.

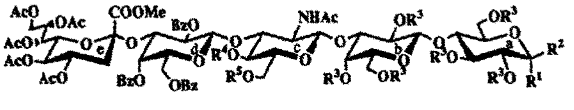
Treatment of **5** with benzyl bromide in *N,N*-dimethylformamide in the presence of sodium hydride for 2 h at 0°C gave the benzyl derivative **6** (94%), which on reductive ring-opening [21] of the benzylidene acetal function with sodium cyanoborohydride–hydrogen chloride in tetrahydrofuran, afforded **7** (85%).

Glycosylation of **5** or **7** with **4** in dichloromethane for 48 h at 8°C in the presence of DMTST (4.0 equiv with respect to the glycosyl donor) and powdered 4A molecular sieves (4A-MS) gave the expected pentasaccharide derivatives **9** (90%) and **13** (83%), respectively. The ^{1}H NMR data for the KDN-Gal unit in **9** [δ 5.07 (d, $J_{1,2}$ 7.9 Hz, H-1d), 5.36 (dd, $J_{2,3}$ 10.4 Hz, H-2d) and 5.32 (br d, $J_{3,4}$ 3.1 Hz, H-4d)], and in **13** [δ 5.08 (d, $J_{1,2}$ 7.9 Hz, H-1d), 5.38 (br d, $J_{3,4}$ 3.4 Hz, H-4d), and 5.47 (dd, $J_{2,3}$ 10.1 Hz, H-2d)] indicated the newly formed glycosidic linkage to be β. In the same way, when reacted with **4**, compound **8** yielded the desired hexasaccharide **17** in 46% yield; significant signals of KDN-Gal unit in the ^{1}H NMR spectrum of **17** [δ 5.22 (d, $J_{1,2}$ 7.6 Hz, H-1e), 5.47 (br d, $J_{3,4}$ 3.1 Hz, H-4e), and 5.68 (dd, 1 H, $J_{2,3}$ 10.1 Hz, H-2e)], supported the structure assigned.

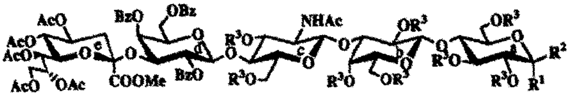
Catalytic hydrogenolysis (10% Pd–C) in ethanol–acetic acid of the benzyl and benzylidene groups in **9** and subsequent *O*-acetylation gave the per-*O*-acetyl derivative **10** (82%). In the same way, hydrogenolysis of the benzyl groups in **13** and **17** followed by acetylation gave **14** (84%) and **18** (80%), respectively. Treatment of compounds **10**, **14**, and **18** with trifluoroacetic acid [19] in dichloromethane for 5 h at 0°C gave the corresponding 1-hydroxy compounds **11**, **15**, and **19** in high yields. Treatment [22-24] of **11**, **15**, and **19** with trichloroacetonitrile in dichloromethane in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) for 2 h at 0°C then gave the α-trichloroacetimidates **12** (93%), **16** (88%), and **20** (86%) (yields after column chromatography). Significant signals in the ^{1}H NMR spectra were at δ 6.48 (d, $J_{1,2}$ 3.7 Hz, H-1a) and 8.65 (C = NH) for **12**, at δ 6.47 (d, $J_{1,2}$ 3.8 Hz, H-1a) and 8.65 (C = NH) for **16**, and δ 6.47 (d, $J_{1,2}$ 3.7 Hz, H-1a) and 8.65 (C = NH) for **20**, which showed the imidates to be α.

Final glycosylation [24,25] of (2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol [25,26] (**21**) with **12**, **16**, and **20** in dichloromethane in the presence of boron trifluoride etherate for 6 h at room temperature gave the corresponding β-glycosides **22** (59%), **25** (64%), and **28** (51%), respectively. The ^{1}H NMR data for the Glc unit of compounds **22**, **25**, and **28** [δ 4.49-4.50 (d, $J_{1,2}$ 7.3–7.7 Hz, H-1a)] indicated the glycosidic linkage to be β.

Selective reduction [27–28] of the azido group in **22**, **25**, and **28** with hydrogen sulfide in aqueous 83% pyridine for 72 h at 0°C and subsequent condensation with octadecanoic acid, using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (WSC) in dichloromethane, gave the corresponding acylated gangliosides

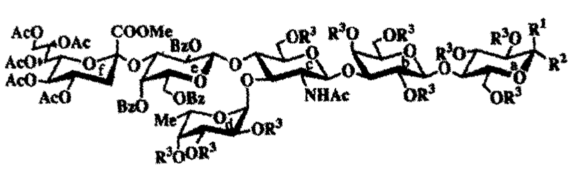


	R^1	R^2	R^3	R^4	R^5
9	H	OSE	Bn	benzylidene	
10	H	OSE	Ac	Ac	Ac
11	H,OH		Ac	Ac	Ac
12	OC(=NH)CCl$_3$	H	Ac	Ac	Ac

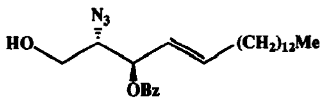


	R^1	R^2	R^3
13	H	OSE	Bn
14	H	OSE	Ac
15	H,OH		Ac
16	OC(=NH)CCl$_3$	H	Ac

23 (89%), **26** (72%), and **29** (91%), respectively. Finally, *O*-deacylation of **23**, **26**, and **29** with sodium methoxide in methanol, with subsequent saponification of the sialate methyl ester group, furnished the desired KDN-gangliosides **24**, **27**, and **30** in high yields. The ^{1}H NMR data of the products thus obtained are consistent with the structures assigned.



	R^1	R^2	R^3
17	H	OSE	Bn
18	H	OSE	Ac
19	H,OH		Ac
20	OC(=NH)CCl$_3$	H	Ac



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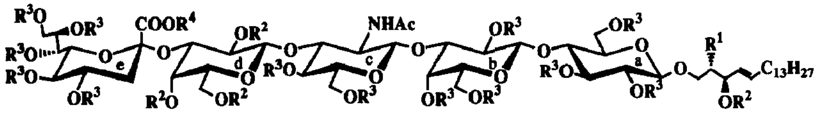
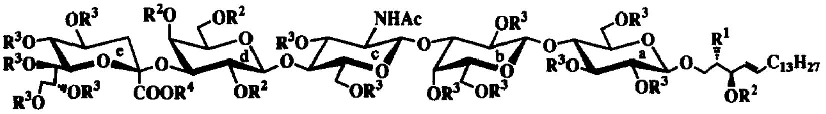


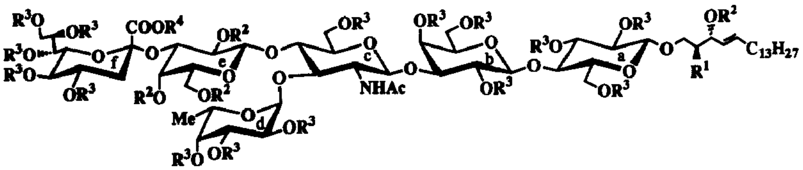
	R^1	R^2	R^3	R^4
22	N_3	Bz	Ac	Me
23	$NHCO(CH_2)_{16}Me$	Bz	Ac	Me
24	$NHCO(CH_2)_{16}Me$	H	H	H



	R^1	R^2	R^3	R^4
25	N_3	Bz	Ac	Me
26	$NHCO(CH_2)_{16}Me$	Bz	Ac	Me
27	$NHCO(CH_2)_{16}Me$	H	H	H

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, and the NMR data were confirmed by use of decoupling techniques. Preparative chromatography was performed on silica gel (Wako Chem-



	R^1	R^2	R^3	R^4
28	N_3	Bz	Ac	Me
29	$NHCO(CH_2)_{16}Me$	Bz	Ac	Me
30	$NHCO(CH_2)_{16}Me$	H	H	H

ical Co., 200 mesh) with the solvent systems specified. Concentrations were conducted in vacuo.

