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Total synthesis of the modified ganglioside de-*N*-acetyl-GM_3 and some analogs

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ABSTRACT

Methyl [methyl 4,7,8,9-tetra-*O*-acetyl-5-(*tert*-butoxycarbonylamino)-3,5-dideoxy-2-thio-D-*glycero*-α-D-*galacto*-2-nonulopyranosid]onate was used for the glycosylation of benzyl *O*-(2,6-di-*O*-benzyl-β-D-galactopyranosyl)- and benzyl *O*-(2,3-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-*O*-pivaloyl-β-D-glucopyranoside to give benzyl *O*-[methyl 4,7,8,9-tetra-*O*-acetyl-5-(*tert*-butoxycarbonylamino)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→3)-*O*-(2,6-di-*O*-benzyl-β-D-galactopyranosyl)- (**21**) and benzyl *O*-[methyl 4,7,8,9-tetra-*O*-acetyl-5-(*tert*-butoxycarbonylamino)-3,5-dideoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosylonate]-(2→6)-*O*-(2,3-di-*O*-benzyl-β-D-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-*O*-pivaloyl-β-D-glucopyranoside (**18**), respectively, accompanied by the β-linked isomers **22** and **19**, respectively. Compounds **18**, **21**, and **22** were converted into the corresponding glycotriosyl donors which, upon coupling with (2*S*,3*R*,4*E*)-3-*O*-benzoyl-2-*N*-tetracosanoylsphingenine, afforded completely protected ganglioside analogs **39**, **40**, and **41**, respectively. Deprotection of **40**, **41**, and **39** completed the synthesis of the modified ganglioside de-*N*-acetyl-GM_3, a stereoisomer, and a regioisomer. The *N*-deprotected forms of **40** and **39**, on successive treatment with methyl isocyanate and *O*-deprotection, gave the *N*-(*N*-methylcarbamoyl) analogs of GM_3 and its regioisomer.

INTRODUCTION

Ganglioside GM_3 [α-D-NeuAc*p*-(2→3)-β-D-Gal*p*-(1→4)-β-D-Glc*p*-(1→1)-Cer], which affects the growth and differentiation of various types of animal cells[1–3], appears also to control the action of epidermal growth factor (EGF) by inhibiting the phosphorylation of its receptor on human ovarian epidermoid carcinoma A-431 cells. In contrast, de-*N*-acetyl-GM_3 enhances EGF-dependent phosphorylation of the EGF receptor[4]. Therefore, *N*-acetyl substitution of sialic acid seems to play a key role in determining the biological functions of gangliosides in cell membranes. These observations prompted us to synthesize de-*N*-acetyl-GM_3 (**1**), a stereoisomer (**2**), a regioisomer (**3**), and two *N*-(*N*-methylcarbamoyl) analogs (**4** and **5**) in order to facilitate further biochemical studies of the functions of gangliosides.

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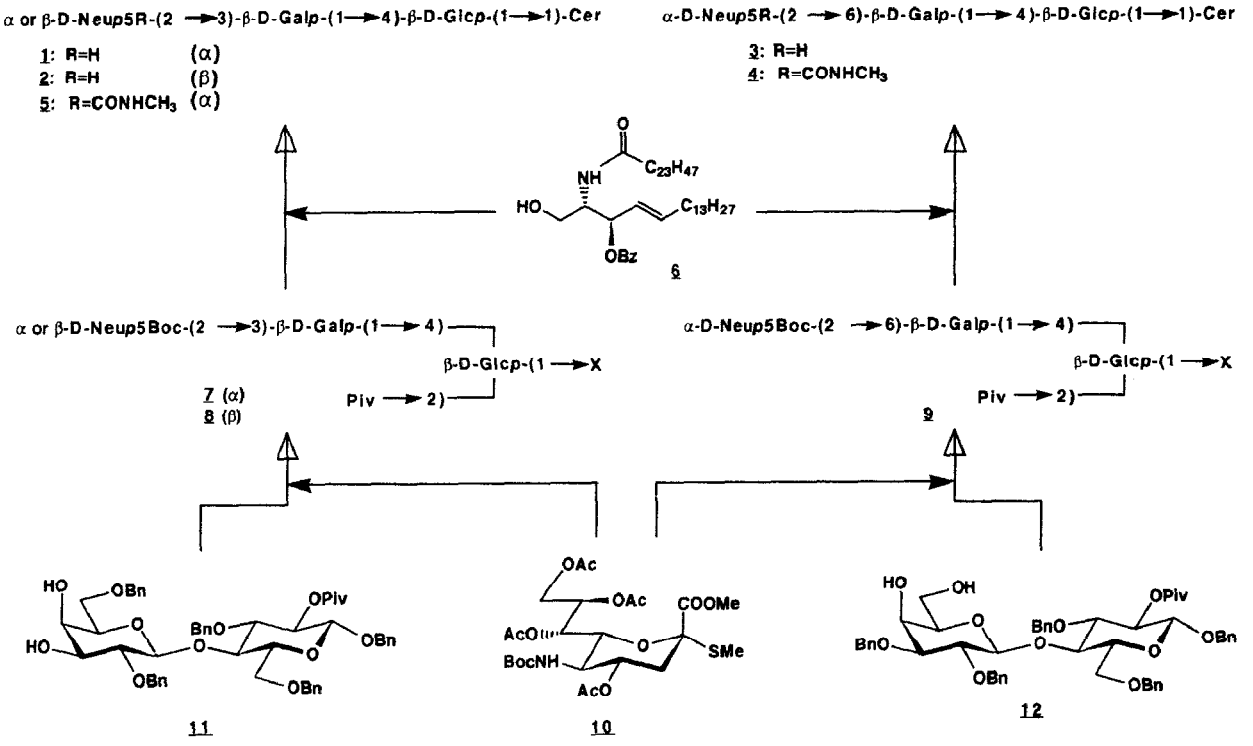


Scheme 1 Piv = pivaloyl = trimethylacetyl

RESULTS AND DISCUSSION

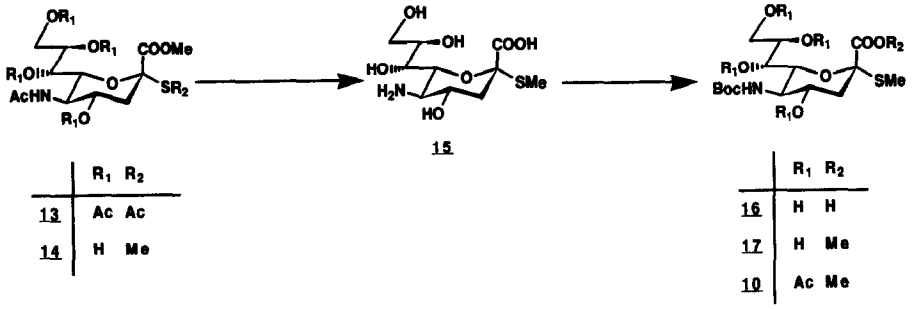
A retrosynthetic analysis of the target structures (**1–5**) suggested their construction from two parts, namely the benzoyl ceramide[5] **6** and one of the glycotriosyl donors **7**, **8**, or **9**. Compounds **7**, **8**, and **9** were further dissected into the glycosyl donor **10** and two properly protected lactose derivatives, **11** and **12**.

The efficiency of the pivaloyl auxiliary group at O-2a of **11** and **12** was established in our previous studies[6]. In order to have a free amino group at the end of synthesis, we introduced a *tert*-butoxycarbonyl group at the 5 position of the neuraminic acid derivative **10**. This compound was elaborated as the glycosyl donor because, as an alkyl thioglycoside, it is stable under basic conditions.

Deacetylation of **13** (ref. 7) by sodium methoxide in methanol followed by methylation with methyl iodide gave **14** in 88% yield for the two steps. Treatment of **14** with aqueous barium hydroxide at reflux gave an amino derivative **15** in 94% yield. Subsequent protection of the amino group of **15** with di-*tert*-butyl dicarbonate in dioxane–methanol–water afforded **16** in 69% yield. Esterification of **16** with diazomethane gave **17** in 81% yield, which was then acetylated with acetic anhydride in pyridine to give **10** in 92% yield.

The crucial coupling of one molar equivalent of glycosyl donor **10** with 1.5 molar equivalents of glycosyl acceptor **12**, which contains a primary hydroxyl group, was performed in the presence of benzeneselenenyl triflate[8] and trimethylsilyl triflate in tetrahydrofuran (THF), giving an 84% yield of a mixture of glycotriosides **18** and **19** (α:β 11:1) that was accompanied by 12% of byproduct **20**. Similarly, the coupling of **10** with **11**, containing two secondary hydroxy groups, was carried out using the same catalysts in dichloromethane–acetonitrile (procedure A) to afford a 46% yield of a mixture of **21** and **22** (α:β 8:1). However, when the above coupling was carried out in dichloromethane alone with the same catalysts (procedure B), the stereoselectivity was significantly changed, so that the β isomer **22** was the major product. This finding was in accord with previous observations[9] that acetonitrile was the solvent of choice for obtaining a thermodynamically less stable glycoside.

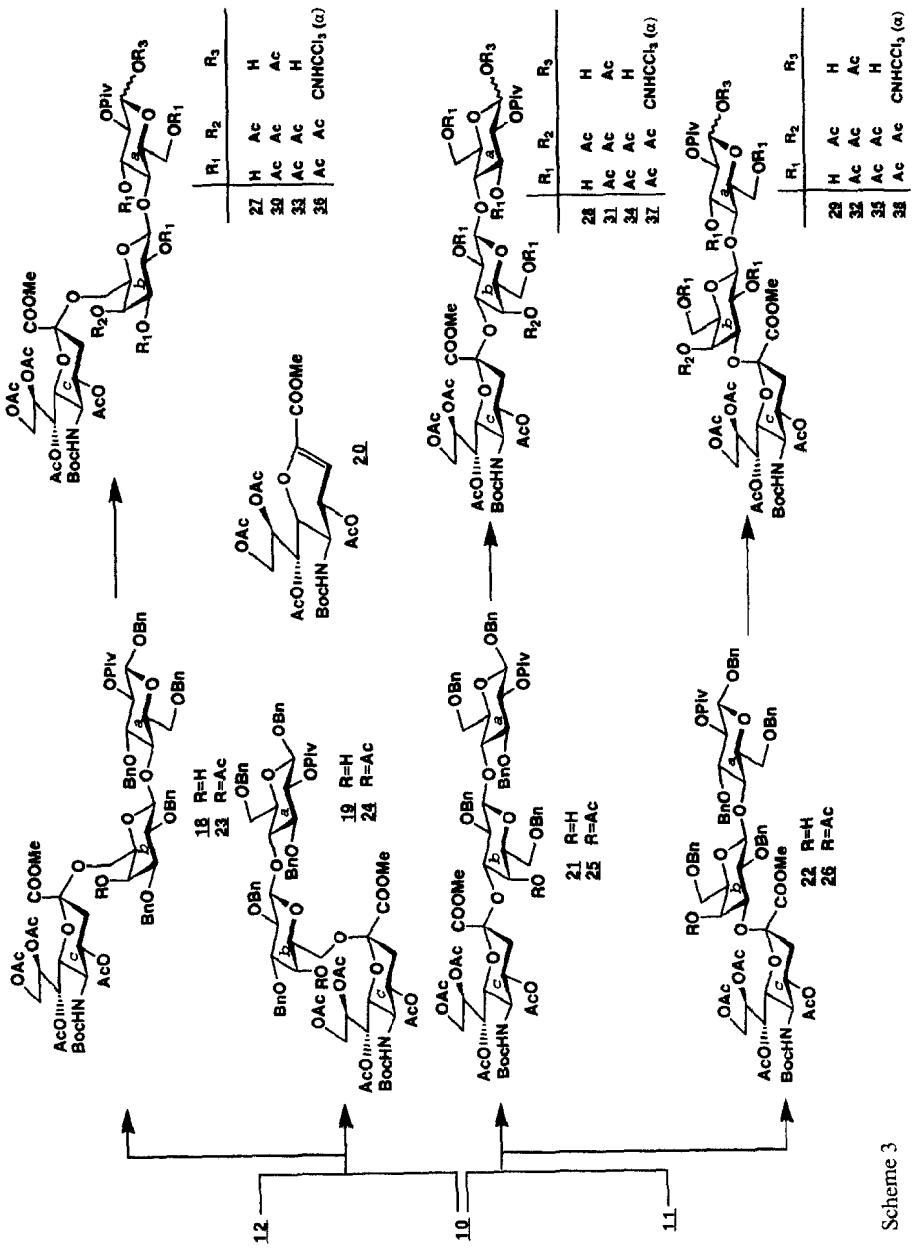
The structures of **18**, **19**, **21**, and **22** were confirmed as follows. Acetylation of **18** and **19** with acetic anhydride and pyridine in the presence of 4-dimethylaminopyridine (DMAP) gave the pentaacetates **23** and **24**, respectively. ^{1}H-N.m.r. data showed that



	R_1	R_2
13	Ac	Ac
14	H	Me

	R_1	R_2
16	H	H
17	H	Me
10	Ac	Me

Scheme 2



Scheme 3

H-4b in **23** and **24** were deshielded to δ 5.495 and 5.658, respectively, indicating that in **18** and **19** a new glycosidic linkage had been introduced at C-6b of the lactose residue. The configurations at C-2c in **18** and **19** were assigned as α and β, respectively, according to the ^{1}H-n.m.r. data. The signal for H-4c in **18** appeared at δ 4.758, whereas that in **19** appeared at δ 5.112, and the $J_{7c,8c}$ values for **18** and **19** were observed to be 8.2 and 2.4 Hz, respectively, in agreement with previous observations[10].

Similarly, the regiochemistry of the new glycosidic linkage in **21** and **22** was determined from the ^{1}H.n.m.r. data for their acetates **25** and **26**, which showed deshielded doublets for H-4b at δ 5.001 and 5.295, respectively, as expected for (2→3)-coupling. The configurations at C-2c in **21** and **22** were assigned as α and β, respectively, based on characteristic signals for H-4c at δ 4.790 and 5.117, respectively.

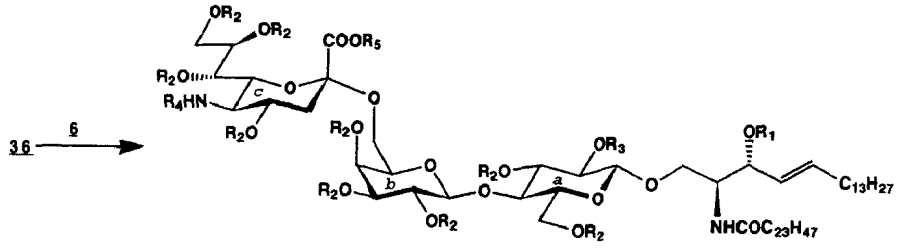
The transformation of **23**, **25**, and **26** into glycosyl donors **9**, **7**, and **8** was performed as follows. The pentaacetates **23**, **25**, and **26** were hydrogenolysed to give **27**, **28**, and **29** which, in turn, were converted into the per-*O*-acetates **30**, **31**, and **32** in 93, 98, and 81% overall yields, respectively.

Regioselective deacetylation of **30**, **31**, and **32** with hydrazinium acetate[11] in *N*,*N*-dimethylformamide afforded 95, 96, and 94% of the hemiacetals **33**, **34**, and **35**, respectively. These were then treated with trichloroacetonitrile in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene[12] (DBU) to give the α-imidates **36** (95%), **37** (98%), and **38** (97%), synthetic equivalents of **9**, **7**, and **8**.

Boron trifluoride etherate-catalysed coupling of the ceramide derivative **6** and the glycosyl donors **36**, **37**, and **38** was performed in the presence of powdered 4A molecular sieves in chloroform to give 55, 71, and 65% of the glycolipids **39**, **40**, and **41**, respectively. Then the deprotection of **39**, **40**, and **41** to produce the target compounds was investigated.

