Carbohydrate Research, 230 (1992) 273–288
Elsevier Science Publishers B.V., Amsterdam

Synthesis of a series of ganglioside GM_3 analogs containing a deoxy-*N*-acetylneuraminic acid residue *

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(Received August 19th, 1991; accepted November 26th, 1991)

ABSTRACT

Ganglioside GM_3 analogs containing 4-, 7-, 8-, and 9-deoxy-*N*-acetylneuraminic acids in the place of *N*-acetylneuraminic acid (Neu5Ac) have been synthesized. Glycosylation of 2-(trimethylsilyl)ethyl *O*-(6-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-2,6-di-*O*-benzoyl-β-D-glucopyranoside with the methyl 2-thioglycoside derivatives of the respective deoxy-*N*-acetylneuraminic acids, using dimethyl(methylthio)sulfonium triflate as a promoter, gave the four required 2-(trimethylsilyl)ethyl α-sialosyl-(2 → 3b)-β-lactosides. These were converted via *O*-acetylation, selective removal of the 2-(trimethylsilyl)ethyl group, and subsequent imidate formation, into the corresponding α-sialosyl-(2 → 3b)-α-lactose trichloroacetimidates **15, 17, 19**, and **21**. Glycosylation of (2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol with **15, 17, 19**, and **21** in the presence of boron trifluoride etherate afforded the expected β glycosides, which were transformed in good yields, via selective reduction of the azido group, coupling with octadecanoic acid, *O*-deacylation, and de-esterification, into the target compounds.

INTRODUCTION

Ganglioside GM_3, as well as other gangliosides, is a polymorphous molecule at the sialic acid and ceramide moieties, and it exhibits various important biological functions, serving as the influenza A virus receptor[2], causing induction of monocytic differentiation of human myeloid cells[3], and enhancing or inhibiting protein kinase activity[4]. In view of these facts, it is an interesting substance for further investigation at the molecular level. As previously noted[1], we have achieved a facile, stereoselective α-glycosidation of sialic acids[5], and synthesized a series of gangliosides and their analogs[5]. In order to elucidate the role of the ceramide and sialic acid parts in the functions of GM_3 we synthesized this ganglioside, analogs containing a variety of lipophilic parts in place of the ceramide, and analogs having truncated (C_7, C_8) sialic acids[6].

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* Synthetic Studies on Sialoglycoconjugates, Part 30. For Part 29 see ref. 1.

In the immediately preceding paper[1], we described the methyl 2-thioglycosides of 4-, 7-, 8-, and 9-deoxy-*N*-acetylneuraminic acids. As part of our continuing efforts on the synthesis and structure–function relationship of gangliosides, we describe here the synthesis of ganglioside GM_3 analogs containing the deoxy sialic acids, in order to clarify the structural features of the sialic acid moiety required for the functions of GM_3.

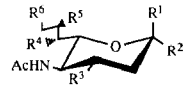
RESULTS AND DISCUSSION

For the synthesis of the desired ganglioside GM_3 analogs we employed the methyl 2-thioglycosides **1–4** of the deoxy-*N*-acetylneuraminic acids[1] as the glycosyl donors and 2-(trimethylsilyl)ethyl *O*-(6-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-2,6-di-*O*-benzoyl-β-D-glucopyranoside[5,7] (**5**) as a suitably protected glycosyl acceptor. The acceptor **5** was coupled with the donors using dimethyl(methylthio)sulfonium triflate[8] (DMTST) as a promoter. According to our method[9], the intermediates could be converted into the end products by introduction of a ceramide moiety.

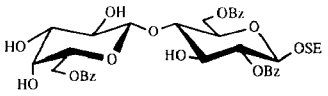
The glycosylation[5,7] of **5** with methyl (methyl 5-acetamido-7,8,9-tri-*O*-acetyl-3,4,5-trideoxy-2-thio-D-*manno*-2-nonulopyranosid)onate[1] (**1**, 2.0 equiv with respect to the acceptor), in acetonitrile for 24 h at −15° in the presence of DMTST (4.0 equiv with respect to **1**) and 3A molecular sieves, gave exclusively the α-glycoside **6** in 38% yield. Acetylation of **6** with acetic anhydride in pyridine gave the acetate **7**. The structure of **7** was unambiguously proved by 270 MHz ^{1}H-NMR spectroscopy. The observed chemical shifts and coupling constants for H-7c (δ 5.47, $J_{6,7}$ 2.6, $J_{7,8}$ 9.3 Hz) and H-8c (δ 5.72) are characteristic of α-glycosidically linked[6a,10–12] sialic acid analogs, and the values for H-2b (δ 5.16, $J_{1,2}$ 8.1, $J_{2,3}$ 10.1 Hz), H-3b (δ 4.67, $J_{3,4}$ 3.1 Hz), and H-4b (δ 5.09) in the lactose unit indicate the position of glycosylation to be C-3b. Other ^{1}H-NMR data are given in the Experimental section and are consistent with the structure assigned.

In essentially the same way, reaction of **5** with methyl (methyl 5-acetamido-8,9-di-*O*-acetyl-4-*O*-benzoyl-3,5,7-trideoxy-2-thio-D-*galacto*-2-nonulopyranosid)onate[1] (**2**), methyl (methyl 5-acetamido-4,7,9-tri-*O*-acetyl-3,5,8-trideoxy-2-thio-D-*galacto*-2-nonulopyranosid)onate[1] (**3**), or methyl (methyl 5-acetamido-4,7,8-tri-*O*-acetyl-3,5,9-trideoxy-2-thio-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate[1] (**4**) furnished the corresponding α-sialosyl-(2 → 3b)-lactosides **8**, **10**, and **12** in 51, 53, and 43% yields, respectively. It is noteworthy that neither the unwanted β-glycoside of sialic acid nor any position isomer was isolated from these glycosylations, as we observed previously[5–7,9]. Acetylation of **8**, **10**, and **12** gave the acetates **9**, **11**, and **13**, respectively, in almost quantitative yields.

Selective removal of the 2-(trimethylsilyl)ethyl group from **7**, **9**, **11** and **13** was performed by treatment[5,13] with boron trifluoride etherate in dichloromethane for 6–8.5 h at 0°, to give the corresponding 1-hydroxy derivatives **14**, **16**, **18**, and **20** in high yields (84–96%).

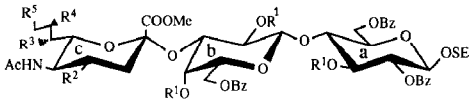


	R^1, R^2	R^3	R^4	R^5	R^6
1	SMe, COOMe	H	OAc	OAc	OAc
2	SMe, COOMe	OBz	H	OAc	OAc
3	SMe, COOMe	OAc	OAc	H	OAc
4	SMe, COOMe	OAc	OAc	OAc	H



5

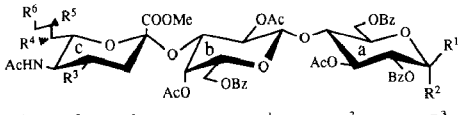
SE = 2-(trimethylsilyl)ethyl
Bz = benzoyl



	R^1	R^2	R^3	R^4	R^5
6	H	H	OAc	OAc	OAc
7	Ac	H	OAc	OAc	OAc
8	H	OBz	H	OAc	OAc
9	Ac	OBz	H	OAc	OAc
10	H	OAc	OAc	H	OAc
11	Ac	OAc	OAc	H	OAc
12	H	OAc	OAc	OAc	H
13	Ac	OAc	OAc	OAc	H

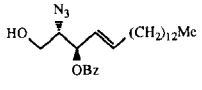
Treatment[5,14,15] of **14, 16, 18**, or **20** with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) for 2 h at 0° gave the corresponding trichloroacetimidates **15, 17, 19**, and **21** as the α-anomers in 82–89% yields.

The glycosylation[5,16] of (2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol[17,18] (**22**) with **15, 17, 19**, or **21** thus obtained, in dichloromethane for 4 h at 0°



	R^1, R^2	R^3	R^4	R^5	R^6
14	H, OH	H	OAc	OAc	OAc
16	H, OH	OBz	H	OAc	OAc
18	H, OH	OAc	OAc	H	OAc
20	H, OH	OAc	OAc	OAc	H

	R^1	R^2	R^3	R^4	R^5	R^6
15	H	$OC(=NH)CCl_3$	H	OAc	OAc	OAc
17	H	$OC(=NH)CCl_3$	OBz	H	OAc	OAc
19	H	$OC(=NH)CCl_3$	OAc	OAc	H	OAc
21	H	$OC(=NH)CCl_3$	OAc	OAc	OAc	H



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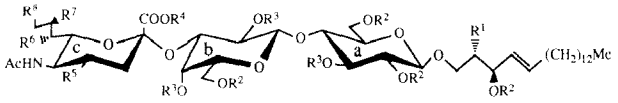

	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8
23	N_3	Bz	Ac	Me	H	OAc	OAc	OAc
24	$NHCO(CH_2)_{16}Me$	Bz	Ac	Me	H	OAc	OAc	OAc
25	$NHCO(CH_2)_{16}Me$	H	H	H	H	OH	OH	OH
26	N_3	Bz	Ac	Me	OBz	H	OAc	OAc
27	$NHCO(CH_2)_{16}Me$	Bz	Ac	Me	OBz	H	OAc	OAc
28	$NHCO(CH_2)_{16}Me$	H	H	H	OH	H	OH	OH
29	N_3	Bz	Ac	Me	OAc	OAc	H	OAc
30	$NHCO(CH_2)_{16}Me$	Bz	Ac	Me	OAc	OAc	H	OAc
31	$NHCO(CH_2)_{16}Me$	H	H	H	OH	OH	H	OH
32	N_3	Bz	Ac	Me	OAc	OAc	OAc	H
33	$NHCO(CH_2)_{16}Me$	Bz	Ac	Me	OAc	OAc	OAc	H
34	$NHCO(CH_2)_{16}Me$	H	H	H	OH	OH	OH	H

in the presence of boron trifluoride etherate and 4A molecular sieves, gave only the desired β-glycosides **23, 26, 29**, and **32**, respectively, in good yields. A significant signal in the ^{1}H-NMR spectra of **23, 26, 29**, and **32** was a one-proton doublet at δ 4.61–4.68 ($J_{1,2}$ 7.7–8.1 Hz, H-1a of the lactose unit), showing the newly formed glycosidic linkages to be β.