*2-(Trimethylsilyl)ethyl O-(methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-*D-glycero-α-D-galacto-*2-nonulopyranosylonate)-(2 → 3)-2,4,6-tri-O-benzoyl-β-*D*-galactopyranoside* (2).—To a solution of 2-(trimethylsilyl)ethyl *O*-(methyl 4,5,7,8,9-penta-*O*-acetyl-3-deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-6-*O*-benzoyl-β-D-galactopyranoside (**1**; 1.83 g, 2.1 mmol) was added, with stirring, a solution of benzoyl chloride (1.0 mL, 8.5 mmol) in CH_2Cl_2 (20 mL) and pyridine (3 mL) at room temperature. After completion of the reaction the mixture was extracted with CH_2Cl_2 and successively washed with 2 M HCl, M Na_2CO_3, and water, dried (Na_2SO_4), and concentrated. Column chromatography (1:3 EtOAc–hexane) of the residue on silica gel (200 g) gave **2** (1.93 g, 85%) as an amorphous mass; $[\alpha]_D$ +31° (*c* 0.5, $CHCl_3$); ν 1750 and 1230 (ester), 860 and 840 (Me_3Si, and 720 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 0.98 (m, 2 H, $Me_3SiCH_2CH_2O$), 1.51, 1.88, 1.90, 2.15, 2.20 (5 s, 15 H, 5 AcO), 1.74 (t, 1 H, $J_{gem} = J_{3'ax,4'} = 12.6$ Hz, H-3′*ax*), 2.63 (dd, 1 H, $J_{3'eq,4'}$ 4.9 Hz, H-3′*eq*), 3.96 (s, 3 H, MeO), 4.61 (t, $J_{4',5'} = J_{5',6'} = 9.8$ Hz, H-5′), 4.88 (ddd, 1 H, $J_{3'ax,4'}$ 14.1 Hz, H-4′), 5.23 (dd, 1 H, $J_{6',7'}$ 3.0, $J_{7',8'}$ 9.8 Hz, H-7′), 5.45 (br d, 1 H, H-4), 5.56 (dd, 1 H, $J_{1,2}$ 8.1, $J_{2,3}$ 9.8 Hz, H-2), 5.63 (m, 1 H, H-8′), 6.16 (d, 1 H, H-1), and 7.39–8.14 (m, 15 H, 3 Ph). Anal. Calcd for $C_{52}H_{62}O_{22}Si$ (1067.1): C, 58.53; H, 5.86. Found: C, 58.29; H, 5.75.

*O-(Methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-*D-glycero-α-D-galacto-*2-nonulopyranosylonate)-(2 → 3)-1-O-acetyl-2,4,6-tri-O-benzoyl-β-*D*-galactopyranose* (3).—To a solution of **2** (1.44 g, 1.4 mmol) in dry toluene (8 mL) and Ac_2O (2 mL), cooled to 0°C, was added boron trifluoride etherate (0.35 mL, 1.3 mmol), and the mixture was stirred for 2 h at 0°C. After completion of the reaction, CH_2Cl_2 was added, and the solution was washed with M Na_2CO_3, dried (Na_2SO_4), and concentrated. Column chromatography (1:3 EtOAc–hexane) of the residue on silica gel (200 g) gave **3** (1.27 g, 93%) as an amorphous mass; $[\alpha]_D$ +43° (*c* 0.44, $CHCl_3$); ν 1750 and 1230 (ester), 860 and 840 (Me_3Si), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 1.43, 1.89, 1.90, 2.04, 2.09, 2.20 (6 s, 18 H, 6 AcO), 2.55 (dd, 1 H, J_{gem} 12.8 Hz, $J_{3'eq,4'}$ 4.7 Hz, H-3′*eq*), 3.70 (dd, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 3.0 Hz, H-3), 3.88 (s, 3 H, MeO), 4.61 (t, 1 H, $J_{4',5'} = J_{5',6'} = 9.8$ Hz, H-5′), 4.88 (ddd, 1 H, $J_{3'ax,4'}$ 14.1 Hz, H-4′), 5.23 (dd, 1 H, $J_{6',7'}$ 3.0, $J_{7',8'}$ 9.8 Hz, H-7′), 5.45 (br d, 1 H, H-4), 5.56 (dd, 1 H, $J_{1,2}$ 8.1, $J_{2,3}$ 9.8 Hz, H-2), 5.56 (dd, 1 H, $J_{1,2}$ 8.1, $J_{2,3}$ 9.8 Hz, H-2), 5.63 (m, 1 H, H-8′), 6.16 (d, 1 H, H-1), and 7.39–8.14 (m, 15 H, 3 Ph). Anal. Calcd for $C_{49}H_{52}O_{23}$ (1008.9): C, 58.33; H, 5.20. Found: C, 58.15; H, 5.04.

*Methyl O-(methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-*D-glycero-α-D-galacto-*2-nonulopyranosylonate)-(2 → 3)-2,4,6-tri-O-benzoyl-1-thio-β-*D*-galactopyranoside* (4).—To a solution of **3** (1.24 g, 1.2 mmol) in dry CH_2Cl_2 (8 mL) cooled to 0°C were added trimethyl(methylthio)silane (0.62 mL, 3.1 mmol) and boron trifluoride etherate (0.35 mL), and the mixture was stirred for 2 h at 0°C, the reaction being monitored by TLC. The solution was diluted with CH_2Cl_2 and successively washed with M Na_2CO_3 and water, dried (Na_2SO_4), and concentrated. Column chromatography (1:3 EtOAc–hexane) of the residue on silica gel (200 g) gave **4** (1.07 g, 87%) as an amorphous mass; $[\alpha]_D$ +38° (*c* 0.39, $CHCl_3$); ν 1740 and 1230 (ester), 860 and 840 (Me_3Si), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 1.51, 1.96, 2.09, 2.13, 2.26, 2.34 (6 s, 18 H, 5 AcO and MeS), 1.71 (t, 1 H, $J_{gem} = J_{3'ax,4'} = 12.8$ Hz, H-3'*ax*), 2.62 (dd, 1 H, $J_{3'eq,4'}$ 4.8 Hz, H-3'*eq*), 3.78 (dd, 1 H, $J_{2,3}$ 9.8, $J_{3,4}$ 3.1 Hz, H-3), 3.94 (s, 3 H, MeO), 4.70 (t, 1 H, $J_{4',5'} = J_{5',6'} = 9.7$ Hz, H-5'), 4.92 (d, 1 H, $J_{1,2}$ 9.8 Hz, H-1), 4.95 (m, 1 H, H-4'), 5.32 (dd, 1 H, $J_{6',7'}$ 2.7, $J_{7',8'}$ 9.9 Hz, H-7'), 5.54 (br d, 1 H, $J_{3,4}$ 3.1 Hz, H-4), 5.64 (t, 1 H, $J_{2,3}$ 9.8 Hz, H-2), 5.72 (m, 1 H, H-8'), and 7.36–8.25 (m, 15 H, 3 Ph). Anal. Calcd for $C_{48}H_{52}O_{21}S$ (997.0): C, 57.83; H, 5.26. Found: C, 57.58; H, 5.12.

2-(Trimethylsilyl)ethyl O-(2-acetamido-3-O-benzyl-4,6-O-benzylidene-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-O-(2,4,6-tri-O-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**6**).—To a solution of 2-(trimethylsilyl)ethyl *O*-(2-acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-β-D-glucopyranoside (**5**; 1.50 g, 1.2 mmol) in *N*,*N*-dimethylformamide (29 mL) was added a suspension of NaH in oil (0.05 mg, 1.3 mmol; 60% of NaH by weight) at 0°C, and the mixture was stirred for 20 min at 0°C. Benzyl bromide (0.15 mL, 1.3 mmol) was added dropwise, and the mixture was stirred for 2 h at 0°C. The reaction was monitored by TLC. When it was complete MeOH (3 mL) was added, the mixture was concentrated, and the residue was extracted with CH_2Cl_2. The extract was washed with water, dried (Na_2SO_4), and concentrated. Column chromatography (100:1 CH_2Cl_2–MeOH) of the residue on silica gel (200 g) gave **6** (1.51 g, 94%) as an amorphous mass; $[\alpha]_D$ −15° (*c* 0.10, $CHCl_3$); ν 3400 (NH), 1670 and 1550 (amide), 860 and 840 (Me_3Si), and 740 and 700 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 0.99 (m, 2 H, $Me_3SiCH_2CH_2O$), 1.40 (s, 3 H, AcN), 5.57 (s, 1 H, Ph*CH*), and 7.10–7.39 (m, 40 H, 8 Ph). Anal. Calcd for $C_{81}H_{93}NO_{16}Si$ (1364.7): C, 71.29; H, 6.87; N, 1.03. Found: C, 71.06; H, 6.86; N, 0.86.