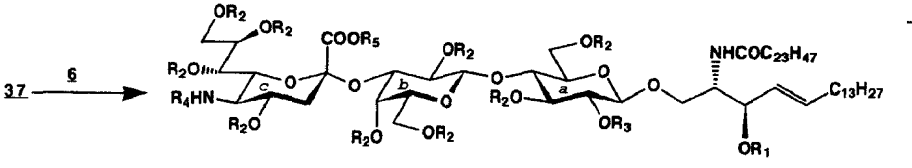
In a preliminary experiment, we attempted the saponification of ester functions before removing the *N*-*tert*-butoxycarbonyl group of the glycolipid derivatives. Saponification of compound **39** was achieved in the conventional way to give **42** in 98% yield. However, the reaction of **42** with trifluoroacetic acid was sluggish, and resulted in unexpected cleavage of the glycosidic bonds. Therefore, deprotection of **39**, **40**, and **41** was carried out as follows. Selective removal of the methyl ester group in **39** and **40** was performed using lithium iodide in pyridine[13] to give **43** and **44** in 64 and 96% yields, respectively. Treatment of **43** and **44** with trifluoroacetic acid gave **45** and **46** in 98 and 100% yields, respectively. Finally, deacylation of **45** and **46** with sodium methoxide was achieved to give target compounds **3** and **1** in 56 and 48% yields, respectively. On the other hand, **41** was treated with trifluoroacetic acid in dichloromethane to give **47** in 94% yield, and saponification of 47 was achieved conventionally to give a 55% yield of an additional target compound, **2**.

Treatment of **39** and **40** with trifluoroacetic acid in dichloromethane gave **48** and **49** in 95 and 99% yields, respectively. These amino derivatives served as key intermediates for the syntheses of the *N*-(*N*-methylcarbamoyl) analogs. Thus, reaction of **48** and **49** with methyl isocyanate in dichloromethane gave the ureides **50** and **51** in 99 and 98% yields, respectively. Saponification of **50** and **51** in aqueous tetrahydrofuran–methanol,



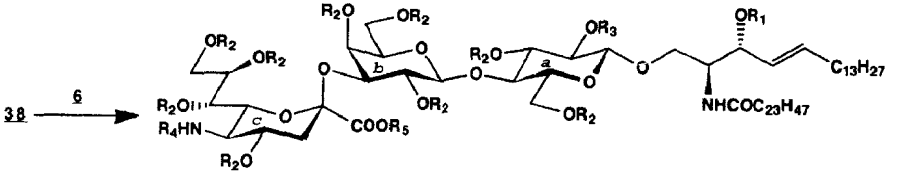
	R_1	R_2	R_3	R_4	R_5
39	Bz	Ac	Piv	Boc	Me
42	H	H	H	Boc	Na
43	Bz	Ac	Piv	Boc	Li
45	Bz	Ac	Piv	H*	H
3	H	H	H	H	Na
48	Bz	Ac	Piv	H	Me
50	Bz	Ac	Piv	CONHMe	Me
4	H	H	H	CONHMe	Na

* CF_3COOH salt



	R_1	R_2	R_3	R_4	R_5
40	Bz	Ac	Piv	Boc	Me
44	Bz	Ac	Piv	Boc	Li
46	Bz	Ac	Piv	H*	H
1	H	H	H	H	Na
49	Bz	Ac	Piv	H	Me
51	Bz	Ac	Piv	CONHMe	Me
5	H	H	H	CONHMe	Na

* CF_3COOH salt



	R_1	R_2	R_3	R_4	R_5
41	Bz	Ac	Piv	Boc	Me
47	Bz	Ac	Piv	H	Me
2	H	H	H	H	Na

Scheme 4

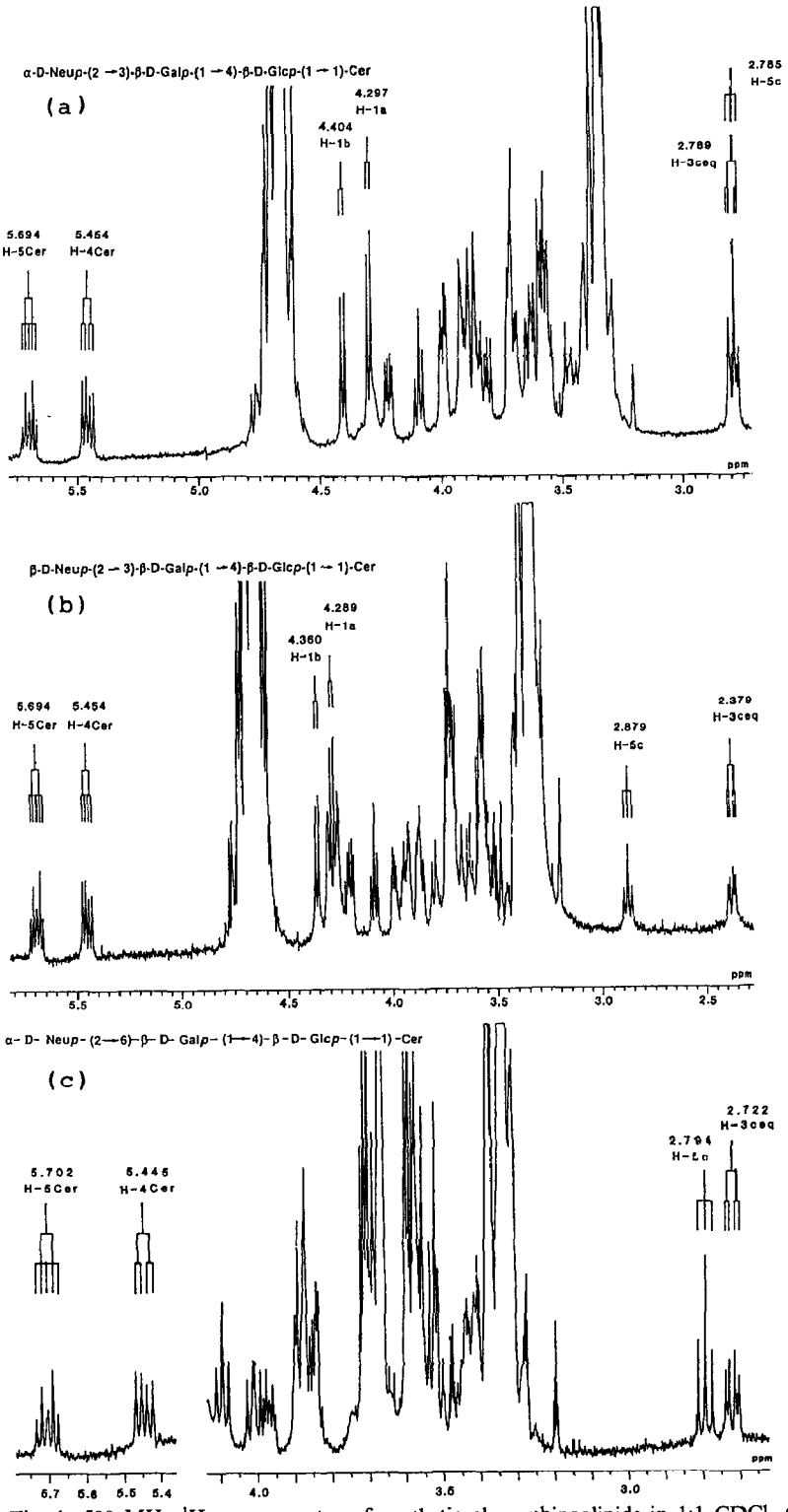


Fig. 1. 500 MHz ^{1}H-n.m.r. spectra of synthetic glycosphingolipids in 1:1 $CDCl_3$–CD_3OD at 24°: (a) de-*N*-acetyl-GM$_3$ (**1**), (b) compound **2**, (c) compound **3**.

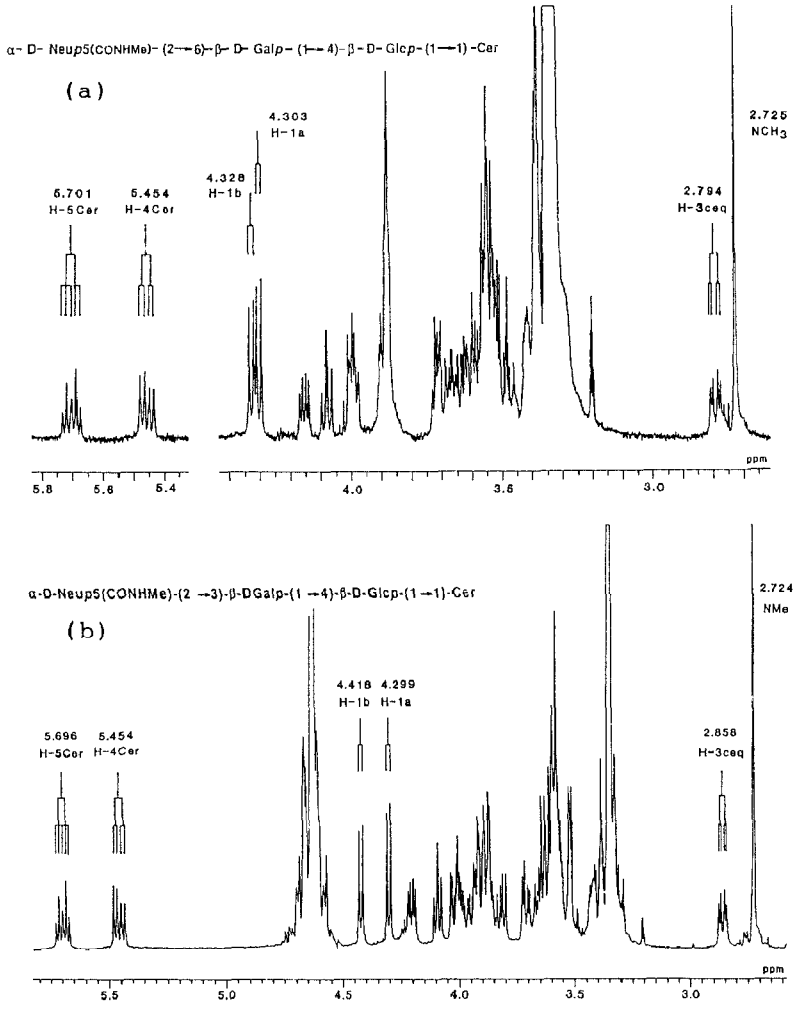


Fig. 2. 500 MHz ^{1}H-n.m.r. spectra of synthetic glycosphingolipids in 1:1 $CDCl_3$–CD_3OD at 24°: (a) compound **4**, (b) compound **5**.

and subsequent purification by Sephadex LH-20 column chromatography gave **4** and **5** in 88 and 92% yields, respectively.

The purity of compounds **1**, **2**, **3**, **4**, and **5** was confirmed by their ^{1}H-n.m.r. spectra (Figs. 1 and 2).

In conclusion, de-*N*-acetyl-GM_3 (**1**), stereoisomer **2**, regioisomer **3**, and analogs **4** and **5** were successfully synthesized using the key glycosyl donor **10**.

EXPERIMENTAL

General. — Melting points were determined with a Büchi-510 melting-point apparatus and are uncorrected. Optical rotations were determined with a JASCO

Model DIP-370 polarimeter, for solutions in $CHCl_3$ at 25°, unless noted otherwise. Flash chromatography was performed on columns of Wakogel C-300 (200–300 mesh). High-performance (h.p.) t.l.c. was done on plates coated with Silica Gel 60-F_{254} (Merck). The 4A molecular sieves were purchased from Nakarai Chemicals. N.m.r. spectra were recorded with a JEOL GX-500 (^1H at 500 MHz, ^{13}C at 125 MHz) spectrometer. Proton and ^{13}C chemical shifts are expressed in p.p.m. downfield from internal Me_4Si, for solutions in $CDCl_3$, unless noted otherwise.

Debenzylidenation of benzyl O-*(2,3-di-*O*-benzyl-4,6-*O*-benzylidene-β-*D*-galacto-pyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-*O*-pivaloyl-β-*D*-glucopyranoside to give* **12**. — To a solution of the title benzylidene derivative[6] (4.00 g, 4.14 mmol) in CH_2Cl_2 (50 mL) was added aq. 90% CF_3COOH (4 mL). The mixture was stirred for 15 min at 20° and diluted with $CHCl_3$ (50 mL). The solution was washed with aq. $NaHCO_3$, aq. NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on Silica gel (200 g) in 4:1 toluene–EtOAc to give **12** (3.02 g, 83%), m.p. 131–134° (recrystallized from CCl_4); $[\alpha]_D$ −2.9° (*c* 1.0); R_F 0.32 in 3:1 toluene–EtOAc; n.m.r.: δ_H 5.118 (dd, 1 H, $J_{1,2}$ 7.9, $J_{2,3}$ 9.3 Hz, H-2a), 4.478 (d, 1 H, H-1a), 4.374 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 4.030 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.3 Hz, H-4a), 3.866 (d, 1 H, $J_{3,4}$ 2.9 Hz, H-4b), 3.628 (t, 1 H, H-3a), 3.602 (dd, 1 H, $J_{2,3}$ 9.3 Hz, H-2b), and 1.138 (s, 9 H, *t*-Bu).

*Methyl (methyl 5-acetamido-3,5-dideoxy-2-thio-*D-glycero-α-D-galacto-*2-nonulo-pyranosid)onate* (**14**). — To a solution of **13** (ref. 7) (10.00 g, 18.2 mmol) in dry MeOH (150 mL) was added 2M NaOMe in MeOH (9 mL). The reaction mixture was stirred for 6 h at 20° then evaporated *in vacuo*. The residue was dissolved in Me_2NCHO (40 mL) and MeI (1.27 mL, 120 mmol) was added. After being stirred for 15 h at 20° the reaction mixture was evaporated *in vacuo*. The residue was chromatographed over Sephadex LH-20 (1 L) in MeOH to give crude **14**, which was recrystallized from MeOH–Me_2CO–Et_2O to give the pure product (5.60 g, 88%), m.p. 185–187°; $[\alpha]_D$ +55.3° (*c* 1.0, MeOH); R_F 0.37 in 19:1 dioxane–H_2O; n.m.r. (CD_3OD): δ_H 3.865–3.808 (m, 2 H, H-8, 9), 3.835 (s, 3 H, OMe), 3.775 (t, 1 H, $J_{4,5} = J_{5,6}$ 10.3 Hz, H-5), 3.657 (ddd, 1 H, $J_{3eq,4}$ 4.6, $J_{3ax,4}$ 11.1 Hz, H-4), 3.625 (dd, 1 H, $J_{8,9'}$ 5.5, $J_{9,9'}$ 11.4 Hz, H-9'), 3.502 (dd, 1 H, $J_{6,7}$ 1.6, $J_{7,8}$ 9.0 Hz, H-7), 3.404 (dd, 1 H, H-6), 2.750 (dd, 1 H, $J_{3eq,3ax}$ 12.8 Hz, H-3*eq*), 2.147 (s, 3 H, SMe), 1.994 (s, 3 H, NAc), and 1.784 (dd, 1 H, H-3*ax*).

Anal. Calc. for $C_{13}H_{23}NO_8S$: C, 44.18; H, 6.56; N, 3.96. Found: C, 43.56; H, 6.44; N, 3.69 (trace of water).

*Methyl 5-amino-3,5-dideoxy-2-thio-*D-glycero-α-D-galacto-*2-nonulopyranosid-onic acid* (**15**). — A mixture of **14** (4.30 g, 12.2 mmol) and $Ba(OH)_2 \cdot 8\,H_2O$ (5.75 g, 18.2 mmol) in water (18 mL) was stirred for 19 h at 90°. Carbon dioxide gas was passed through the reaction mixture until no further precipitate would form. The precipitate was removed by filtration, and the filtrate was brought to pH 4.2 by addition of Amberlite IRC-50 (H^+ form). After filtration to remove the resin, the solution was treated with activated charcol and lyophilized to give **15** (3.40 g, 94%), m.p. >300° (recrystallized from MeOH); $[\alpha]_D$ +18.9° (*c* 1.0, H_2O); R_F 0.39 in 3:1 dioxane–H_2O; n.m.r. (D_2O): δ_H 3.933 (ddd, 1 H, $J_{8,9}$ 2.6, $J_{8,9'}$ 5.9, $J_{7,8}$ 8.4 Hz, H-8), 3.879 (dd, 1 H, $J_{9,9'}$ 12.1 Hz, H-9), 3.850 (dd, 1 H, $J_{6,7}$ 2.4, $J_{5,6}$ 10.4 Hz, H-6), 3.762 (dd, 1 H, H-7), 3.517 (dt, 1

H, $J_{3eq,4}$ 4.8, $J_{3ax,4} = J_{4,5}$ 10.8 Hz, H-4), 3.697 (dd, 1 H, H-9′), 3.196 (t, 1 H, H-5), 2.813 (dd, 1 H, $J_{3eq,3ax}$ 12.6 Hz, H-3*eq*), 2.127 (s, 3 H, SMe), and 1.774 (dd, 1 H, H-3*ax*).

