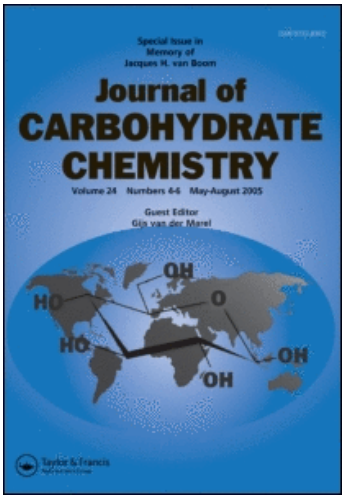


Journal of Carbohydrate Chemistry

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

Synthetic Studies on Sialoglycoconjugates. 3: Synthesis of 5-Acetamido-3,5-Dideoxy-l-*Arabino*-2-Heptulosonic Acid Derivatives and Analogs

Akira Hasegawa[a]; Yukiyasu Ito[a]; Hideharu Ishida[a]; Makoto Kiso[a]
[a] Department of Applied Bioorganic Chemistry, Gifu University, Gifu, Japan

To cite this Article Hasegawa, Akira , Ito, Yukiyasu , Ishida, Hideharu and Kiso, Makoto(1989) 'Synthetic Studies on Sialoglycoconjugates. 3: Synthesis of 5-Acetamido-3,5-Dideoxy-l-*Arabino*-2-Heptulosonic Acid Derivatives and Analogs', Journal of Carbohydrate Chemistry, 8: 1, 125 — 133
To link to this Article: DOI: 10.1080/07328308908047997
URL: http://dx.doi.org/10.1080/07328308908047997

J. CARBOHYDRATE CHEMISTRY, 8(1), 125-133 (1989)

SYNTHETIC STUDIES ON SIALOGLYCOCONJUGATES 3: SYNTHESIS OF 5-ACETAMIDO-3,5-DIDEOXY-L-ARABINO-2-HEPTULOSONIC ACID DERIVATIVES AND ANALOGS

Akira Hasegawa, Yukiyasu Ito, Hideharu Ishida, and Makoto Kiso

Department of Applied Bioorganic Chemistry,
Gifu University, Gifu 501-11, Japan

Received September 28, 1988 - Final Form November 3, 1988

ABSTRACT

5-Acetamido-3,5-dideoxy-L-arabino-2-heptulosonic acid derivatives and analogs (shorter carbon-chain analogs of N-acetylneuraminic acid) were synthesized. Periodate oxidation followed by sodium borohydride reduction and O-acetylation of methyl [2-(trimethylsilyl)ethyl 5-acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosid)onate (3), prepared by condensation of the 2-β-chloro derivative of pentaacetylneuraminic acid methyl ester (1) with trimethylsilylethanol and subsequent O-deacetylation, gave methyl (trimethylsilylethyl 5-acetamido-4,7-di-O-acetyl-3,5-dideoxy-β-L-arabino-2-heptulopyranosid)onate (4). Starting from compound 4, the 7-bromo, 2-α-chloro, and 2-β-thio analogs were synthesized.

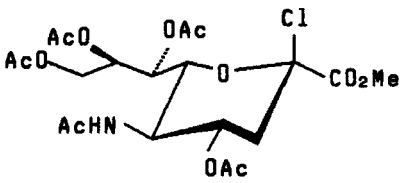
INTRODUCTION

Many derivatives and analogs of N-acetylneuraminic acid play important role in various biological processes[1] as the terminal units of carbohydrate chain of cell-surface sialoglycoconjugates. Recently, many kinds of free sialic acid have been isolated in nature and characterized.[2] In view of these facts, there has been a great deal of activity in recent years in the syntheses[2a,3-18] of the derivatives and analogs of N-acetylneuraminic acid. We now describe the synthesis of 5-acetamido-3,5-dideoxy-L-arabino-heptulosonic acid (C_7-Neu5Ac) derivatives and the analogs.