2-(Trimethylsilyl)ethyl O-(2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-O-(2,4,6-tri-O-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside (**7**).—To a solution of **6** (1.50 g, 1.1 mmol) in dry tetrahydrofuran (7.5 mL) was added 3A molecular sieves (3A-MS, 2 g), the mixture was stirred for 5 h at room temperature, and sodium cyanoborohydride (1.0 g) was gradually added. After the reagent had dissolved, HCl in ether was added dropwise at 0°C until the evolution of gas ceased. The reaction was monitored by TLC, and when it was complete, the mixture was 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 (1:2 EtOAc–hexane) of the residue on silica gel (200 g) gave **7** (1.28 g, 85%) as an amorphous mass; $[\alpha]_D$ −10° (*c* 0.88, $CHCl_3$); ν 3400 (OH), 1660 and 1550 (amide), 860 and 840 (Me_3Si), and 740 and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 0.99 (m, 2 R, $Me_3SiCH_2CH_2O$), 1.42 (s, 3 H, AcN), and 6.99–7.33 (m, 40 H, 8 Ph). Anal. Calcd for $C_{81}H_{95}NO_{16}Si$ (1366.7): C, 71.18; H, 7.01; N, 1.02. Found: C, 71.05; H, 6.90; N, 0.83.

*2-(Trimethylsilyl)ethyl O-(methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-*D-glycero-*α*-D-galacto-*2-nonulopyranosylonate)-(2 → 3)-O-(2,4,6-tri-O-benzoyl-β-D-galactopyranosyl)-(1 → 3)-O-(2-acetamido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-O-(2,4,6-tri-O-benzyl-β--galactopyranosyl)-(1 → 4)-2,3,6-tri-O-benzyl-β-D-gluco-*

pyranoside (**9**).—To a solution of **4** (235 mg, 0.24 mmol) and 2-(trimethylsilyl)ethyl *O*-(2-acetamido-4,6-*O*-benzylidene-2-deoxy-*β*-D-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-benzyl-*β*-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-benzyl-*β*-D-glucopyranoside (**5**, 200 mg, 0.16 mmol) in CH_2Cl_2 (3 mL) was added 4A molecular sieves (4A-MS, 600 mg), and the mixture was stirred for 6 h at room temperature, then cooled to 0°C. A mixture of dimethyl(methylthio)sulfonium triflate (DMTST; 244 mg, 0.94 mmol) and 4A-MS (240 mg) was added, the mixture was stirred for 48 h at 8°C, and the reaction was monitored by TLC. The solids were collected and washed with CH_2Cl_2, and the combined filtrate was washed with M Na_2CO_3 and water, dried (Na_2SO_4), and concentrated. Column chromatography (1:2 EtOAc–hexane) of the residue on silica gel (50 g) gave **9** (314 mg, 90%) as an amorphous mass; $[\alpha]_D$ +2.1° (*c* 1.0, $CHCl_3$); ν 3400 (NH), 1750 and 1540 (ester), 1670 and 1560 (amide), 860 and 840 (Me_3Si), and 740 and 720 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 1.00 (m, 2 H, $Me_3SiCH_2CH_2O$), 1.40–2.16 (6 s, 18 H, 5 AcO and 1 AcN), 2.45 (dd, 1 H, J_{gem} 12.2, $J_{3eq,4}$ 4.6 Hz, H-3e*eq*), 3.81 (s, 3 H, MeO), 5.07 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1d), 5.24 (dd, 1 H, $J_{6,7}$ 2.7, $J_{7,8}$ 9.8 Hz, H-7e), 5.32 (br d, 1 H, $J_{3,4}$ 3.1 Hz, H-4d), 5.36 (dd, 1 H, $J_{2,3}$ 10.4 Hz, H-2d), 5.56 (s, 1 H, PhC*H*), 5.63 (m, 1 H, H-8e), and 7.11–8.17 (m, 50 H, 10 Ph). Anal. Calcd for $C_{121}H_{135}NO_{37}Si$ (2223.5): C, 65.36; H, 6.12; N, 0.63. Found: C, 65.13; H, 6.09; N, 0.36.

2-(Trimethylsilyl)ethyl O-*(methyl 4,5,7,8,9-penta-*O*-acetyl-3-deoxy-*D-glycero-*α*-D-galacto*-2-nonulopyranosylonate)-(2 → 3)-*O*-(2,4,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-(1 → 3)-*O*-(2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-acetyl-β-*D*-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranoside* (**10**).—A solution of **9** (125 mg, 56 μmol) in EtOH (30 mL) and AcOH (4 mL) was hydrogenolyzed in the pesence of 10% Pd–C (125 mg) for 48 h at 40°C, then filtered and concentrated. The residue was acetylated with Ac_2O (3 mL) and pyridine (5 mL) for 12 h at 40°C. Column chromatography (80:1 CH_2Cl_2–MeOH) of the product on silica gel (50 g) gave **10** (89.3 mg, 82%) as an amorphous mass; $[\alpha]_D$ +15° (*c* 1.7, $CHCl_3$); ν 3450 (NH), 1750 and 1230 (ester), 1670 and 1540 (amide), 860 and 840 (Me_3Si), and 720 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 1.02 (m, 2 H, $Me_3SiCH_2CH_2O$), 1.48–2.11 (14 s, 42 H, 13 AcO and 1 AcN), 2.45 (dd, 1 H, J_{gem} 12.4, $J_{3eq,4}$ 4.4 Hz, H-3e*eq*), 3.83 (s, 3 H, MeO), 5.37 (br d, 1 H, $J_{3,4}$ 3.42 Hz, H-4d), 5.64 (m, 1 H, H-8e), and 7.16–8.18 (m, 15 H, 3 Ph). Anal. Calcd for $C_{88}H_{111}NO_{45}Si$ (1930.9): C, 54.74; H, 5.79; N, 0.73. Found: C, 54.45; H, 5.51; N, 0.50.

O-*(Methyl 4,5,7,8,9-penta-*O*-acetyl-3-deoxy-*D-glycero-*α*-D-galacto*-2-nonulopyranosylonate)-(2 → 3)-*O*-(2,4,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-(1 → 3)-*O*-(2-acetamido-4,6-di-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-acetyl-β-*D*-galactopyranosyl)-(1 → 4)-2,3,6-tri-*O*-acetyl-*D*-glucopyranose* (**11**).—To a solution of **10** (80 mg, 41 μmol) in CH_2Cl_2 (0.5 mL) cooled to 0°C was added CF_3CO_2H (1.2 mL), and the mixture was stirred for 5 h at 0°C. The reaction was monitored by TLC, and when it was complete EtOAc (3 mL) was added and the solution was concentrated. Column chromatography (30:1 CH_2Cl_2–MeOH) of the residue on silica gel (50 g) gave **11** (75.9 mg, quantitative) as an amorphous mass; $[\alpha]_D$ +15° (*c* 1.7, $CHCl_3$); ν 3400 (NH, OH), 1740 and 1230 (ester), 1680 and 1540 (amide), and 720 cm ^{1}(Ph). Anal. Calcd for $C_{83}H_{99}NO_{45}$ (1830.7): C, 54.46; H, 5.45; N, 0.77. Found: C, 54.30; H, 5.36; N, 0.56.