Selective reduction[5,19] of the azido group in **23, 26, 29**, or **32** with hydrogen sulfide in aqueous 83% pyridine for 48 h at room temperature, and subsequent condensation with octadecanoic acid, using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (WSC) in dichloromethane furnished good yields of the corresponding acylated ganglioside analogs **24, 27, 30**, and **33**, respectively. *O*-Deacylation of **24, 27, 30**, and **33** with sodium methoxide in methanol, with subsequent saponification of the sialate methyl ester group, yielded the desired products **25, 28, 31**, and **34** in almost quantitative yields. The ^{1}H-NMR data of the products thus obtained are consistent with the structures assigned.

The work described above shows that the use of the methyl 2-thioglycosides of sialic acids as glycosyl donors in acetonitrile in the presence of DMTST is effective for obtaining the α-glycosides of the sialic acids.

EXPERIMENTAL

General methods.—Optical rotations were determined with a Union PM-201 polarimeter at 25°, 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 O-*(methyl 5-acetamido-7,8,9-tri*-O-*acetyl-3,4,5-trideoxy-α*-D-manno-*2-nonulopyranosylonate)-(2 → 3)*-O-*(6*-O-*benzoyl-β*-D-*galactopyranosyl)-(1 → 4)-2,6-di*-O-*benzoyl-β*-D-*glucopyranoside* (**6**).—To a solution of methyl (methyl 5-acetamido-7,8,9-tri-*O*-acetyl-3,4,5-trideoxy-2-thio-D-*manno*-2-nonulopyranosid)-onate[1] (**1**, 1.6 g, 3.45 mmol) and 2-(trimethylsilyl)ethyl *O*-(6-*O*-benzoyl-β-D-galactopyranosyl)-(1 → 4)-2,6-di-*O*-benzoyl-β-D-glucopyranoside[5] (**5**, 1.35 g, 1.79 mmol) in dry MeCN (17 mL) was added molecular sieves 3 A (MS-3A, 5.0 g), and the mixture was stirred overnight at room temperature, then cooled to −30°. To the cooled mixture was added, with stirring, a mixture (5.0 g, 50% DMTST by weight) of dimethyl(methylthio)sulfonium triflate (DMTST) and MS-3A, and the stirring was continued for 24 h at −15°. The solids were filtered off and washed thoroughly 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 to a syrup that was chromatographed on a column of silica gel (150 g), with 3:1 EtOAc–hexane, to give **6** (800 mg, 37.5%) as an amorphous mass, $[\alpha]_D$ + 24.2° (*c* 0.97, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.98 (m, 2 H, $Me_3SiCH_2CH_2$), 1.54–2.50 (m, 4 H, H-3c*ax*, 3c*eq*, 4c*ax*, 4c*eq*), 2.04 (s, 3 H, AcN), 2.07, 2.18, 2.26 (3 s, 9 H, 3 AcO), 3.86 (s, 3 H, MeO), 4.75 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1b), 4.76 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1a), 5.38 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2a), 5.52 (m, 2 H, H-7c,8c), 5.91 (d, 1 H, $J_{5,NH}$ 9.9 Hz, N*H*), and 7.37–8.20 (m, 15 H, 3 Ph).

Anal. Calcd for $C_{56}H_{71}NO_{24}Si$ (1170.3): C, 57.47; H, 6.12; N, 1.20. Found: C, 57.39; H, 6.09; N, 1.18.

2-(Trimethylsilyl)ethyl O-*(methyl 5-acetamido-7,8,9-tri*-O-*acetyl-3,4,5-trideoxy-α*-D-manno-*2-nonulopyranosylonate)-(2 → 3)*-O-*(2,4-di*-O-*acetyl-6*-O-*benzoyl-β*-D-*galactopyranosyl)-(1 → 4)-3*-O-*acetyl-2,6-di*-O-*benzoyl-β*-D-*glucopyranoside* (**7**).—Compound **6** (430 mg, 0.37 mmol) was acetylated with acetic anhydride (10 mL)–pyridine (12 mL) overnight at room temperature. The product was purified by column chromatography (70:1 CH_2Cl_2–MeOH) on silica gel (60 g), to give **7** (400 mg, 84%) as an amorphous mass, $[\alpha]_D$ +19.8° (*c* 2.2, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.96 (m, 2 H, $Me_3SiCH_2CH_2$), 1.41 (m, 1 H, $J_{4ax,5}$ 10.5 Hz, H-4c*ax*), 1.62 (m, 1 H, H-3c*eq*), 1.99 (s, 3 H, AcN), 2.11, 2.13, 2.14, 2.16, 2.24, 2.32 (6 s, 18 H, 6 AcO), 3.77 (s, 3 H, MeO), 4.67 (dd, 1 H, $J_{2,3}$ 10.1, $J_{3,4}$ 3.1 Hz, H-3b), 4.78 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1a), 5.02 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 5.09 (br. d, 1 H, H-4b), 5.16 (dd, 1 H, H-2b), 5.32 (dd, 1 H, H-2a), 5.47 (dd, 1 H, $J_{6,7}$ 2.6, $J_{7,8}$ 9.3 Hz, H-7c), 5.60 (t, 1 H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H-3a), 5.72 (m, 1 H, H-8c), and 7.27–8.19 (m, 15 H, 3 Ph).

Anal. Calcd for $C_{62}H_{77}NO_{27}Si$ (1296.4): C, 57.44; H, 5.99; N, 1.08. Found: C, 57.49; H, 6.20; N, 0.95.

2-(Trimethylsilyl)ethyl O-*(methyl 5-acetamido-8,9-di*-O-*acetyl-4*-O-*benzoyl-3,5,7-trideoxy-α*-D-galacto-*2-nonulopyranosylonate)-(2 → 3)*-O-*(6*-O-*benzoyl-β*-D-*galacto-pyranosyl)-(1 → 4)-2,6-di*-O-*benzoyl-β*-D-*glucopyranoside* (**8**).—Glycosylation of **5** (360 mg, 0.48 mmol) with **2** (ref. 1) (490 mg, 0.93 mmol) in CH_3CN (7 mL) in the presence of DMTST (1.0 g) and MS-3A (20 g) for 24 h at −15°, then workup as

described for the preparation of **6**, gave **8** (400 mg, 51%) as an amorphous mass, $[\alpha]_D$ +1.9° (*c* 0.4, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.99 (m, 2 H, $Me_3SiCH_2CH_2$), 1.84–2.09 (m, 2 H, H-7c,7′c), 1.97 (s, 3 H, AcN), 2.11, 2.16 (2 s, 6 H, 2 AcO), 2.29 (t, 1 H, $J_{3ax,3eq} = J_{3ax,4} = 12.6$ Hz, H-3c*ax*), 2.95 (dd, 1 H, $J_{3eq,4}$ 4.6 Hz, H-3c*eq*), 3.92 (s, 3 H, MeO), 4.69 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1b), 4.77 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1a), 4.88 (dd, 1 H, $J_{5,6}$ 3.3, $J_{6,6'}$ 12.4 Hz, H-6a), 5.24 (ddd, 1 H, H-4c), 5.37 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2a), 5.49 (m, 1 H, H-8), and 7.35–8.19 (m, 20 H, 4 Ph).

Anal. Calcd for $C_{61}H_{73}NO_{24}Si$ (1232.2): C, 59.45; H, 5.97; N, 1.14. Found: C, 59.43; H, 5.89; N, 1.09.

