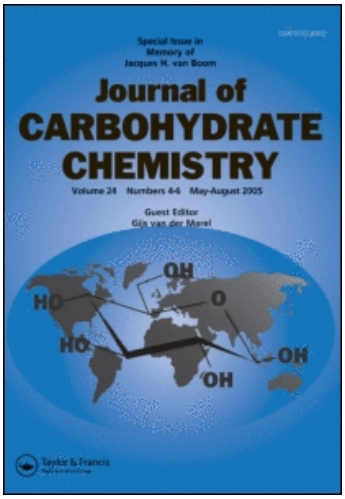

Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

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To cite this Article Terada, Tomohiro , Kiso, Makoto and Hasegawa, Akira(1993) 'Synthetic Studies on Sialoglycoconjugates 44: Synthesis of KDN-Gangliosides Gm_4 and GM_3', Journal of Carbohydrate Chemistry, 12: 4, 425 — 440
To link to this Article: DOI: 10.1080/07328309308019398
URL: http://dx.doi.org/10.1080/07328309308019398

J. CARBOHYDRATE CHEMISTRY, 12(4&5), 425-440 (1993)

SYNTHETIC STUDIES ON SIALOGLYCOCONJUGATES 44: SYNTHESIS OF KDN-GANGLIOSIDES GM_4 and GM_3

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Received October 23, 1992 - Final Form December 23, 1992

ABSTRACT

Ganglioside GM_4 and GM_3 analogs, containing 3-deoxy-D-*glycero*-D-*galacto*-2-nonulopyranosonic acid (KDN) in place of *N*-acetylneuraminic acid, have been synthesized. KDN, prepared by the condensation of oxalacetic acid with D-mannose, was converted into methyl (phenyl 4,5,7,8,9-penta-*O*-acetyl-3-deoxy-2-thio-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (**2**) *via* methyl esterification, *O*-acetylation and replacement of the anomeric acetoxy group with phenylthio. Glycosylation of **2** with 2-(trimethylsilyl)ethyl 6-*O*-benzoyl-β-D-galactopyranoside (**3**) or 2-(trimethylsilyl)ethyl *O*-(6-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2,6-di-*O*-benzoyl-β-D-glucopyranoside (**4**) was performed, using *N*-iodosuccinimide-trimethylsilyl trifluoromethanesulfonate as the glycosyl promoter, to give 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 (**5**) and 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-galactopyranosyl)-(1→4)-(2,6-di-*O*-benzoyl-β-D-glucopyranoside (**9**), respectively. Compounds **5** and **9** were converted *via* *O*-acetylation, selective removal of the 2-(trimethylsilyl)ethyl group and subsequent imidate formation, into the corresponding trichloroacetimidates **8** and **12**, respectively. Glycosylation of (2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol (**13**) with **8** and **12** in the presence of boron trifluoride etherate afforded the expected β-glycosides **14** and **17**, which were transformed *via* selective reduction of the azido group, coupling with octadecanoic acid, *O*-deacylation and de-esterification, into the target gangliosides **16** and **19** in high yields.

INTRODUCTION

Sialic acids[2] are well known as important constituents of cell-surface glycoproteins and glycolipids and are involved in a variety of the biological functions of the

sialoglycoconjugates. Recently, a novel type of sialic acid, 3-deoxy-D-*glycero*-D-*galacto*-2-nonulopyranosylonic acid (KDN) having a hydroxyl group in place of an acetamido group at C-5 of *N*-acetylneuraminic acid (Neu5Ac), was reported by Inoue,[3] who isolated it from rainbow trout egg vitelline envelope. In 1991 KDN-ganglioside GM_3 was isolated[4] from rainbow trout sperm, indicating the possibility of the widespread distribution of this class of ganglioside in nature. However, the biological function of KDN-ganglioside has not been investigated in detail, because a limited quantity of the required material was available. We have reported[5] the systematic syntheses of gangliosides and their analogs, syntheses based on the facile dimethyl(methylthio)sulfonium triflate (DMTST) or *N*-iodosuccinimide-trifluoromethanesulfonic acid promoted, stereoselective α- glycosidation[6,7] of sialic acid with suitably protected galactose and lactose residues in acetonitrile medium. As a part of our continuing studies on the preparation and structure-function relationships of gangliosides, we describe here the first total synthesis of KDN-gangliosides GM_3 and GM_4. Here, *N*-acetylneuraminic acid residue is replaced by 3-deoxy-D-*glycero*-D-*galacto*-2-nonulopyranosylonic acid, thus allows us investigations of the biological function of KDN-gangliosides, and also the elucidation of the role of the C-5 hydroxyl group in the Neu5Ac residue in biological systems.

RESULTS AND DISCUSSION

For the synthesis of the desired KDN-gangliosides GM_4 and GM_3, we employed the phenyl 2-thioglycoside **2** of 3-deoxy-D-*glycero*-D-*galacto*-2-nonulopyranosonic acid[8] as the glycosyl donor and 2-(trimethylsilyl)ethyl 6-*O*-benzoyl-β-D-galactopyranoside[9] (**3**) and 2-(trimethylsilyl)ethyl *O*-(6-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2,6-di-*O*-benzoyl-β-D-glucopyranoside[10] (**4**) as the suitably protected glycosyl acceptor.

The aceptor **3** or **4** was coupled with the donor using *N*-iodosuccinimide[7,11] (NIS)-trimethylsilyl trifluoromethanesulfonate (TMS·OTf) as a promoter. According to our method,[10] the intermediates could be converted into the end products by introduction of a ceramide moiety.

Methyl 3-deoxy-2,4,5,7,8,9-hexa-*O*-acetyl-D-*glycero*-D-*galacto*-2-nonulopyranosonate (**1**)[12] was obtained in 51% yield by condensation[8] of oxalacetic acid with D-mannose and subsequent methyl esterification and *O*-acetylation. Treatment of compound **1** with thiophenol in dichloromethane in the presence of boron trifluoride etherate gave methyl (phenyl 4,5,7,8,9-penta-*O*-acetyl-3-deoxy-2-thio-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (**2**) in 92% yield as ~1:3 (α:β) anomeric mixture.