*O-(Methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-*D-glycero-*α*-D-galacto-*2-nonulopyranosylonate)-(2 → 3)-O-(2,4,6-tri-O-benzoyl-β-D-galactopyranosyl)-(1 → 3)-O-(2-acetamido-4,6-di-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-O-(2,4,6-tri-O-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-O-acetyl-D-glucopyranosyl trichloroacetimidate* (**12**).-To a stirred solution of **11** (73.7 mg, 40 μmol) in CH_2Cl_2 (0.6 mL) cooled to −5°C was added trichloroacetonitrile (0.5 mL), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 30 mg), and Drierite (30 mg), and the mixture was stirred for 1 h at 0°C then directly applied to a column of silica gel (50 g) eluted with 30:1 CH_2Cl_2–MeOH. Concentration of the eluate gave **12** (73.6 mg, 93%) as an amorphous mass; $[\alpha]_D$ +36° (c 1.3, $CHCl_3$); ν 3350 (NH), 1740 and 1230 (ester), 1680 and 1540 (amide), and 720 cm^{-1} (Ph); ^{1}H NMR ($CDCl_3$): δ 1.48–2.22 (14 s, 42 H, 13 AcO and 1 AcN), 2.50 (dd, 1 H, J_{gem} 12.6, $J_{3eq,4}$ 4.9 Hz, H-3e*eq*), 3.83 (s, 3 H, MeO), 5.04 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 10.1 Hz, H-2a), 5.50 (t, 1 H, $J_{3,4}$ 10.1 Hz, H-3a), 5.64 (m, 1 H, H-8e), 6.48 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1a), 7.43-8.19 (m, 15 H, 3 Ph), and 8.65 (s, 1 H, C = N*H*). Anal. Calcd for $C_{85}H_{99}Cl_3N_2O_{45}$ (1975.1): C, 51.69; H, 5.05; N, 1.42. Found: C, 51.64; H, 4.96; N, 1.13.

*2-(Trimethylsilyl)ethyl O-(methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-*D-glycero-*α*-D-galacto-*2-nonulopyranosylonate)-(2 → 3)-O-(2,4,6-tri-O-benzoyl-β-D-galactopyranosyl)-(1 → 4)-O-(2-acetamido-3,6-di-O-benzyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-O-(2,4,6-tri-O-benzyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-O-benzyl-β-D-glucopyranoside* (**13**).—To a solution of **4** (218 mg, 0.22 mmol) and **7** (200 mg, 0.15 mmol) in CH_2Cl_2 (3 mL) was added 4A-MS (600 mg), and the mixture was stirred for 6 h at room temperature, then cooled to 0°C. A mixture of DMTST (226 mg, 0.88 mmol) and 4A-MS (217 mg) was added, and the mixture was stirred for 48 h at 8°C, with monitoring by TLC. The solids were collected and washed with CH_2Cl_2, and the combined filtrate was washed with M Na_2CO_3 and water, dried (Na_2SO_4), and concentrated. Column chromatography (1:2 EtOAc–hexane) of the residue on silica gel (50 g) gave **13** (281 mg, 83%) as an amorphous mass; $[\alpha]_D$ +10° (c 0.86, $CHCl_3$); ν 3400 (NH), 1750 and 1550 (ester), 1670 and 1560 (amide), 860 and 840 (Me_3Si), and 740 and 720 cm $-^{1}$ (Ph); ^{1}H NMR ($CDCl_3$): 8 0.97 (m, 2 H, $Me_3SiCH_2CH_2O$), 1.42–2.15 (6 s, 18 H, 5 AcO and 1 AcN), 2.52 (dd, 1 H, J_{gem} 12.8, $J_{3eq,4}$ 4.9 Hz, H-3e*eq*), 3.84 (s, 3 H, MeO), 5.08 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1d), 5.14 (d, 1 H, $J_{NH,CH}$ 8.9 Hz, NH), 5.24 (dd, 1 H, $J_{6,7}$ 2.7, $J_{7,8}$ 10.1 Hz, H-7e), 5.38 (br d, 1 H, $J_{3,4}$ 3.4 Hz, H-4d), 5.47 (dd, 1 H, $J_{2,3}$ 10.1 Hz, H-2d), 5.70 (m, 1 H, H-8e), and 7.08–8.23 (m, 55 H, 11 Ph). Anal. Calcd for $C_{128}H_{143}NO_{37}Si$ (2315.6): C, 66.39; H, 6.22; N, 0.60. Found: C, 66.54; H, 5.77; N, 0.58.

*2-(Trimethylsilyl)ethyl O-(methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-*D-glycero-*α*-D-galacto-*2-nonulopyranosylonate)-(2 → 3)-O-(2,4,6-tri-O-benzoyl-β-D-galactopyranosyl)-(1 → 4)-O-(2-acetamido-3,6-di-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-O-(2,4,6-tri-O-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside* (**14**).—A solution of **13** (311 mg, 0.13 mmol) in EtOH (45 mL) and AcOH (7.8 mL) was hydrogenolysed in the presence of 10% Pd–C (370 mg) for 48 h at 40°C, then filtered and concentrated. The residue was acetylated with Ac_2O (5 mL) and pyridine (10 mL) for 12 h at 40°C. Column chromatography (80:1 CH_2Cl_2–MeOH) of the product on silica gel (80 g) gave **14** (217 mg, 84%) as an amorphous mass; $[\alpha]_D$ +17° (*c* 0.61, $CHCl_3$); ν 3400 (NH), 1750 and 1230 (ester), 1670 and 1540 (amide), 860 and 840 (Me_3Si), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 0.98 (m, 2 H, $Me_3SiCH_2CH_2O$), 1.42–2.15 (14 s, 42 H, 13 AcO and 1 AcN), 2.52 (dd, 1 H, J_{gem} 12.8, $J_{3eq,4}$ 4.9 Hz, H-3e*eq*), 3.83 (s, 3 H, MeO), 5.65 (m, 1 H, H-8e), and 7.48–8.19 (m, 15 H, 3 Ph). Anal. Calcd for $C_{88}H_{111}NO_{45}Si$ (1930.9): C, 54.74; H, 5.79; N, 0.73. Found: C, 54.58; H, 5.58; N, 0.43.

*O-(Methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-*D-glycero-*α*-D-galacto*-2-nonulopyranosylonate)-(2 → 3)-O-(2,4,6-tri-O-benzoyl-β-*D*-galactopyranosyl)-(1 → 4)-O-(2-acetamido-3,6-di-O-acetyl-2-deoxy-β-*D*-glucopyranosyl)-(1 → 3)-O-(2,4,6-tri-O-acetyl-β-*D*-galactopyranosyl)-(1 → 4)-2,3,6-tri-O-acetyl-*D*-glucopyranose* (**15**).—To a solution of **14** (73.3 mg, 38 μmol) in CH_2Cl_2 (0.5 mL) cooled to 0°C was added CF_3CO_2H (1.2 mL), and the mixture was stirred for 5 h at 0°C. The reaction was monitored by TLC, and when it was complete EtOAc (3 mL) was added and the solution was concentrated. Column chromatography (30:1 CH_2Cl_2–MeOH) of the residue on silica gel (50 g) gave **15** (69.5 mg, quantitative) as an amorphous mass; ν 3400 (NH, OH), 1740 and 1230 (ester), 1670 and 1560 (amide), and 710 cm^{-1} (Ph). Anal. Calcd for $C_{83}H_{99}NO_{45}$ (1830.7): C, 54.46; H, 5.45; N, 0.77. Found: C, 54.18; H, 5.41; N, 0.64.

*O-(Methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-*D-glycero-*α*-D-galacto*-2-nonulopyranosylonate)-(2 → 3)-O-(2,4,6-tri-O-benzoyl-β-*D*-galactopyranosyl)-(1 → 4)-O-(2-acetamido-3,6-di-O-acetyl-2-deoxy-β-*D*-glucopyranosyl)-(1 → 3)-O-(2,4,6-tri-O-acetyl-β-*D*-galactopyranosyl)-(1 → 4)-2,3,6-tri-O-acetyl-α-*D*-glucopyranosyl trichloroacetimidate* (**16**).—To a stirred solution of **15** (69.5 mg, 38 μmol) in CH_2Cl_2 (0.6 mL) cooled to −5°C was added trichloroacetonitrile (0.5 mL), DBU (30 mg), and Drierite (100 mg), and the mixture was stirred for 1 h at 0°C then directly applied to a column of silica gel (50 g) eluted with 30:1 CH_2Cl_2–MeOH, to give **16** (66.0 mg, 88%) as an amorphous mass; $[\alpha]_D$ +36° (*c* 1.3, $CHCl_3$); ν 3350 (NH), 1750 and 1230 (ester), 1680 and 1540 (amide), and 720 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): δ 1.45–2.14 (14 s, 42 H, 13 AcO and 1 AcN), 2.51 (dd, 1 H, J_{gem} 12.6, $J_{3eq,4}$ 4.8 Hz, H-3e*eq*), 4.58 (t, 1 H, $J_{4,5} = J_{5,6} = 10.3$ Hz, H-5e), 5.04 (dd, 1 H, $J_{1,2}$ 3.8, $J_{2,3}$ 10.1 Hz, H-2a), 5.50 (t, 1 H, $J_{3,4}$ 10.1 Hz, H-3a), 5.64 (m, 1 H, H-8e), 6.47 (d, 1 H, H-1a), 7.46–8.17 (m, 15 H, 3 Ph), and 8.65 (s, 1 H, C = N*H*). Anal. Calcd for $C_{85}H_{99}Cl_3N_2O_{45}$ (1975.1): C, 51.69; H, 5.05; N, 1.42. Found: C, 51.61; H, 4.88; N, 1.19.