Anal. Calc. for $C_{10}H_{19}NO_7S$: C, 40.40; H, 6.44; N, 4.71. Found: C, 39.70; H, 6.51; N, 4.66 (trace of water).

Methyl [methyl 4,7,8,9-tetra-O-*acetyl-5-(tert-butoxycarbonylamino)-3,5-dideoxy-2-thio*-D-glycero-α-D-galacto-*2-nonulopyranosid]onate* (**10**). — A mixture of **15** (5.08 g, 17.1 mmol), di-*tert*-butyl dicarbonate (18.66 g, 85.5 mmol), and Et_3N (7.15 mL, 51.3 mmol) in 1:1:1 dioxane–H_2O–MeOH (24 mL) was stirred for 1.5 h at 60°, then evaporated *in vacuo*. The residue was dissolved in H_2O (200 mL), and the solution was washed with EtOAc (400 mL) and evaporated *in vacuo*. The residue was chromatographed over DIAION HP-20 (1.4 L) with a linear gradient of H_2O–MeOH to give the triethylamine salt of **16** (6.05 g, 71%). This product was dissolved in MeOH and the solution was brought to pH 3.0 by addition of Dowex-50 (H^+) at 0°, filtered, and evaporated *in vacuo* to give **16** as the free acid (4.70 g, 69%), m.p. 197° (dec.) (recrystallized from EtOH–Et_2O–hexane); $[\alpha]_D$ +70.8° (*c* 1.0, MeOH); R_F 0.53 in 17:3 dioxane–H_2O; n.m.r. (CD_3OD): δ_H 3.970–3.829 (m, 2 H, H-8, 9), 3.685–3.594 (m. 3 H, H-4, 7, 9′), 3.463 (t, 1 H, $J_{4,5} = J_{5,6}$ 10.1 Hz, H-5), 3.406 (br.d, 1 H, H-6), 2773 (dd, 1 H, $J_{3eq,4}$ 4.8, $J_{3eq,3ax}$ 12.5 Hz, H-3*eq*), 2.156 (s, 3 H, SMe), 1.741 (t, 1 H, $J_{3ax,4}$ 11.9 Hz, H-3*ax*), and 1.442 (s, 9 H, *t*-Bu).

To a solution of **16** (1.87 g, 4.7 mmol) in MeOH (14 mL) was added dropwise an ethereal solution of CH_2N_2 until t.l.c. showed that the reaction was complete. After evaporation of the reaction mixture *in vacuo*, the residue was chromatographed on silica gel (57 g) in 23:2 $CHCl_3$–MeOH to give **17** (1.59 g, 82%), $[\alpha]_D$ +45.2° (*c* 1.0, MeOH); R_F 0.47 in 17:3 $CHCl_3$–MeOH; n.m.r. (CD_3OD): δ_H 3.867–3.803 (m, 2 H, H-8, 9), 3.825 (s, 3 H, OMe), 3.639–3.568 (m, 3 H, H-9′, 4, 7), 3.481 (t, 1 H, $J_{4,5} = J_{5,6}$ 10.1 Hz, H-5), 3.383 (dd, 1 H, $J_{6,7}$ 1.6 Hz, H-6), 2.730 (dd, 1 H, $J_{3eq,4}$ 4.8, $J_{3eq,3ax}$ 12.8 Hz, H-3*eq*), 2.140 (s, 3 H, SMe), 1.769 (dd, 1 H, $J_{3ax,4}$ 11.7 Hz, H-3*ax*), and 1.440 (s, 9 H, *t*-Bu).

A mixture of **17** (585 mg, 1.42 mmol) and DMAP (37 mg, 0.30 mmol) in Ac_2O (7.1 mL) and pyridine (7.1 mL) was stirred for 19 h at 20° and then evaporated *in vacuo*. The residue was taken up in $CHCl_3$ (100 mL) and the organic layer was successively washed with 0.1 M aq. HCl (50 mL), H_2O (50 mL), aq. $NaHCO_3$ (50 mL), and aq. NaCl (100 mL), dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on silica gel (60 g) in 19:1 $CHCl_3$–THF to give **10** (764 mg, 93%), $[\alpha]_D$ +24.4° (*c* 1.1); R_F 0.49 in 9:1 $CHCl_3$–THF; n.m.r.: δ_H 5.442–5.380 (m, 2 H, H-7, 8), 4.788 (dt, 1 H, $J_{3eq,4}$ 4.2, $J_{3ax,4} = J_{4,5}$ 10.8 Hz, H-4), 4.304 (dd, 1 H, $J_{8,9}$ 2.4, $J_{9,9'}$ 12.3 Hz, H-9), 4.210 (d, 1 H, $J_{NH,5}$ 10.3 Hz, N*H*), 4.097 (dd, 1 H, $J_{8,9'}$ 4.9 Hz, H-9′), 3.802 (s, 3 H, OMe), 3.820–3.714 (m, 2 H, H-5,6), 2.737 (dd, 1 H, $J_{3eq,3ax}$ 12.6 Hz, H-3*eq*), 2.162, 2.137, 2.108, 2.047, and 2.036 (5 s, 15 H, 4 OAc and SMe), 1.953 (t, 1 H, H-3*ax*), 1.390 (s, 9 H, *t*-Bu); δ_C 155.1 (*t*-BuO*C*=O), 82.8 (C-2), 52.9 (OMe), 50.5 (C-5), 38.0 (C-3), 28.1 [(*C*H_3)$_3$C], and 12.0 (SMe).

Anal. Calc. for $C_{24}H_{37}NO_{13}S$: C, 49.73; H, 6.43; N, 2.42. Found: C, 50.05; H, 6.49; N, 2.18.

Benzyl O-*[methyl 4,7,8,9-tetra*-O-*acetyl-5-(*tert-*butoxycarbonylamino)-3,5-dideoxy*-D-glycero-α- (**18**) *and* -β-D-galacto-*2-nonulopyranosylonate]-(2→6)*-O-*(2,3-di-*

*O-benzyl-β-*D*-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-*O*-pivaloyl-β-*D*-glucopyranoside* (**19**). — A mixture of **10** (232 mg, 0.40 mmol), **12** (531 mg, 0.60 mmol), and 4A molecular sieves (2.0 g) in THF (8 mL) was stirred for 3 h at 20° under Ar. The mixture was cooled to −78° and AgOTf (125 mg, 0.48 mmol) in THF (2 mL), PhSeCl (95 mg, 0.49 mmol) in THF (2 mL), and Me_3SiOTf (0.078 mL, 0.40 mmol) were added. After stirring for 20 min at −78°, the reaction mixture was diluted with EtOAc (150 mL) and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$ and aq. NaCl, then dried ($MgSO_4$). The solvents were evaporated *in vacuo*, and the residue was chromatographed on silica gel (60 g) in 19:1 $CHCl_3$–THF to give **18** (431 mg, 77%), **19** (39 mg, 7%) and **20** (25 mg, 12%).

Compound **18** had $[\alpha]_D$ −12.8° (*c* 1.0); R_F 0.28 in 37:3 $CHCl_3$–THF; n.m.r.: δ_H 5.414 (dd, 1 H, $J_{6,7}$ 2.0, $J_{7,8}$ 8.2 Hz, H-7c), 5.344 (ddd, 1 H, $J_{8,9}$ 2.7, $J_{8,9'}$ 6.0 Hz, H-8c), 5.111 (dd, 1 H, $J_{1,2}$ 8.1, $J_{2,3}$ 9.5 Hz, H-2a), 4.758 (m, 1 H, H-4c), 4.470 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1b), 4.463 (d, 1 H, H-1a), 4.300 (dd, 1 H, $J_{9,9'}$ 12.5 Hz, H-9c), 4.191 (d, 1 H, $J_{NH,5}$ 10.6 Hz, N*H*), 4.08–4.03 (m, 3 H, H-4a, 4b, 9'c), 3.980 (dd, 1 H, $J_{5,6}$ 10.8 Hz, H-6c), 3.745 (s, 3 H, OMe), 3.390 (dd, 1 H, $J_{3,4}$ 3.3, $J_{2,3}$ 9.5 Hz, H-3b), 2.656 (d, 1 H, $J_{OH,4}$ 3.3 Hz, O*H*-4b), 2.356 (dd, 1 H, $J_{3eq,4}$ 4.2 and $J_{3eq,3ax}$ 13.0 Hz, H-3c*eq*), 2.121, 2.090, 2.045, and 1.971 (4 s, 12 H, 4 OAc), 1.751 (t, 1 H, $J_{3ax,4}$ 12.5 Hz, H-3c*ax*), 1.393 (s, 9 H, *t*-BuO), 1.119 (s, 9 H, *t*-BuC=O); δ_C 176.8 (*t*-Bu*C*=O), 155.1 (*t*-BuO*C*=O), 102.7 (C-1a), 99.8 (C-1b), 99.0 (C-2c), 28.2 [(*C*H$_3$)$_3$CO], and 27.2 [(*C*H$_3$)$_3$CC=O].

Anal. Calc. for $C_{75}H_{93}NO_{25}$: C, 63.95; H, 6.65; N, 0.99. Found: C, 64.16; H, 6.68; N, 1.00.

Compound **19** had $[\alpha]_D$ −20.0° (*c* 1.0); R_F 0.40 in 37:3 $CHCl_3$–THF; n.m.r.: δ_H 5.445 (t, 1 H, $J_{6,7} = J_{7,8}$ 2.4 Hz, H-7c), 5.412 (td, 1 H, $J_{8,9'}$ 2.4, $J_{8,9}$ 8.1 Hz, H-8c), 5.112 (dt, 1 H, $J_{3ceq,4}$ 4.8, $J_{3cax,4} = J_{4,5}$ 10.4 Hz, H-4c), 5.085 (dd, 1 H, $J_{1,2}$ 8.1, $J_{2,3}$ 9.2 Hz, H-2a), 4.452 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1b), 4.436 (d, 1 H, H-1a), 4.327 (d, 1 H, $J_{NH,5}$ 10.3 Hz, N*H*), 4.287 (dd, 1 H, $J_{9,9'}$ 12.5 Hz, H-9c), 4.051 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.0 Hz, H-4a), 3.659 (s, 3 H, OMe), 3.616 (t, 1 H, H-3a), 3.591 (m, 2 H, H-2b, 5c), 2.483 (dd, 1 H, $J_{3eq,3ax}$ 13.0 Hz, H-3c*eq*), 2.135, 2.028, 2.026, and 1.842 (4 s, 12 H, 4 OAc), 1.739 (dd, 1 H, H-3c*ax*), 1.401 (s, 9 H, *t*-BuO), 1.108 (s, 9 H, *t*-BuC=O); δ_C 176.8 (*t*-Bu*C*=O), 155.2 (*t*-BuO*C*=O), 102.9 (C-1a), 99.7 (C-1b), 98.1 (C-2c), 28.2 [(*C*H$_3$)$_3$CO], and 27.1 [(*C*H$_3$)$_3$CC=O].

Anal. Calc. for $C_{75}H_{93}NO_{25}$: C, 63.95; H, 6.65; N, 0.99. Found: C, 64.23; H, 6.79; N, 0.95.

Compound **20** had $[\alpha]_D$ +58.7° (*c* 1.0); R_F 0.29 in 37:3 $CHCl_3$–THF; n.m.r.: δ_H 5.996 (d, 1 H, $J_{3,4}$ 3.3 Hz, H-3), 5.550 (t, 1 H, $J_{7,8} = J_{6,7}$ 4.2 Hz, H-7), 5.467 (dd, 1 H, $J_{4,5}$ 7.3 Hz, H-4), 5.373 (ddd, 1 H, $J_{8,9}$ 3.4, $J_{8,9'}$ 6.7 Hz, H-8), 4.582 (dd, 1 H, $J_{9,9'}$ 12.3 Hz, H-9), 4.548 (d, 1 H, $J_{NH,5}$ 9.9 Hz, N*H*), 4.327 (dd, 1 H, $J_{5,6}$ 8.8 Hz, H-6), 4.187 (dd, 1 H, H-9'), 4.083 (q, 1 H, H-5), 3.797 (s, 3 H, OMe), 2.126, 2.075, and 2.060 (6 H) (3 s, 12 H, 4 OAc), and 1.413 (s, 9 H, *t*-Bu).

Anal. Calc. for $C_{23}H_{33}NO_{13}$: C, 51.97; H, 6.26; N, 2.64. Found: C, 47.83; H, 5.69; N, 2.30 (contamination with $CHCl_3$).

Benzyl O-*[methyl 4,7,8,9-tetra-*O*-acetyl-5-*(tert-*butoxycarbonylamino)-3,5-dideoxy-*D*-glycero-α-* (**21**) *and -β-*D*-galacto-2-nonulopyranosylonate]-(2→3)-*O*-(2,6-di-* O-

*benzyl-β-*D*-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-*O*-pivaloyl-β-*D*-glucopyranoside* (**22**). — *Procedure A.* A mixture of 4A molecular sieves (1.0 g), compound **10** (116 mg, 0.20 mmol), and compound **11** (350 mg, 0.40 mmol) in CH_2Cl_2 (3 mL) and MeCN (3 mL) was stirred for 21 h at 20° under Ar. After cooling to − 78° this mixture was treated with solutions of AgOTf (63 mg, 0.24 mmol) in MeCN (1 mL) and PhSeCl (47 mg, 0.24 mmol) in CH_2Cl_2 (1 mL), and Me_3SiOTf (0.039 mL, 0.20 mmol). After stirring for 1 h at − 78°, the mixture was diluted with EtOAc (100 mL) and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$ and aq. NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on silica gel (50 g) in 9:1 toluene–THF to give **21** (117 mg, 41%), **22** (14 mg, 5%), and **20** (27 mg, 26%).

Procedure B. A mixture of 4A molecular sieves (1.0 g), compound **10** (116 mg, 0.20 mmol), and compound **11** (264 mg, 0.30 mmol) in CH_2Cl_2 (8 mL) was stirred for 4 h at 20° under Ar. A solution of AgOTf (63 mg, 0.24 mmol) in toluene (1.5 mL), PhSeCl (46 mg, 0.24 mmol) in CH_2Cl_2 (1 mL), and Me_3SiOTf (0.047 mL, 0.24 mmol) were added to this mixture at − 78°. After stirring for an additional 50 min, the mixture was diluted with $CHCl_3$ (50 mL) and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$ and aq. NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on silica gel (26 g) in 7:3 hexane-EtOAc to give **21** (14 mg, 5%), **22** (124 mg, 44%) and **20** (42 mg, 40%).

Compound **21** had $[\alpha]_D$ − 8.8° (*c* 1.0); R_F 0.53 in 3:1 toluene–THF; n.m.r.: δ_H 5.397 (m, 2 H, H-7c, 8c), 5.113 (dd, 1 H, $J_{1,2}$ 8.1, $J_{2,3}$ 9.5 Hz, H-2a), 4.790 (m, 2 H, H-4c, C*H*$_2$Ph), 4.537 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 4.440 (d, 1 H, H-1a), 4.259 (br. d, 1 H, $J_{9,9'}$ 12.1 Hz, H-9c), 4.182 (d, 1 H, $J_{NH,5}$ 10.6 Hz, N*H*), 4.059 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.2 Hz, H-4a), 3.966 (dd, 1 H, $J_{8,9'}$ 5.1 Hz, H-9'c), 3.753 (s, 3 H, OMe), 3.616 (t, 1 H, H-3a), 2.714 (br. d, 1 H, $J_{OH,4}$ 2.6 Hz, O*H*-4b), 2.520 (dd, 1 H, $J_{3eq,4}$ 4.4 and $J_{3eq,3ax}$ 12.8 Hz, H-3c*eq*), 2.072, 2.015, 1.980, and 1.900 (4 s, 12 H, 4 OAc), 1.380 (s, 9 H, *t*-BuO), 1.126 (s, 9 H, *t*-BuC = O); δ_C 176.7 (*t*-BuC = O), 155.1 (*t*-BuOC = O), 102.5 (C-1a), 99.7 (C-1b), 98.4 (C-2c), 28.1 [(*C*H$_3$)$_3$CO], and 27.1 [(*C*H$_3$)$_3$CC = O].