2-(Trimethylsilyl)ethyl O-*(methyl 5-acetamido-8,9-di*-O-*acetyl-4*-O-*benzoyl-3,5,7-trideoxy-α*-D-galacto-*2-nonulopyranosylonate)-(2 → 3)*-O-*(2,4-di*-O-*acetyl-6*-O-*benzoyl-β*-D-*galactopyranosyl)-(1 → 4)-3*-O-*acetyl-2,6-di*-O-*benzoyl-β*-D-*glucopyranoside* (**9**).—Compound **8** (200 mg, 0.16 mmol) was acetylated with acetic anhydride (5 mL)—pyridine (10 mL) overnight at room temperature. Workup as described for **7** gave **9** (210 mg, 96%) as an amorphous mass, $[\alpha]_D$ −0.6° (*c* 1.2, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.98 (m, 2 H, $Mc_3SiCH_2CH_2$), 1.89–2.05 (m, 2 H, H-7c,7′c), 1.96 (s, 3 H, AcN), 2.11 (2), 2.13, 2.22, 2.31, (5 s, 15 H, 5 AcO), 2.85 (dd, 1 H, $J_{3ax,3eq}$ 12.3, $J_{3eq,4}$ 4.8 Hz, H-3c*eq*), 3.49 (m, 1 H, H-6c), 3.86 (s, 3 H, MeO), 4.78 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 4.80 (dd, 1H, $J_{2,3}$ 9.8, $J_{3,4}$ 3.3 Hz, H-3b), 5.02 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 5.17 (dd, 1 H, H-2b), 5.18 (br. d, 1 H, H-4b), 5.19 (m, 1 H, H-4c), 5.33 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2a), 5.64 (t, 1 H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H-3a), 5.66 (d, 1 H, $J_{5,NH}$ 9.5 Hz, N*H*, and m, 1 H, H-8c), and 7.39–8.18 (m, 20 H, 4 Ph).

Anal. Calcd for $C_{67}H_{79}NO_{27}Si$ (1358.4): C, 59.23; H, 5.86; N, 1.03. Found: C, 59.09; H, 5.91; N, 1.08.

2-(Trimethylsilyl)ethyl O-*(methyl 5-acetamido-4,7,9-tri*-O-acetyl-3,5,8-trideoxy-*α*-D-galacto-*2-nonulopyranosylonate)-(2 → 3)*-O-*(6*-O-*benzoyl-β*-D-*galactopyranosyl)-(1 → 4)-2,6-di*-O-*benzoyl-β*-D-*glucopyranoside* (**10**).—Glycosylation of **5** (656 mg, 0.87 mmol) with compound **3** (ref. 1) (806 mg, 1.74 mmol) in CH_3CN (10 mL) in the presence of DMTST (1.76 g) and MS-3A (2.0 g) for 24 h at −15°, and workup as described for **6**, gave **10** (540 mg, 53%) as an amorphous mass, $[\alpha]_D$ −0.4° (*c* 1.7, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.98 (m, 2 H, $Me_3SiCH_2CH_2$), 1.92–2.06 (m, 2 H, H-8c,8′c), 2.00 (s, 3 H, AcN), 2.11, 2.15, 2.22 (3 s, 9 H, 3 AcO), 2.85 (dd, 1 H, $J_{3ax,3eq}$ 13.1, $J_{3eq,4}$ 4.7 Hz, H-3c*eq*), 3.57 (dd, 1 H, H-6c), 3.67 (m, 1 H, $Me_3SiCH_2CH_2$), 3.92 (s, 3 H, MeO), 4.56 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1b), 4.76 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1a), 5.07–5.18 (m, 2 H, H-4c,7c), 5.37 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2a), 5.69 (d, 1 H, $J_{5,NH}$ 9.0 Hz, N*H*), and 7.07–8.20 (m, 15 H, 3 Ph).

Anal. Calcd for $C_{56}H_{71}NO_{24}Si$ (1170.3): C, 57.47; H, 6.12; N, 1.20. Found: C, 57.55; H, 6.20; N, 1.25.

2-(Trimethylsilyl)ethyl O-*(methyl 5-acetamido-4,7,9-tri*-O-*acetyl-3,5,8-trideoxy-α*-D-galacto-*2-nonulopyranosylonate)-(2 → 3)*-O-*(2,4-di*-O-*acetyl-6*-O-*benzoyl-β*-D-*ga-lactopyranosyl)-(1 → 4)-3*-O-*acetyl-2,6-di*-O-*benzoyl-β*-D-*glucopyranoside* (**11**).—Compound **10** (360 mg, 0.31 mmol) was acetylated with acetic anhydride (6 mL)–pyridine (7 mL) overnight at room temperature. Workup as described for **7**

gave **11** (333 mg, 83.5%) as an amorphous mass, $[\alpha]_D$ +1.4° (*c* 1.9, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.98 (m, 2 H, $Me_3SiCH_2CH_2$), 1.85 (t, 1 H, $J_{3ax,3eq} = J_{3ax,4}$ = 12.6 Hz, H-3*ax*), 1.96–2.17 (m, 2 H, H-8c,8'c), 1.97 (s, 3 H, AcN), 2.10, 2.11 (2), 2.13, 2.23, 2.31 (6 s, 18 H, 6 AcO), 2.68 (dd, 1 H, $J_{3eq,4}$ 4.9 Hz, H-3c*eq*), 3.47 (dd, 1 H, $J_{5,6}$ 10.5, $J_{6,7}$ 2.1 Hz, H-6c), 3.65, 4.07 (2 s, 2 H, $Me_3SiCH_2CH_2$), 3.88 (s, 3 H, MeO), 4.16 (q, 1 H, $J_{4,5} = J_{5,6} = J_{5,NH}$ = 10.5 Hz, H-5c), 4.68 (dd, 1 H, $J_{2,3}$ 10.1, $J_{3,4}$ 3.3 Hz, H-3b), 4.78 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1a), 4.83 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 5.17 (dd, 1H, H-2b), 5.19 (m, 1 H, H-7c), 5.26 (br. d, 1 H, H-4b), 5.33 (dd, 1 H, $J_{2,3}$ 9.4 Hz, H-2a), 5.59 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.4 Hz, H-3a), 5.86 (d, 1 H, N*H*), and 7.39–8.16 (m, 15 H, 3 Ph)

Anal. Calcd for $C_{62}H_{77}NO_{27}Si$ (1296.4): C, 57.44; H, 5.99; N, 1.08. Found: C, 57.49; H, 6.12; N, 1.10.

2-(Trimethylsilyl)ethyl O-*(methyl 5-acetamido-4,7,8-tri*-O-*acetyl-3,5,9-trideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosylonate)-(2 → 3)*-O-*(6*-O-*benzoyl-β*-D-*galacto-pyranosyl)-(1 → 4)-2,6-di*-O-*benzoyl-β*-D-*glucopyranoside* (**12**).—Glycosylation of **5** (900 mg, 1.2 mmol) with compound **4** (ref. 1) (1.1 g, 2.4 mmol) in CH_3CN (10 mL) in the presence of DMTST (1.5 g) and MS-3A (3.0 g) for 24 h at −15°, and subsequent processing as described for **6**, gave **12** (600 mg, 43%) as an amorphous mass, $[\alpha]_D$ +8.3° (*c* 0.7, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.98 (m, 2 H, $Me_3SiCH_2CH_2$), 1.14 (d, 3 H, $J_{8,9}$ 6.2 Hz, CH_3CH), 2.01 (s, 3 H, AcN), 2.12, 2.15, 2.26 (3 s, 9 H, 3 AcO), 2.80 (dd, 1 H, $J_{3ax,3eq}$ 13.0, $J_{3eq,4}$ 4.6 Hz, H-3c*eq*), 3.68 (m, 1 H, $Me_3SiCH_2CH_2$), 3.90 (s, 3 H, MeO), 4.68 (dd, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 4.76 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1a), 4.87 (dd, 1 H, $J_{5,6}$ 2.9, $J_{6,6'}$ 11.9 Hz, H-6a), 5.15 (2 m, 2 H, H-4c,8c), 5.22 (dd, 1 H, $J_{6,7}$ 1.7, $J_{7,8}$ 9.2 Hz, H-7c), 5.36 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2a), and 7.40–8.20 (m, 15 H, 3 Ph).

Anal. Calcd for $C_{56}H_{71}NO_{24}Si$ (1170.3): C, 57.47; H, 6.12; N, 1.20. Found: C, 57.30; H, 6.29; N, 1.18.

2-(Trimethylsilyl)ethyl O-*(methyl 5-acetamido-4,7,8-tri*-O-*acetyl-3,5,9,trideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosylonate)-(2→3)*-O-*(2,4-di*-O-*acetyl-6*-O-*benzoyl-β*-D-*galactopyranosyl)-(1 → 4)-3*-O-*acetyl-2,6-di*-O-*benzoyl-β*-D-*glucopyranoside* (**13**).—Compound **12** (450 mg, 0.38 mmol) was acetylated with acetic anhydride (7 mL)–pyridine (10 mL) overnight at room temperature. Processing as described for **7** gave **13** (420 mg, 84%) as an amorphous mass, $[\alpha]_D$ +1.6° (*c* 0.6, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.98 (m, 2 H, $Me_3SiCH_2CH_2$), 1.23 (d, 3 H, $J_{8,9}$ 6.6 Hz, CH_3CH), 1.96 (s, 3 H, AcN), 1.99, 2.11, 2.12, 2.16, 2.23, 2.32 (6 s, 18 H, 6 AcO), 2.68 (dd, 1 H, $J_{3ax,3eq}$ 12.6, $J_{3eq,4}$ 4.4 Hz, H-3c*eq*), 3.68, 4.08 (2 m, 2 H, $Me_3SiCH_2CH_2$), 3.95 (s, 3 H, MeO), 4.67 (dd, 1 H, $J_{2,3}$ 10.3, $J_{3,4}$ 3.3 Hz, H-3b), 4.78 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 4.96 (m, 1 H, H-4c), 4.97 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1a), 5.11 (br. d, 1 H, H-4b), 5.32 (dd, 1 H, $J_{6,7}$ 1.8, $J_{7,8}$ 9.9 Hz, H-7c), 5.34 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2a), 5.47 (m, 1 H, H-8c), 5.58 (t, 1 H, $J_{2,3} = J_{3,4}$ = 9.5 Hz, H-3a), and 7.39–8.20 (m, 15 H, 3 Ph).

