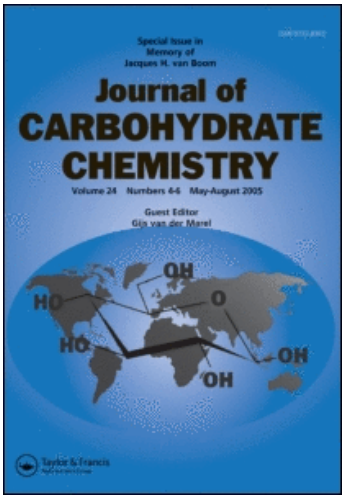

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Synthetic Studies on Sialoglycoconjugates 8: Synthesis of 8-*EPI-N*-Acetylenuraminic Acid Derivatives

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SYNTHETIC STUDIES ON SIALOGLYCOCONJUGATES 8: SYNTHESIS OF 8-EPI-N-ACETYLENURAMINIC ACID DERIVATIVES

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ABSTRACT

Methyl [2-(trimethylsilyl)ethyl 5-acetamido-3,5-dideoxy-L-glycero-α-D-galacto-2-nonulopyranosid]onate (6) and its 8-epi-N-acetylneuraminic acid derivatives were synthesized from methyl [2-(trimethylsilyl)ethyl 5-acetamido-4,7-di-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosid]onate (1) and methyl [2-(trimethylsilyl)ethyl 5-acetamido-3,5-dideoxy-4,7-di-O-2-(trimethylsilyl)ethoxymethyl-D-glycero-α-D-galacto-2-nonulopyranosid]onate (2).

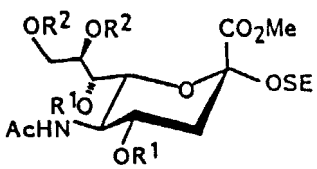
INTRODUCTION

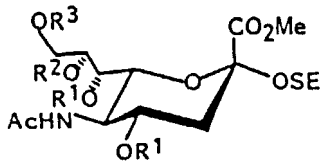
N-Acetylneuraminic acid, its derivatives and analogs play important roles in various biological processes[1-4] as the terminal units of the carbohydrate chain of cell-surface sialoglycoconjugates such as glycolipids and glycoproteins. It is of interest to study the relationship between the structure of the sialic acid moiety in sialoglycoconjugates, especially gangliosides, and the sialoglycoconjugate functions. We now describe the synthesis of 5-acetamido-3,5-dideoxy-L-glycero-α-D-galacto-2-nonulosonic acid (8-epi-Neu5Ac) derivatives as the glycosyl acceptor or intermediate of the glycosyl donor for the synthesis of sialoglycoconjugate analogs.

RESULTS AND DISCUSSION

Treatment of methyl [2-(trimethylsilyl)ethyl 5-acetamido-4,7-di-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosid]onate[5] (1) or methyl [2-(trimethylsilyl)ethyl 5-acetamido-3,5-dideoxy-4,7-di-O-2-(trimethylsilyl)ethoxymethyl-D-glycero-α-D-galacto-2-nonulopyranosid]onate[6] (2)

with methanesulfonyl chloride in pyridine afforded the corresponding 8,9-di-O-mesyl derivatives (3 and 4) in high yields, respectively. Treatment of compound 3 with cesium acetate in the presence of 18-Crown-6 in N,N-dimethylformamide for 16 h at 110-120 °C, subsequent methyl esterification using methyl p-toluenesulfonate and triethylamine, and O-acetylation, gave methyl [2-(trimethylsilyl)ethyl 5-acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-L-glycero-α-D-galacto-2-nonulopyranosid]onate (5) as crystals in 71% yield. The ^{1}H NMR spectrum of 5 revealed the presence of one acetamido