Anal. Calc. for $C_{75}H_{93}NO_{25}$: C, 63.95; H, 6.65; N, 0.99. Found: C, 63.47; H, 6.73; N, 0.97.

Compound **22** had $[\alpha]_D$ − 12.3° (*c* 1.0); R_F 0.61 in 3:1 toluene–THF; n.m.r.: δ_H 5.298 (dd, 1 H, $J_{6,7}$ 2.9, $J_{7,8}$ 4.0 Hz, H-7c), 5.217 (ddd, 1 H, $J_{8,9}$ 2.6, $J_{8,9'}$ 7.7 Hz, H-8c), 5.312 (dd, 1 H, $J_{1,2}$ 8.1, $J_{2,3}$ 9.5 Hz, H-2a), 5.117 (dt, 1 H, $J_{3ceq,4}$ 4.8, $J_{3cax,4} = J_{4,5}$ 10.3 Hz, H-4c), 4.756 (dd, 1 H, $J_{9,9'}$ 12.3 Hz, H-9c), 4.538 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1b), 4.446 (d, 1 H, H-1a), 4.251 (dd, 1 H, $J_{5,6}$ 11.0 Hz, H-6c), 4.130 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.5 Hz, H-4a), 4.014 (dd, 1 H, H-9'c), 2.638 (s, 3 H, OMe), 2.544 (dd, 1 H, $J_{3eq,3ax}$ 13.6 Hz, H-3c*eq*), 2.110, 2.090, 1.988, and 1.978 (4 s, 12 H, 4 OAc), 1.937 (dd, 1 H, H-3c*ax*), 1.402 (s, 9 H, *t*-BuO), 1.117 (s, 9 H, *t*-BuC = O); δ_C 176.7 (*t*-BuC = O), 155.2 (*t*-BuOC = O), 102.6 (C-1a), 99.7 (C-1b), 99.3 (C-2c), 28.2 [(*C*H$_3$)$_3$CO], and 27.1 [(*C*H$_3$)$_3$CC = O].

Anal. Calc. for $C_{75}H_{93}NO_{25}$: C, 63.95; H, 6.65; N, 0.99. Found: C, 64.14; H, 6.81; N, 0.87.

Benzyl O-*[methyl 4,7,8,9-tetra-*O*-acetyl-5-(*tert*-butoxycarbonylamino)-3,5-dideoxy-*D*-glycero-α-*D*-galacto-2-nonulopyranosylonate]-(2→6)-*O*-(4-*O*-acetyl-2,3-di-*O*-*

*benzyl-β-*D*-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-*O*-pivaloyl-β-*D*-glucopyranoside* (**23**). — A mixture of **18** (428 mg, 0.30 mmol) and DMAP (74 mg, 0.61 mmol) in Ac_2O (0.51 mL, 6.1 mmol) and pyridine (2.28 mL) was stirred for 3 h at 20°. The reaction mixture was evaporated *in vacuo*. The residue was chromatographed on silica gel (50 g) in 19:1 $CHCl_3$–THF to give **23** (400 mg, 91%), $[\alpha]_D$ −15.6° (*c* 0.8); R_F 0.40 in 37:3 $CHCl_3$–THF; n.m.r.: δ_H 5.495 (d, 1 H, $J_{3,4}$ 2.6 Hz, H-4b), 5.392 (dd, 1 H, $J_{6,7}$ 1.8, $J_{7,8}$ 8.4 Hz, H-7c), 5.315 (ddd, 1 H, $J_{8,9}$ 3.0, $J_{8,9'}$ 5.6 Hz, H-8c), 5.133 (dd, 1 H, $J_{1,2}$ 7.9, $J_{2,3}$ 9.3 Hz, H-2a), 4.477 (d, 1 H, H-1a), 4.245 (dd, 1 H, $J_{9,9'}$ 12.5 Hz, H-9c), 4.170 (d, 1 H, $J_{NH,5}$ 10.6 Hz, N*H*), 4.024 (dd, 1 H, H-9′c), 3.985 (dd, 1 H, $J_{5,6}$ 11.4 Hz, H-6c), 3.722 (s, 3 H, OMe), 2.480 (dd, 1 H, $J_{3eq,4}$ 4.2 and $J_{3eq,3ax}$ 13.0 Hz, H-3c*eq*), 2.091, 2.080, 2.058, 2.019, and 1.986 (5 s, 15 H, 5 OAc), 1.845 (t, 1 H, H-3c*ax*), 1.384 (s, 9 H, *t*-BuO), 1.119 (s, 9 H, *t*-BuC=O); δ_C 176.7 (*t*-Bu*C*=O), 155.1 (*t*-BuO*C*=O), 102.2 (C-1a), 99.7 (C-1b), 99.0 (C-2c), 28.1 [(*C*H$_3$)$_3$CO], and 27.1 [(*C*H$_3$)$_3$CC=O].

Anal. Calc. for $C_{77}H_{95}NO_{26}$: C, 63.76; H, 6.60; N, 0.97. Found: C, 63.57; H, 6.56; N, 1.00.

*Benzyl O-[methyl 4,7,8,9-tetra-*O*-acetyl-5-(*tert*-butoxycarbonylamino)-3,5-dideoxy-*D*-*glycero*-β-*D*-galacto-2-nonulopyranosylonate]-(2→6)-*O*-(4-*O*-acetyl-2,3-di-*O*-benzyl-β-*D*-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-*O*-pivaloyl-β-*D*-glucopyranoside* (**24**). — Compound **19** (6.8 mg, 4.8 μmol) was converted into **24** (6.9 mg, 98%) as described for the synthesis of compound **23**. For **24**, $[\alpha]_D$ −14.7° (*c* 0.9); R_F 0.50 in 37:3 $CHCl_3$–THF; n.m.r.: δ_H 5.658 (d, 1 H, $J_{3,4}$ 2.9 Hz, H-4b), 5.450 (t, 1 H, $J_{6,7} = J_{7,8}$ 2.7 Hz, H-7c), 5.264 (dt, 1 H, $J_{3ceq,4}$ 4.8, $J_{3cax,4} = J_{4,5}$ 10.9 Hz, H-4c), 5.076 (dd, 1 H, $J_{1,2}$ 7.9, $J_{2,3}$ 9.3 Hz, H-2a), 5.041 (td, 1 H, $J_{8,9'}$ 2.6, $J_{8,9}$ 8.1 Hz, H-8c), 4.724 (dd, 1 H, $J_{9,9'}$ 12.1 Hz, H-9c), 4.491 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1b), 4.440 (d, 1 H, H-1a), 4.111 (dd, 1 H, H-9′c), 4.089 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.2 Hz, H-4a), 3.861 (q, 1 H, $J_{4,5} = J_{NH,5} = J_{5,6}$ 10.4 Hz, H-5c), 3.833 (dd, 1 H, $J_{5,6}$ 4.6, $J_{6,6'}$ 11.0 Hz, H-6a), 3.754 (s, 3 H, OMe), 3.696 (dd, 1 H, $J_{5,6'}$ 1.8 Hz, H-6′a), 3.616 (dd, 1 H, H-6c), 3.614 (t, 1 H, H-3a), 3.527 (dd, 1 H, $J_{2,3}$ 9.5 Hz, H-2b), 2.503 (dd, 1 H, $J_{3eq,3ax}$ 12.8 Hz, H-3c*eq*), 2.277, 2.147, 2.032, 2.003, and 1.922 (5 s, 15 H, 5 OAc), 1.735 (dd, 1 H, H-3c*ax*), 1.414 (s, 9 H, *t*-BuO), and 1.108 (s, 9 H, *t*-BuC=O).

Anal. Calc. for $C_{77}H_{95}NO_{26}$: C, 63.76; H, 6.60; N, 0.97. Found: C, 63.68; H, 6.63; N, 0.90.

*Benzyl O-[methyl 4,7,8,9-tetra-*O*-acetyl-5-(*tert*-butoxycarbonylamino)-3,5-dideoxy-*D*-*glycero*-α-*D*-galacto-2-nonulopyranosylonate]-(2→3)-*O*-(4-*O*-acetyl-2,6-di-*O*-benzyl-β-*D*-galactopyranosyl)-(1→4)-3,6-di-*O*-benzyl-2-*O*-pivaloyl-β-*D*-glucopyranoside* (**25**). — Compound **21** (167 mg, 0.12 mmol) was converted into **25** (160 mg, 93%) as described for the synthesis of compound **23**. For **25**, $[\alpha]_D$ −18.2° (*c* 1.0); R_F 0.45 in 19:1 $CHCl_3$–THF; n.m.r.: δ_H 5.603 (ddd, 1 H, $J_{8,9}$ 2.6, $J_{8,9'}$ 5.1, $J_{7,8}$ 8.8 Hz, H-8c), 5.415 (dd, 1 H, $J_{6,7}$ 2.2 Hz, H-7c), 5.100 (dd, 1 H, $J_{1,2}$ 8.1, $J_{2,3}$ 9.5 Hz, H-2a), 5.001 (d, 1 H, $J_{3,4}$ 3.7 Hz, H-4b), 4.724 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1b), 4.483 (dd, 1 H, $J_{2,3}$ 9.9 Hz, H-3b), 4.407 (d, 1 H, H-1a), 4.273 (dd, 1 H, $J_{9,9'}$ 12.5 Hz, H-9c), 4.152 (d, 1 H, $J_{NH,5}$ 10.6 Hz, N*H*), 4.065 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.2 Hz, H-4a), 3.998 (dd, 1 H, H-9′c), 3.815 (s, 3 H, OMe), 3.596 (t, 1 H, H-3a), 3.448 (dd, 1 H, H-2b), 2.608 (dd, 1 H, $J_{3eq,4}$ 4.8 and $J_{3eq,3ax}$ 12.8 Hz, H-3c*eq*), 2.067, 2.017, 1.989, 1.973, and 1.774 (5 s, 15 H, 5 OAc), 1.814 (t, 1 H, $J_{3ax,4}$ 12.6 Hz, H-3c*ax*), 1.371 (s, 9

H, *t*-BuO), 1.124 (s, 9 H, *t*-BuC = O); δ_C 176.6 (*t*-Bu*C* = O), 155.2 (*t*-BuO*C* = O), 102.1 (C-1a), 99.6 (C-1b), 97.3 (C-2c), 28.1 [(*C*H$_3$)$_3$CO], and 27.1 [(*C*H$_3$)$_3$CC = O].

Anal. Calc. for $C_{77}H_{95}NO_{26}$: C, 63.76; H, 6.60; N, 0.97. Found: C, 64.01; H, 6.75; N, 0.91.

Benzyl O-*[methyl 4,7,8,9-tetra*-O-*acetyl-5-(*tert-*butoxycarbonylamino)-3,5-dideoxy*-D-glycero-*β*-D-galacto-*2-nonulopyranosylonate]-(2→3)*-O-*(4*-O-*acetyl-2,6-di*-O-*benzyl-β*-D-*galactopyranosyl)-(1→4)-3,6-di*-O-*benzyl-2*-O-*pivaloyl-β*-D-*glucopyranoside* (**26**). — Compound **22** (152 mg, 0.11 mmol) was converted into **26** (148 mg, 95%) as described for the synthesis of compound **23**. For **26**, $[\alpha]_D$ −20.5° (*c* 1.1); R_F 0.58 in 19:1 $CHCl_3$–THF; n.m.r.: δ_H 5.459 (t, 1 H, $J_{6,7} = J_{7,8}$ 2.6 Hz, H-7c), 5.295 (m, 2 H, H-4b, 8c), 5.100 (dd, 1 H, $J_{1,2}$ 7.9, $J_{2,3}$ 9.3 Hz, H-2a), 5.015 (dd, 1 H, $J_{8,9}$ 2.9, $J_{9,9'}$ 12.1 Hz, H-9c), 5.003 (dt, 1 H, $J_{3eq,4}$ 4.4, $J_{3ax,4} = J_{4,5}$ 11.1 Hz, H-4c), 4.529 (dd, 1 H, $J_{3,4}$ 2.9, $J_{2,3}$ 9.9 Hz, H-3b), 4.413 (d, 1 H, H-1a), 4.101 (t, 1 H, $J_{3,4} = J_{4,5}$ 9.2 Hz, H-4a), 3.914 (dd, 1 H, $J_{8,9'}$ 9.2 Hz, H-9′c), 3.581 (t, 1 H, H-3a), 3.490 (dd, 1 H, $J_{1,2}$ 8.1 Hz, H-2b), 3.403 (s, 3 H, OMe), 3.316 (ddd, 1 H, $J_{5,6}$ 2.6 and $J_{5,6'}$ 4.0 Hz, H-5a), 2.593 (dd, 1 H, $J_{3eq,3ax}$ 13.2 Hz, H-3c*eq*), 2.123, 2.078, 2.034, 1.978, and 1.848 (5 s, 15 H, 5 OAc), 1.789 (dd, 1 H, H-3c*ax*), 1.417 (s, 9 H, *t*-BuO), 1.138 (s, 9 H, *t*-BuC = O); δ_C 176.7 (*t*-Bu*C* = O), 155.4 (*t*-BuO*C* = O), 102.3 (C-1a), 99.6 (C-1b), 99.2 (C-2c), 28.2 [(*C*H$_3$)$_3$CO], and 27.1 [(*C*H$_3$)$_3$CC = O].

Anal. Calc. for $C_{77}H_{95}NO_{26}$: C, 63.76; H, 6.60; N, 0.97. Found: C, 63.65; H, 6.66; N, 0.93.

Crude O-*[methyl 4,7,8,9-tetra*-O-*acetyl-5-(*tert-*butoxycarbonylamino)-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosylonate]-(2→6)*-O-*(4*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)-2*-O-*pivaloyl*-D-*glucopyranose* (**27**). — A mixture of **23** (391 mg, 0.27 mmol) and 10% Pd-C (271 mg) in EtOH (5.4 mL) was stirred for 22 h at 20° under H_2. After filtration through Celite, the solution was evaporated *in vacuo* to give crude **27** (260 mg, 96%). This product was used for the next step without further purification, $[\alpha]_D$ +7.6° (*c* 1.1, MeOH); R_F 0.49 and 0.45 in 4:1 $CHCl_3$–MeOH.

Crude O-*[methyl 4,7,8,9-tetra*-O-*acetyl-5-(*tert-*butoxycarbonylamino)-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosylonate]-(2→3)*-O-*(4*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)-2*-O-*pivaloyl*-D-*glucopyranose* (**28**). — Compound **25** (144 mg, 0.1 mmol) was converted into **28** (98 mg, 99%) as described for the synthesis of compound **27**. For **28**, $[\alpha]_D$ +26.3° (*c* 1.0, MeOH); R_F 0.52 and 0.46 in 9:1 $CHCl_3$–MeOH.

Crude O-*[methyl 4,7,8,9-tetra*-O-*acetyl-5-(*tert-*butoxycarbonylamino)-3,5-dideoxy*-D-glycero-β-D-galacto-*2-nonulopyranosylonate]-(2→3)*-O-*(4*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)-2*-O-*pivaloyl*-D-*glucopyranose* (**29**). — Compound **26** (141 mg, 0.097 mmol) was converted into **29** (97 mg, 97%) as described for the synthesis of compound **27**. For **29**, $[\alpha]_D$ +26.7° (*c* 1.0, MeOH); R_F 0.45 and 0.46 in 9:1 $CHCl_3$–MeOH.

O-*[Methyl 4,7,8,9-tetra*-O-*acetyl-5-(*tert-*butoxycarbonylamino)-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosylonate]-(2→6)*-O-*(2,3,4-tri*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)-1,3,6-tri*-O-*acetyl-2*-O-*pivaloyl-α,β*-D-*glucopyranose* (**30**). — A solution of crude **27** (250 mg, 0.25 mmol) and DMAP (61 mg, 0.50 mmol) in 1:2 Ac_2O–pyridine (7.5 mL) was stirred for 3 h at 20° and then evaporated *in vacuo*. The

residue was chromatographed on silica gel (20 g) with 23:2 toluene–MeOH to give **30** (291 mg, 96%), $[\alpha]_D$ −0.6° (*c* 0.7); R_F 0.49 and 0.44 in 7:3 toluene–THF; n.m.r.: δ_H 6.297 (d, 0.5 H, $J_{1,2}$ 3.7 Hz, H-1aα), 5.728 (d, 0.5 H, $J_{1,2}$ 8.4 Hz, H-1aβ), 4.766 (dt, 1 H, $J_{3eq,4}$ 3.9, $J_{3ax,4}$ = $J_{4,5}$ 11.2 Hz, H-4c), 3.800 and 3.791 (2 s, 3 H, OMe), 2.504 (m, 1 H, H-3c*eq*), 1.870 (br. t, 1 H, $J_{3eq,3ax}$ 11.5 Hz, H-3c*ax*), 1.390 (s, 9 H, *t*-BuO), 1.135, and 1.131 (2 s, 9 H, *t*-BuC = O).