Anal. Calcd for $C_{62}H_{77}NO_{27}Si$ (1296.4): C, 57.44; H, 5.99; N, 1.08. Found: C, 57.29; H, 6.18; N, 1.05.

O-(*Methyl 5-acetamido-7,8,9-tri*-O-*acetyl-3,4,5-trideoxy*-α-D-manno-*2-nonulopyranosylonate*)-(2 → 3)-O-(*2,4-di*-O-*acetyl-6*-O-*benzoyl*-β-D-*galactopyranosyl*)-(1 → 4)-*3*-O-*acetyl-2,6-di*-O-*benzoyl*-D-*glucopyranose* (**14**).—To a stirred solution of **7** (400 mg, 0.31 mmol) in CH_2Cl_2 (10 mL), cooled to 0°, was added dropwise $BF_3 \cdot OEt_2$ (0.5 mL). The mixture was stirred for 6 h at 0°, the course of the reaction being monitored by TLC. Dichloromethane (50 mL) was added to the mixture, and the solution was successively washed with M Na_2CO_3 and water, dried (Na_2SO_4), and evaporated. The residue was chromatographed on a column of silica gel (30 g) with 60:1 CH_2Cl_2–MeOH to give compound **14** (350 mg, 95%) as an amorphous mass, $[\alpha]_D$ +53.0° (*c* 1.5, $CHCl_3$); IR: *ν* 3700–3140 (OH, NH), 1670 and 1530 (amide), and 710 cm^{-1} (Ph).

Anal. Calcd for $C_{57}H_{65}NO_{27}$ (1196.1): C, 57.23; H, 5.48; N, 1.17. Found: C, 57.24; H, 5.60; N, 1.15.

O-(*Methyl 5-acetamido-7,8,9-tri*-O-*acetyl-3,4,5-trideoxy*-α-D-manno-*2-nonulopyranosylonate*)-(2 → 3)-O-(*2,4-di*-O-*acetyl-6*-O-*benzoyl*-β-D-*galactopyranosyl*)-(1 → 4)-*3*-O-*acetyl-2,6-di*-O-*benzoyl*-α-D-*glucopyranosyl trichloroacetimidate* (**15**).—To a stirred solution of **14** (350 mg, 0.29 mmol) in CH_2Cl_2 (4 mL), cooled to 0°, were added Cl_3CCN (1.0 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 40 mg). The mixture was stirred for 2 h at 0° and then concentrated. The residue was chromatographed on a column of silica gel (20 g) with 70:1 CH_2Cl_2–MeOH to give compound **15** (320 mg, 82%) as an amorphous mass, $[\alpha]_D$ +56.0° (*c* 1.5, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 1.20–2.30 (m, 4 H, H-3c*ax*, 3c*eq*, 4c*ax*, 4c*eq*), 1.87 (s, 3 H, AcN), 1.99 (2), 2.03, 2.07, 2.14, 2.19 (6 s, 18 H, 6 AcO), 3.66 (s, 3 H, MeO), 4.82 (dd, 1 H, $J_{2,3}$ 10.1, $J_{3,4}$ 3.1 Hz, H-3b), 4.95 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1b), 4.98 (br. d, 1 H, H-4b), 5.07 (dd, 1 H, H-2b), 5.28 (dd, 1 H, $J_{1,2}$ 3.8, $J_{2,3}$ 9.5 Hz, H-2), 5.35 (dd, 1 H, $J_{6,7}$ 2.6, $J_{7,8}$ 9.1 Hz, H-7c), 5.57 (m, 1 H, H-8c), 5.87 (t, 1 H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H-3a), 6.65 (d, 1 H, H-1a), 7.27–8.07 (m, 15 H, 3 Ph), and 8.55 (s, 1 H, C=N*H*).

Anal. Calcd for $C_{59}H_{65}Cl_3N_2O_{27}$ (1340.5): C, 52.86; H, 4.89; N, 2.09. Found: C, 52.71; H, 5.14; N, 2.13.

O-(*Methyl 5-acetamido-8,9-di*-O-*acetyl-4*-O-*benzoyl-3,5,7-trideoxy*-α-D-galacto-*2-nonulopyranosylonate*)-(2 → 3)-O-(*2,4-di*-O-*acetyl-6*-O-*benzoyl*-β-D-*galactopyranosyl*)-(1 → 4)-*3*-O-*acetyl-2,6-di*-O-*benzoyl*-D-*glucopyranose* (**16**).—Selective removal of the 2-(trimethylsilyl)ethyl group in **9** (210 mg, 0.15 mmol) with $BF_3 \cdot OEt_2$ (0.24 mL) in CH_2Cl_2 (4 mL), as described for the preparation of **14**, gave compound **16** (185 mg, 93.5%) as an amorphous mass, $[\alpha]_D$ +27.5° (*c* 1.4, $CHCl_3$); IR: *ν* 3700–3200 (OH, NH), 1730 and 1220 (ester), 1660 and 1540 (amide), and 710 cm^{-1} (Ph).

Anal. Calcd for $C_{62}H_{67}NO_{27}$ (1258.2): C, 59.18; H, 5.37; N, 1.11. Found: C, 59.03; H, 5.41; N, 1.15.

O-(*Methyl 5-acetamido-8,9-di*-O-*acetyl-4*-O-*benzoyl-3,5,7-trideoxy*-α-D-galacto-*2-nonulopyranosylonate*)-(2 → 3)-O-(*2,4-di*-O-*acetyl-6*-O-*benzoyl*-β-D-*galactopyranosyl*)-(1 → 4)-*3*-O-*acetyl-2,6-di*-O-*benzoyl*-α-D-*glucopyranosyl trichloroacetimidate*

(**17**).—To a stirred solution of **16** (182 mg, 0.14 mmol) in CH_2Cl_2 (2.5 mL), cooled to 0°, were added Cl_3CCN (0.5 mL) and DBU (20 mg). After completion of the reaction workup as described for **15** gave **17** (180 mg, 89%) as an amorphous mass, $[\alpha]_D$ +32.0° (*c* 0.95, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 1.82–2.04 (m, 2 H, H-7c,7′c), 1.83 (s, 3 H, AcN), 1.97, 1.98, 2.06, 2.11, 2.18 (5 s, 15 H, 5 AcO), 2.73 (dd, 1 H, $J_{3ax,3eq}$ 12.4, $J_{3eq,4}$ 4.7 Hz, H-3c*eq*), 3.34 (m, 1 H, H-6c), 3.75 (s, 3 H, MeO), 3.92 (q, 1 H, $J_{4,5} = J_{5,6} = J_{5,NH}$ = 10.3 Hz, H-5c), 4.69 (dd, 1 H, $J_{2,3}$ 10.0, $J_{3,4}$ 3.2 Hz, H-3b), 4.95 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1b), 5.06 (m, 1 H, H-4c), 5.07 (m, 2 H, H-2b,4b), 5.28 (dd, 1 H, $J_{1,2}$ 3.8, $J_{2,3}$ 10.3 Hz, H-2a), 5.51 (d, 1 H, N*H*), 5.54 (m, 1 H, H-8c), 5.86 (t, 1 H, $J_{2,3} = J_{3,4}$ = 10.3 Hz, H-3a), 6.67 (d, 1 H, H-1a), 7.27–8.07 (m, 20 H, 4 Ph), and 8.54 (s, 1 H, C=N*H*);

Anal. Calcd for $C_{65}H_{67}Cl_3N_2O_{27}$ (1402.6): C, 55.66; H, 4.82; N, 2.00. Found: C, 55.53; H, 4.89; N, 2.08.

O-(*Methyl 5-acetamido-4,7,9-tri*-O-*acetyl-3,5,8-trideoxy-α*-D-galacto-*2-nonulopyranosylonate)-(2 → 3)*-O-*(2,4-di*-O-*acetyl-6*-O-*benzoyl-β*-D-*galactopyranosyl)-(1 → 4)-3*-O-*acetyl-2,6-di*-O-*benzoyl*-D-*glucopyranose* (**18**).—To a stirred solution of **11** (333 mg, 0.26 mmol) in CH_2Cl_2 (4.5 mL), cooled to 0°, was added $BF_3 \cdot OEt_2$ (0.36 mL), and the mixture was stirred for 8.5 h at 0°. Workup as described for **14** gave **18** (298 mg, 96%) as an amorphous mass, $[\alpha]_D$ +34.5° (*c* 0.94, $CHCl_3$); IR: ν 3700–3150 (OH, NH), 1750 and 1230 (ester), 1670 and 1540 (amide), and 710 cm^{-1} (Ph).