*2-(Trimethylsilyl)ethyl O-(methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-*D-glycero-*α*-D-galacto*-2-nonulopyranosylonate)-(2 → 3)-O-(*2,4,6-tri-O*-benzoyl-β-*D*-galactopyranosyl)-(1 → 4)-O-[(2,3,4-tri-O-benzyl-α-*L*-fucopyranosyl-(1 → 3)]-O-(2-acetamido-6-O-benzyl-2-deoxy-β-*D*-glucopyranosyl)-(1 → 3)-O-(2,4,6-tri-O-benzyl-β-*D*-galactopyranosyl)-(1 → 4)-2,3,6-tri-O-benzyl-β-*D*-glucopyranoside* (**17**).—To a solution of **4** (653 mg, 0.65 mmol) and **8** (464 mg, 0.27 mmol) in CH_2Cl_2 (2.5 mL) was added 4A-MS (1.5 g), and the mixture was stirred for 6 h at room temperature, then cooled to 0°C. A mixture of DMTST (846 mg, 3.3 mmol) and 4A-MS (850 mg) was added, and the suspension was stirred for 48 h at 8°C, while the reaction was monitored by

TLC. The solids were collected and washed with CH_2Cl_2, and the combined filtrate was washed with M Na_2CO_3 and water, dried (Na_2SO_4), and concentrated. Column chromatography (1:2 EtOAc–hexane) of the residue on silica gel (80 g) gave **17** (334.5 mg, 46%) as an amorphous mass; $[\alpha]_D$ +12° (*c* 1.8, $CHCl_3$); ν 3400 (NH), 1750 and 1540 (ester), 1670 and 1560 (amide), 860 and 840 (Me_3Si), and 740 and 710 cm^{-1} (Ph); ^{1}H NMR ($CDCl_3$): δ 0.98 (m, 2 H, $Me_3SiCH_2CH_2O$), 1.02 (d, 3 H, $J_{5,6}$ 6.7 Hz, H-6d), 1.46–2.24 (6 s, 18 H, 5 AcO and 1 AcN), 2.50 (dd, 1 H, J_{gem} 12.8, $J_{3eq,4}$ 4.9 Hz, H-3f*eq*), 3.88 (s, 3 H, MeO), 4.97 (d, 1 H, $J_{1,2}$ 3.1 Hz, H-1d), 5.22 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1e), 5.31 (dd, 1 H, $J_{6,7}$ 2.8, $J_{7,8}$ 9.8 Hz, H-7f), 5.47 (br d, 1 H, $J_{3,4}$ 3.1 Hz, H-4e), 5.62 (m, 1 H, H-8f), 5.68 (dd, 1 H, $J_{2,3}$ 10.1 Hz, H-2e), and 7.03–8.05 (m, 65 H, 13 Ph). Anal. Calcd for $C_{148}H_{165}NO_{41}Si$ (2642.0): C, 67.28; H, 6.30; N, 0.53. Found: C, 67.28; H, 6.20; N, 0.42.

*2-(Trimethylsilyl)ethyl O-(methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-*D-glycero-*α*-D-galacto-*2-nonulopyranosylonate)-(2 → 3)-O-(2,4,6-tri-O-benzoyl-β-D-galactopyranosyl)-(1 → 4)-O-[(2,3,4-tri-O-acetyl-α-L-fucopyranosyl-(1 → 3)]-O-(2-acetamido-6-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-O-(2,4,6-tri-O-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-O-acetyl-β-D-glucopyranoside* (**18**).—A solution of **17** (100 mg, 38 μmol) in EtOH (13 mL) and AcOH (4.8 mL) was hydrogenolysed in the presence of 10% Pd–C (87 mg) for 48 h at 40°C, then filtered and concentrated. The residue was acetylated with Ac_2O (4 mL) and pyridine (8 mL) for 12 h at 40°C. Column chromatography (50:1 CH_2Cl_2–MeOH) of the product on silica gel (50 g) gave **18** (65.8 mg, 80%) as an amorphous mass; $[\alpha]_D$ −22° (*c* 0.75, $CHCl_3$); ν 3400 (NH), 1750 and 1230 (ester), 1670 and 1550 (amide), 860 and 840 (Me_3Si), and 710 cm^{-1} (Ph); ^{1}H NMR ($CDCl_3$): δ 0.95 (m, 2 H, $Me_3SiCH_2CH_2O$), 1.20 (d, 3 H, $J_{5,6}$ 6.6 Hz, H-6d), 1.53–2.13 (16 s, 48 H, 15 AcO and 1 AcN), 2.49 (dd, 1 H, J_{gem} 12.8, $J_{3eq,4}$ 4.8 Hz, H-3f*eq*), 3.84 (s, 3 H, MeO), 4.98 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1d), 5.16 (d, 1 H, $J_{1,2}$ 9.4 Hz, H-1e), 5.68 (m, 1 H, H-8f), and 7.45–8.16 (m, 15 H, 3 Ph). Anal. Calcd for $C_{98}H_{125}NO_{51}Si$ (2161.1): C, 54.47; H, 5.83; N, 0.65. Found: C, 54.18; H, 5.82; N, 0.54.

*O-(Methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-*D-glycero-*α*-D-galacto-*2-nonulopyranosylonate)-(2 → 3)-O-(2,4,6-tri-O-benzoyl-β-D-galactopyranosyl)-(1 → 4)-O-[(2,3,4-tri-O-acetyl-α-L-fucopyranosyl)-(1 → 3)]-O-(2-acetamido-6-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-O-(2,4,6-tri-O-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-tri-O-acetyl-D-glucopyranose* (**19**).—To a solution of **18** (57.8 mg, 27 μmol) in CH_2Cl_2 (1.5 mL) cooled to 0°C was added CF_3CO_2H (3 mL), and the mixture was stirred for 5 h at 0°C. The reaction was monitored by TLC, and when it was complete EtOAc (5 mL) was added and the solution was concentrated. Column chromatography (40:1 CH_2Cl_2–MeOH) of the residue on silica gel (50 g) gave **19** (48.6 mg, 88%) as an amorphous mass; ν 3400 (NH, OH), 1750 and 1230 (ester), 1680 and 1560 (amide), and 710 cm^{-1} (Ph). Anal. Calcd for $C_{93}H_{113}NO_{51}$ (2060.9): C, 54.20; H, 5.53; N, 0.68. Found: C, 54.05; H, 5.33; N, 0.59.