1 R^1 = Ac , R^2 = H

2 R^1 = SEM , R^2 = H

3 R^1 = Ac , R^2 = Ms

4 R^1 = SEM , R^2 = Ms

SE = $Me_3SiCH_2CH_2$-

SEM = $Me_3SiCH_2CH_2OCH_2$-

Ms = $MeSO_2$-

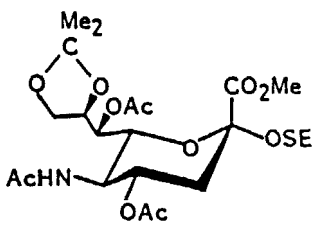
5 R^1 = R^2 = R^3 = Ac

6 R^1 = R^2 = R^3 = H

7 R^1 = SEM , R^2 = R^3 = Ac

8 R^1 = SEM , R^2 = H , R^3 = TBDMS

TBDMS = $Me_3C(Me)_2Si$-



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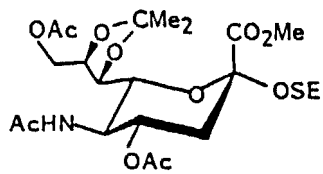

10

and four O-acetyl groups at δ 1.86, 2.00, 2.01, 2.07, and 2.08, methyl ester group at δ 3.81, H-3e as a doublet of doublets at δ 2.59 ($J_{3a,3e}$ = 12.8 Hz, $J_{3e,4}$ = 4.6 Hz), and H-7 at δ 5.30 (dd, $J_{6,7}$ = 1.5 Hz, $J_{7,8}$ = 8.8 Hz). Other NMR data are given in the Experimental Section, and are

consistent with structure 5. O-Deacetylation of 5 with sodium methoxide in methanol gave compound 6 as crystals. According to a similar procedure as described for the preparation of 5, compound 4 afforded the desired 8-epi-Neu5Ac derivative 7 in 80% yield. 8-epi-Neu5Ac derivative having a free hydroxyl group at C-8 was prepared from compound 7. O-Deacetylation of 7 and subsequent tert-butyldimethylsilylation in pyridine gave methyl [2-(trimethylsilyl)ethyl 5-acetamido-9-O-tert-butyldimethylsilyl-3,5-dideoxy-4,7-di-O-2-(trimethylsilyl)ethoxymethyl-L-glycero-α-D-galacto-2-nonulopyranosid]onate (8) in 89% yield.

On the other hand, the isopropylidenation[7] of compound 6 using 2,2-dimethoxypropane in N,N-dimethylformamide containing a trace of p-toluenesulfonic acid monohydrate, followed by O-acetylation gave a mixture from which a crystalline product 9 in 54% yield and a syrupy compound 10 in 27% yield were isolated by column chromatography. The ^{1}H NMR spectrum of 9 showed the presence of one isopropylidene group at δ 1.28 and 1.36 (2s, Me_2C), one N-acetyl at δ 1.83, and two O-acetyl groups at δ 2.00 and 2.09, H-4 at δ 4.74 ($J_{3a,4}$ = 12.1 Hz, $J_{3e,4}$ = 4.8 Hz, and $J_{4,5}$ = 10.3 Hz), and H-7 as a doublet of doublets at δ 5.05 ($J_{6,7}$ = 2.4 Hz, $J_{7,8}$ = 8.4 Hz), and these data were consistent with the 8,9-O-isopropylidene derivative 9. Significant signals in the ^{1}H NMR spectrum of 10 were two three-proton singlets at δ 1.39 (Me_2C), a three-proton singlet at δ 1.90 (N-acetyl), two three-proton singlets at δ 2.03 and 2.10 (O-acetyl), H-4 at δ 4.86 (ddd, $J_{3a,4}$ = 12.2 Hz, $J_{3e,4}$ = 4.8 Hz, and $J_{4,5}$ = 10.3 Hz), and H-8 at δ 4.39 (ddd, $J_{8,9}$ = $J_{8,9'}$ = 4.4 Hz), indicating the structure of the 7,8-O-isopropylidene derivative 10.

EXPERIMENTAL

General Procedures. Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. Specific rotations were determined with a Union PM-201 polarimeter at 25 °C, and IR spectra were recorded with a Jasco IRA-1 spectrophotometer. ^{1}H NMR spectra were recorded with a Jeol JNM-GX270 (270 MHz) spectrometer, and the NMR data were confirmed by use of decoupling techniques. Preparative chromatography was performed on silica gel (Waco Co.; 200 mesh) with the solvent systems specified. Concentrations were conducted in vacuo.