Anal. Calcd for $C_{57}H_{65}NO_{27}$ (1196.1): C, 57.23; H, 5.48; N, 1.17. Found: C, 57.05; H, 5.63; N, 1.08.

O-(*Methyl 5-acetamido-4,7,9-tri*-O-*acetyl-3,5,8-trideoxy-α*-D-galacto-*2-nonulopyranosylonate)-(2 → 3)*-O-*(2,4-di*-O-*acetyl-6*-O-*benzoyl-β*-D-*galactopyranosyl)-(1 → 4)-3*-O-*acetyl-2,6-di*-O-*benzoyl-α*-D-*glucopyranosyl trichloroacetimidate* (**19**).—To a stirred solution of **18** (294 mg, 0.25 mmol) in CH_2Cl_2 (3.7 mL), cooled to 0°, were added Cl_3CCN (1.0 mL) and DBU (40 mg), and the mixture was stirred for 2 h at 0°. Processing as described for **15** gave **19** (293 mg, 89%) as an amorphous mass, $[\alpha]_D$ +37.5° (*c* 1.7, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): 1.72 (t, 1 H, $J_{3ax,3eq} = J_{3ax,4}$ = 12.6 Hz, H-3c*ax*), 1.85 (s, 3 H, AcN), 1.94–2.14 (m, 2 H, H-8c,8′c), 1.97, 1.98, 2.01, 2.04, 2.13, 2.21 (6 s, 18 H, 6 AcO), 2.57 (dd, 1 H, $J_{3eq,4}$ 4.8 Hz, H-3c*eq*), 3.35 (dd, 1 H, $J_{5,6}$ 10.4, $J_{6,7}$ 2.1 Hz, H-6c), 3.77 (s, 3 H, MeO), 4.04 (q, 1 H, $J_{4,5} = J_{5,6} = J_{5,NH}$ = 10.4 Hz, H-5c), 4.69 (dd, 1 H, $J_{2,3}$ 9.9, $J_{3,4}$ 3.3 Hz, H-3b), 4.78 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 4.94 (dt, 1 H, H-4c), 5.08 (m, 1 H, H-7c), 5.09 (dd, 1 H, H-2b), 5.17 (br. d, 1 H, H-4b), 5.29 (dd, 1 H, $J_{1,2}$ 3.8, $J_{2,3}$ 10.0 Hz, H-2a), 5.85 (t, 1 H, $J_{2,3} = J_{3,4}$ = 10.0 Hz, H-3a), 6.67 (d, 1 H, H-1a), 7.28–8.13 (m, 15 H, 3 Ph), and 8.58 (s, 1 H, C=N*H*).

Anal. Calcd for $C_{59}H_{65}Cl_3N_2O_{27}$ (1340.5): C, 52.86; H, 4.89; N, 2.09. Found: C, 52.71; H, 5.03; N, 2.13.

O-(*Methyl 5-acetamido-4,7,8-tri*-O-*acetyl-3,5,9-trideoxy*-D-glycero-*α*-D-galacto-*2-nonulopyranosylonate)-(2 → 3)*-O-*(2,4-di*-O-*acetyl-6*-O-*benzoyl-β*-D-*galactopyranosyl)-(1 → 4)-3*-O-*acetyl-2,4-di*-O-*benzoyl*-D-*glucopyranose* (**20**).—To a stirred solu-

tion of **13** (390 mg, 0.3 mmol) in CH_2Cl_2 (8 mL), cooled to 0°, was added $BF_3 \cdot OEt_2$ (0.3 mL) and the mixture was stirred for 6 h at 0°. Processing as described for **14** gave **20** (300 mg, 84%) as an amorphous mass, $[\alpha]_D$ +30.5° (*c* 0.9, $CHCl_3$); IR: ν 3700–3160 (OH, NH), 1750 and 1230 (ester), 1680 and 1560 (amide), and 720 cm^{-1} (Ph).

Anal. Calcd for $C_{57}H_{65}NO_{27}$ (1196.1): C, 57.23; H, 5.48; N, 1.17. Found: C, 57.28; H, 5.45; N, 1.01.

O-*(Methyl 5-acetamido-4,7,8-tri*-O-*acetyl-3,5,9-trideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosylonate)-(2 → 3)*-O-*(2,4-di*-O-*acetyl-6*-O-*benzoyl-β*-D-*galactopyranosyl)-(1 → 4)*-3-O-*acetyl-2,6-di*-O-*benzoyl-α*-D-*glucopyranosyl trichloroacetimidate* (**21**).—To a stirred solution of **20** (240 mg, 0.2 mmol) in CH_2Cl_2 (3 mL), cooled to 0°, were added Cl_3CCN(0.6 mL) and DBU (30 mg), and the mixture was stirred for 2 h at 0°. Processing as described for **15** gave **21** (220 mg, 82%) as an amorphous mass, $[\alpha]_D$ +31.6° (*c* 1.0, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 1.08 (d, 3 H, $J_{8,9}$ 6.2 Hz, CH_3CH), 1.66 (t, 1 H, $J_{3ax,3eq} = J_{3ax,4} = 12.5$ Hz, H-3c*ax*), 1.83 (s, 3 H, AcN), 1.85, 1.99, 2.02, 2.04, 2.12, 2.20 (6 s, 18 H, 6 AcO), 2.56 (dd, 1 H, $J_{3eq,4}$ 4.4 Hz, H-3c*eq*), 3.58 (d, 1 H, $J_{5,6}$ 10.6, $J_{6,7}$ 2.9 Hz, H-6c), 3.72 (s, 3 H, MeO), 4.07 (q, 1 H, $J_{4,5} = J_{5,6} = J_{5,NH} = 10.6$ Hz, H-5c), 4.56 (dd, 1 H, $J_{2,3}$ 10.3, $J_{3,4}$ 3.1 Hz, H-3b), 4.85 (ddd, 1 H, H-4c), 4.88 (br. d, 1 H, H-4b), 4.90 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 5.05 (dd, 1 H, H-2b), 5.13 (dd, 1 H, $J_{7,8}$ 9.9 Hz, H-7c), 5.27 (dd, 1 H, $J_{1,2}$ 3.7, $J_{2,3}$ 9.7 Hz, H-2a), 5.38 (m, 1 H, H-8c), 5.83 (t, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3a), 6.66 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1a), and 7.27–8.54 (m, 15 H, 3 Ph).

Anal. Calcd for $C_{59}H_{65}Cl_3N_2O_{27}$ (1340.5): C, 52.86; H, 4.89; N, 2.09. Found: C, 52.70; H, 4.91; N, 1.88.

O-*(Methyl 5-acetamido-7,8,9-tri*-O-*acetyl-3,4,5-trideoxy-α*-D-manno-*2-nonulopyranosylonate)-(2 → 3)*-O-*(2,4-di*-O-*acetyl-6*-O-*benzoyl-β*-D-*galactopyranosyl)-(1 → 4)*-O-*(3*-O-*acetyl-2,6-di*-O-*benzoyl-β*-D-*glucopyranosyl)-(1 → 1)-(2*S,3R,4E*)-*2-azido-3*-O-*benzoyl-4-octadecene-1,3-diol* (**23**).—To a solution of **15** (180 mg, 0.13 mmol) and (2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol[17,18] (**22**, 100 mg, 0.23 mmol) in dry CH_2Cl_2 (4 mL) was added MS-4A (AW-300, 2.5 g), the mixture was stirred for 30 min at room temperature, and then cooled to 0°. Boron trifluoride etherate (0.07 mL) was added to the mixture, and this was stirred for 4 h at 0°, the progress of the reaction being monitored by TLC. The precipitate was filtered off and washed thoroughly with CH_2Cl_2. The combined filtrate was washed successively with M Na_2CO_3 and water, dried (Na_2SO_4), and evaporated to a syrup that was chromatographed on a column of silica gel (30 g), with 70:1 CH_2Cl_2–MeOH, to give compound **23** (170 mg, 79%) as an amorphous mass, $[\alpha]_D$ +7.8° (*c* 1.5, $CHCl_3$); ν 3500 (NH), 2940 and 2850 (Me, CH_2), 2100 (N_3), 1740 and 1230 (ester), 1660 and 1540 (amide), and 710 cm^{-1} (Ph); ^{1}H-NMR ($CDCl_3$): δ 0.87 (t, 3 H, $J_{17,18}$ 6.6 Hz, CH_3CH_2), 1.24 (s, 22 H, 11 CH_2), 1.50 (m, 1 H, H-4c*ax*), 1.86 (s, 3 H, AcN), 1.99 (2), 2.03 (2), 2.12, 2.18 (6 s, 18 H, 6 AcO), 3.65 (s, 3 H, MeO), 4.55 (dd, 1 H, $J_{2,3}$ 10.1, $J_{3,4}$ 3.1 Hz, H-3b), 4.68 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1a), 4.90 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1b), 4.96 (br. d, 1 H, H-4b), 5.01 (dd, 1 H, H-2b), 5.24 (dd, 1 H, $J_{2,3}$ 8.1

Hz, H-2a), 5.35 (dd, 1 H, $J_{6,7}$ 2.9, $J_{7,8}$ 9.1 Hz, H-7c), 5.49 (t, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3a), 5.66 (dt, 1 H, $J_{4,5}$ 14.0, $J_{5,6} = J_{5,6'} = 7.0$ Hz, H-5 of sphingosine), and 7.26–8.12 (m, 20 H, 4 Ph).