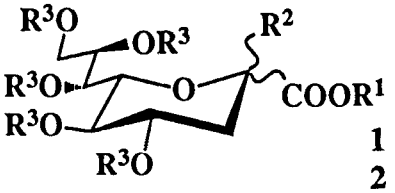
Glycosylation[7] of **3** with **2** (1.5 equiv with respect to the acceptor), in acetonitrile for 2 h at - 40 °C in the presence of NIS (2.0 equiv with respect to the donor)-TMS·OTf (0.2 equiv with respect to **2**) and molecular sieves 3Å, gave exclusively the α-glycoside, 2-(trimethylsilyl)ethyl *O*-(methyl 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 (**5**) in 49% yield. In essentially the same way, reaction of **4** with **2** furnished the α-sialyl-(2→3')-lactoside **9** in 46% yield. 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.[5a,6a] Acetylation of **5** and **9** gave the acetates **6** and **10**, respectively, in almost quantitative yields. The structures of **6** and **10** were unambiguously proved by 270 MHz ^{1}H NMR spectroscopy. The observed chemical shift and coupling constants of KDN units for H-3*eq* (δ 2.65, $J_{3eq,4}$ = 4.8 Hz, Jgem = 12.8 Hz for **6**; 2.75, $J_{3eq,4}$ = 4.0 Hz, Jgem = 12.5 Hz for **10**), for H-4 (δ 4.94 for **6**; 5.02 for **10**), and for H-7 (δ 5.39, $J_{7,8}$ = 9.5 Hz for **6**; 5.50, $J_{7,8}$ = 9.4 Hz for **10**), are characteristic of α-glycosidically linked[13] sialic acid analogs, and the values for H-3 (δ 4.57, $J_{2,3}$ = 9.9 Hz, $J_{3,4}$ = 3.3 Hz) in galactose unit, and H-3' (δ 4.70, $J_{2',3'}$ = 9.3 Hz, $J_{3',4'}$ = 3.3 Hz) in the lactose unit indicate the position of glycosylation to be C-3 and C-3', respectively. Other ^{1}H NMR data are given in the Experimental Section and are consistent with the structures assigned.

Selective removal of the 2-(trimethylsilyl)ethyl group from **6** and **10** was performed by treatment[10,14] with boron trifluoride etherate in dichloromethane for 5 h at 0 °C, to give the corresponding 1-hydroxy derivatives **7** and **11** in almost quantitative yields, after column chromatography.

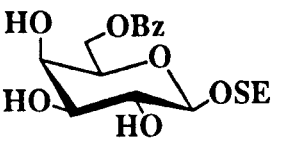
Treatment[10,15] of **7** or **11** with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) for 3 h at 0 °C gave the corresponding trichloroacetimidates **8** and **12** as the α-anomers in 90% and 91% yields, respectively. The glycosylation[10,16] of (2*S*, 3*R*, 4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol[17,18] (**13**) with **8** or **12** thus obtained, in dichloromethane for 5 h at 0 °C in the presence of boron trifluoride etherate and molecular sieves 4Å, gave only the desired β-glycosides **14** and **17** in 89 and 84% yields, respectively.

A significant signal in the ^{1}H NMR spectra of **14** and **17** was a one-proton doublet at δ 4.70 ($J_{1,2}$ = 8.1 Hz, H-1 for the galactose unit) or at δ 4.68 ($J_{1,2}$ = 7.7 Hz, H-1 for the lactose unit), showing the newly formed glycosidic linkage to be β.

Selective reduction[17,19] of the azido group in **14** or **17** with hydrogen sulfide in aqueous 83% pyridine for 48 h at 0 °C and subsequent condensation with octadecanoic acid, using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (WSC) in dichloromethane



1 R^1 = Me, R^2 = OAc, R^3 = Ac
2 R^1 = Me, R^2 = SPh, R^3 = OAc



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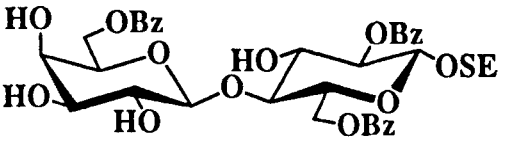

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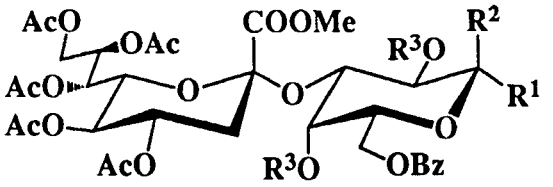
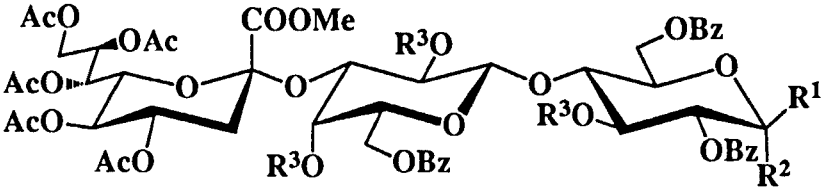
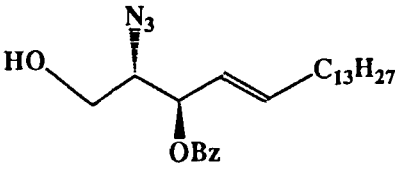


	R^1	R^2	R^3
5	OSE	H	H
6	OSE	H	Ac
7		H,OH	Ac
8	H	$OC(=NH)CCl_3$	Ac



	R^1	R^2	R^3
9	OSE	H	H
10	OSE	H	Ac
11		H,OH	Ac
12	H	$OC(=NH)CCl_3$	Ac



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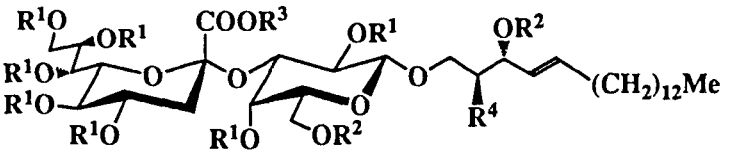
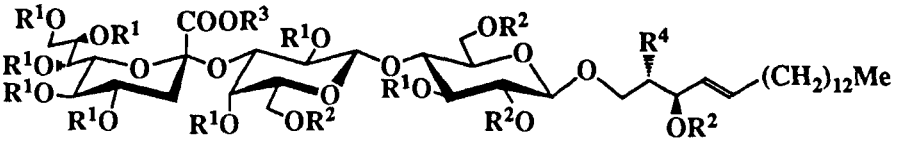