Methyl [2-(Trimethylsilyl)ethyl 5-Acetamido-4,7-di-O-acetyl-3,5-dideoxy-8,9-di-O-methanesulfonyl-D-glycero-α-D-galacto-2-nonulopyranosid]onate (3). To an ice-cooled solution of methyl [2-(trimethylsilyl)ethyl 5-acetamido-4,7-di-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulo-

pyranosid]onate[5] (1; 254 mg, 0.5 mmol) in dry pyridine (2 mL) was added methanesulfonyl chloride (460 mg), and the mixture was kept overnight at 0 °C. The mixture was concentrated, the residue extracted with dichloromethane, and the extract successively washed with 2M hydrochloric acid, M sodium carbonate, and water, dried (sodium sulfate), and concentrated. The residue was chromatographed on a column of silica gel (30 g) using (a) dichloromethane, (b) 150:1, and (c) 100:1 dichloromethane-methanol as the eluants. Eluant (c) gave compound 3 (300 mg, 90%) as an amorphous mass: mp 64-66 °C, $[\alpha]_D$ +1.1° (c 0.2, chloroform); IR (KBr) 3400 (NH), 1750 and 1240 (ester), 1670 and 1540 (amide), 1180 (SO_2), and 860 and 840 cm^{-1} (TMS); ^1H NMR ($CDCl_3$) δ 0.90 (m, 2H, $Me_3Si\underline{CH_2}CH_2O$), 1.88 (s, 3H, AcN), 1.93 (dd, 1H, $J_{3a,3e}$ = 12.8 Hz, $J_{3a,4}$ = 12.1 Hz, H-3a), 2.02, 2.16 (2s, 6H, 2AcO), 2.62 (dd, 1H, $J_{3e,4}$ = 4.8 Hz, H-3e), 3.07, 3.17 (2s, 6H, 2MeS), 3.84 (s, 3H, MeO), 3.47, 3.88 (2ddd, 2H, J_{gem} = 7.0 Hz, $J_{SiCH,CHO}$ = 8.8 Hz, $Me_3Si\text{-}CH_2\underline{CH_2}O$), 4.01 (q, 1H, $J_{4,5} = J_{5,6} = J_{5,NH}$ = 9.9 Hz, H-5), 4.09 (dd, 1H, $J_{6,7}$ = 1.8 Hz, H-6), 4.33 (dd, 1H, $J_{8,9'}$ = 7.3 Hz, $J_{9,9'}$ = 11.7 Hz, H-9'), 4.77 (dd, 1H, $J_{8,9}$ = 2.6 Hz, H-9), 4.92 (ddd, 1H, H-4), 5.20 (ddd, 1H, H-8), 5.45 (dd, 1H, $J_{6,7}$ = 1.8 Hz, $J_{7,8}$ = 4.0 Hz, H-7), and 5.63 (d, 1H, NH).

Anal. Calcd for $C_{23}H_{41}NO_{15}S_2Si$: C, 41.61; H, 6.22; N, 2.11. Found: C, 41.53; H, 6.25; N, 2.18.

Methyl [2-(Trimethylsilyl)ethyl 5-Acetamido-3,5-dideoxy-8,9-O-methanesulfonyl-4,7-di-O-2-(trimethylsilyl)ethoxymethyl-D-glycero-α-D-galacto-2-nonulopyranosid]onate (4). To an ice-cooled solution of methyl [2-(trimethylsilyl)ethyl 5-acetamido-3,5-dideoxy-4,7-di-O-2-(trimethylsilyl)ethoxymethyl-D-glycero-α-D-galacto-2-nonulopyranosid]onate[6] (2; 130 mg, 0.19 mmol) in dry pyridine (1.3 mL) was added methanesulfonyl chloride (150 mg), and the mixture was kept overnight at 0 °C. Processing described in the preparation of 3 gave the 8,9-dimesylate 4 (150 mg, 95%) as a syrup: $[\alpha]_D$ -4.6° (c 1.9, chloroform); IR (film) 3300 (NH), 1740 and 1250 (ester), 1660 and 1540 (amide), 1170 (SO_2), and 860 and 840 cm^{-1} (TMS); ^1H NMR ($CDCl_3$) δ 0.81-0.96 (m, 6H, $3Me_3Si\underline{CH_2}CH_2O$), 1.69 (dd, 1H, $J_{3a,3e}$ = 12.8 Hz, $J_{3a,4}$ = 12.5 Hz, H-3a), 1.93 (s, 3H, AcN), 2.72 (dd, 1H, $J_{3e,4}$ = 4.6 Hz, H-3e), 3.05, 3.14 (2s, 6H, 2MeS), 3.78 (s, 3H, MeO), 4.15 (near d, 1H, $J_{5,6}$ = 10.2 Hz, H-6), 4.48 (dd, 1H, $J_{8,9'}$ = 7.3 Hz, $J_{9,9'}$ = 11.9 Hz, H-9'), 4.61, 4.66, 4.73, and 4.82 (4d, 4H, $2OCH_2O$), 4.84 (dd, 1H, $J_{8,9}$ = 2.4 Hz, H-9), 5.00 (m, 1H, H-8), and 5.88 (d, 1H, $J_{NH,5}$ = 8.1 Hz, NH).