Anal. Calcd for $C_{82}H_{102}N_4O_{29}$ (1607.7): C, 61.26; H, 6.40; N, 3.49. Found: C, 61.33; H, 6.59; N, 3.38.

O-*(Methyl 5-acetamido-7,8,9-tri*-O-*acetyl-3,4,5-trideoxy-α*-D-manno-*2-nonulopyranosylonate)-(2 → 3)*-O-*(2,4-di*-O-*acetyl-6*-O-*benzoyl-β*-D-*galactopyranosyl)-(1 → 4)*-O-*(3*-O-*acetyl-2,6-di*-O-*benzoyl-β*-D-*glucopyranosyl)-(1 → 1)-(2*S,*3*R,*4*E*)-3-*O-benzoyl-2-octadecanamido-4-octadecene-1,3-diol* (**24**).—Hydrogen sulfide was bubbled through a solution of **23** (120 mg, 0.07 mmol) in pyridine (5 mL) and water (1 mL) for 2 days while the solution was stirred at room temperature, the course of the reaction being monitored by TLC. The mixture was concentrated and the residue dissolved in CH_2Cl_2 (6 mL). Octadecanoic acid (50 mg, 0.17 mmol) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (WSC, 50 mg) were added to the solution, and the mixture was stirred overnight at room temperature. After completion of the reaction, CH_2Cl_2 (50 mL) was added to the mixture, and the solution was washed with water, dried (Na_2SO_4), and concentrated to a syrup that was chromatographed on a column of silica gel (30 g), with 75:1 CH_2Cl_2–MeOH, to give compound **24** (110 mg, 80%) as an amorphous mass, $[\alpha]_D$ +18.0° (*c* 2.0, $CHCl_3$), IR: ν 3350 (NH), 2940 and 2840 (Me, CH_2), 1740 and 1220 (ester), 1660 and 1530 (amide), and 710 cm^{-1} (Ph); ^{1}H-NMR ($CDCl_3$): δ 0.87 (t, 6 H, $J_{17,18}$ 6.5 Hz, 2 CH_3CH_2), 1.26 (s, 50 H, 25 CH_2), 1.87 (s, 3 H, AcN), 2.00 (2), 2.02, 2.03, 2.12, 2.16 (6 s, 18 H, 6 AcO), 3.66 (s, 3 H, MeO), 4.55 (dd, 1 H, $J_{2,3}$ 10.5, $J_{3,4}$ 3.3 Hz, H-3b), 4.60 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 4.86 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 4.98 (br. d, 1 H, H-4b), 5.02 (dd, 1 H, $J_{3,4}$ 9.0 Hz, H-2b), 5.18 (dd, 1 H, $J_{1,2}$ 7.7, $J_{2,3}$ 9.9 Hz, H-2a), 5.37 (dd, 1 H, $J_{6,7}$ 2.7, $J_{7,8}$ 9.1 Hz, H-7c), 5.48 (t, 1 H, $J_{2,3} = J_{3,4} = 9.9$ Hz, H-3a), 5.55 (m, 1 H, H-8c), 5.65 (d, 1 H, $J_{5,NH}$ 9.3 Hz, N*H*), 5.75 (dt, 1 H, $J_{4,5} = 14.1$, $J_{5,6} = J_{5,6'} = 6.6$ Hz, H-5 of ceramide), and 7.26–8.13 (m, 20 H, 4 Ph).

Anal. Calcd for $C_{100}H_{138}N_2O_{30}$ (1848.2): C, 64.98; H, 7.53; N, 1.52. Found: C, 64.79; H, 7.66; N, 1.51.

O-*(5-Acetamido-3,4,5-trideoxy-α*-D-manno-*2-nonulopyranosylonic acid)-(2 → 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* (**25**).—To a solution of **24** (105 mg, 0.057 mmol) in MeOH (3.5 mL) was added NaOMe (30 mg), and the mixture was stirred for 6 h at room temperature, the course of the reaction being monitored by TLC. Water (0.5 mL) was added and the mixture was stirred for 24 h at room temperature, then treated with Amberlite IR-120 (H^+) resin to neutralize the base. The resin was filtered off and washed with MeOH, and the combined filtrate and washings were concentrated. Column chromatography (MeOH) of the residue on Sephadex LH-20 (40 g) gave **25** (66 mg, quantitative) as an amorphous mass, $[\alpha]_D$ – 14.0° (*c* 1.2, 1:1 MeOH–$CHCl_3$); ^{1}H-NMR (1:1 $CDCl_3$–CD_3OD): δ 0.89 (t, 6 H, $J_{17,18}$ 6.6 Hz, 2 CH_3CH_2), 1.28 (s, 50 H, 25 CH_2), 1.98 (s, 3 H, AcN), 4.30 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 4.42 (d, 1 H, $J_{1,2}$ 7.5 Hz, H-1b), 5.43 (dd, 1 H, $J_{3,4}$ 7.0, $J_{4,5}$ 15.4 Hz, H-4

of ceramide), and 5.68 (dt, 1 H, $J_{5,6} = J_{5,6'} = 6.6$ Hz, H-5 of ceramide).

Anal. Calcd for $C_{59}H_{108}N_2O_{20}$ (1165.5): C, 60.80; H, 9.34; N, 2.40. Found: C, 60.58; H, 9.49; N, 2.43.

O-*(Methyl 5-acetamido-8,9-di-*O*-acetyl-4-*O*-benzoyl-3,5,7-trideoxy-α-*D-galacto-*2-nonulopyranosylonate)-(2 → 3)-*O*-(2,4-di-*O*-acetyl-6-*O*-benzoyl-β-*D-*galactopyranosyl)-(1 → 4)-*O*-(3-*O*-acetyl-2,6-di-*O*-benzoyl-β-*D-*glucopyranosyl)-(1 → 1)-(2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol* (**26**).—Coupling of **17** (110 mg, 0.08 mmol) and **22** (90 mg, 0.19 mmol), as described for **23**, gave **26** (80 mg, 61%) as an amorphous mass, $[\alpha]_D$ +8.5 (*c* 0.7, $CHCl_3$); ν 3400 (NH), 2950 and 2840 (Me, CH_2), 2100 (N_3), 1730 and 1220 (ester), 1660 and 1540 (amide), and 710 cm^{-1} (Ph); ^{1}H-NMR ($CDCl_3$): δ 0.81 (t, 3 H, $J_{17,18}$ 6.6 Hz, C*H*$_3$CH$_2$), 1.18 (*s*, 22 H, 11 C*H*$_2$), 1.63–1.87 (m, 2 H, H-7c,7'c), 1.77 (s, 3 H, AcN), 1.90, 1.92, 1.95, 2.02, 2.10 (5 s, 15 H, 5 AcO), 2.65 (dd, 1 H, $J_{3ax,3eq}$ 12.6, $J_{3eq,4}$ 4.6 Hz, H-3c*eq*), 3.29 (dt, 1 H, $J_{5,6} = J_{6,7'} = 10.3$, $J_{6,7} = 2.5$ Hz, H-6c), 3.67 (s, 3 H, MeO), 4.01 (q, 1 H, $J_{4,5} = J_{5,6} = J_{5,NH} = 10.3$ Hz, H-5c), 4.60 (dd, 1 H, $J_{2,3}$ 10.1, $J_{3,4}$ 3.3 Hz, H-3b), 4.61 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1a), 4.83 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1b), 4.97 (dd, 1 H, H-2b), 4.98 (br. d, 1 H, H-4b), 4.99 (m, 1 H, H-4c), 5.17 (dd, 1 H, $J_{2,3}$ 9.9 Hz, H-3a), 5.46 (m, 1 H, H-8c), 5.47 (dd, 1 H, $J_{3,4}$ 8.4, $J_{4,5}$ 14.5 Hz, H-4 of sphingosine), 5.60 (dt, 1 H, $J_{5,6} = J_{5,6'} = 6.6$ Hz, H-5 of sphingosine), and 7.19–8.00 (m, 25 H, 5 Ph).

Anal. Calcd for $C_{87}H_{107}N_4O_{29}$ (1669.8): C, 62.57; H, 6.46; N, 3.36. Found: C, 62.51; H, 6.48; N, 3.29.