*O-(Methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-*D-glycero-*α*-D-galacto-*2-nonulopyranosylonate)-(2 → 3)-O-(2,4,6-tri-O-benzoyl-β-D-galactopyranosyl)-(1 → 4)-O-[(2,3,4-tri-O-acetyl-α-L-fucopyranosyl)-(1 → 3)]-O-(2-acetamido-6-O-acetyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-O-(2,4,6-tri-O-acetyl-β-D-galactopyranosyl)-(1 → 4)-2,3,6-*

*tri-O-acetyl-*D*-glucopyranosyl trichloroacetimidate* (**20**).—To a stirred solution of **19** (48.6 mg, 24 μmol) in CH_2Cl_2 (0.7 mL) cooled to −5°C were added trichloroacetonitrile (0.3 mL), DBU (30 mg), and Drierite (200 mg), then the mixture was stirred for 1 h at 0°C and directly applied to a column of silica gel (40 g) eluted with 40:1 CH_2Cl_2–MeOH, to give **20** (44.5 mg, 86%) as an amorphous mass; $[\alpha]_D$ +4.1° (*c* 0.73, $CHCl_3$); *ν* 3400 (NH), 1740 and 1230 (ester), 1680 and 1540 (amide), and 720 cm^{-1} (Ph); ^{1}H NMR ($CDCl_3$): δ 1.21 (d, 3 H, $J_{5,6}$ 6.4 Hz, H-6d), 1.52–2.35 (16 s, 48 H, 15 AcO and 1 AcN), 1.54 (t, 1 H, $J_{gem} = J_{3ax,4}$ = 12.8 Hz, H-3f*ax*), 2.47 (dd, 1 H, $J_{3eq,4}$ 4.8 Hz, H-3f*eq*), 3.49 (dd, 1 H, $J_{2,3}$ 9.9, $J_{3,4}$ 3.7 Hz, H-3e), 3.84 (s, 3 H, MeO), 5.04 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 10.1 Hz, H-2a), 5.30 (dd, 1 H, $J_{6,7}$ 2.9, $J_{7,8}$ 10.3 Hz, H-7f), 5.51 (t, 1 H, $J_{1,2} = J_{2,3}$ = 9.9 Hz, H-2e), 5.67 (m, 1 H, H-8f), 6.47 (d, 1 H, H-1a), 7.15–8.12 (m, 15 H, 3 Ph), and 8.65 (s, 1 H, C = N*H*). Anal. Calcd for $C_{95}H_{113}Cl_3N_2O_{51}$ (2205.3): C, 51.74; H, 5.17; N, 1.27. Found: C, 51.47; H, 5.07; N, 1.25.

O-*(Methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-*D-glycero-α-D-galacto-*2-nonulopyranosylonate)-(2 → 3)-O-(2,4,6-tri-O-benzoyl-β-*D*-galactopyranosyl)-(1 → 3)-O-(2-acetamido-6-O-acetyl-2-deoxy-β-*D*-glucopyranosyl)-(1 → 3)-O-(2,4,6-tri-O-acetyl-β-*D*-galactopyranosyl)-(1 → 4)-2,3,6-tri-O-acetyl-β-*D*-glucopyranosyl)-(1 → 1)-(2*S,3R,4E*)-2-azido-3-O-benzoyl-4-octadecene-1,3-diol* (**22**).—To a solution of **12** (58.9 mg, 30 μmol) and (2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol (**21**; 25.6 mg, 60 μmol) in CH_2Cl_2 (1 mL) were added 4A-MS (600 mg) and the mixture was stirred for 5 h at room temperature, then cooled to 0°C. Boron trifluoride etherate (0.02 mL) was added to the mixture, and this was stirred for 6 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_2 and water, dried (Na_2SO_4), and concentrated. Column chromatography (100:1 CH_2Cl_2–MeOH) of the residue on silica gel (30 g) gave **22** (39.6 mg, 59%) as an amorphous mass; $[\alpha]_D$ +11° (*c* 1.0, $CHCl_3$); *ν* 3400 (NH), 2100 (azido), 1740 and 1230 (ester), 1670 and 1550 (amide), and 720 cm^{-1} (Ph); ^{1}H NMR ($CDCl_3$): (sphingosine) δ 0.88 (t, 3 H, C*H*3), 1.24 (s, 22 H, 11 CH_2), 5.92 (dt, 1 H, $J_{4,5}$ 14.3, $J_{5,6} = J_{5,6'}$ = 6.8 Hz, H-5); (pentasaccharide) δ 1.60 (t, 1 H, $J_{gem} = J_{3ax,4}$ = 12.6 Hz, H-3e*ax*), 1.47–2.18 (14 s, 42 H, 13 AcO and 1 AcN), 2.48 (dd, 1 H, $J_{3eq,4}$ 4.3 Hz, H-3e*eq*), 3.83 (s, 3 H, MeO), 4.49 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), and 7.41–8.18 (m, 20 H, 4 Ph). Anal. Calcd for $C_{108}H_{136}N_4O_{47}$ (2242.3): C, 57.85; H, 6.11; N, 2.50. Found: C, 57.28; H, 5.83; N, 2.28.

O-*(Methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-*D-glycero-α-D-galacto-*2-nonulopyranosylonate)-(2 → 3)-O-(2,4,6-tri-O-benzoyl-β-*D*-galactopyranosyl)-(1 → 3)-O-(2-acetamido-4,6-di-O-acetyl-2-deoxy-β-*D*-glucopyranosyl)-(1 → 3)-O-(2,4,6-tri-O-acetyl-β-*D*-galactopyranosyl)-(1 → 4)-2,3,6-tri-O-acetyl-β-*D*-glucopyranosyl)-(1 → 1)-(2*S,3R, 4E*)-3-benzoyl-2-octadecanamido-4-octadecene-1,3-diol* (**23**).—Hydrogen sulfide was bubbled through a solution of **22** (58.9 mg, 26 μmol) in pyridine (10 mL) and water (2 mL) for 72 h while the solution was stirred at 0°C. The course of the reaction was monitored by TLC. The mixture was concentrated to a syrup, which was dissolved in dry CH_2Cl_2 (2 mL). Octadecanoic acid (10 mg, 35 μmol) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (WSC; 7.0 mg, 37 μmol) were added to the solution, and the mixture was stirred overnight at room temperature. Dichloromethane (30 mL) was added, and the solution was washed with water, dried (Na_2SO_4), and concentrated. Column chromatography (60:1 CH_2Cl_2–MeOH) of the residue on silica gel (30 g) afforded **23** (58.0 mg, 89%) as an amorphous mass; $[\alpha]_D$ +20° (*c* 0.79, $CHCl_3$); ν 3400 (NH), 2950 and 2900 (methyl, methylene), 1750 and 1230 (ester), 1680 and 1540 (amide), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): (ceramide) δ 0.88 (t, 6 H, 2 CH_3), 1.24 (s, 52 H, 26 CH_2), 5.73 (d, 1 H, $J_{NH,CH}$ 9.2 Hz, N*H*), 5.86 (dt, 1 H, $J_{4,5}$ 14.8, $J_{5,6} = J_{5,6'}$ = 6.4 Hz, H-5); (pentasaccharide) δ 1.47–2.18 (14 s, 42 H, 13 AcO and 1 AcN), 2.50 (dd, 1 H, J_{gem} 12.4, $J_{3eq,4}$ 4.8 Hz, H-3e*eq*), 3.83 (s, 3 H, MeO), 5.64 (m, 1 H, H-8e), and 7.41–8.18 (m, 20 H, 4 Ph). Anal. Calcd for $C_{126}H_{172}N_2O_{48}$ (2482.7): C, 60.96; H, 6.98; N, 1.13. Found: C, 60.95; H, 6.89; N, 0.85.

O-*(3-Deoxy-*D-glycero-α-D-galacto-*2-nonulopyranosylonic acid)-(2 → 3)-*O-*β-*D-*galactopyranosyl-(1 → 3)-*O-*(2-acetamido-2-deoxy-β-*D-*glucopyranosyl)-(1 → 3)-*O-*β-*D-*galactopyranosyl-(1 → 4)-*O-*β-*D-*glucopyranosyl-(1 → 1)-(2*S,*3*R,*4*E*)-2-octadecanamido-4-octadecene-1,3-diol* (**24**).—To a solution of **23** (38.5 mg, 16 μmol) in MeOH (5 mL) was added NaOMe (30 mg), and the mixture was stirred for 8 h at room temperature; the course of the reaction was monitored by TLC (4:2:2 BuOH–EtOH–H_2O). Potassium hydroxide (0.2 M, 5 mL) was added to the mixture and this was stirred for 12 h at room temperature, neutralized with Dowex-50 (H^+) resin, and filtered. The resin was washed with 1:1 H_2O–MeOH, and combined filtrate and washings was concentrated to a syrup that was chromatographed on a column of Sephadex LH-20 (50 g) with 5:4:0.7 $CHCl_3$–MeOH–H_2O to give **24** (21.6 mg, 93%) as an amorphous mass; $[\alpha]_D$ −6.8° (*c* 0.2, 1:1 $CHCl_3$–MeOH); ν 3500–3300 (OH, NH), 2940 and 2840 (methyl, methylene), 1715 (COOH), and 1660 and 1550 cm^{-1} (amide); ^1H NMR [55°C, 49:1 $(CD_3)_2SO$–D_2O]: δ 0.95 (t, 6 H, 2CH_3), 1.34 (s, 52 H, 26 CH_2), 1.55 (t, 2 H, COCH_2CH_2), 2.73 (dd, 1 H, J_{gem} 12.8, $J_{3eq,4}$ 4.7 Hz, H-3*eq*), 4.26 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 4.38 (d, 1 H, $J_{1,2}$ 7.2 Hz, H-1d), 4.68 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1b), 4.81 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1c), 5.46 (dd, 1 H, $J_{3,4}$ 7.6, $J_{4,5}$ 14.8 Hz, H-4 of ceramide), and 5.65 (dt, 1 H, $J_{5,6} = J_{5,6'}$ = 6.8 Hz, H-5 of ceramide). Anal. Calcd for $C_{71}H_{128}N_2O_{31}$ (1505.8): C, 56.63; H, 8.57; N, 1.86. Found: C, 56.47; H, 8.47; N, 1.82.