Anal. Calcd for $C_{31}H_{65}NO_{15}S_2Si$: C, 44.31; H, 7.71; N, 1.67. Found: C, 44.25; H, 7.90; N, 1.65.

Methyl [2-(Trimethylsilyl)ethyl 5-Acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-L-glycero-α-D-galacto-2-nonulopyranosid]onate (5). To a solution of 3 (332 mg, 0.5 mmol) in dry N,N-dimethylformamide (DMF; 3 mL) were added cesium acetate (500 mg) and 18-Crown-6 (264 mg), and the mixture was heated, with stirring, for 16 h at 110-120 °C (bath); the course of the reaction being monitored by TLC. The mixture was concentrated to leave a syrup which extracted with dichloromethane, and the extract successively washed with 2M hydrochloric acid and water, dried (sodium sulfate), and concentrated. To a solution of the residue in dry DMF (2 mL) were added methyl p-toluenesulfonate (115 mg) and triethylamine (1.3 mL), and the mixture was stirred for 7 h at room temperature. Acetic anhydride (1 mL) and pyridine (2 mL) were added into the mixture, and it was heated overnight at 45 °C, and then concentrated to a syrup which was extracted with dichloromethane. The extract was successively washed with 2M hydrochloric acid, M sodium carbonate, and water, dried (sodium sulfate), and concentrated to a syrup, which was chromatographed on a column of silica gel (30 g) using dichloromethane and 100:1 dichloromethane-methanol. The latter eluant gave compound 5 (210 mg, 71%) as crystals. Recrystallization from ether-hexane gave needles: mp 149-151 °C, $[\alpha]_D$ -19.5° (c 0.2, chloroform); IR (KBr) 3310 (NH), 1750 and 1230 (ester), 1660 and 1550 (amide), and 860 and 840 cm^{-1} (TMS); ^1H NMR ($CDCl_3$) δ 0.90 (m, 2H, $Me_3Si\underline{CH_2}CH_2O$), 1.86 (s, 3H, AcN), 1.94 (dd, 1H, $J_{3a,3e}$ = 12.8 Hz, $J_{3a,4}$ = 12.4 Hz, H-3a), 2.00, 2.01, 2.07, and 2.08 (4s, 12H, 4AcO), 2.59 (dd, 1H, $J_{3e,4}$ = 4.6 Hz, H-3e), 3.81 (s, 3H, MeO), 3.43, 3.88 (2ddd, 2H, J_{gem} = 7.1 Hz, $J_{SiCH,CHO}$ = 8.4 Hz, $Me_3SiCH_2\underline{CH_2}O$), 3.98-4.11 (m, 2H, H-5,6), 4.50 (dd, 1H, $J_{8,9'}$ = 4.4 Hz, $J_{9,9'}$ = 12.6 Hz, H-9'), 4.60 (dd, 1H, $J_{8,9}$ = 2.4 Hz, H-9), 4.88 (ddd, 1H, H-4), 5.27 (d, 1H, $J_{NH,5}$ = 9.7 Hz, NH), 5.30 (dd, 1H, $J_{6,7}$ = 1.5 Hz, $J_{7,8}$ = 8.8 Hz, H-7), and 5.39 (ddd, 1H, $J_{8,9'}$ = 4.4 Hz, H-8).

Anal. Calcd for $C_{25}H_{41}NO_{13}Si$: C, 50.74; H, 6.98; N, 2.37. Found: C, 50.68; H, 6.83; N, 2.35.