O-*(Methyl 5-acetamido-8,9-di-*O*-acetyl-4-*O*-benzoyl-3,5,7-trideoxy-α-*D-galacto-*2-nonulopyranosylonate)-(2 → 3)-*O*-(2,4-di-*O*-acetyl-6-*O*-benzoyl-β-*D-*galactopyranosyl)-(1 → 4)-*O*-(3-*O*-acetyl-2,6-di-*O*-benzoyl-β-*D-*glucopyranosyl)-(1 → 1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol* (**27**).—Selective reduction of the azido group in **26** (60 mg, 0.04 mmol) with H_2S, and subsequent coupling with octadecanoic acid (25 mg, 0.09 mmol) in the presence of WSC (40 mg) as described for **24** afforded compound **27** (54 mg, 78%) as an amorphous mass, $[\alpha]_D$ +8.5 (*c* 1.0, $CHCl_3$); ^{1}H-NMR ($CDCl_3$) δ 0.88 (t, 6 H, $J_{17,18}$ 6.5 Hz, 2 C*H*$_3$CH$_2$), 1.26 (s, 50 H, 25 C*H*$_2$), 1.76–1.95 (m, 2 H, H-7c,7'c), 1.84 (s, 3 H, AcN), 1.97, 2.00, 2.01, 2.09, 2.15 (5 s, 15 H, 5 AcO), 2.72 (dd, 1 H, $J_{3ax,3eq}$ 12.3, $J_{3eq,4}$ 4.6 Hz, H-3c*eq*), 3.36 (m, 1 H, H-6c), 3.74 (s, 3 H, MeO), 4.68 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 4.87 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1b), 5.02 (dd, 1 H, $J_{2,3}$ 9.9 Hz, H-2b), 5.05 (m, 1 H, H-4c), 5.06 (br. d, 1 H, H-4c), 5.18 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2a), 5.48 (m, 1 H, H-8c), 5.52 (t, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3a), 5.66 (d, 1 H, N*H*), 5.77 (dt, 1 H, $J_{4,5} = 14.0$, $J_{5,6} = J_{5,6'} = 7.0$ Hz, H-5 of ceramide), and 7.27–8.07 (m, 25 H, 5 Ph).

Anal. Calcd for $C_{105}H_{140}N_2O_{30}$ (1910.3): C, 66.01; H, 7.39; N, 1.47. Found C, 65.86; H, 7.41; N, 1.45.

O-*(5-Acetamido-3,5,7-trideoxy-α-*D-galacto-*2-nonulopyranosylonic acid)-(2 → 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* (**28**).—Deacylation and saponification of **27** (54 mg, 0.03 mmol), as described for **25**, yielded compound **28** (35 mg, quantitative) as an amorphous mass, $[\alpha]_D$ −9.2° (*c* 0.7, 1:1 MeOH–$CHCl_3$); ^{1}H-NMR (1:1

$CDCl_3$–CD_3OD): δ 0.89 (t, 6 H, $J_{17,18}$ 6.6 Hz, 2 CH_3CH_2), 1.28 (s, 50 H, 25 CH_2), 1.99 (s, 3 H, AcN), 2.78 (dd, 1 H, H-3c*eq*), 4.31, 4.43 (2 d, 2 H, $J_{1,2}$ 7.5 Hz, H-1a,b), 5.45 (dd, 1 H, $J_{3,4}$ 7.0, $J_{4,5}$ 15.2 Hz, H-4 of ceramide), and 5.69 (dt, 1 H, $J_{5,6} = J_{5,6'} = 6.6$ Hz, H-5 of ceramide).

Anal. Calcd for $C_{59}H_{108}N_2O_{20}$ (1165.5): C, 60.80; H, 9.34; N, 2.40. Found: C, 60.55; H, 9.49; N, 2.42.

O-*(Methyl 5-acetamido-4,7,9-tri*-O-*acetyl-3,5,8-trideoxy-α*-D-*galacto-2-nonulopyranosylonate)-(2 → 3)*-O-*(2,4-di*-O-*acetyl-6*-O-*benzoyl-β*-D-*galactopyranosyl)-(1 → 4)*-O-*(3*-O-*acetyl-2,6-di*-O-*benzoyl-β*-D-*glucopyranosyl)-(1 → 1)-(2*S,*3*R,*4*E*)-2-azido-3*-O-*benzoyl-4-octadecene-1,3-diol* (**29**).—Coupling of **19** (183 mg, 0.14 mmol) and **22** (145 mg, 0.34 mmol), as described for **23**, gave compound **29** (167 mg, 75.5%) as an amorphous mass, $[\alpha]_D$ – 9.5° (*c* 1.3, $CHCl_3$); IR: ν 3500–3300 (NH), 2940 and 2840 (Me, CH_2), 2100 (N_3), 1720 and 1220 (ester), 1670 and 1540 (amide), and 710 cm^{-1} (Ph); ^{1}H-NMR ($CDCl_3$): δ 0.88 (t, 3 H, $J_{17,18}$ 6.5 Hz, CH_3CH_2), 1.25 (s, 22 H, 11 CH_2), 1.72 (t, 1 H, $J_{3ax,3eq} = J_{3ax,4} = 12.6$ Hz, H-3c*ax*), 1.85 (s, 3 H, AcN), 1.90–2.15 (m, 2 H, H-8c,8'c), 1.97, 1.99, 2.01 (2), 2.12, 2.19 (6 s, 18 H, 6 AcO), 2.56 (dd, 1 H, $J_{3eq,4}$ 4.6 Hz, H-3c*eq*), 3.35 (dd, 1 H, $J_{5,6}$ 10.4, $J_{6,7}$ 2.0 Hz, H-6c), 3.77 (s, 3 H, MeO), 4.00 (q, 1 H, $J_{4,5} = J_{5,6} = J_{5,NH} = 10.4$ Hz, H-5c), 4.58 (dd, 1 H, $J_{2,3}$ 9.9, $J_{3,4}$ 3.3 Hz, H-3b), 4.69 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 4.72 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1b), 4.94 (ddd, 1 H, H-4c), 5.04 (dd, 1 H, H-2b), 5.15 (br. d, 1 H, H-4b), 5.22 (d, 1 H, N*H*), 5.26 (dd, 1 H, $J_{2,3}$ 9.2 Hz, H-2a), 5.43 (m, 1 H, H-7c), 5.48 (t, H, $J_{2,3} = J_{3,4} = 9.2$ Hz, H-3a), 5.54 (dd, 1 H, $J_{3,4}$ 8.2, $J_{4,5}$ 15.0 Hz, H-4 of sphingosine), 5.69 (dt, 1 H, $J_{5,6} = J_{5,6'} = 6.6$ Hz, H-5 of sphingosine), and 7.27–8.09 (m, 20 H, 4 Ph).

Anal. Calcd for $C_{82}H_{102}N_4O_{29}$ (1607.7): C, 61.26; H, 6.40; N, 3.49. Found: C, 61.18; H, 6.59; N, 3.45.

O-*(Methyl 5-acetamido-4,7,9-tri*-O-*acetyl-3,5,8-trideoxy-α*-D-galacto-*2-nonulopyranosylonate)-(2 → 3)*-O-*(2,4-di*-O-*acetyl-6*-O-*benzoyl-β*-D-*galactopyranosyl)-(1 → 4)*-O-*(3*-O-*acetyl-2,6-di*-O-*benzoyl-β*-D-*glucopyranosyl)-(1 → 1)-(2*S,*3*R,*4*E*)-3*-O-*benzoyl-2-octadecanamido-4-octadecene-1,3-diol* (**30**).—Selective reduction of the azide group in **29** (165 mg, 0.1 mmol) and subsequent coupling with octadecanoic acid (50 mg, 0.18 mmol), as described for **24**, afforded compound **30** (150 mg, 78.5%) as an amorphous mass, $[\alpha]_D$ +5.4° (*c* 1.2, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): δ 0.88 (t, 6 H, $J_{17,18}$ 6.6 Hz, 2 CH_3CH_2), 1.26 (s, 50 H, 25 CH_2), 1.85 (s, 3 H, AcN), 1.88–2.16 (m, 2 H, H-8c,8'c), 1.97, 1.99 (2), 2.00, 2.11, 2.16 (6 s, 18 H, 6 AcO), 2.55 (dd, 1 H, $J_{3ax,3eq}$ 12.9, $J_{3eq,4}$ 4.7 Hz, H-3c*eq*), 3.36 (dd, 1 H, $J_{5,6}$ 10.1, $J_{6,7}$ 2.1 Hz, H-6c), 3.77 (s, 3 H, MeO), 4.09 (q, 1 H, $J_{4,5} = J_{5,6} = J_{5,NH} = 10.1$ Hz, H-5c), 4.55 (dd, 1 H, $J_{2,3}$ 10.4, $J_{3,4}$ 3.5 Hz, H-3b), 4.60 (d, 1 H, $J_{1,2}$ 8.6 Hz, H-1a), 4.68 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 4.93 (ddd, 1 H, H-4c), 5.02 (dd, 1 H, H-2b), 5.14 (br. d, 1 H, H-4b), 5.19 (dd, 1 H, $J_{2,3}$ 9.7 Hz, H-2a), 5.47 (t, 1 H, $J_{2,3} = J_{3,4} = 9.7$ Hz, H-3a), 5.78 (dt, 1 H, $J_{3,4} = 15.0$, $J_{5,6} = J_{5,6'} = 6.7$ Hz, H-5 of ceramide), and 7.25–8.03 (m, 20 H, 4 Ph).