Anal. Calc. for $C_{52}H_{75}NO_{31}$: C, 51.61; H, 6.25; N, 1.16. Found: C, 52.29; H, 6.45; N, 1.08 (trace of toluene).

O-*[Methyl 4,7,8,9-tetra*-O-*acetyl-5-(*tert-*butoxycarbonylamino)-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosylonate]-(2→3)*-O-*(2,4,6-tri*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)-1,3,6-tri*-O-*acetyl-2*-O-*pivaloyl-α,β*-D-*glucopyranose* (**31**). — Compound **28** (94 mg, 0.095 mmol) was converted into **31** (113 mg, 99%) as described for the synthesis of compound **30**. For **31**, $[\alpha]_D$ +17.1° (*c* 1.0); R_F 0.53 and 0.49 in 7:3 toluene–THF; n.m.r.: δ_H 6.293 (d, 0.5 H, $J_{1,2}$ 3.7 Hz, H-1aα), 5.715 (d, 0.5 H, $J_{1,2}$ 8.4 Hz, H-1aβ), 5.276 (t, 0.5 H, $J_{2,3}$ = $J_{3,4}$ 9.5 Hz, H-3aα), 5.036 (dd, 0.5 H, $J_{2,3}$ 9.5 Hz, H-2aβ), 4.795 (m, 1 H, H-4c), 3.835, and 3.830 (2 s, 3 H, OMe), 2.589 (m, 1 H, H-3c*eq*), 1.379 (s, 9 H, *t*-BuO), 1.135, and 1.124 (2 s, 9 H, *t*-BuC = O).

Anal. Calc. for $C_{52}H_{75}NO_{31}$: C, 51.61; H, 6.25; N, 1.16. Found: C, 51.84; H, 6.37; N, 1.05.

O-*[Methyl 4,7,8,9-tetra*-O-*acetyl-5-(*tert-*butoxycarbonylamino)-3,5-dideoxy*-D-glycero-β-D-galacto-*2-nonulopyranosylonate]-(2→3)*-O-*(2,4,6-tri*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)-1,3,6-tri*-O-*acetyl-2*-O-*pivaloyl-α,β*-D-*glucopyranose* (**32**). — Compound **29** (94 mg, 0.095 mmol) was converted into **32** (96 mg, 84%) as described for the synthesis of compound **30**. For **32**, $[\alpha]_D$ +20.4° (*c* 1.0); R_F 0.46 and 0.41 in 3:1 toluene–THF; n.m.r.: δ_H 6.292 (d, 0.6 H, $J_{1,2}$ 3.7 Hz, H-1aα), 5.706 (d, 0.4 H, $J_{1,2}$ 8.4 Hz, H-1aβ), 5.375 (dd, 0.6 H, $J_{8,9}$ 2.6, $J_{9,9'}$ 12.5 Hz, H-9cα), 5.350 (dd, 0.4 H, $J_{8,9}$ 2.6, $J_{9,9'}$ 13.2 Hz, H-9cβ), 5.117 (dd, 0.6 H, $J_{1,2}$ 8.4, $J_{2,3}$ 10.3 Hz, H-2bα), 5.101 (dd, 0.4 H, $J_{1,2}$ 8.4, $J_{2,3}$ 10.3 Hz, H-2bβ), 5.056 (dd, 0.4 H, $J_{2,3}$ 9.5 Hz, H-2aβ), 4.968 (dd, 0.6 H, $J_{2,3}$ 10.3 Hz, H-2aα), 4.964 (m, 1 H, H-4c), 4.791 (dd, 0.6 H, $J_{3,4}$ 2.9 Hz, H-3bα), 4.770 (dd, 0.4 H, $J_{3,4}$ 2.9 Hz, H-3bβ), 4.629 (dd, 0.6 H, $J_{6,7}$ 2.0, $J_{5,6}$ 9.9 Hz, H-6cα), 4.616 (dd, 0.4 H, $J_{6,7}$ 2.2, $J_{5,6}$ 10.6 Hz, H-6cβ), 4.507 (d, 1 H, $J_{NH,5}$ 10.6 Hz, N*H*), 4.379 (d, 0.6 H, H-1bα), 4.376 (d, 0.4 H, H-1bβ), 3.835 (s, 1.8 H, OMeα), 3.830 (s, 1.2 H, OMeβ), 3.665 (q, 1 H, $J_{4,5}$ 10.3 Hz, H-5c), 2.444 (dd, 0.6 H, $J_{3eq,4}$ 4.6, $J_{3eq,3ax}$ 13.4 Hz, H-3c*eq*α), 2.441 (dd, 0.4 H, $J_{3eq,4}$ 4.6, $J_{3eq,3ax}$ 13.4 Hz, H-3c*eq*β), 1.762 (dd, 0.6 H, $J_{3ax,4}$ 11.9 Hz H-3c*ax*α), 1.755 (dd, 0.4 H $J_{3ax,4}$ 11.9 Hz, H-3c*ax*β), 1.398 (s, 9 H, *t*-BuO), 1.138 (s, 3.6 H, *t*-BuC = Oβ), and 1.124 (s, 5.4 H, *t*-BuC = Oα).

Anal. Calc. for $C_{52}H_{75}NO_{31}$: C, 51.61; H, 6.25; N, 1.16. Found: C, 51.70; H, 6.35; N, 1.01.

O-*[Methyl 4,7,8,9-tetra*-O-*acetyl-5-(*tert-*butoxycarbonylamino)-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosylonate]-(2→6)*-O-*(2,3,4-tri*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)-3,6-di*-O-*acetyl-2*-O-*pivaloyl*-D-*glucopyranose* (**33**). — A mixture of **30** (287 mg, 0.24 mmol) and $H_2NNH_2 \cdot AcOH$ (27 mg, 0.30 mmol) in Me_2NCHO (4.7 mL) was stirred for 6 min at 50°, and then diluted with $CHCl_3$ (100 mL). The organic

layer was washed with water (50 mL). The aqueous layer was re-extracted with $CHCl_3$ (150 mL) and the combined organic layers washed with aq. NaCl (50 mL), dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on silica gel (30 g) to give **33** (227 mg, 95% based on **30** consumed; 39 mg of **30** was recovered), $[\alpha]_D$ + 5.9° (*c* 1.2); R_F 0.43 in 13:7 toluene–THF; n.m.r.: δ_H 3.793 (s, 0.9 H, OMe), 3.774 (s, 2.1 H, OMe), 2.550 (dd, 0.3 H, $J_{3eq,4}$ 4.8, $J_{3eq,3ax}$ 12.8 Hz, H-3c*eq*), 2.540 (dd, 0.7 H, $J_{3eq,4}$ 4.8, $J_{3eq,3ax}$ 12.8 Hz, H-3c*eq*), 1.869 (dd, 1 H, $J_{3ax,4}$ 12.1 Hz, H-3c*ax*), 1.387 (s, 9 H, *t*-BuO), 1.192 (s, 6.3 H, *t*-BuC = O), and 1.187 (s, 2.7 H, *t*-BuC = O).

Anal. Calc. for $C_{50}H_{73}NO_{30}$: C, 51.41; H, 6.30; N, 1.20. Found: C, 51.14; H, 6.22; N, 1.22.

O-*[Methyl 4,7,8,9-tetra*-O-*acetyl-5-(*tert-*butoxycarbonylamino)-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosylonate]-(2→3)*-O-*(2,4,6-tri*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)-3,6-di*-O-*acetyl-2*-O-*pivaloyl*-D-*glucopyranose* (**34**). — Compound **31** (106 mg, 0.088 mmol) was converted into **34** (91 mg, 96% based on **31** consumed; 8 mg of **31** was recovered) as described for the synthesis of compound **33**. For **34**, $[\alpha]_D$ + 25.8° (*c* 1.0); R_F 0.45 in 13:7 toluene–THF; n.m.r.: δ_H 5.565 (t, 0.7 H, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3aα), 5.376 (d, 0.7 H, $J_{1,2}$ 3.7 Hz, H-1aα), 5.294 (t, 0.3 H, $J_{2,3} = J_{3,4}$ 9.2 Hz, H-3a*β*), 4.974 (dd, 0.7 H, $J_{1,2}$ 8.1, $J_{2,3}$ 10.3 Hz, H-2bα), 4.931 (dd, 0.3 H, $J_{1,2}$ 8.1, $J_{2,3}$ 9.9 Hz, H-2b*β*), 4.880 (d, 1 H, $J_{3,4}$ 3.3 Hz, H-4b), 4.784 (dt, 1 H, $J_{3eq,4}$ 4.0, $J_{3ax,4} = J_{4,5}$ 11.4 Hz, H-4c), 4.762 (dd, 0.7 H, H-2aα), 4.749 (dd, 0.3 H, $J_{1,2}$ 9.3 Hz, H-2a*β*), 4.506 (dd, 1 H, H-3b), 4.134 (d, 1 H, $J_{NH,5}$ 10.6 Hz, N*H*), 3.831 (s, 3 H, OMe), 3.772 (q, 1 H, $J_{5,6}$ 10.3 Hz, H-5c), 3.523 (dd, 1 H, $J_{6,7}$ 1.8 Hz, H-6c), 2.588 (dd, 1 H, $J_{3eq,3ax}$ 12.8 Hz, H-3c*eq*), 2.239, 2.237, 2.144, 2.116, 2.110, 2.087, 2.084, 2.077, 2.058, 2.056, 2.021, and 2.010 (12 s, 27 H, 9 OAc), 1.646 (dd, 0.7 H, H-3c*ax*α), 1.639 (dd, 0.3 H, H-3c*ax*β), 1.378 (s, 9 H, *t*-BuO), and 1.179 (s, 9 H, *t*-BuC = O).

Anal. Calc. for $C_{50}H_{73}NO_{30}$: C, 51.41; H, 6.30; N, 1.20. Found: C, 51.11; H, 6.26; N, 1.18.

O-*[Methyl 4,7,8,9-tetra*-O-*acetyl-5-(*tert-*butoxycarbonylamino)-3,5-dideoxy*-D-glycero-β-D-galacto-*2-nonulopyranosylonate]-(2→3)*-O-*(2,4,6-tri*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)-3,6-di*-O-*acetyl-2*-O-*pivaloyl*-D-*glucopyranose* (**35**). — Compound **32** (89 mg, 0.074 mmol) was converted into **35** (77 mg, 94% based on **32** consumed; 5 mg of **32** was recovered) as described for the synthesis of compound **33**. For **35**, $[\alpha]_D$ + 75.3° (*c* 1.0); R_F 0.45 in 13:7 toluene–THF; n.m.r.: δ_H 5.538 (t, 1 H, $J_{2,3} = J_{3,4}$ 9.9 Hz, H-3a), 5.487 (t, 1 H, $J_{7,8} = J_{6,7}$ 1.8 Hz, H-7c), 5.379 (d, 0.7 H, $J_{1,2}$ 4.0 Hz, H-1aα), 5.352 (dd, 0.3 H, $J_{8,9}$ 1.6, $J_{9,9'}$ 12.1 Hz, H-9c*β*), 5.342 (dd, 0.7 H, $J_{8,9}$ 2.2, $J_{9,9'}$ 12.1 Hz, H-9cα), 5.278 (br. s, 1 H, H-4b), 5.242 (br. d, 1 H, $J_{8,9'}$ 9.8 Hz, H-8c), 5.113 (dd, 0.7 H, $J_{1,2}$ 8.1, $J_{2,3}$ 10.3 Hz, H-2bα), 5.097 (dd, 0.3 H, $J_{1,2}$ 8.1, $J_{2,3}$ 10.3 Hz, H-2b*β*), 4.970 (m, 1 H, H-4c), 4.694 (dd, 0.3 H, H-1a*β*), 4.626 (dd, 0.7 H, $J_{5,6}$ 10.4 Hz, H-6cα), 4.619 (dd, 0.3 H, $J_{5,6}$ 10.6 Hz, H-6c*β*), 4.502 (d, 0.7 H, $J_{NH,5}$ 10.6 Hz, N*H*α), 4.493 (d, 0.3 H, $J_{NH,5}$ 10.6 Hz, N*H*β), 4.396 (d, 0.7 H, H-1bα), 4.366 (d, 0.3 H, H-1b*β*), 3.837 (s, 2.1 H, OMeα), 3.835 (s, 0.9 H, OMe*β*), 3.661 (q, 1 H, $J_{4,5}$ 10.6 Hz, H-5c), 2.442 (dd, 1 H, $J_{3eq,4}$ 4.6, $J_{3eq,3ax}$ 13.4 Hz, H-3c*eq*), 2.282, 2.279, 2.137, 2.132, 2.129, 2.081, 2.057, 2.055, 2.052, 2.029, 2.025, and 1.990 (12 s, 27 H, 9 OAc), 1.756 (dd, 1 H, $J_{3ax,4}$ 12.6 Hz, H-3c*ax*), 1.397 (s, 9 H, *t*-BuO), and 1.182 (s, 9 H, *t*-BuC = O).

Anal. Calc. for $C_{50}H_{73}NO_{30}$: C, 51.41; H, 6.30; N, 1.20. Found: C, 51.15; H, 6.21; N, 1.17.

Conversion of **33** *into the trichloroacetimidate* **36**. — A solution of **33** (217 mg, 0.186 mmol), CCl_3CN (0.190 mL, 1.86 mmol), and DBU (0.032 mL, 0.205 mmol) in $(ClCH_2)_2$ (3.7 mL) was stirred for 4 h at 0°. The reaction mixture was directly chromatographed on silica gel (24 g) in 1:1 toluene–EtOAc to give **36** (225 mg, 95% based on **33** consumed; 6 mg of **33** was recovered), $[\alpha]_D$ + 19.2° (*c* 1.2); R_F 0.46 in 7:13 toluene–EtOAc; n.m.r.: δ_H 8.640 (s, 1 H, C = N*H*), 6.515 (d, 1 H, $J_{1,2}$ 4.0 Hz, H-1a), 5.585 (t, 1 H, $J_{2,3} = J_{3,4}$ 9.7 Hz, H-3a), 5.418–5.357 (m, 2 H, H-4b, 7c), 5.319 (ddd, 1 H, $J_{8,9}$ 2.8, $J_{8,9'}$ 6.1, $J_{7,8}$ 9.3 Hz, H-8c), 5.110 (dd, 1 H, $J_{1,2}$ 7.9, $J_{2,3}$ 10.4 Hz, H-2b), 5.049 (dd, 1 H, H-2a), 4.986 (dd, 1 H, $J_{3,4}$ 3.3 Hz, H-3b), 4.765 (dt, 1 H, $J_{3eq,4}$ 4.0, $J_{3ax,4} = J_{4,5}$ 11.3 Hz, H-4c), 4.579 (d, 1 H, H-1b), 4.283 (dd, 1 H, $J_{9,9'}$ 12.3 Hz, H-9c), 4.195 (d, 1 H, $J_{NH,5}$ 10.6 Hz, N*H*), 4.054 (dd, 1 H, H-9′c), 3.983 (dd, 1 H, $J_{6,7}$ 1.5, $J_{5,6}$ 10.6 Hz, H-6c), 3.791 (s, 3 H, OMe), 2.540 (dd, 1 H, $J_{3eq,3ax}$ 12.6 Hz, H-3c*eq*), 2.162, 2.148, 2.109, 2.090, 2.049, 2.043 (6 H), 2.030 and 1.951 (8 s, 27 H, 9 OAc), 1.390 (s, 9 H, *t*-BuO), and 1.139 (s, 9 H, *t*-BuC = O).