Methyl [2-(Trimethylsilyl)ethyl 5-Acetamido-3,5-dideoxy-L-glycero-α-D-galacto-2-nonulopyranosid]onate (6). To a solution of 5 (1.3 g, 2.2 mmol) in methanol (50 mL) was added sodium methoxide (50 mg), and the mixture was kept for one h at room temperature, and then treated with Amberlite IR-120 (H^+) resin to remove the base; the resin was filtered off, and washed with methanol. The filtrate and washings were combined, and concentrated, whereupon the residue crystallized. Recrystallization from methanol-ether gave compound 6 (890 mg, 96%) as needles: mp 214-215 °C, $[\alpha]_D$ -1.0° (c 0.2, methanol); IR (KBr) 3400 (OH), 3300 (NH), 1740 and 1240 (ester), 1640 and 1580 (amide), and 860 and 840 cm^{-1} (TMS); ^1H NMR (1:1

CD_3OD-$CDCl_3$) δ 0.85 (t, 2H, $J_{gem} = J_{SiCH,CHO} = 8.1$ Hz, $Me_3SiCH_2CH_2O$), 1.70 (t, 1H, $J_{3a,3e} = J_{3a,4} = 12.5$ Hz, H-3a), 1.99 (s, 3H, AcN), 2.63 (dd, 1H, $J_{3e,4} = 4.4$ Hz, H-3e), 3.39 (q, 1H, $Me_3SiCH_2CH_2O$), 3.52 (dd, 1H, $J_{5,6} = 9.9$ Hz, $J_{6,7} = 1.8$ Hz, H-6), 3.53 (dd, 1H, $J_{7,8} = 7.0$ Hz, H-7), 3.74-3.87 (m, 5H, H-5,8,9,9', $Me_3SiCH_2CH_2O$), and 3.80 (s, 3H, MeO).

Anal. Calcd for $C_{17}H_{33}NO_9Si$: C, 48.20; H, 7.85; N, 3.31. Found: C, 48.15; H, 7.85; N, 3.26.

Methyl [2-(Trimethylsilyl)ethyl 5-Acetamido-8,9-di-O-acetyl-3,5-dideoxy-4,7-di-O-2-(trimethylsilyl)ethoxymethyl-L-glycero-α-D-galacto-2-nonulopyranosid]onate (7). To a solution of 4 (150 mg, 0.36 mmol) in dry DMF (1.5 mL) were added cesium acetate (300 mg) and 18-Crown-6 (150 mg), the mixture was heated, with stirring, for 19 h at 110-120 °C (bath), and then concentrated. The residue was extracted with dichloromethane, and the extract successively washed with 2M hydrochloric acid and water, dried (sodium sulfate), and concentrated. The residue was dissolved in dry DMF (1.5 mL), and methyl p-toluenesulfonate (110 mg), triethylamine (1.1 mL), and Drierite (50 mg) were added in situ, and the mixture was stirred overnight at room temperature. Pyridine (2 mL) and acetic anhydride (1 mL) were added to the solution, and the mixture was kept for 8 h at room temperature and concentrated to leave a syrup, which was extracted with dichloromethane. The same procedure as used for the preparation of 5 gave compound 7 (110 mg, 80%) as a syrup: $[\alpha]_D$ -21° (c 0.2, chloroform); IR (film) 3280 (NH), 1750 and 1220 (ester), 1650 and 1550 (amide), and 860 and 840 cm^{-1} (TMS); ^1H NMR ($CDCl_3$) δ 0.83-1.00 (m, 6H, $3Me_3SiCH_2CH_2O$), 1.66 (dd, 1H, $J_{3a,3e} = 12.6$ Hz, $J_{3a,4} = 11.2$ Hz, H-3a), 1.95 (s, 3H, AcN), 2.03, 2.08 (2s, 6H, 2AcO), 2.80 (dd, 1H, $J_{3e,4} = 4.8$ Hz, H-3e), 3.24-3.94 (m, 8H, H-5,7, $3Me_3SiCH_2CH_2O$), 3.82 (s, 3H, MeO), 4.26 (ddd, 1H, $J_{3a,4} = 11.2$ Hz, $J_{3e,4} = 4.8$ Hz, $J_{4,5} = 10.1$ Hz, H-4), 4.33 (dd, 1H, $J_{5,6} = 12.3$ Hz, $J_{6,7} = 1.7$ Hz, H-6), 4.50 (dd, 1H, $J_{8,9'} = 2.4$ Hz, $J_{9,9'} = 12.6$ Hz, H-9'), 4.60 (dd, 1H, $J_{8,9} = 5.5$ Hz, H-9), 4.65, 4.70, 477, and 4.80 (4d, 4H, $2OCH_2O$), 5.37 (ddd, 1H, $J_{7,8} = 7.9$ Hz, H-8), and 5.95 (d, 1H, $J_{NH,5} = 7.5$ Hz, NH).