	R^1	R^2	R^3	R^4
14	Ac	Bz	Me	N_3
15	Ac	Bz	Me	$NHCO(CH_2)_{16}Me$
16	H	H	H	$NHCO(CH_2)_{16}Me$



	R^1	R^2	R^3	R^4
17	Ac	Bz	Me	N_3
18	Ac	Bz	Me	$NHCO(CH_2)_{16}Me$
19	H	H	H	$NHCO(CH_2)_{16}Me$

furnished high yields (88 and 89%) of the corresponding acylated gangliosides **15** and **18**, respectively. Finally, *O*-deacylation of **15** and **18** with sodium methoxide in methanol, with subsequent saponification of the sialate methyl ester group, yielded the desired KDN-gangliosides **16** and **19** in quantitative yields. The ^1H NMR data of the products thus obtained are consistent with the structures assigned.

In conclusion, the first total synthesis of KDN-gangliosides GM_3 and GM_4 has been achieved by use of the phenyl 2-thioglycoside of KDN as a glycosyl donor, suitably protected galactose and lactose derivatives as acceptors, and *N*-iodosuccinimide-TMS•OTf as a promoter.

EXPERIMENTAL

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

Methyl 2,4,5,7,8,9-Hexa-*O*-acetyl-3-deoxy-D-*glycero*-D-*galacto*-2-nonulopyranosonate (1). To a stirred solution of Na_2CO_3 (5.65 g, 53.3 mmol) in water (25 mL) was added D-mannose (24 g, 0.13 mol) followed by a slow addition of oxalacetic acid (6 g, 45.4 mmol) while the basicity of the solution was kept at pH 11 by addition of 10 M NaOH. The mixture was stirred for 2 h at room temperature then concentrated. Column chromatography (0.3 M formic acid) of the residue on Dowex-1 resin (formate form) gave crude 3-deoxy-D-*glycero*-D-*galacto*-2-nonulopyranosonic acid (KDN), which was used for the next reaction without further purification. To a suspension of KDN, thus obtained, in methanol (150 mL) was added Dowex-50 (H^+) resin (25 g) and the mixture was stirred for 24 h at room temperature, filtered, and the resin was washed with methanol. The combined filtrate and washings were concentrated. To a suspension of the residue in acetic anhydride (150 mL) was slowly added pyridine (150 mL) at 0 °C, and the mixture was stirred for 12 h at room temperature, concentrated, and the residue was extracted with dichloromethane. The extract was successively washed with 2 M hydrochloric acid, M Na_2CO_3 and water, dried (Na_2SO_4), and concentrated. Column chromatography (2:3 ethyl acetate-hexane) of the residue gave **1** (12.4 g, 51%) as an amorphous mass: ^1H NMR ($CDCl_3$) δ 2.01, 2.02, 2.04, 2.05, 2.07 and 2.16 (6s, 18H, 6AcO), 2.45 (dd, H-3*ax*), 2.62 (dd, $J_{3eq,4}$ = 5.1 Hz, Jgem = 13.4 Hz, H-3*eq*), 3.78 (s, MeOβ), 3.80 (s, MeOα), 4.19 (dd, $J_{8,9}$ = 7.2

Hz, $J_{9,9'}$ = 12.6 Hz, H-9), 4.20 (dd, $J_{5,6}$ = 10.1 Hz, $J_{6,7}$ = 2.2 Hz, H-6), 4.43 (dd, $J_{8,9'}$ = 2.4 Hz, H-9'), 4.97 (t, $J_{4,5} = J_{5,6}$ = 10.1 Hz, H-5), 5.15 (ddd, H-8α), 5.27 (ddd, H-4α), 5.39 (dd, $J_{7,8}$ = 6.4, H-7α), and 5.54 (m, H-8β); anomeric ratio (α:β) was estimated as ~1:10 from the ratio of intensities of the methyl ester signals.

Anal. Calcd for $C_{22}H_{30}O_{15}$ (534.5): C, 49.44; H, 5.66. Found: C, 49.36; H, 5.83.

Methyl (Phenyl 4,5,7,8,9-Penta-*O*-acetyl-3-deoxy-2-thio-D-*glycero*-D-*galacto*-2-nonulopyranosid)onate (2). To a solution of **1** (3.27 g, 6.12 mmol) in dichloromethane (50 mL), were added at 0 °C thiophenol (6.91 mL, 6.73 mmol) and boron trifluoride etherate (1.88 mL, 15.3 mmol), and the mixture was stirred for 3 h at room temperature, while the reaction was monitored by TLC. The mixture was extracted with dichloromethane (100 mL) and washed successively with M Na_2CO_3 and water, dried (Na_2SO_4) and concentrated. Column chromatography (2:3 ethyl acetate-hexane) of the residue gave amorphous **2** (3.27 g, 92%): ^{1}H NMR ($CDCl_3$) δ 2.73 (dd, $J_{3eq,4}$ = 5.1 Hz, Jgem = 13.9 Hz, H-3*eq*-β), 2.89 (dd, $J_{3eq,4}$ = 4.8 Hz, Jgem = 12.8 Hz, H-3*eq*-α), 4.90 (ddd, H-4α), 5.44 (ddd, H-4β), 3.56 (s, MeO-α), and 3.67 (s, MeO-β); the anomeric ratio (α:β) was estimated as ~1:3 from the ratio of intensities of the methyl ester signals.

Anal. Calcd for $C_{26}H_{32}O_{13}S$ (584.6): C, 53.42; H, 5.52. Found: C, 53.41; H, 5.47.