O-*(Methyl 4,5,7,8,9-penta-*O*-acetyl-3-deoxy-*D-glycero-α-D-galacto-*2-nonulopyranosylonate)-(2 → 3)-*O-*(2,4,6-tri-*O*-benzoyl-β-*D-*galactopyranosyl)-(1 → 4)-*O-*(2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-*D-*glucopyranosyl)-(1 → 3)-*O-*(2,4,6-tri-*O*-acetyl-β-*D-*galactopyranosyl)-(1 → 4)-*O-*2,3,6-tri-*O*-acetyl-β-*D-*glucopyranosyl)-(1 → 1)-(2*S,3R,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol* (**25**).—To a solution of **16** (56.1 mg, 28 μmol) and **21** (24.4 mg, 57 μmol) in CH_2Cl_2 (1 mL) was added 4A-MS (600 mg), and the mixture was stirred for 5 h at room temperature then cooled to 0°C. Boron trifluoride etherate (0.02 mL) was added to the mixture, and this was stirred for 6 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 (100:1 CH_2Cl_2–MeOH) of the residue on silica gel (30 g) gave **25** (41.0 mg, 64%) as an amorphous mass; $[\alpha]_D$ +6.5° (*c* 0.92, $CHCl_3$); ν

3400 (NH), 2100 (azide), 1750 and 1230 (ester), 1650 and 1550 (amide), and 710 cm^{-1} (Ph); ^{1}H NMR (CDCl$_3$): (sphingosine) δ 0.88 (t, 3 H, C*H*3), 1.25 (s, 22 H, 11 C*H*$_2$), 5.91 (dt, 1 H, $J_{4,5}$ 14.6, $J_{5,6} = J_{5,6'} = 6.7$ Hz, H-5); (pentasaccharide) δ 1.48–2.14 (14 s, 42 H, 13 AcO and 1 AcN), 2.52 (dd, 1 H, J_{gem} 12.8, $J_{3eq,4}$ 4.8 Hz, H-4e*eq*), 3.82 (s, 3 H, MeO), 4.49 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1a), 5.65 (m, 1 H, H-8e), and 7.45–8.18 (m, 20 H, 4 Ph). Anal. Calcd for $C_{108}H_{136}N_4O_{47}$ (2242.3): C, 57.85; H, 6.11; N, 2.50. Found: C, 57.33; H, 5.81; N, 2.37.

O-*(Methyl 4,5,7,8,9-penta-*O*-acetyl-3-deoxy-*D-glycero-α-D-galacto*-2-nonulopyranosylonate)-(2 → 3)-*O*-(2,4,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-(1 → 4)-*O*-(2-acetamido-3,6-di-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-acetyl-β-*D*-galactopyranosyl)-(1 → 4)-*O*-(2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl)-(1 → 1)-(2*S, 3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol* (**26**).—Hydrogen sulfide was bubbled through a solution of **25** (48.8 mg, 22 μmol) in pyridine (10 mL) and water (2 mL) for 72 h while the solution was stirred at 0°C. The course of the reaction was monitored by TLC. The mixture was concentrated to a syrup, which was dissolved in dry CH$_2$Cl$_2$ (2 mL). Octadecanoic acid (12.4 mg, 44 μmol) and WSC (8.34 mg, 44 μmol) were added to the solution, and the mixture was stirred overnight at room temperature. Dichloromethane (30 mL) was added, and the solution was washed with water, dried (Na$_2$SO$_4$), and concentrated. Column chromatography (60 : 1 CH$_2$Cl$_2$–MeOH) of the residue on silica gel (30 g) afforded **26** (38.8 mg, 72%) as an amorphous mass; $[\alpha]_D$ +11° (*c* 0.79, CHCl$_3$); ν 3400 (NH), 2950 and 2900 (methyl, methylene), 1750 and 1230 (ester), 1670 and 1560 (amide), and 720 cm^{-1} (Ph); ^{1}H NMR (CDCl$_3$): (ceramide) δ 0.88 (t, 6 H, 2 C*H*$_3$), 1.25 (s, 52 H, 26 C*H*$_2$), 5.73 (d, 1 H, $J_{NH,CH}$ 9.3 Hz, N*H*), 5.86 (dt, 1 H, $J_{4,5}$ 14.6, $J_{5,6} = J_{5,6'} = 6.8$ Hz, H-5); (pentasaccharide) δ 1.48–2.14 (14 s, 42 H, 13 AcO and 1 AcN), 2.52 (dd, 1 H, J_{gem} 12.5, $J_{3eq,4}$ 4.6 Hz, H-3e*eq*), 3.82 (s, 3 H, MeO), 5.70 (m, 1 H, H-8e), and 7.40–8.18 (m, 20 H, 4 Ph). Anal. Calcd for $C_{126}H_{172}N_2O_{48}$ (2482.7): C, 60.96; H, 6.98; N, 1.13. Found: C, 60.91; H, 6.81; N, 0.81.

O-*(3-Deoxy-*D-glycero-α-D-galacto*-2–nonulopyranosylonic acid)-(2 → 3)-*O*-β-*D*-galactopyranosyl-(1 → 4)-*O*-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1 → 3)-*O*-β-*D*-galactopyranosyl-(1 → 4)-*O*-β-*D*-glucopyranosyl-(1 → 1)-(2*S*,3*R*,4*E*)-2-octadecanamido-4-octadecene-1,3-diol* (**27**).—To a solution of **26** (38.5 mg, 16 μmol) in MeOH (5 mL) was added NaOMe (30 mg), and the mixture was stirred for 8 h at room temperature; the course of the reaction was monitored by TLC (4 : 2 : 2 BuOH–EtOH–H$_2$O). Potassium hydroxide (0.2 M, 5 mL) was added to the mixture, and this was stirred for 12 h at room temperature, neutralized with Dowex-50 (H$^+$) resin, and filtered. The resin was washed with 1 : 1 H$_2$O–MeOH, and combined filtrate and washings was concentrated to a syrup that was chromatographed on a column of Sephadex LH-20 (50 g) with 5 : 4 : 0.7 CHCl$_3$–MeOH–H$_2$O to give **27** (20.6 mg, 88%) as an amorphous mass; $[\alpha]_D$ −10.6° (*c* 0.2, 1 : 1 CHCl$_3$–MeOH); ν 3500–3300 (OH, NH), 2940 and 2840 (methyl, methylene), 1720 (COOH), and 1660 and 1540 cm^{-1} (amide); ^{1}H NMR [55°C, 49 : 1 (CD$_3$)$_2$SO–D$_2$O]: δ 0.95 (t, 6 H, 2C*H*$_3$), 1.33 (s, 52 H, 26 C*H*$_2$), 1.54 (t, 2 H, COC*H*$_2$CH$_2$), 2.71 (dd, 1 H, J_{gem} 12.9, $J_{3eq,4}$ 5.0 Hz, H-3e*eq*), 4.26 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1a), 4.37 (d, 1 H, $J_{1,2}$ 7.0 Hz, H-1d), 4.65 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1b), 4.76 (d, 1 H, $J_{1,2}$ 7.6 Hz, H-1c), 5.45 (dd, 1 H, $J_{3,4}$ 7.8, $J_{4,5}$ 15.0 Hz, H-4 of ceramide), and 5.64 (dt, 1 H, $J_{5,6} = J_{5,6'} = 7.0$ Hz, H-5 of ceramide). Anal. Calcd for $C_{71}H_{128}N_2O_{31}$ (1505.8): C, 56.63; H, 8.57; N, 1.86. Found: C, 56.60; H, 8.29; N, 1.58.