Anal. Calcd for $C_{33}H_{65}NO_{13}Si_3$: C, 51.60; H, 8.52; N, 1.82. Found: C, 51.43; H, 8.69; N, 1.80.

Methyl [2-(Trimethylsilyl)ethyl 5-Acetamido-9-O-tert-butyldimethylsilyl-L-glycero-α-D-galacto-2-nonulopyranosid]onate (8). To a solution of 7 (385 mg, 0.5 mmol) in dry methanol (10 mL) was added sodium methoxide (30 mg), and the mixture was kept for one h at room temperature, and treated with Amberlite IR-120 (H^+) resin to remove the base. The product was dissolved in pyridine (5 mL), and tert-butyldimethylsilyl chloride (110 mg)

was added. The mixture was stirred at room temperature; after 2 h, the reaction was complete. Methanol (1 mL) was added, and the solution was concentrated to a syrup, which was extracted with dichloromethane. The extract was successively washed with 2M hydrochloric acid, M sodium carbonate, and water, dried (sodium sulfate), and concentrated. The residue was chromatographed on a column of silica gel (30 g) using dichloromethane and then 100:1 dichloromethane-methanol as the eluants. The latter eluant gave compound 8 (355 mg, 89%) as a syrup: $[\alpha]_D$ -7.5° (c 0.4, chloroform); IR (film) 3300 (NH), 1750 and 1250 (ester), 1660 and 1560 (amide), and 860 and 840 cm^{-1} (TMS); ^1H NMR ($CDCl_3$) δ 0.83-0.99 (m, 15H, $3Me_3SiCH_2CH_2O$, Me_3CSiMe_2), 1.74 (dd, 1H, $J_{3a,3e}$ = 12.7 Hz, $J_{3a,4}$ = 11.7 Hz, H-3a), 1.92 (s, 3H, AcN), 2.74 (dd, 1H, $J_{3e,4}$ = 4.4 Hz, H-3e), 3.38 (q, 1H, $J_{gem} = J_{SiCH,CHO}$ = 8.6 Hz, $Me_3SiCH_2CH_2O$), 3.55-3.93 (m, 10H, H-5,7,8,9,9', and $3Me_3SiCH_2CH_2O$), 3.99 (ddd, 1H, $J_{4,5}$ = 10.3 Hz, H-4), 4.06 (near d, 1H, $J_{5,6}$ = 10.3 Hz, H-6), 4.66, 4.70, 4.73, and 4.89 (4d, 4H, $2OCH_2O$), and 5.65 (d, 1H, $J_{NH,5}$ = 8.3 Hz, NH).

Anal. Calcd for $C_{29}H_{61}NO_{10}Si_3$: C, 52.65; H, 9.46; N, 1.75. Found: C, 52.56; H, 9.60; N, 1.75.