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 (5). To a solution of **3** (112.5 mg 0.192 mmol) and 2-(trimethylsilyl)ethyl 6-*O*-benzoyl-β-D-galactopyranoside[9] (**3**; 49.3 mg, 0.128 mmol) in dry acetonitrile (2 mL) were added molecular sieves 3Å (MS-3Å; 300 mg), the mixture was stirred for 6 h at room temperature. To the cooled (-40 °C) mixture was added, with stirring, *N*-iodosuccinimide (NIS; 86.6 mg, 0.385 mmol) and trimethylsilyl trifluoromethanesulfonate (TMS·OTf ; 7 μL, 0.038 mmol), and the stirring was continued for 2 h at -40 °C. The precipitate was filtered off and washed with dichloromethane. The filtrate and washings were combined and the solution was successively washed with M Na_2CO_3, M $Na_2S_2O_3$ and water, dried (Na_2SO_4), and concentrated. Column chromatography (1:1 ethyl acetate-hexane) of the residue on silica gel (30 g) gave amorphous **5** (48.1 mg, 49%): $[\alpha]_D$ -5.2° (*c* 0.9, $CHCl_3$); ^{1}H NMR ($CDCl_3$) Gal unit δ 1.07 (m, 2H, $Me_3SiCH_2CH_2O$), 4.53 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 4.54 (dd, 1H, $J_{5,6}$ = 7.1 Hz, $J_{6,6'}$ = 11.4 Hz, H-6), 4.62 (dd, 1H, $J_{5,6'}$ = 5.7 Hz, H-6), and 7.41-8.05 (m, 5H, Ph); KDN unit δ 2.01-2.13 (5s, 15H, 5AcO), 2.78 (dd, 1H,

$J_{3eq,4}$ = 3.7 Hz, Jgem = 12.6 Hz, H-3*eq*), 3.78 (s, 3H, MeO), 4.13 (dd, 1H, $J_{5,6}$ = 9.5 Hz, $J_{6,7}$ = 2.0 Hz, H-6), 4.90 (t, 1H, $J_{4,5} = J_{5,6}$ = 9.5 Hz, H-5), 4.92 (ddd, 1H, $J_{3ax,4}$ = 12.5 Hz, H-4), 5.36 (dd, 1H, $J_{7,8}$ = 9.5 Hz, H-7), and 5.48 (ddd, 1H, $J_{8,9}$ = 7.2 Hz, $J_{8,9'}$ = 4.4 Hz, H-8).

Anal. Calcd for $C_{38}H_{54}O_{20}Si$ (858.9): C, 53.14; H, 6.34. Found: C, 52.99; H, 6.30.

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-di-*O*-acetyl-6-*O*-benzoyl-β-D-galactopyranoside (6). Compound **5** (250 mg, 0.26 mmol) was treated with acetic anhydride (2 mL)-pyridine (4 mL) overnight at room temperature, and the product was purified by column chromatography with 1:1 ethyl acetate-hexane as the eluent, to give amorphous **6** (273.5 mg, quantitative): $[\alpha]_D$ -21° (*c* 0.5, $CHCl_3$); IR (KBr) 1750 and 1230 (ester), 860 and 840 (TMS), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$) Gal unit δ 0.99 (m, 2H, $Me_3SiCH_2CH_2O$), 4.22 (dd, 1H, $J_{5,6}$ = 4.0 Hz, $J_{6,6'}$ = 11.4 Hz, H-6), 4.23 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 4.40 (dd, 1H, $J_{5,6'}$ = 6.6 Hz, H-6'), 4.57 (dd, 1H, $J_{2,3}$ = 9.9 Hz, $J_{3,4}$ = 3.3 Hz, H-3), 5.04 (dd, 1H, H-2), 5.06 (broad d, 1H, H-4), and 7.39-8.04 (m, 5H, Ph); KDN unit δ 2.65 (dd, 1H, $J_{3eq,4}$ = 4.8 Hz, Jgem = 12.8 Hz, H-3*eq*), 3.72 (dd, 1H, $J_{5,6}$ = 9.5 Hz, $J_{6,7}$ = 2.6 Hz, H-6), 3.78 (s, 3H, MeO), 4.07 (dd, 1H, $J_{8,9}$ = 5.2 Hz, Jgem = 12.8 Hz, H-9), 4.29 (dd, 1H, $J_{8,9'}$ = 2.5 Hz, H-9'), 4.85 (t, 1H, $J_{4,5} = J_{5,6}$ = 9.5 Hz, H-5), 4.94 (m, 1H, H-4), 5.39 (dd, 1H, $J_{7,8}$ = 9.5 Hz, H-7), 5.57 (m, 1H, H-8); *O*-acetyl groups δ 1.97, 1.98, 2.03, 2.04, 2.10, 2.14 and 2.19 (7s, 21H, 7AcO).

Anal. Calcd for $C_{42}H_{58}O_{22}Si$ (943.0): C, 53.50; H, 6.20. Found: C, 53.41; H, 6.25.

***O*-(Methyl 4,5,7,8,9-Penta-*O*-acetyl-3-deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-2,4-di-*O*-acetyl-6-*O*-benzoyl-D-galacto-pyranose (7).** To a stirred solution of **6** (228.3 mg, 0.27 mmol) in dichloromethane (4 mL) cooled to 0 °C was added trifluoroacetic acid (4 mL), and the mixture was stirred for 5 h at 0 °C. Dichloromethane (30 mL) was added to the mixture, and the solution was washed successively with M Na_2CO_3 and water, dried (Na_2SO_4), and concentrated. Column chromatography (100:1 dichloromethane-methanol) of the residue gave amorphous **7** (196 mg, 96%): IR (KBr) 3550-3400 (OH), 1750 and 1230 (ester), and 710 cm^{-1} (Ph).

Anal. Calcd for $C_{37}H_{46}O_{22}$ (842.8): C, 52.73; H, 5.50. Found: C, 52.70; H, 5.71.