O-*(Methyl 4,5,7,8,9-penta-*O*-acetyl-3-deoxy-*D-glycero-α-D-galacto-*2-nonulopyranosylonate)-(2 → 3)-*O*-(2,4,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-(1 → 4)-*O*-[(2,3,4-tri-*O*-acetyl-α-*L*-fucopyranosyl)-(1 → 3)]-*O*-(2-acetamido-6-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-acetyl-β-*D*-galactopyranosyl)-(1 → 4)-*O*-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl)-(1 → 1)-(2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol* (**28**).—To a solution of **20** (36.6 mg, 17 μmol) and **21** (14.5 mg, 34 μmol) in CH_2Cl_2 (0.7 mL) was added 4A-MS (300 mg), and the mixture was stirred for 5 h at room temperature then cooled to 0°C. Boron trifluoride etherate (0.04 mL) was added to the mixture, and this was stirred for 6 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 (60:1 CH_2Cl_2–MeOH) of the residue on silica gel (30 g) gave **28** (21.0 mg, 51%) as an amorphous mass; $[\alpha]_D$ −18° (*c* 0.70, $CHCl_2$); ν 3400 (NH), 2100 (azide), 1740 and 1230 (ester), 1660 and 1550 (amide), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_2$): (ceramide) δ 0.88 (t, 3 H, CH_3), 1.24 (s, 22 H, 11 CH_2), 5.89 (dt, 1 H, $J_{4,5}$ 13.4, $J_{5,6} = J_{5,6'} = 6.4$ Hz, H-5); (pentasaccharide) δ 1.43–2.12 (16 s, 48 H, 15 AcO and 1 AcN), 2.47 (dd, 1 H, J_{gem} 12.6, $J_{3eq,4}$ 4.9 Hz, H-3*eq*), 3.45 (dd, 1 H, $J_{2,3}$ 10.4, $J_{3,4}$ 3.5 Hz, H-3e), 3.84 (s, 3 H, MeO), 4.50 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1a), 5.22 (br d, 1 H, H-4e), 5.68 (m, 1 H, H-8f), and 7.42–8.16 (m, 20 H, 4 Ph). Anal. Calcd for $C_{118}H_{150}N_4O_{53}$ (2472.5): C, 57.32; H, 6.12; N, 2.27. Found: C, 57.23; H, 5.83; N, 2.26.

O-*(Methyl 4,5,7,8,9-penta-*O*-acetyl-3-deoxy-*D-glycero-α-D-galacto-*2-nonulopyranosylonate)-(2 → 3)-*O*-(2,4,6-tri-*O*-benzoyl-β-*D*-galactopyranosyl)-(1 → 4)-*O*-[(2,3,4-tri-*O*-acetyl-α-*L*-fucopyranosyl)-(1 → 3)]-*O*-(2-acetamido-6-*O*-acetyl-2-deoxy-β-*D*-glucopyranosyl)-(1 → 3)-*O*-(2,4,6-tri-*O*-acetyl-β-*D*-galactopyranosyl)-(1 → 4)-*O*-2,3,6-tri-*O*-acetyl-β-*D*-glucopyranosyl)-(1 → 1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol* (**29**).—Hydrogen sulfide was bubbled through a solution of **28** (21.0 mg, 8.5 μmol) in pyridine (10 mL) and water (2 mL) for 72 h while the solution was stirred at 0°C. The course of the reaction was monitored by TLC. The mixture was concentrated to a syrup, which was dissolved in dry CH_2Cl_2 (2 mL). Octadecanoic acid (5.41 mg, 19 μmol and WSC (3.7 mg, 19 μmol) were added to the solution, and the mixture was stirred overnight at room temperature. Dichloromethane (30 mL) was added, and the solution was washed with water, dried (Na_2SO_4), and concentrated. Column chromatography (60:1 CH_2Cl_2–MeOH) of the residue on silica gel (20 g) afforded **29** (21.0 mg, 91%) as an amorphous mass; $[\alpha]_D$ −13° (*c* 0.45, $CHCl_3$); ν 3400 (NH), 2950 and 2900 (methyl, methylene), 1750 and 1230 (ester), 1670 and 1540 (amide), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$): (ceramide) δ 0.88 (t, 6 H, 2 CH_3), 1.25 (s, 52 H, 26 CH_2), 5.86 (dt, 1 H, $J_{4,5}$ 14.8, $J_{5,6} = J_{5,6'} = 6.9$ Hz, H-5); (hexasaccharide) δ 1.53–2.12 (16 s, 48 H, 15 AcO and 1 AcN), 2.47 (dd, 1 H, J_{gem} 12.7, $J_{3eq,4}$ 5.1 Hz, H-3f*eq*), 3.44 (dd, 1 H, $J_{2,3}$ 10.3, $J_{3,4}$ 3.8 Hz, H-3e), 3.83 (s, 3 H, MeO), 4.97 (d, 1 H, H-4e), 5.68 (m, 1 H, H-8f), and 7.43–8.16 (m, 20 H, 4 Ph). Anal. Calcd for $C_{136}H_{186}N_2O_{54}$ (2712.9): C, 60.21; H, 6.91; N, 1.03. Found: C, 59.97; H, 6.77; N, 0.75.

*O-(3-Deoxy-*D-glycero-α-D-galacto*-2-nonulopyranosylonic acid)-(2 → 3)-O-β-*D*-galactopyranosyl-(1 → 4)-O-[α-*L*-fucopyranosyl-(1 → 3)]-O-(2-acetamido-2-deoxy-β-*D*-glucopyranosyl)-(1 → 3)-O-β-*D*-galactopyranosyl-(1 → 4)-O-β-*D*-glucopyranosyl-(1 → 1)-(2*S*,3*R*,4*E*)-2-octadecanamido-4-octadecene-1,3-diol* (**30**).—To a solution of **29** (21 mg, 7.7 μmol) in MeOH (5 mL) was added NaOMe (30 mg), and the mixture was stirred for 8 h at room temperature; the course of the reaction was monitored by TLC (4:2:2 BuOH–EtOH–H_2O). Potassium hydroxide (0.2 M, 5 mL) was added to the mixture, and this was stirred for 12 h at room temperature, neutralized with Dowex-50 (H^+) resin, and filtered. The resin was washed with 1:1 H_2O–MeOH, and the combined filtrate and washings was concentrated to a syrup that was chromatographed on a column of Sephadex LH-20 (50 g) with 5:4:0.7 $CHCl_3$–MeOH–H_2O to give **30** (11.7 mg, 91%) as an amorphous mass; $[\alpha]_D$ −16.0° (*c* 0.2, 1:1 $CHCl_3$–MeOH); ν 3500–3350 (OH, NH), 2940 and 2840 (methyl, methylene), 1720 (COOH), and 1660 and 1540 cm^{-1} (amide); ^1H NMR [55°C, 49:1 $(CD_3)_2SO$–D_2O]: δ 0.95 (t, 6 H, 2CH_3), 1.27 (s, 52 H, 26 CH_2), 1.84 (t, 2 H, COCH_2CH_2), 2.81 (dd, 1 H, J_{gem} 12.9, $J_{3eq,4}$ 4.9 Hz, H-3*eq*), 4.17 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1a), 4.39 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1d), 4.53 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 4.94 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1c), 5.08 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1d), 5.40 (dd, 1 H, $J_{3,4}$ 7.8, $J_{4,5}$ 15.0 Hz, H-4 of ceramide), and 5.59 (dt, 1 H, $J_{5,6} = J_{5,6'} = 6.8$ Hz, H-5 of ceramide). Anal. Calcd for $C_{77}H_{138}N_2O_{35}$ (1651.9): C, 55.99; H, 8.42; N, 1.70. Found: C, 55.83; H, 8.23; N, 1.61.

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