Methyl [2-(Trimethylsilyl)ethyl 5-Acetamido-4,7-di-O-acetyl-3,5-dideoxy-8,9-O-isopropylidene-L-glycero-α-D-galacto-2-nonulopyranosid]onate (9) and Methyl [2-(Trimethylsilyl)ethyl 5-Acetamido-4,9-di-O-acetyl-3,5-dideoxy-7,8-O-isopropylidene-L-glycero-α-D-galacto-2-nonulopyranosid]onate (10). To a solution of 6 (850 mg, 2 mmol) in dry DMF (10 mL) were added 2,2-dimethoxypropane (2 mL) and p-toluenesulfonic acid monohydrate (15 mg). The mixture was stirred at room temperature while the progress of the reaction was monitored by TLC; after 2 h, the starting material was no longer detectable. Pyridine (5 mL) and acetic anhydride (4 mL) were added to the stirring mixture, and it was kept for 4 h at 60 °C, and then concentrated to a syrup, which was extracted with dichloromethane. The extract was successively washed with 2M hydrochloric acid, M sodium carbonate, and water, dried (sodium sulfate), and concentrated to a syrup, which was chromatographed on a column of silica gel (100 g) using (a) dichloromethane, (b) 150:1, and (c) 100:1 dichloromethane-methanol as the eluants. Eluant (b) gave compound 10 (300 mg, 27%) as a syrup, and eluant (c) afforded 9 (590 mg, 54%) as crystals. Compound 9 had mp 74-76 °C, $[\alpha]_D$ -25° (c 0.2, chloroform); IR (KBr) 3300 (NH), 1750 and 1230 (ester), 1660 and 1550 (amide), and 850 cm^{-1} (TMS, Me_2C); ^1H NMR ($CDCl_3$) δ 0.84 (t, 2H, $J_{gem} = J_{SiCH,CHO}$ = 7.7 Hz, $Me_3SiCH_2CH_2O$), 1.28, 1.36 (2s, 6H, Me_2C), 1.83 (s, 3H, AcN), 2.00, 2.09 (2s, 6H, 2AcO), 2.51 (dd, 1H, $J_{3a,3e}$ = 12.8 Hz, $J_{3e,4}$ = 4.8 Hz, H-3e), 3.34 (q, 1H, $J_{gem} = J_{SiCH,CHO}$ = 7.7 Hz, $Me_3SiCH_2CH_2O$), 3.78

(s, 3H, MeO), 3.97 (q, 1H, $J_{4,5} = J_{5,6} = J_{5,NH} = 10.3$ Hz, H-5), 4.12 (dd, 1H, $J_{8,9} = 6.2$ Hz, $J_{9,9'} = 9.0$ Hz, H-9), 4.35 (ddd, 1H, $J_{7,8} = 8.4$ Hz, $J_{8,9} = J_{8,9'} = 6.2$ Hz, H-8), 4.74 (ddd, 1H, $J_{3a,4} = 12.1$ Hz, H-4), 5.05 (dd, 1H, $J_{6,7} = 2.4$ Hz, H-7), and 5.82 (d, 1H, NH).

Anal. Calcd for $C_{24}H_{41}NO_{11}Si$: C, 52.63; H, 7.54; N, 2.56. Found: C, 52.58; H, 7.60; N, 2.58.

Compound 10 had $[\alpha]_D$ -54.5° (c 1.9, chloroform); IR (film) 3300 (NH), 1750 and 1240 (ester), 1660 and 1550 (amide), and 860 and 850 cm^{-1} (TMS, Me_2C); ^1H NMR ($CDCl_3$) δ 0.85 (t, 1H, $J_{gem} = J_{SiCH,CHO} = 8.1$ Hz, Me_3SiCH_2-CH_2O), 1.39 (s, 6H, Me_2C), 1.90 (s, 3H, AcN), 2.03, 2.10 (2s, 6H, 2AcO), 2.52 (dd, 1H, $J_{3a,3e} = 12.5$ Hz, $J_{3e,4} = 4.8$ Hz, H-3e), 3.62 (dd, 1H, $J_{5,6} = 10.3$ Hz, $J_{6,7} = 2.6$ Hz, H-6), 3.77 (dd, 1H, $J_{7,8} = 8.8$ Hz, H-7), 3.80 (s, 3H, MeO), 3.43, 3.83 (2q, 2H, $J_{gem} = J_{SiCH,CHO} = 8.1$ Hz, $Me_3SiCH_2CH_2O$), 4.04 (q, 1H, $J_{4,5} = J_{5,6} = J_{5,NH} = 10.3$ Hz, H-5), 4.20 (m, 2H, H-9,9'), 4.39 (ddd, 1H, $J_{8,9} = J_{8,9'} = 4.4$ Hz, H-8), 4.86 (ddd, 1H, $J_{3a,4} = 12.2$ Hz, H-4), and 5.54 (d, 1H, NH).

Anal. Found: C, 52.49; H, 7.66; N, 2.51.

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