***O*-(Methyl 4,5,7,8,9-Penta-*O*-acetyl-3-deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-2,4-di-*O*-acetyl-6-*O*-benzoyl-α-D-galactopyranosyl trichloroacetimidate (8).** To a stirred solution of **7** (200 mg, 0.21 mmol) in dichloromethane (3 mL) were added at -5 °C trichloroacetonitrile (0.05 mL, 0.51 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 12 mg), and Drierite (200 mg). The mixture was stirred for 3 h at 0 °C and applied directly on a column of silica gel (40 g). Elution with 200:1 dichloromethane-methanol gave amorphous **8** (213 mg, 91%): $[\alpha]_D$ +12.0° (*c* 0.2, $CHCl_3$); IR (KBr) 3350 (NH), 1750 and 1230 (ester), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$) Gal unit δ 5.05 (dd, 1H, $J_{2,3}$ = 7.0 Hz, $J_{3,4}$ = 3.3 Hz, H-2), 5.15 (broad d, 1H, $J_{3,4}$ = 3.3 Hz, H-4), 6.55 (d, 1H, $J_{1,2}$ = 4.0 Hz, H-1), 7.34-8.04 (m, 5H, Ph), and 8.69 (s, 1H, C=NH); KDN unit δ 2.70 (dd, 1H, $J_{3eq,4}$ = 4.7 Hz, Jgem = 9.7 Hz, H-3*eq*), 3.75 (dd, 1H, $J_{5,6}$ = 6.2 Hz, $J_{6,7}$ = 2.0 Hz, H-6), 3.81 (s, 3H, MeO), 4.79 (t, 1H, $J_{4,5} = J_{5,6}$ = 6.2 Hz, H-5), 4.95 (m, 1H, H-4), 5.40 (dd, 1H, $J_{7,8}$ = 9.9 Hz, H-7), and 5.06 (m, 1H, H-8); *O*-acetyl groups δ 1.97-2.12 (7s, 21H, 7AcO).

Anal. Calcd for $C_{39}H_{46}Cl_3NO_{22}$ (987.2): C, 47.45; H, 4.70; N, 1.42. Found: C, 47.41; H, 4.86; N, 1.39.

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*-(6-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2,6-di-*O*-benzoyl-β-D-glucopyranoside (9). To a solution of compound **2** (200 mg, 0.342 mmol) and 2-(trimethylsilyl)ethyl *O*-(6-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-2,6-di-*O*-benzoyl-β-D-glucopyranoside[10] (**4**; 175 mg, 0.23 mmol) in dry acetonitrile (6 mL) were added MS-3Å (700 mg) and the mixture was stirred for 6 h at room temperature. To the cooled (-40 °C) mixture were added NIS (160 mg, 0.71 mmol) and TMS·OTf (13 μL, 0.068 mmol), and the mixture was stirred for 2 h at -40 °C, while the course of the reaction was monitored by TLC. The precipitate was filtered off and washed with dichloromethane. The filtrate and washings were combined, and the solution was successively washed with M Na_2CO_3, M $Na_2S_2O_3$ and water, dried (Na_2SO_4), and concentrated to a syrup which was chromatographed on a column of silica gel (30 g) with 1:1 ethyl acetate-hexane to gave amorphous **9** (130 mg 46%): $[\alpha]_D$ +11.5 ° (*c* 0.4, $CHCl_3$); IR (KBr) 3450-3250 (OH), 1750 and 1220 (ester), 860 and 840 (TMS), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$) Lac unit δ 0.99 (m, 2H, $Me_3SiCH_2CH_2O$), 4.70 (d, 1H, $J_{1',2'}$ = 7.9 Hz, H-1'), 4.75 (d, 1H, $J_{1,2}$ = 8.1 Hz, H-1), 4.87 (dd, 1H, $J_{2',3'}$ = 12.1 Hz, $J_{3',4'}$ = 3.5 Hz, H-3'), 5.38 (dd, 1H, H-2), and 7.42-8.19 (m, 15H, 3Ph); KDN unit δ 2.09-2.23 (5s, 15H, 5AcO), 2.86 (dd, 1H, $J_{3eq,4}$ = 4.4 Hz, Jgem = 13.2 Hz, H-3*eq*), 3.84 (dd, 1H, $J_{5,6}$ = 9.3 Hz, $J_{6,7}$ = 1.8 Hz, H-6),

3.91 (s, 3H, MeO), 4.99 (t, 1H, $J_{4,5} = J_{5,6} = 9.3$ Hz, H-5), 5.06 (m, 1H, H-4), 5.42 (dd, 1H, $J_{7,8} = 9.7$ Hz, H-7), and 5.47 (m, 1H, H-8).

Anal. Calcd for $C_{58}H_{72}O_{27}Si$ (1229.3): C, 56.67; H, 5.90. Found: C, 56.63; H, 5.84.

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-di-*O*-acetyl-6-*O*-benzoyl-β-D-galactopyranosyl)-(1→4)-3-*O*-acetyl-2,6-di-*O*-benzoyl-β-D-glucopyranoside (10). Compound **9** (100 mg, 0.081 mmol) was treated with acetic anhydride (2 mL)-pyridine (4 mL) overnight at room temperature, and the product was purified by chromatography on a column of silica gel (20 g) with 1:1 ethyl acetate-hexane as the eluent, to give amorphous **10** (109 mg, theoretical): $[\alpha]_D$ +6.1 ° (*c* 0.56, $CHCl_3$); ^1H NMR ($CDCl_3$) Lac unit δ 0.98 (m, 2H, $Me_3SiCH_2CH_2O$), 4.70 (dd, 1H, $J_{2',3'} = 9.3$ Hz, $J_{3',4'} = 3.3$ Hz, H-3'), 4.78 (d, 1H, $J_{1,2} = 8.1$ Hz, $J_{2,3} = 9.5$ Hz, H-1), 4.98 (d, 1H, $J_{1',2'} = 9.5$ Hz, H-1'), 5.11 (broad d, 1H, H-4'), 5.33 (dd, 1H, H-2), and 5.58 (t, 1H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H-3); KDN unit δ 2.75 (dd, 1H, $J_{3eq,4} = 4.0$ Hz, Jgem = 12.5 Hz, H-3*eq*), 3.80 (dd, 1H, $J_{5,6} = 9.5$ Hz, $J_{6,7} = 2.6$ Hz, H-6), 3.95 (s, 3H, MeO), 4.95 (t, 1H, $J_{4,5} = J_{5,6} = 9.5$ Hz, H-5), 5.02 (m, 1H, H-4), 5.50 (dd, 1H, $J_{7,8} = 9.4$ Hz, H-7), and 5.70 (m, 1H, H-8); *O*-acyl groups δ 2.07-2.32 (8s, 24H, 8AcO), and 7.49-8.18 (m, 15H, 3Ph).