Conversion of **34** *into the trichloroacetimidate* **37**. — Compound **34** (83 mg, 0.071 mmol) was converted into **37** (86 mg, 98% based on **34** consumed; 5 mg of **34** was recovered) as described for the synthesis of compound **36**. For **37**, $[\alpha]_D$ + 34.4° (*c* 1.2); R_F 0.43 in 2:3 toluene–EtOAc; n.m.r.: δ_H 8.637 (s, 1 H, C = N*H*), 6.515 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1a), 5.606 (t, 1 H, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3a), 5.513 (m, 2 H, H-8c, 7c), 5.053 (dd, 1 H, H-2a), 4.965 (dd, 1 H, $J_{1,2}$ 8.1, $J_{2,3}$ 10.3 Hz, H-2b), 4.886 (dd, 1 H, $J_{4,5}$ 0.7, $J_{3,4}$ 3.3 Hz, H-4b), 4.795 (dt, 1 H, $J_{3eq,4}$ 4.0, $J_{3ax,4} = J_{4,5}$ 11.7 Hz, H-4c), 4.695 (d, 1 H, H-1b), 4.508 (dd, 1 H, H-3b), 4.135 (d, 1 H, $J_{NH,5}$ 10.6 Hz, N*H*), 3.835 (s, 3 H, OMe), 3.773 (q, 1 H, $J_{5,6}$ 10.6 Hz, H-5c), 3.520 (dd, 1 H, $J_{6,7}$ 1.8 Hz, H-6c), 2.593 (dd, 1 H, $J_{3eq,3ax}$ 12.5 Hz, H-3c*eq*), 2.249, 2.147, 2.087, 2.082, 2.079 (6 H), 2.060, 2.028 and 2.009 (8 s, 27 H, 9 OAc), 1.647 (t, 1 H, H-3c*ax*), 1.377 (s, 9 H, *t*-BuO), and 1.130 (s, 9 H, *t*-BuC = O).

Conversion of **35** *into the trichloroacetimidate* **38**. — Compound **35** (68 mg, 0.058 mmol) was converted into **38** (70 mg, 97% based on **35** consumed; 4 mg of **35** was recovered) as described for the synthesis of compound **36**. For **38**, $[\alpha]_D$ + 31.5° (*c* 1.0); R_F 0.47 in 2:3 toluene–EtOAc; n.m.r.: δ_H 8.652 (s, 1 H, C = N*H*), 6.494 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1a), 5.578 (t, 1 H, $J_{2,3} = J_{3,4}$ 9.7 Hz, H-3a), 5.494 (t, 1 H, $J_{6,7} = J_{7,8}$ 2.0 Hz, H-7c), 5.379 (dd, 1 H, $J_{8,9}$ 2.6, $J_{9,9'}$ 12.1 Hz, H-9c), 5.274 (d, 1 H, $J_{3,4}$ 2.6 Hz, H-4b), 5.237 (td, 1 H, $J_{8,9'}$ 9.9 Hz, H-8c), 5.134 (dd, 1 H, $J_{1,2}$ 8.2, $J_{2,3}$ 10.4 Hz, H-2b), 5.066 (dd, 1 H, H-2a), 4.974 (dt, 1 H, $J_{3eq,4}$ 4.8, $J_{3ax,4} = J_{4,5}$ 11.2 Hz, H-4c), 4.789 (dd, 1 H, H-3b), 4.631 (dd, 1 H, $J_{5,6}$ 10.6 Hz, H-6c), 4.497 (d, 1 H, $J_{NH,5}$ 10.6 Hz, N*H*), 4.434 (d, 1 H, H-1b), 4.099 (ddd, 1 H, $J_{5,6}$ 1.6, $J_{5,6'}$ 4.2, $J_{4,5}$ 10.1 Hz, H-5a), 3.898 (t, 1 H, H-4a), 3.830 (s, 3 H, OMe), 3.768 (dd, 1 H, H-9′c), 3.662 (q, 1 H, H-5c), 2.444 (dd, 1 H, $J_{3eq,3ax}$ 13.5 Hz, H-3c*eq*), 2.280, 2.139, 2.109, 2.082, 2.052 (6 H), 2.036, 2.030 and 1.992 (8 s, 27 H, 9 OAc), 1.762 (dd, 1 H, H-3c*ax*), 1.397 (s, 9 H, *t*-BuO), and 1.135 (s, 9 H, *t*-BuC = O).

O-*[Methyl 4,7,8,9-tetra*-O-*acetyl-5-(*tert-*butoxycarbonylamino)-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosylonate]-(2→6)*-O-*(2,3,4-tri*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(3,6-di*-O-*acetyl-2*-O-*pivaloyl-β*-D-*glucopyranosyl)-(1→1)-(2*S,*3*R,*4*E*)-3*-O-*benzoyl-2*-N-*tetracosanoylsphingenine* (**39**). — To a mixture of **36** (225

mg, 0.171 mmol), **6** (259 mg, 0.343 mmol), and powdered 4A molecular sieves (940 mg) in $CHCl_3$ (7 mL) was added $BF_3 \cdot OEt_2$ (0.027 mL, 0.220 mmol) at 0° under Ar. The reaction mixture was stirred for 8 h at 0°, then diluted with $CHCl_3$ (70 mL) and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$ and aq. NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on silica gel (47 g) with 23:2 $CHCl_3$–THF to give **39** (177 mg, 55%), $[\alpha]_D$ − 12.3° (*c* 0.2); R_F 0.39 in 9:1 $CHCl_3$–THF; n.m.r.: δ_H 8.000 (d, 2 H, *J* 7.0 Hz, $C_6H_5C=O$), 7.553 (t, 1 H, *J* 7.3 Hz, $C_6H_5C=O$), 7.435 (t, 2 H, *J* 7.7 Hz, $C_6H_5C=O$), 5.865 (td, 1 H, $J_{5,6}$ 7.1, $J_{4,5}$ 15.0 Hz, H-5cer), 5.774 (d, 1 H, $J_{NH,2}$ 9.2 Hz, N*H*cer), 5.532 (t, 1 H, $J_{2,3} = J_{3,4}$ 7.5 Hz, H-3cer), 5.456 (dd, 1 H, H-4cer), 5.386 (bd, 1 H, $J_{7,8}$ 9.2 Hz, H-7c), 5.377 (bs, 1 H, H-4b), 5.313 (ddd, 1 H, $J_{8,9}$ 2.9, $J_{8,9'}$ 5.9 Hz, H-8c), 5.219 (t, 1 H, $J_{2,3} = J_{3,4}$ 9.3 Hz, H-3a), 5.052 (dd, 1 H, $J_{1,2}$ 7.7, $J_{2,3}$ 10.3 Hz, H-2b), 4.965 (dd, 1 H, $J_{3,4}$ 3.5 Hz, H-3b), 4.898 (dd, 1 H, $J_{1,2}$ 7.9 Hz, H-2a), 4.771 (dt, 1 H, $J_{3eq,4}$ 4.4, $J_{3ax,4} = J_{4,5}$ 10.7 Hz, H-4c), 4.508 (d, 1 H, H-1b), 4.452 (m, 1 H, H-2cer), 4.427 (d, 1 H, H-1a), 4.199 (d, 1 H, $J_{NH,5}$ 10.6 Hz, N*H*), 4.060 (dd, 1 H, $J_{9,9'}$ 12.3 Hz, H-9c), 4.016 (dd, 1 H, $J_{1,2}$ 3.3, $J_{1,1'}$ 9.9 Hz, H-1cer), 3.821 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4a), 3.795 (s, 3 H, OMe), 3.595 (dd, 1 H, $J_{1',2}$ 4.4 Hz, H-1′cer), 3.557 (ddd, 1 H, $J_{5,6}$ 2.0, $J_{5,6'}$ 5.7 Hz, H-5a), 3.336 (dd, 1 H, $J_{5,6}$ 7.7, $J_{5,6'}$ 10.6 Hz, H-5b), 2.544 (dd, 1 H, $J_{3eq,3ax}$ 13.0 Hz, H-3c*eq*), 2.168, 2.134, 2.111, 2.053, 2.031 (6 H), 2.006, 1.937 and 1.910 (8 s, 27 H, 9 OAc), 1.874 (t, 1 H, H-3c*ax*), 1.392 (s, 9 H, *t*-BuO), 1.146 (s, 9 H, *t*-BuC=O), 0.880 (t, 3 H, *J* 6.8 Hz, CH_2CH_3), 0.878 (t, 3 H, *J* 6.8 Hz, CH_2CH_3); δ_C 177.1 (*t*-Bu*C*=O), 155.0 (*t*-BuO*C*=O), 100.8, 100.4 (C-1a,1b), and 99.1 (C-2c).

Anal. Calc. for $C_{99}H_{158}N_2O_{33}$: C, 62.44; H, 8.36; N, 1.47. Found: C, 59.12; H, 7.80; N, 1.27 (trace of $CHCl_3$).

O-*[Methyl 4,7,8,9-tetra*-O-*acetyl-5-(*tert-*butoxycarbonylamino)-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosylonate]-(2→3)*-O-*(2,4,6-tri*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(3,6-di*-O-*acetyl-2*-O-*pivaloyl-β*-D-*glucopyranosyl)-(1→1)-(2*S,*3*R,*4*E*)-3*-O-*benzoyl-2*-N-*tetracosanoylsphingenine* (**40**). — To a mixture of **37** (86 mg, 0.065 mmol), **6** (99 mg, 0.131 mmol), and powdered 4A molecular sieves (350 mg) in $CHCl_3$ (3.9 mL) was added $BF_3 \cdot OEt_2$ (0.016 mL, 0.130 mmol) at 0° under Ar. The reaction mixture was stirred for 5 h at 0°, then diluted with $CHCl_3$ (40 mL) and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$ and aq. NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on silica gel (19 g) with $CHCl_3$ to give **40** (88 mg, 71%), $[\alpha]_D$ + 5.2° (*c* 0.2); R_F 0.44 in 3:1 toluene–acetone; n.m.r.: δ_H 7.995 (dd, 2 H, *J* 1.5, *J* 7.0 Hz, $C_6H_5C=O$), 7.547 (tt, 1 H, *J* 1.5, *J* 7.3 Hz, $C_6H_5C=O$), 7.429 (t, 2 H, *J* 7.7 Hz, $C_6H_5C=O$), 5.862 (td, 1 H, $J_{5,6}$ 7.0, $J_{4,5}$ 15.4 Hz, H-5cer), 5.738 (d, 1 H, $J_{NH,2}$ 9.2 Hz, N*H*cer), 5.541 (t, 1 H, $J_{2,3} = J_{3,4}$ 7.3 Hz, H-3cer), 5.457 (dd, 1 H, H-4cer), 5.206 (t, 1 H, $J_{2,3} = J_{3,4}$ 9.3 Hz, H-3a), 4.907 (dd, 1 H, $J_{1,2}$ 7.9, $J_{2,3}$ 10.4 Hz, H-2b), 4.886 (dd, 1 H, $J_{1,2}$ 7.7 Hz, H-2a), 4.866 (d, 1 H, $J_{3,4}$ 2,6 Hz, H-4b), 4.786 (dt, 1 H, $J_{3eq,4}$ 4.4, $J_{3ax,4} = J_{4,5}$ 12.1 Hz, H-4c), 4.628 (d, 1 H, H-1b), 4.501 (dd, 1 H, H-3b), 4.434 (m, 1 H, H-2cer), 4.423 (d, 1 H, H-1a), 4.126 (d, 1 H, $J_{NH,5}$ 11.0 Hz, N*H*), 3.827 (s, 3 H, OMe), 3.767 (q, 1 H, $J_{5,6}$ 10.3 Hz, H-5c), 3.604 (dd, 1 H, $J_{1,2}$ 4.0, $J_{1,1'}$ 9.9 Hz, H-1cer), 2.580 (dd, 1 H, $J_{3eq,3ax}$ 12.5 Hz, H-3c*eq*), 2.205, 2.146, 2.087, 2.077, 2.071, 2.067, 2.006 (6 H), and 1.906 (8 s, 27 H, 9 OAc), 1.632 (t, 1 H, H-3c*ax*), 1.378 (s, 9 H, *t*-BuO), 1.142 (s, 9 H,

t-BuC=O), 0.880 (t, 3 H, *J* 6.6 Hz, CH_2CH_3), 0.878 (t, 3 H, *J* 7.0 Hz, CH_2CH_3); δ_c 177.1 (*t*-Bu*C*=O), 155.2 (*t*-BuO*C*=O), 101.0 (C-1a), 100.4 (C-1b), 96.7 (C-2c), 28.1 [$(CH_3)_3CO$], and 27.0 [$(CH_3)_3CC$=O].

Anal. Calc. for $C_{99}H_{158}N_2O_{33}$: C, 62.44; H, 8.36; N, 1.47. Found: C, 62.07; H, 8.34; N, 1.38.

O-*[Methyl 4,7,8,9-tetra*-O-*acetyl-5-(*tert-*butoxycarbonylamino)-3,5-dideoxy*-D-glycero-*β*-D-galacto-*2-nonulopyranosylonate]-(2→3)*-O-*(2,4,6-tri*-O-*acetyl-β*-D-*galactopyranosyl)-(1→4)*-O-*(3,6-di*-O-*acetyl-2*-O-*pivaloyl-β*-D-*glucopyranosyl)-(1→1)-(2S,3R,4E)-3*-O-*benzoyl-2*-N-*tetracosanoylsphingenine* (**41**). — To a mixture of **38** (70 mg, 0.053 mmol), **6** (80 mg, 0.106 mmol), and powdered 4A molecular sieves (280 mg) in $CHCl_3$ (2.0 mL) was added $BF_3 \cdot OEt_2$ (0.013 mL, 0.106 mmol) at 0° under Ar. The reaction mixture was stirred for 7 h at 0°, then diluted with $CHCl_3$ (40 mL) and filtered through Celite. The filtrate was washed with aq. $NaHCO_3$ and aq. NaCl, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on silica gel (19 g) in $CHCl_3$ to give **41** (66 mg, 65%), $[\alpha]_D$ +4.4° (*c* 1.4); R_F 0.61 in 3:1 toluene–acetone; n.m.r.: δ_H 7.989 (dd, 2 H, *J* 1.1, *J* 8.4 Hz, C_6H_5C=O), 7.556 (tt, 1 H, *J* 1.5, *J* 7.3 Hz, C_6H_5C=O), 7.431 (t, 2 H, *J* 8.1 Hz, C_6H_5C=O), 5.871 (td, 1 H, $J_{5,6}$ 6.9, $J_{4,5}$ 15.4 Hz, H-5cer), 5.706 (d, 1 H, $J_{NH,2}$ 9.5 Hz, N*H*cer), 5.526 (t, 1 H, $J_{2,3} = J_{3,4}$ 7.7 Hz, H-3cer), 5.484 (t, 1 H, $J_{6,7} = J_{7,8}$ 1.8 Hz, H-7c), 5.451 (dd, 1 H, H-4cer), 5.352 (dd, 1 H, $J_{8,9}$ 2.6 and $J_{9,9'}$ 12.1 Hz, H-9c), 5.258 (d, 1 H, $J_{3,4}$ 2.9 Hz, H-4b), 5.237 (td, 1 H, $J_{8,9'}$ 10.3 Hz, H-8c), 5.183 (t, 1 H, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3a), 5.006 (dd, 1 H, $J_{1,2}$ 8.2, $J_{2,3}$ 10.4 Hz, H-2b), 4.953 (ddd, 1 H, $J_{3eq,4}$ 4.4, $J_{4,5}$ 10.6, $J_{3ax,4}$ 11.7 Hz, H-4c), 4.912 (dd, 1 H, $J_{1,2}$ 7.9 Hz, H-2a), 4.762 (dd, 1 H, H-3b), 4.619 (dd, 1 H, $J_{5,6}$ 10.4 Hz, H-6c), 4.471 (d, 1 H, $J_{NH,5}$ 10.6 Hz, N*H*), 4.465 (m, 1 H, H-2cer), 4.416 (d, 1 H, H-1a), 4.330 (d, 1 H, H-1b), 3.815 (s, 3 H, OMe), 3.788 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4a), 3.768 (dd, 1 H, H-9'c), 3.656 (q, 1 H, H-5c), 3.590 (dd, 1 H, $J_{1,2}$ 4.0, $J_{1,1'}$ 9.5 Hz, H-1cer), 3.488 (ddd, 1 H, $J_{5,6}$ 1.8, $J_{5,6'}$ 4.8 Hz, H-5a), 2.428 (dd, 1 H, $J_{3eq,3ax}$ 13.4 Hz, H-3c*eq*), 2.265, 2.135, 2.094, 2.055, 2.031, 2.011 (6 H), 1.984, and 1.943 (8 s, 27 H, 9 OAc), 1.745 (dd, 1 H, H-3c*ax*), 1.395 (s, 9 H, *t*-BuO), 1.148 (s, 9 H, *t*-BuC=O), 0.880 (t, 3 H, *J* 6.8 Hz, CH_2CH_3), 0.878 (t, 3 H, *J* 7.1 Hz, CH_2CH_3); δ_C 177.1 (*t*-Bu*C*=O), 155.4 (*t*-BuO*C*=O), 101.1 (C-1a), 100.5 (C-1b), 99.5 (C-2c), 28.2 [$(CH_3)_3CO$], and 27.0 [$(CH_3)_3CC$=O].