Anal. Calcd for $C_{100}H_{138}N_2O_{30}$ (1848.2): C, 64.98; H, 7.53; N, 1.52. Found: C, 64.70; H, 7.68; N, 1.50.

O-*(5-Acetamido-3,5,8-trideoxy-α-*D-galacto-*2-nonulopyranosylonic acid)-(2 → 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* (**31**).—Deacylation and saponification of **30** (149 mg, 0.08 mmol), as described for **25**, yielded compound **31** (90 mg, quantitative) as an amorphous mass, $[\alpha]_D$ −1.2° (*c* 1.0, 1 : 1 MeOH–$CHCl_3$); IR: *ν* 3500-3300 (OH, NH), 2940 and 2850 (Me, CH_2), 1720 (COOH), and 1640 and 1550 cm^{-1} (amide); ^{1}H-NMR (1 : 1 $CDCl_3$–CD_3OD): *δ* 0.89 (t, 6 H, $J_{17,18}$ 6.5 Hz, 2 C*H*$_3$CH$_2$), 1.27 (s, 50 H, 25 CH_2), 1.99 (s, 3 H, AcN), 2.71 (dd, 1 H, H-3c*eq*), 4.30 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 4.42 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1b), 5.45 (dd, 1H, $J_{3,4}$ 7.3, $J_{4,5}$ 15.0 Hz, H-4 of ceramide), and 5.69 (dt, 1 H, $J_{5,6} = J_{5,6'} = 6.4$ Hz, H-5 of ceramide).

Anal. Calcd for $C_{59}H_{108}N_2O_{20}$ (1165.5): C, 60.80; H, 9.34; N, 2.40. Found: C, 60.73; H, 9.51; N, 2.32.

O-*(Methyl 5-acetamido-4,7,8-tri-*O-*acetyl-3,5,9-trideoxy-*D-glycero-*α-*D-galacto-*2-nonulopyranosylonate)-(2 → 3)-*O-*(2,4-di-*O-*acetyl-6-*O-*benzoyl-β-*D-*galactopyranosyl)-(1 → 4)-*O-*(3-*O-*acetyl-2,6-di-*O-*benzoyl-β-*D-*glucopyranosyl)-(1 → 1)-(2*S,*3*R,*4*E*)-2-azido-3-*O-*benzoyl-4-octadecene-1,3-diol* (**32**).—Coupling of **21** (100 mg, 0.07 mmol) with **22** (70 mg, 0.16 mmol), as described for **23**, gave compound **32** (110 mg, 92.5%) as an amorphous mass, $[\alpha]_D$ −8.6° *c* 1.1, $CHCl_3$); IR: *ν* 3400 (NH), 2940 and 2840 (Me, CH_2), 2100 (N_3), 1730 and 1220 (ester), 1650 and 1530 (amide), and 710 cm^{-1} (Ph); ^{1}H-NMR ($CDCl_3$): *δ* 0.87 (t, 3 H, $J_{17,18}$ 6.5 Hz, C*H*$_3$CH$_2$), 1.10 (d, 3 H, $J_{8,9}$ 6.2 Hz,C*H*$_3$CH), 1.24 (s, 22 H, 11 CH_2), 1.87 (s, 3 H, AcN), 1.88, 1.99, 2.01, 2.03, 2.11, 2.19 (6 s, 18 H, 6 AcO), 2.55 (dd, 1 H, $J_{3eq,3ax}$ 12.3, $J_{3eq,4}$ 4.4 Hz, H-3c*eq*), 3.57 (dd, 1 H, $J_{5,6}$ 10.6, $J_{6,7}$ 2.9 Hz, H-6c), 3.71 (s, 3 H, MeO), 4.68 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1a), 4.85 (m, 1 H, H-4c), 4.86 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1b), 4.99 (br d, 1 H, H-4b), 5.00 (dd, 1 H, $J_{2,3}$ 10.1 Hz, H-2b), 5.15 (dd, 1 H, H-7c), 5.25 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2a), 5.40 (m, 1 H, H-8c), 5.47 (t, 1 H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H-3a), 5.65 (m, 1 H, H-5 of sphingosine), and 7.26–8.07 (m, 20 H, 4 Ph).

Anal. Calcd for $C_{82}H_{102}N_4O_{29}$ (1607.7): C, 61.26; H, 6.40; N, 3.49. Found: C, 61.33; H, 6.51; N, 3.45.

O-*(Methyl 5-acetamido-4,7,8-tri-*O-*acetyl-3,5,9-trideoxy-*D-glycero-*α-*D-galacto-*2-nonulopyranosylonate)-(2 → 3)-*O-*(2,4-di-*O-*acetyl-6-*O-*benzoyl-β-*D-*galactopyranosyl)-(1 → 4)-*O-*(3-*O-*acetyl-2,6-di-*O-*benzoyl-β-*D-*glucopyranosyl)-(1 → 1)-(2*S,*3*R,*4*E*)-3-*O-*benzoyl-2-octadecanamido-4-octadecene-1,3-diol*(**33**).—Selective reduction of the azido group in **32** (110 mg, 0.06 mmol) and subsequent coupling with octadecanoic acid (44 mg, 0.15 mmol), as described for **24**, afforded compound **33** (97 mg, 77%) as an amorphous mass, $[\alpha]_D$ −5.0° (*c* 1.0, $CHCl_3$); ^{1}H-NMR ($CDCl_3$): *δ* 0.87 (t, 6 H, $J_{17,18}$ 6.6 Hz, 2 C*H*$_3$CH$_2$), 1.11 (d, 3 H, $J_{8,9}$ 6.2 Hz, C*H*$_3$CH), 1.26 (s, 50 H, 25 CH_2), 1.65 (t, 1 H, $J_{3ax,3eq} = J_{3ax,4} = 12.5$ Hz, H-3c*ax*), 1.83 (s, 3 H, AcN), 1.88, 1.99, 2.00, 2.03, 2.10, 2.18 (6 s, 18 H, 6 AcO), 2.58 (dd, 1 H, $J_{3ax,3eq}$ 12.5 Hz, $J_{3eq,4}$ 4.3 Hz, H-3c*eq*), 3.58 (dd, 1 H, $J_{5,6}$ 10.6, $J_{6,7}$

2.9 Hz, H-6c), 3.71 (s, 3 H, MeO), 4.55 (dd, 1 H, $J_{2,3}$ 9.9, $J_{3,4}$ 3.3 Hz, H-3b), 4.60 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 4.82 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1b), 5.06 (dd, 1 H, H-2b), 5.14 (dd, 1 H, $J_{7,8}$ 7.3 Hz, H-7c), 5.19 (dd, 1 H, $J_{2,3}$ 9.9 Hz, H-2a), 5.40 (m, 1 H, H-8c), 5.43 (t, 1 H, $J_{2,3} = J_{3,4} = 9.9$ Hz, H-3a), 5.76 (dt, 1 H, $J_{4,5} = 14.0$, $J_{5,6} = J_{5,6'} =$ 6.6 Hz, H-5 of ceramide), and 7.26–8.07 (m, 20 H, 4 Ph).

Anal. Calcd for $C_{100}H_{138}N_2O_{30}$ (1848.2): C, 64.98; H, 7.53; N, 1.52. Found: C, 64.71; H, 7.53; N, 1.49.

O-*(5-Acetamido-3,5,9-trideoxy-*D-glycero-*α-*D-galacto-*2-nonulopyranosylonic acid)-(2 → 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* (**34**).—Deacylation and saponification of **33** (91 mg, 0.049 mmol), as described for **25**, yielded compound **34** (52 mg, 90%) as an amorphous mass, $[\alpha]_D -0.5°$ (*c* 1.2, 1:1 $CHCl_3$–MeOH); IR: *ν* 3700–3300 (OH, NH) 2940 and 2850 (Me, CH_2), 1720 (COOH), and 1660 and 1540 cm^{-1} (amide); ^{1}H-NMR (1:1 $CDCl_3$–CD_3OD): δ 0.88 (t, 6 H, $J_{17,18}$ 6.5 Hz, 2 CH_3CH_2), 1.27 (s, 50 H, 25 CH_2), 2.03 (s, 3 H, AcN) 2.85 (dd, 1 H, H-3c*eq*), 4.31 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 4.42 (d, 1 H, 7.6 Hz, H-1b), 5.43 (dd, 1 H, $J_{3,4}$ 7.7, $J_{4,5}$ 15.0 Hz, H-4 of ceramide), and 5.68 (dt, 1 H, $J_{5,6} = J_{5,6'} = 6.8$ Hz, H-5 of ceramide).

Anal. Calcd for $C_{59}H_{108}N_2O_{20}$ (1165.5): C, 60.80; H, 9.34; N, 2.40. Found: C, 60.73; H, 9.61; N, 2.39.

ACKNOWLEDGMENT

This work was supported in part by a Grant-in-Aid (No. 03255207) for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture of Japan.

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