Anal. Calcd for $C_{64}H_{78}O_{30}Si$ (1355.4): C, 56.71; H, 5.80. Found: C, 56.55; H, 5.98.

***O*-(Methyl 4,5,7,8,9-Penta-*O*-acetyl-3-deoxy-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-D-glucopyranose (11).** To a stirred solution of **10** (100 mg, 0.075 mmol) in dichloromethane (2 mL) cooled to 0 °C was added trifluoroacetic acid (2 mL). The mixture was stirred for 5 h at 0 °C. Dichloromethane (20 mL) was added, and the solution was successively washed with M Na_2CO_3 and water, dried (Na_2SO_4), and concentrated. Column chromatography (150:1 dichloromethane-methanol) of the residue gave amorphous **11** (92 mg, 98%): IR (KBr) 3350 (OH), 1750 and 1230 (ester) and 710 cm^{-1} (Ph).

Anal. Calcd for $C_{59}H_{66}O_{30}$ (1255.2): C, 56.46; H, 5.30. Found: C, 56.21; H, 5.44.

***O*-(Methyl 4,5,7,8,9-Penta-*O*-acetyl-3-deoxy-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 (12).** To a stirred solution of **11** (125 mg, 0.1 mmol)

in dichloromethane (2 mL) was added at -50 °C trichloroacetonitrile (30 μL, 0.30 mmol) and Drierite (200 mg), and the mixture was stirred for 3 h at 0 °C, while the reaction was monitored by TLC. The mixture was directly applied on a column of silica gel (20 g) and eluted with 150:1 dichloromethane-methanol, to give amorphous **12** (131 mg, 90%): $[\alpha]_D$ +22.0 ° (*c* 0.3, $CHCl_3$); IR (KBr) 3550 (NH), 1750 and 1230 (ester), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$) Lac unit δ 4.60 (dd, 1H, $J_{2',3'}$ = 7.0 Hz, $J_{3',4'}$ = 3.3 Hz, H-3'), 4.88 (dd, 1H, $J_{1',2'}$ = 8.1 Hz, H-1'), 5.01 (broad d, 1H, H-4'), 5.85 (t, 1H, $J_{2,3} = J_{3,4}$ = 9.5 Hz, H-3), 6.67 (d, 1H, $J_{1,2}$ = 3.3 Hz, H-1), and 8.54 (s, 1H, C=NH); KDN unit δ 2.64 (dd, 1H, $J_{3eq,4}$ = 4.0 Hz, Jgem = 12.1 Hz, H-3*eq*), 3.68 (dd, 1H, $J_{5,6}$ = 9.5 Hz, $J_{6,7}$ = 2.9 Hz, H-6), 3.73 (s, 3H, MeO), 4.86 (t, 1H, $J_{4,5} = J_{5,6}$ = 9.5 Hz, H-5), 5.39 (dd, 1H, $J_{7,8}$ = 9.2 Hz, H-7), and 5.54 (m, 1H, H-8); *O*-acyl groups δ 1.96-2.20 (8s, 24H, 8AcO) and 7.35-8.12 (m, 15H, 3Ph).

Anal. Calcd for $C_{61}H_{66}Cl_3NO_{30}$ (1399.6): C, 52.35; H, 4.75; N, 1.00. Found: C, 52.18; H, 4.93; N, 1.08.

***O*-(Methyl 4,5,7,8,9-Penta-*O*-acetyl-3-deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-acetyl-6-*O*-benzoyl-β-D-galactopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol (14).** To a solution of **8** (184 mg, 0.19 mmol) and (2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol[17] (**13**; 160 mg, 0.37 mmol) in dichloromethane (5 mL) were added molecular sieves 4Å (MS-4Å; 500 mg), and the mixture was stirred for 3 h at room temperature. Boron trifluoride etherate (0.14 mL) was added at 0 °C to the mixture, and this was stirred for 5 h at 0 °C. The precipitate was filtered off and washed with dichloromethane. 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 dichloromethane-methanol) of the residue gave amorphous **14** (208 mg, 89%): $[\alpha]_D$ -22.5° (*c* 0.36, $CHCl_3$); IR (KBr) 2100 (N_3), 1750 and 1230 (ester), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$) Gal unit δ 4.60 (dd, 1H, $J_{2,3}$ = 10.3 Hz, $J_{3,4}$ = 3.3 Hz, H-3), 4.70 (d, 1H, $J_{1,2}$ = 8.1 Hz, H-1), 5.07 (broad d, 1H, H-4); KDN unit δ 2.66 (dd, 1H, $J_{3eq,4}$ = 4.9 Hz, Jgem = 12.8 Hz, H-3*eq*), 3.74 (dd, 1H, $J_{5,6}$ = 9.5 Hz, $J_{6,7}$ = 2.5 Hz, H-6), 3.78 (s, 3H, MeO), 4.85 (t, 1H, $J_{4,5} = J_{5,6}$ = 9.5 Hz, H-5), 4.94 (ddd, 1H, $J_{3ax,4}$ = 13.3 Hz, H-4), 5.42 (dd, 1H, $J_{7,8}$ = 9.5 Hz, H-7), 5.64 (m, 1H, H-8); sphingosine unit δ 0.87 (t, 3H, $MeCH_2$), 1.23 (s, 22H, $11CH_2$), 5.94 (dt, 1H, $J_{4,5}$ = 14.3 Hz, $J_{5,6} = J_{5',6'}$ = 6.6 Hz, H-5); *O*-acyl groups δ 1.97-2.23 (7s, 21H, 7AcO) and 7.38-8.06 (m, 10H, 2Ph).