Anal. Calc. for $C_{99}H_{158}N_2O_{33}$: C, 62.44; H, 8.36; N, 1.47. Found: C, 62.20; H, 8.40; N, 1.43.

O-*[Sodium 5-(*tert-*butoxycarbonylamino)-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosylonate]-(2→6)*-O-*β*-D-*galactopyranosyl-(1→4)*-O-*β*-D-*glucopyranosyl-(1→1)-(2S,3R,4E)-2*-N-*tetracosanoylsphingenine* (**42**). — To a solution of **39** (11 mg, 5.8 μmol) in 1:1 THF–MeOH (0.35 mL) was added 3M NaOH (0.035 mL). The reaction mixture was stirred for 3 h at 20°, then evaporated *in vacuo*. The residue was chromatographed over Sephadex LH-20 (10 mL) in 5:5:1 $CHCl_3$–MeOH–H_2O to give **42** (7.7 mg, 98%), $[\alpha]_D$ −4.5° (*c* 0.2, pyridine); R_F 0.44 in 5:4:1 $CHCl_3$–MeOH–H_2O; n.m.r. [49:1 $(CD_3)_2SO$–D_2O, 50°]: δ_H 5.548 (td, 1 H, $J_{5,6}$ 6.7, $J_{4,5}$ 15.0 Hz, H-5cer), 5.355 (dd, 1 H, $J_{3,4}$ 7.1 Hz, H-4cer), 4.211 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1b), 4.176 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 2.631 (dd, 1 H, $J_{3eq,4}$ 4.4, $J_{3eq,3ax}$ 11.9 Hz, H-3c*eq*), 1.388 (s, 9 H, *t*-Bu), and 0.854 (t, 6 H, *J* 6.8 Hz, 2 CH_2CH_3).

Cleavage of methyl ester of **39** *to give* **43**. — A solution of **39** (10.0 mg, 5.3 μmol) in pyridine (0.3 mL) was added dropwise onto LiI (7.1 mg, 0.053 mmol, dried at 60° for 3 h *in vacuo*), and the mixture was heated for 2 h at reflux under Ar. The crude mixture was chromatographed over Sephadex LH-20 (16 mL) in MeOH and then on silica gel (1.0 g) with 23:2 $CHCl_3$–MeOH to give **43** (6.4 mg, 64%), R_F 0.47 in 17:3 $CHCl_3$–MeOH; n.m.r.: δ_H 8.002 (d, 2 H, *J* 7.3 Hz, $C_6H_5C=O$), 7.555 (t, 1 H, *J* 7.3 Hz, $C_6H_5C=O$), 7.435 (t, 2 H, *J* 7.7 Hz, $C_6H_5C=O$), 5.864 (td, 1 H, $J_{5,6}$ 7.1, $J_{4,5}$ 15.0 Hz, H-5cer), 5.465 (dd, 1 H, $J_{3,4}$ 7.3 Hz, H-4cer), 1.390 (s, 9 H, *t*-BuO), 1.152 (s, 9 H, *t*-BuC=O), 0.879 (t, 3 H, *J* 6.6 Hz, CH_2CH_3), and 0.878 (t, 3 H, *J* 7.0 Hz, CH_2CH_3).

Cleavage of methyl ester of **40** *to give* **44**. — Compound **40** (21 mg, 0.011 mmol) was converted into **44** (20 mg, 96%) as described for the synthesis of compound **43**. For **44**, $[\alpha]_D$ + 15.6° (*c* 0.6); R_F 0.46 in 17:3 $CHCl_3$–MeOH; n.m.r. (CD_3OD): δ_H 8.001 (dd, 2 H, *J* 1.5, *J* 8.4 Hz, $C_6H_5C=O$), 7.594 (tt, 1 H, *J* 1.5, *J* 7.3 Hz, $C_6H_5C=O$), 7.462 (t, 2 H, *J* 7.7 Hz, $C_6H_5C=O$), 5.877 (td, 1 H, $J_{5,6}$ 7.3, $J_{4,5}$ 15.0 Hz, H-5cer), 5.568 (t, 1 H, $J_{2,3} = J_{3,4}$ 7.3 Hz, H-3cer), 5.502 (dd, 1 H, H-4cer), 5.440 (dd, 1 H, $J_{6,7}$ 2.6, $J_{7,8}$ 9.5 Hz, H-7c), 5.298 (br. d, 1 H, H-4b), 5.201 (t, 1 H, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3a), 5.012 (m, 1 H, H-4c), 4.416 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1a), 2.594 (br. dd, 1 H, H-3c*eq*), 2.262, 2.115, 2.100, 2.085, 2.060, 2.058, 2.007, 1.974, and 1.961 (9 s, 27 H, 9 OAc), 1.390 (s, 9 H, *t*-BuO), 1.151 (s, 9 H, *t*-BuC=O), 0.897 (t, 3 H, *J* 7.0 Hz, CH_2CH_3), and 0.895 (t, 3 H, *J* 7.0 Hz, CH_2CH_3).

N-*Deprotection of* **43** *to give* **45**. — To a solution of **43** (6.4 mg, 3.4 μmol) in 1:1 CH_2Cl_2–MeOH (0.068 mL) was added CF_3COOH (0.068 mL), and the mixture was stirred for 8 h at 0°. After evaporation *in vacuo*, the residue was chromatographed over Sephadex LH-20 (6 mL) in MeOH to give **45** (6.3 mg, 98%), R_F 0.33 in 45:5:1 $CHCl_3$–MeOH–Et_3N; n.m.r. (1:1 $CDCl_3$–CD_3OD): δ_H 7.993 (d, 2 H, *J* 7.7 Hz, $C_6H_5C=O$), 7.589 (t, 1 H, *J* 7.3 Hz, $C_6H_5C=O$), 7.457 (t, 2 H, *J* 7.7 Hz, $C_6H_5C=O$), 5.871 (td, 1 H, $J_{5,6}$ 7.1, $J_{4,5}$ 15.8 Hz, H-5cer), 5.492 (dd, 1 H, $J_{3,4}$ 7.9 Hz, H-4cer), 1.144 (s, 9 H, *t*-Bu), 0.896 (t, 3 H, *J* 6.6 Hz, CH_2CH_3), and 0.894 (t, 3 H, *J* 6.6 Hz, CH_2CH_3).

N-*Deprotection of* **44** *to give* **46**. — Compound **44** (17 mg, 8.8 μmol) was converted into **46** (17 mg, 99%) as described for the synthesis of compound **45**. For **46**, $[\alpha]_D$ − 0.2° (*c* 1.1); R_F 0.34 in 4:1 $CHCl_3$–MeOH; n.m.r. (CD_3OD): δ_H 8.003 (dd, 2 H, *J* 1.5, *J* 8.4 Hz, $C_6H_5C=O$), 7.594 (t, 1 H, *J* 7.7 Hz, $C_6H_5C=O$), 7.493 (t, 2 H, *J* 8.1 Hz, $C_6H_5C=O$), 5.882 (td, 1 H, $J_{5,6}$ 6.6, $J_{4,5}$ 15.4 Hz, H-5cer), 5.687 (br. d, 1 H, *J* 10.3 Hz, H-8c), 5.571 (t, 1 H, $J_{2,3} = J_{3,4}$ 7.3 Hz, H-3cer), 5.500 (dd, 1 H, H-4cer), 5.501 (br. d, 1 H, $J_{7,8}$ 9.2 Hz, H-7c), 5.194 (t, 1 H, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3a), 5.141 (m, 1 H, H-4c), 3.862 (t, 1 H, $J_{4,5}$ 9.5 Hz, H-4a), 2.819 (br. t, 1 H, H-5c), 2.666 (br. d, 1 H, H-3c*eq*), 2.201, 2.171, 2.080, 2.075, 2.071 (6 H), 2.054, 1.999, and 1.994 (8 s, 27 H, 9 OAc), 1.153 (s, 9 H, *t*-Bu), 0.897 (t, 3 H, *J* 7.0 Hz, CH_2CH_3), and 0.896 (t, 3 H, *J* 6.6 Hz, CH_2CH_3).

O-[*Sodium 5-amino-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosylonate*]-(2→6)-O-β-D-*galactopyranosyl*-(1→4)-O-β-D-*glucopyranosyl*-(1→1)-(2S, 3R, 4E)-2-N-*tetracosanoylsphingenine* (**3**). — To a solution of **45** (6.3 mg, 3.3 μmol) in THF (0.05 mL) was added M NaOMe in MeOH (0.1 mL). The reaction mixture was stirred for 90 min at 20°, then evaporated *in vacuo*. The residue was chromatographed over Sephadex LH-20 (6 mL) in 5:5:1 $CHCl_3$–MeOH–H_2O to give **3** (2.3 mg, 56%), $[\alpha]_D$

+ 17.7° (*c* 0.1, pyridine); R_F 0.30 in 5:4:1 $CHCl_3$–MeOH–H_2O; n.m.r. [49:1 $(CD_3)_2SO$–D_2O, 50°]: δ_H 5.545 (td, 1 H, $J_{5,6}$ 6.9, $J_{4,5}$ 15.4 Hz, H-5cer), 5.357 (dd, 1 H, $J_{3,4}$ 7.1 Hz, H-4cer), 4.194 (d, 1 H, $J_{1,2}$ 7.3 Hz, H-1b), 4.162 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 0.854 (t, 6 H, *J* 6.8 Hz, 2 CH_2CH_3); (1:1 $CDCl_3$–CD_3OD): δ_H 5.702 (td, 1 H, $J_{5,6}$ 7.1, $J_{4,5}$ 14.7 Hz, H-5cer), 5.445 (dd, 1 H, $J_{3,4}$ 7.7 Hz, H-4cer), 2.794 (t, 1 H, $J_{4,5}$ = $J_{5,6}$ 9.7 Hz, H-5c), 2.722 (dd, 1 H, $J_{3eq,4}$ 4.8, $J_{3eq,3ax}$ 12.5 Hz, H-3c*eq*), 1.625 (t, 1 H, $J_{3ax,4}$ 11.9 Hz, H-3c*ax*), 0.891 (t, 3 H, *J* 6.6 Hz, CH_2CH_3), and 0.889 (t, 3 H, *J* 7.0 Hz, CH_2CH_3).

O-*(Sodium 5-amino-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosylonate)-(2→3)*-O-*β*-D-*galactopyranosyl-(1→4)*-O-*β*-D-*glucopyranosyl-(1→1)*-(2S, *3*R, *4*E*)-2*-N-*tetracosanoylsphingenine* (**1**). — Compound **46** (16.5 mg, 8.7 μmol) was converted into **1** (5.2 mg, 48%) as described for the synthesis of compound **3**. For **1**, $[\alpha]_D$ + 50.8° (*c* 0.2, pyridine); R_F 0.29 in 5:4:1 $CHCl_3$–MeOH–H_2O; n.m.r. [49:1 $(CD_3)_2SO$–D_2O, 35°]: δ_H 5.536 (td, 1 H, $J_{5,6}$ 6.6, $J_{4,5}$ 15.4 Hz, H-5cer), 5.349 (dd, 1 H, $J_{3,4}$ 7.0 Hz, H-4cer), 4.190 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1b), 4.158 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1a), 3.887 (t, 1 H, $J_{2,3}$ 7.7 Hz, H-3cer), 2.660 (dd, 1 H, $J_{3eq,4}$ 4.8, $J_{3eq,3ax}$ 11.7 Hz, H-3c*eq*), 0.853 (t, 6 H, *J* 7.0 Hz, 2 CH_2CH_3); (1:1 $CDCl_3$–CD_3OD): δ_H 5.694 (td, 1 H, $J_{5,6}$ 7.0, $J_{4,5}$ 15.0 Hz, H-5cer), 5.454 (dd, 1 H, $J_{3,4}$ 7.7 Hz, H-4cer), 4.404 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 4.297 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 4.092 (t, 1 H, $J_{2,3}$ 8.1 Hz, H-3cer), 2.789 (dd, 1 H, $J_{3eq,4}$ 5.5, $J_{3eq,3ax}$ 12.1 Hz, H-3c*eq*), 2.785 (t, 1 H, $J_{4,5}$ = $J_{5,6}$ 9.5 Hz, H-5c), 1.681 (t, 1 H, $J_{3ax,4}$ 12.1 Hz, H-3c*ax*), and 0.890 (t, 6 H, *J* 7.0 Hz, 2 CH_2CH_3).

N-*Deprotection of* **41** *to give* **47**. — To a solution of **41** (8.1 mg, 4.3 μmol) in CH_2Cl_2 (0.043 mL) was added CF_3COOH (0.086 mL). The mixture was stirred for 2 h at 0°, then diluted with $CHCl_3$ (10 mL), washed with aq. $NaHCO_3$ (10 mL) and aq. NaCl (20 mL), dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on silica gel (0.9 g) in 17:3 $CHCl_3$–THF to give **47** (7.1 mg, 94%), $[\alpha]_D$ − 0.3° (*c* 0.5); R_F 0.31 in 3:1 $CHCl_3$–THF; n.m.r.: δ_H 7.993 (d, 2 H, *J* 7.3 Hz, C_6H_5C = O), 7.558 (t, 1 H, *J* 7.3 Hz, C_6H_5C = O), 7.434 (t, 2 H, *J* 7.3 Hz, C_6H_5C = O), 5.872 (td, 1 H, $J_{5,6}$ 7.1, $J_{4,5}$ 15.6 Hz, H-5cer), 5.724 (d, 1 H, $J_{NH,2}$ 9.2 Hz, N*H*cer), 5.689 (br. s, 1 H, H-7c), 5.526 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ 7.8 Hz, H-3cer), 5.451 (dd, 1 H, H-4cer), 5.316 (m, 2 H, H-8c, 9c), 5.250 (d, 1 H, $J_{3,4}$ 3.7 Hz, H-4b), 5.185 (t, 1 H, $J_{2,3}$ = $J_{3,4}$ 9.6 Hz, H-3a), 5.071 (dd, 1 H, $J_{1,2}$ 8.3, $J_{2,3}$ 11.0 Hz, H-2b), 4.912 (dd, 1 H, $J_{1,2}$ 7.7 Hz, H-2a), 4.857 (ddd, 1 H, $J_{3eq,4}$ 4.6, $J_{4,5}$ 10.1, $J_{3ax,4}$ 11.9 Hz, H-4c), 4.696 (dd, 1 H, H-3b), 4.456 (m, 1 H, H-2cer), 4.414 (d, 1 H, H-1a), 4.325 (dd, 1 H, $J_{5,6}$ 8.3 Hz, H-6c), 4.309 (d, 1 H, H-1b), 3.815 (s, 3 H, OMe), 3.765 (t, 1 H, $J_{4,5}$ 8.7 Hz, H-4a), 3.588 (dd, 1 H, $J_{1,2}$ 4.1, $J_{1,1'}$ 9.6 Hz, H-1cer), 2.409 (dd, 1 H, $J_{3eq,3ax}$ 13.8 Hz, H-3c*eq*), 2.290 (t, 1 H, H-5c), 2.243, 2.160, 2.080, 2.065, 2.047, 2.032, 2.010, 2.006, and 1.944 (9 s, 27 H, 9 OAc), 1.147 (s, 9 H, *t*-Bu), and 0.880 (t, 6 H, *J* 6.9 Hz, 2 CH_2CH_3).