Anal. Calcd for $C_{62}H_{83}N_3O_{24}$ (1254.3): C, 59.37; H, 6.67; N, 3.35. Found: C, 59.29; H, 6.63; N, 3.42.

***O*-(Methyl 4,5,7,8,9-Penta-*O*-acetyl-3-deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-di-*O*-acetyl-6-*O*-benzoyl-β-D-galactopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol (15).** Hydrogen sulfide was bubbled at 0 °C through a solution of **14** (168 mg, 0.134 mmol) in pyridine (10 mL) and water (2 mL) for 48 h, while the course of the reaction was monitored by TLC. The mixture was concentrated to a syrup which was dissolved in dry dichloromethane (7 mL). Octadecanoic acid (76.2 mg, 0.27 mmol) and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (WSC; 51.5 mg, 0.27 mmol) were added to the solution, and the mixture was stirred overnight at room temperature. Dichloromethane (30 mL) was added, the solution was washed with water, dried (Na_2SO_4), and concentrated. Column chromatography (125:1 dichloromethane-methanol) of the residue afforded amorphous **15** (176 mg, 88%): $[\alpha]_D$ -28.5° (*c* 2.9, $CHCl_3$); IR (KBr) 3450 (NH), 2950 and 2850 (Me, methylene), 1750 and 1230 (ester), 1650 and 1560 (amide), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$) Gal unit δ 4.60 (dd, 1H, $J_{2,3}$ = 10.3 Hz, $J_{3,4}$ = 3.3 Hz, H-3), 4.63 (d, 1H, $J_{1,2}$ = 8.1 Hz, H-1), 5.04 (broad d, 1H, H-4); KDN unit δ 2.65 (dd, 1H, $J_{3eq,4}$ = 4.8 Hz, Jgem = 12.8 Hz, H-3*eq*), 3.71 (dd, 1H, $J_{5,6}$ = 9.7 Hz, $J_{6,7}$ = 2.9 Hz, H-6), 3.77 (s, 3H, MeO), 4.85 (t, 1H, $J_{4,5} = J_{5,6}$ = 9.7 Hz, H-5), 4.93 (m, 1H, H-4), 5.40 (dd, 1H, $J_{7,8}$ = 9.3 Hz, H-7), 5.56 (m, 1H, H-8); ceramide unit δ 0.88 (t, 6H, 2*Me*CH_2), 1.25 (s, 50H, 25CH_2), 5.57 (d, 1H, $J_{NH,2}$ = 7.7 Hz, NH), 5.85 (dt, 1H, $J_{4,5}$ = 14.1 Hz, $J_{5,6} = J_{5,6'}$ = 6.4 Hz, H-5); *O*-acyl groups δ 1.97-2.17 (7s, 21H, 7AcO) and 7.37-8.03 (m, 10H, 2Ph).

Anal. Calcd for $C_{80}H_{119}NO_{25}$ (1494.8): C, 64.28; H, 8.02; N, 0.94. Found: C, 64.12; H, 8.15; N, 1.05.

***O*-(3-Deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonic acid)-(2→3)-*O*-(β-D-galactopyranosyl)-(1→1)-(2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-octadecanamido-4-octadecene-1,3-diol (16).** To a solution of **15** (80 mg, 0.054 mmol) in methanol (5 mL) was added sodium methoxide (30 mg), and the mixture was stirred for 6 h at room temperature, while the course of the reaction was monitored by TLC (4:2:2 butanol-ethanol-water). 0.2M Potassium hydroxide (5 mL) was added to the mixture and this was stirred for 8 h at room temperature, neutralized with Amberlite IR-120 (H^+) resin, and filtered. The resin was washed with 1:1 water-methanol, and the combined filtrate and washings were concentrated to a syrup. Chromatography on a column of Sephadex LH-20 (50 g) with 1:1 methanol-chloroform gave amorphous **16** (51.8 mg, theoretical): $[\alpha]_D$ -17.2° (*c* 0.1 $CHCl_3$); ^1H NMR [$(CD_3)_2SO$, at 55 °C] δ 0.85 (t, 6H, 2*Me*CH_2), 1.24 (s, 50H, 25CH_2), 2.61 (dd, 1H, $J_{3eq,4}$ = 4.8 Hz, Jgem = 12.1 Hz, H-3*eq* for KDN), 4.09 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1 for Gal), 5.36 (dd, 1H, $J_{3,4}$ =

6.9 Hz, $J_{4,5}$ = 15.0 Hz, H-4 for ceramide), and 5.55 (dt, 1H, $J_{5,6} = J_{5,6'}$ = 6.1 Hz, H-5 for ceramide).

Anal. Calcd for $C_{51}H_{85}NO_{16}$ (968.2): C, 63.27; H, 8.85; N, 1.45. Found: C, 63.14; H, 8.93; N, 1.50.

***O*-(Methyl 4,5,7,8,9-Penta-*O*-acetyl-3-deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate)-(2→3)-*O*-(2,4-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 (17).** To a solution of **12** (127 mg, 0.09 mmol) and (2*S*,3*R*,4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol (**13**; 78 mg, 0.18 mmol) in dichloromethane (5 mL) were added MS-4Å (500 mg), and the mixture was stirred for 3 h at room temperature. Boron trifluoride etherate (30 μL) was added at 0 °C to the mixture, and this was stirred for 5 h at 0 °C. The precipitate was filtered off and washed with dichloromethane, and the combined filtrate and washings were successively washed with M Na_2CO_3 and water, dried (Na_2SO_4), and concentrated. Column chromatography (100:1 dichloromethane-methanol) of the residue gave amorphous **17** (127 mg, 84%): $[\alpha]_D$ +1.2° (*c* 0.34, $CHCl_3$); ^1H NMR ($CDCl_3$) Lac unit δ 4.59 (dd, 1H, $J_{2',3'}$ = 9.9 Hz, $J_{3',4'}$ = 2.9 Hz, H-3'), 4.68 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1), 4.84 (d, 1H, $J_{1',2'}$ = 9.9 Hz, H-1'), 5.25 (t, 1H, $J_{2,3}$ = 7.7 Hz, H-2), and 5.48 (t, 1H, $J_{3,4}$ = 7.7 Hz, H-3); KDN unit δ 2.63 (dd, 1H, $J_{3eq,4}$ = 4.8 Hz, Jgem = 12.8 Hz, H-3*eq*), 3.66 (dd, 1H, $J_{5,6}$ = 9.5 Hz, $J_{6,7}$ = 2.5 Hz, H-6), 3.72 (s, 3H, MeO), 4.83 (t, 1H, $J_{4,5} = J_{5,6}$ = 9.5 Hz, H-5), 5.38 (dd, 1H, $J_{7,8}$ = 9.5 Hz, H-7), and 5.54 (m, 1H, H-8); sphingosine unit δ 0.89 (t, 3H, *Me*CH_2), 1.24 (s, 22H, 11CH_2), 5.94 (dt, 1H, $J_{4,5}$ = 14.2 Hz, $J_{5,6} = J_{5',6'}$ = 7.0 Hz, H-5); *O*-acyl groups δ 1.97-2.18 (8s, 24H, 8AcO) and 7.34-8.06 (m, 20H, 4Ph).