O-*(Sodium 5-amino-3,5-dideoxy*-D-glycero-*β*-D-galacto-*2-nonulopyranosylonate)-(2→3)*- O-*β*-D-*galactopyranosyl-(1→4)*-O-*β*-D-*glucopyranosyl-(1→1)-(2*S, *3*R, *4*E*)-2*-N-*tetracosanoylsphingenine* (**2**). — To a solution of **47** (6.6 mg, 3.7 μmol) in THF (0.25 mL) was added M NaOMe in MeOH (0.11 mL). The mixture was stirred for 2 h at 20°, and water (0.10 mL) was added. The mixture was then stirred for an additional 4 h at 20°, and the solvents were evaporated *in vacuo*. The residue was purified by chromatography over Sephadex LH-20 (8 mL) in 5:4:1 $CHCl_3$–MeOH–H_2O and then by

high-performance t.l.c. in 5:4:1 $CHCl_3$–MeOH–H_2O to give **2** (2.5 mg, 55%), $[\alpha]_D$ −19.5° (*c* 0.1, pyridine); R_F 0.36 in 5:4:1 $CHCl_3$–MeOH–H_2O; n.m.r. (1:1 $CDCl_3$–CD_3OD): δ_H 5.694 (td, 1 H, $J_{5,6}$ 7.0, $J_{4,5}$ 15.0 Hz, H-5cer), 5.454 (dd, 1 H, $J_{3,4}$ 7.7 Hz, H-4cer), 4.360 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1b), 4.289 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 4.091 (t, 1 H, $J_{2,3}$ 7.7 Hz, H-3cer), 2.879 (t, 1 H, $J_{4,5} = J_{5,6}$ 9.7 Hz, H-5c), 2.379 (dd, 1 H, $J_{3eq,4}$ 4.6 and $J_{3eq,3ax}$ 12.3 Hz, H-3c*eq*), 1.646 (t, 1 H, $J_{3ax,4}$ 12.1 Hz, H-3c*ax*), and 0.890 (t, 6 H, *J* 6.8 Hz, 2 CH_2CH_3).

N-*Deprotection of* **39** *to give* **48**. — Compound **39** (21 mg, 0.011 mmol) was converted into **48** (18 mg, 95% based on **39** consumed; 1.2 mg of **39** was recovered) as described for the synthesis of compound **47**. For **48**, $[\alpha]_D$ −7.2° (*c* 0.7); R_F 0.34 in 4:1 $CHCl_3$–THF; n.m.r.: δ_H 8.002 (d, 2 H, *J* 8.4 Hz, $C_6H_5C=O$), 7.553 (t, 1 H, *J* 7.5 Hz, $C_6H_5C=O$), 7.435 (t, 2 H, *J* 7.7 Hz, $C_6H_5C=O$), 5.864 (td, 1 H, $J_{5,6}$ 7.2, $J_{4,5}$ 15.0 Hz, H-5cer), 5.738 (d, 1 H, $J_{NH,2}$ 9.5 Hz, NHcer), 5.538 (t, 1 H, $J_{2,3} = J_{3,4}$ 7.5 Hz, H-3cer), 5.480 (dd, 1 H, $J_{6,7}$ 1.5, $J_{7,8}$ 9.5 Hz, H-7c), 5.459 (dd, 1 H, H-4cer), 5.423 (dd, 1 H, $J_{4,5}$ 0.9, $J_{3,4}$ 3.5 Hz, H-4b), 5.339 (ddd, 1 H, $J_{8,9}$ 2.4, $J_{8,9'}$ 4.0 Hz, H-8c), 5.225 (t, 1 H, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3a), 5.047 (dd, 1 H, $J_{1,2}$ 7.9, $J_{2,3}$ 10.4 Hz, H-2b), 4.961 (dd, 1 H, H-3b), 4.898 (dd, 1 H, $J_{1,2}$ 7.7 Hz, H-2a), 4.570 (ddd, 1 H, $J_{3eq,4}$ 4.4, $J_{4,5}$ 9.9, $J_{3ax,4}$ 12.1 Hz, H-4c), 4.532 (d, 1 H, H-1b), 4.453 (m, 1 H, H-2cer), 4.435 (d, 1 H, H-1a), 4.343 (dd, 1 H, $J_{9,9'}$ 12.5 Hz, H-9c), 4.244 (dd, 1 H, H-9′c), 4.014 (dd, 1 H, $J_{1,2}$ 3.3, $J_{1,1'}$ 9.9 Hz, H-1cer), 3.799 (s, 3 H, OMe), 3.751 (dd, 1 H, $J_{5,6}$ 9.9 Hz, H-6c), 3.599 (dd, 1 H, $J_{1',2}$ 4.0 Hz, H-1′cer), 2.611 (dd, 1 H, $J_{3eq,3ax}$ 12.8 Hz, H-3c*eq*), 2.552 (t, 1 H, H-5c), 2.206, 2.140, 2.124, 2.077, 2.066, 2.013 (6 H), 1.931, and 1.915 (8 s, 27 H, 9 OAc), 1.646 (t, 1 H, H-3c*ax*), 1.143 (s, 9 H, *t*-Bu), 0.880 (t, 3 H, *J* 6.8 Hz, CH_2CH_3), and 0.878 (t, 3 H, *J* 6.8 Hz, CH_2CH_3).

N-*Deprotection of* **40** *to give* **49**. — Compound **40** (31 mg, 0.016 mmol) was converted into **49** (29 mg, 99%) as described for the synthesis of compound **47**. For **49**, $[\alpha]_D$ +1.8° (*c* 1.2); R_F 0.26 in 4:1 $CHCl_3$–THF; n.m.r.: δ_H 7.998 (dd, 2 H, *J* 1.5, *J* 8.4 Hz, $C_6H_5C=O$), 7.551 (tt, 1 H, *J* 1.1, *J* 7.3 Hz, $C_6H_5C=O$), 7.432 (t, 2 H, *J* 8.1 Hz, C_6H_5-C=O), 5.868 (td, 1 H, $J_{5,6}$ 7.0, $J_{4,5}$ 15.0 Hz, H-5cer), 5.737 (d, 1 H, $J_{NH,2}$ 9.5 Hz, NHcer), 5.541 (t, 1 H, $J_{2,3} = J_{3,4}$ 7.3 Hz, H-3cer), 5.461 (dd, 1 H, H-4cer), 5.192 (t, 1 H, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3a), 4.660 (ddd, 1 H, $J_{3eq,4}$ 4.4, $J_{4,5}$ 9.9, $J_{3ax,4}$ 11.7 Hz, H-4c), 4.552 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 4.420 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 3.820 (s, 3 H, OMe), 3.599 (dd, 1 H, $J_{1,2}$ 4.0, $J_{1,1'}$ 9.9 Hz, H-1cer), 3.421 (d, 1 H, $J_{5,6}$ 10.3 Hz, H-6c), 2.626 (dd, 1 H, $J_{3eq,3ax}$ 12.5 Hz, H-3c*eq*), 2.537 (t, 1 H, H-5c), 2.161, 2.157, 2.117, 2.082, 2.075, 2.070, 2.059, 1.992, and 1.933 (9 s, 27 H, 9 OAc), 1.411 (t, 1 H, H-3c*ax*), 1.144 (s, 9 H, *t*-Bu), and 0.879 (t, 6 H, *J* 6.6 Hz, 2 CH_2CH_3).

Conversion of **48** *into the ureide* **50**. — A mixture of **48** (7.0 mg, 3.9 μmol) and MeNCO (0.1 mL) in CH_2Cl_2 (0.2 mL) was stirred for 1 h at 20°. The reaction mixture was evaporated *in vacuo*, and the residue was chromatographed on silica gel (0.7 g) in 7:3 $CHCl_3$–THF to give **50** (7.1 mg, 99%), $[\alpha]_D$ −6.1° (*c* 0.5); R_F 0.27 in 7:3 $CHCl_3$–THF; n.m.r.: δ_H 8.000 (d, 2 H, *J* 8.4 Hz, $C_6H_5C=O$), 7.553 (t, 1 H, *J* 7.3 Hz, $C_6H_5C=O$), 7.434 (t, 2 H, *J* 7.9 Hz, $C_6H_5C=O$), 5.864 (td, 1 H, $J_{5,6}$ 6.6, $J_{4,5}$ 15.4 Hz, H-5cer), 5.753 (d, 1 H, $J_{NH,2}$ 9.2 Hz, NHcer), 5.533 (t, 1 H, $J_{2,3} = J_{3,4}$ 7.3 Hz, H-3cer), 5.457 (dd, 1 H, H-4cer), 5.392 (dd, 1 H, $J_{4,5}$ 0.9, $J_{3,4}$ 3.5 Hz, H-4b), 5.353 (dd, 1 H, $J_{6,7}$ 2.0, $J_{7,8}$ 9.0 Hz, H-7c), 5.309

(ddd, 1 H, $J_{8,9'}$ 2.8, $J_{8,9}$ 5.8 Hz, H-8c), 5.221 (t, 1 H, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3a), 5.055 (dd, 1 H, $J_{1,2}$ 7.7, $J_{2,3}$ 10.3 Hz, H-2b), 4.969 (dd, 1 H, H-3b), 4.898 (dd, 1 H, $J_{1,2}$ 8.1 Hz, H-2a), 4.868 (ddd, 1 H, $J_{3eq,4}$ 4.8, $J_{4,5}$ 9.9, $J_{3ax,4}$ 12.5 Hz, H-4c), 4.515 (d, 1 H, H-1b), 4.449 (m, 1 H, H-2cer), 4.429 (d, 1 H, H-1a), 4.174 (q, 1 H, *J* 4.9 Hz, MeN*H*), 4.067 (dd, 1 H, $J_{9,9'}$ 12.5 Hz, H-9c), 3.954 (d, 1 H, $J_{NH,5}$ 9.2 Hz, N*H*), 3.803 (s, 3 H, OMe), 3.596 (dd, 1 H, $J_{1,2}$ 4.0 and $J_{1,1'}$ 9.9 Hz, H-1cer), 2.707 (d, 3 H, *Me*NH), 2.534 (dd, 1 H, $J_{3eq,3ax}$ 13.0 Hz, H-3c*eq*), 2.189, 2.136, 2.118, 2.044, 2.030, 2.026, 2.007, 1.937, and 1.913 (9 s, 27 H, 9 OAc), 1.146 (s, 9 H, *t*-Bu), 0.880 (t, 3 H, *J* 6.6 Hz, CH_2CH_3), 0.878 (t, 3 H, *J* 7.0 Hz, CH_2CH_3); δ_C 177.0 (t-Bu*C*=O), 100.8, 100.5 (C-1a, 1b), 99.1 (C-2c), and 27.3 [$(CH_3)_3C$].

Conversion of **49** *into the ureide* **51**. — Compound **49** (11 mg, 6.2 μmol) was converted into **51** (11 mg, 98%) as described for the synthesis of compound **50**. For **51**, $[\alpha]_D$ +5.1° (*c* 0.5); R_F 0.42 in 19:1 $CHCl_3$–MeOH; n.m.r.: δ_H 7.996 (d, 2 H, *J* 8.4 Hz, $C_6H_5C=O$), 7.549 (t, 1 H, *J* 7.5 Hz, $C_6H_5C=O$), 7.430 (t, 2 H, *J* 7.7 Hz, $C_6H_5C=O$), 5.864 (td, 1 H, $J_{5,6}$ 6.6, $J_{4,5}$ 15.4 Hz, H-5cer), 5.742 (d, 1 H, $J_{NH,2}$ 9.2 Hz, N*H*cer), 5.540 (t, 1 H, $J_{2,3} = J_{3,4}$ 7.3 Hz, H-3cer), 5.499 (ddd, 1 H, $J_{8,9}$ 2.9, $J_{8,9'}$ 5.5, $J_{7,8}$ 11.2 Hz, H-8c), 5.457 (dd, 1 H, H-4cer), 5.452 (dd, 1 H, $J_{6,7}$ 2.9 Hz, H-7c), 5.205 (t, 1 H, $J_{2,3} = J_{3,4}$ 9.5 Hz, H-3a), 4.630 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 4.529 (dd, 1 H, $J_{3,4}$ 3.3, $J_{2,3}$ 10.3 Hz, H-3b), 4.424 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 4.418 (q, 1 H, *J* 4.8 Hz, MeN*H*), 3.938 (q, 1 H, $J_{NH,5} = J_{4,5} = J_{5,6}$ 8.4 Hz, H-5c), 3.837 (s, 3 H, OMe), 3.601 (dd, 1 H, $J_{1,2}$ 4.2, $J_{1,1'}$ 10.1 Hz, H-1cer), 3.580 (d, 1 H, H-6c), 2.685 (d, 3 H, *J* 5.1 Hz, *Me*NH), 2.544 (dd, 1 H, $J_{3eq,4}$ 4.8, $J_{3eq,3ax}$ 12.5 Hz, H-3c*eq*), 2.214, 2.155, 2.097, 2.077 (6 H), 2.071, 2.006, 2.003, and 1.901 (8 s, 27 H, 9 OAc), 1.680 (t, 1 H, $J_{3ax,4}$ 12.5 Hz, H-3c*ax*), 1.143 (s, 9 H, *t*-Bu), 0.879 (t, 6 H, *J* 6.2 Hz, 2 CH_2CH_3); δ_C 177.1 (t-Bu*C*=O), 101.0 (C-1a), 100.4 (C-1b), 96.8 (C-2c), and 27.0 [$(CH_3)_3C$].

O-*[Sodium 5-(3-methylureido)-3,5-dideoxy*-D-glycero-α-D-galacto-*2-nonulopyranosylonate]-(2→6)*-O-*β*-D-*galactopyranosyl-(1→4)*-O-*β*-D-*glucopyranosyl-(1→1)-(2*S, *3*R, *4*E*)-2*-N-*tetracosanoylsphingenine* (**4**). — Compound **50** (4.9 mg, 2.6 μmol) was converted into **4** (3.0 mg, 88%) as described for the synthesis of compound **42**. For **4**, $[\alpha]_D$ −0.7° (*c* 0.1, pyridine); R_F 0.39 in 5:4:1 $CHCl_3$–MeOH–H_2O; n.m.r. (1:1 $CDCl_3$–CD_3OD): δ_H 5.701 (td, 1 H, $J_{5,6}$ 7.1, $J_{4,5}$ 15.0 Hz, H-5cer), 5.454 (dd, 1 H, $J_{3,4}$ 7.5 Hz, H-4cer), 4.328 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1b), 4.303 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 2.794 (dd, 1 H, $J_{3eq,4}$ 4.2, $J_{3eq,3ax}$ 12.3 Hz, H-3c*eq*), 2.725 (s, 3 H, *Me*NH), 1.666 (t, 1 H, $J_{3ax,4}$ 11.7 Hz, H-3c*ax*), and 0.890 (t, 6 H, *J* 7.0 Hz, 2 CH_2CH_3).

O-*[Sodium 5-(3-methylureido)-3,5-dideoxy*-D-glycero-α-D-*galacto-2-nonulopyranosylonate]-(2→3)*-O-*β*-D-*galactopyranosyl-(1→4)*-O-*β*-D-*glucopyranosyl-(1→1)-(2*S, *3*R, *4*E*)-2*-N-*tetracosanoylsphingenine* (**5**). — Compound **51** (7.3 mg, 3.9 μmol) was converted into **5** (4.7 mg, 92%) as described for the synthesis of compound **42**. For **5**, $[\alpha]_D$ −0.9° (*c* 0.3, pyridine); R_F 0.45 in 5:4:1 $CHCl_3$–MeOH–H_2O; n.m.r. (1:1 $CDCl_3$–CD_3OD): δ_H 5.696 (td, 1 H, $J_{5,6}$ 6.2, $J_{4,5}$ 15.4 Hz, H-5cer), 5.454 (dd, 1 H, $J_{3,4}$ 7.7 Hz, H-4cer), 4.418 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1b), 4.299 (d, 1 H, $J_{1,2}$ 7.7 Hz, H-1a), 4.089 (t, 1 H, $J_{2,3}$ 8.1 Hz, H-3cer), 4.019 (dd, 1 H, $J_{3,4}$ 3.3, $J_{2,3}$ 9.9 Hz, H-3b), 3.626 (dd, 1 H, H-2b), 2.858 (dd, 1 H, $J_{3eq,4}$ 4.4, $J_{3eq,3ax}$ 12.5 Hz, H-3c*eq*), 2.724 (s, 3 H, *Me*NH), 1.743 (t, 1 H, $J_{3ax,4}$ 11.7 Hz, H-3c*ax*), and 0.891 (t, 6 H, *J* 6.8 Hz, 2 CH_2CH_3).

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