Anal. Calcd for $C_{84}H_{103}N_3O_{32}$ (1666.7): C, 60.53; H, 6.23; N, 2.52. Found: C, 60.34; H, 6.41; N, 2.51.

***O*-(Methyl 4,5,7,8,9-Penta-*O*-acetyl-3-deoxy-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 (18).** Hydrogen sulfide was bubbled at 0 °C through a stirred solution of **17** (90 mg, 0.054 mmol) in pyridine (10 mL) and water (2 mL) for 48 h. The mixture was concentrated to a syrup which was dissolved in dry dichloromethane (7 mL). Octadecanoic acid (30.7 mg, 0.11 mmol) and WSC (21 mg, 0.11 mmol) 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. The residue was chromatographed with 150:1 dichloromethane-methanol to give amorphous **18** (92 mg, 89%): $[\alpha]_D$ +17.5° (*c* 1.1, $CHCl_3$); IR (KBr) 3450 (NH), 2950 and 2850 (Me, methylene), 1750 and 1230 (ester), 1660 and 1540 (amide), and 710 cm^{-1} (Ph); ^1H NMR ($CDCl_3$) Lac unit δ 4.56 (d, 1H, $J_{1,2}$ = 7.9 Hz, H-1), 4.75 (broad d, 1H, $J_{3',4'}$= 2.9 Hz, H-4'), 4.95 (d, 1H, $J_{1',2'}$ = 9.9 Hz, H-1'), 5.15 (dd, 1H, $J_{2,3}$ = 8.2 Hz, H-2), and 5.44 (t, 1H, $J_{3,4}$ = 8.2 Hz, H-3); KDN unit δ 2.63 (dd, 1H, $J_{3eq,4}$ = 4.2 Hz, Jgem = 12.5 Hz, H-3*eq*), 3.68 (dd, 1H, $J_{5,6}$ = 6.8 Hz, $J_{6,7}$ = 2.8 Hz, H-6), 3.73 (s, 3H, MeO), 4.80 (t, 1H, $J_{4,5}$ = $J_{5,6}$ = 6.8 Hz, H-5), 4.88 (m, 1H, H-4), 5.54 (m, 1H, H-8); ceramide unit δ 0.88 (t, 6H, 2*Me*CH_2), 1.26 (s, 50H, 25CH_2), 5.58 (d, 1H, $J_{NH,2}$ = 6.6 Hz, NH), and 5.74 (dt, 1H, $J_{4,5}$ = 14.1 Hz, $J_{5,6}$ = $J_{5,6'}$ = 7.3 Hz, H-5); *O*-acyl groups δ 1.96-2.16 (8s, 24H, 8AcO) and 7.26-8.06 (m, 20H, 4Ph).

Anal. Calcd for $C_{102}H_{139}NO_{33}$ (1907.2): C, 64.24; H, 7.35; N, 0.73. Found: C, 64.13; H, 7.30; N, 0.78.

***O*-(3-Deoxy-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 (19).** To a solution of **18** (80 mg, 0.054 mmol) in methanol (5 mL) was added sodium methoxide (30 mg), and the mixture was stirred for 6 h at room temperature, while the course of the reaction was monitored by TLC (4:2:2 butanol-ethanol-water). 0.2M Potassium hydroxide (5 mL) was added and the mixture was stirred for 8 h at room temperature. After neutralization with Amberlite IR-120 (H^+) resin, and filtration, the resin was washed with 1:1 methanol-chloroform, and the combined filtrate and washings were concentrated. Column chromatography (1:1 methanol-chloroform) on Sephadex LH-20 (40 g) gave amorphous **19** (54 mg, theoretical): $[\alpha]_D$ -12.0° (*c* 0.1, $CHCl_3$); ^1H NMR [$(CD_3)_2SO$, at 55 °C] δ 0.85 (t, 6H, 2*Me*CH_2), 1.15 (s, 50H, 25CH_2), 2.61 (dd, 1H, $J_{3eq,4}$ = 4.1 Hz, Jgem = 12.6 Hz, H-3*eq* for KDN), 4.03 (d, 1H, $J_{1,2}$ = 7.7 Hz, H-1 for Lac), 4.23 (d, 1H, $J_{1',2'}$ = 7.6 Hz, H-1' for Lac), 5.35 (dd, 1H, $J_{3,4}$ = 7.6 Hz, $J_{4,5}$ = 14.7 Hz, H-4 for ceramide), and 5.56 (dt, 1H, $J_{5,6}$ = $J_{5,6'}$ = 6.9 Hz, H-5 for ceramide).

Anal. Calcd for $C_{69}H_{105}NO_{21}$ (1284.6): C, 64.52; H, 8.24; N, 1.09. Found: C, 64.44; H, 8.42; N, 1.03.

ACKNOWLEDGMENT

This work was supported in part by a Grant-in-Aid (No.03255207 and No.04250102) for the Scientific Research on Priority Areas from the Ministry of Education, Science and Culture of Japan.

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