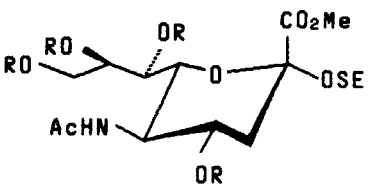
RESULTS AND DISCUSSION

Koenigs-Knorr reaction of methyl 5-acetamido-4.7.8.9-tetra-O-acetyl-2-chloro-2,3,5-trideoxy-D-glycero-β-D-galacto-2-nonulopyranosonate[19] (1) with 2-(trimethylsilyl)ethanol in dry dichloromethane in the presence of silver carbonate, silver perchlorate and powdered molecular sieves 4A, gave the α-glycoside (2) of N-acetylneuraminic acid derivative in 89% yield as crystals, which served as a convenient starting-material for the synthesis of the title compounds. The anomeric configuration was unambiguously proved by ^{1}H NMR spectroscopy. The observed chemical shifts and coupling constants of 2 (δ 2.57, $J_{3a,3e}$ = 12.7 Hz, $J_{3e,4}$ = 4.4 Hz for H-3e, and δ 4.83, $J_{3a,4}$ = 12.7 Hz, $J_{4,5}$ = 9.3 Hz for H-4) are characteristic for the α-glycosidic linkage[20] of N-acetylneuraminic acid. O-Deacetylation of 2 with sodium methoxide in methanol gave 3 as needles. When treated with sodium metaperiodate in methanol followed by sodium borohydride reduction, and acetylated with acetic anhydride in pyridine, compound 3 afforded methyl [2-(trimethylsilyl)ethyl 5-acetamido-4,7-di-O-acetyl-3,5-dideoxy-β-L-arabino-2-heptulopyranosid]onate (4) as crystals in good yield. The ^{1}H NMR spectrum of 4 exhibited four sharp singlets, each integrating for three protons, at δ 1.93, 2.06, 2.12, and 3.82, which demonstrated the presence of one N-acetyl, two O-acetyl, and one methyl ester group; H-3e appeared at δ 2.56 ($J_{3a,3e}$ = 12.4 Hz, $J_{3e,4}$ = 4.4 Hz) as a doublet of doublets, and H-4 at δ 4.87 (ddd, $J_{3a,4}$ = 12.1 Hz, $J_{4,5}$ = 10.3 Hz), indicating structure 4. The observed chemical shifts and coupling constants for H-3e and H-4 are similar to those of the α-glycosides[20] of N-acetylneuraminic acid, and could be used for determination of the anomeric configuration of the glycosides. Treatment of compound 5, derived from 4 by O-deacetylation with sodium methoxide in methanol, with N-bromosuccinimide in the presence of triphenylphosphine in N,N-dimethylformamide according to the procedure described by Hanessian et al.[21] gave methyl [2-(trimethylsilyl)ethyl 5-acetamido-7-bromo-3,5,7-trideoxy-β-L-arabino-2-heptulopyranosid]onate (6) in 61% yield as a syrup, which was acetylated to compound 7. There were five significant signals in ^{1}H NMR spectrum of 7, three three-proton singlets at δ 1.94 (N-acetyl), 2.04 (O-acetyl), and 3.81 (COOMe), a one-proton doublet of doublets at δ 2.57 ($J_{3a,3e}$ = 12.8 Hz, $J_{3e,4}$ = 4.8 Hz, H-3e), and at δ 4.91 ($J_{4,5}$ = 9.9 Hz, H-4). Other ^{1}H NMR data are consistent with 7.

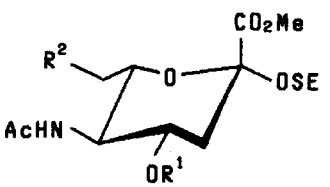
On the other hand, treatment[22] of compound 4 with boron trifluoride etherate in acetonitrile gave crystalline 5-acetamido-4,7-di-O-acetyl-3,5-dideoxy-α-L-arabino-2-heptulopyranosonate (8) in 88% yield, which was



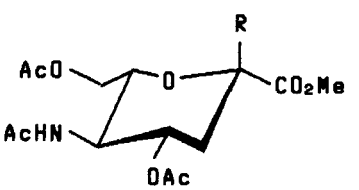
1



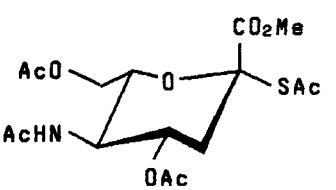
2 R=Ac
3 R=H
SE=$Me_3SiCH_2CH_2$



4 R^1=Ac, R^2=OAc
5 R^1=H, R^2=OH
6 R^1=H, R^2=Br
7 R^1=Ac, R^2=Br



8 R=OH
9 R=Cl



10

converted into the 2α-chloro derivative 9 of triacetylheptulosonic acid methyl ester on treatment with hydrogen chloride in dry dichloromethane. When reacted with potassium thioacetate in dry dichloromethane, compound 9 yielded methyl 5-acetamido-4,7-di-O-acetyl-2-S-acetyl-3,5,-dideoxy-2-thio-β-L-arabino-2-heptulopyranosonate (10) in 85% yield. ^{1}H NMR spectrum exhibited five three-proton singlets, at δ 1.94 (AcN), 2.05 (AcO), 2.31 (AcS), and 3.82 (COOMe). H-3e and H-4 appeared at δ 2.75 ($J_{3a,3e}$ = 12.8 Hz, $J_{3e,4}$ = 4.5 Hz) and at δ 4.99 ($J_{3a,4}$ = 11.5 Hz, $J_{4,5}$ = 10.3 Hz), respectively, indicating of the β-S-acetate structure.[16] Other ^{1}H NMR data are consistent with structure 10.

Compounds 4-10, obtained herein, will be used for the analog synthesis of sialoglycoconjugates.

EXPERIMENTAL

General Procedures. Melting points were determined with a Yanagimoto micro melting points apparatus and are uncorrected. Specific rotations were determined with a Union MP-201 polarimeter at 25 °C, and IR spectra were recorded with a JASCO IR-1 spectrophotometer. ^{1}H NMR spectra were recorded with a JEOL JMN-GX 270 spectrometer. Preparative chromatography was performed on silica gel (Waco Co., 200 mesh) with the solvent systems specified. Concentrations and evaporations were conducted in vacuo.

Methyl [2-(Trimethylsilyl)ethyl 5-Acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosid]onate (2). A suspension of 2-(trimethylsilyl)ethanol (5.7 mL), silver carbonate (11 g), silver perchlorate (200 mg), and molecular sieves 4A (4.0 g) in dichloromethane (50 mL) was stirred for 5 h at room temperature. A suspension of methyl 5-acetamido-4,7,8,9-tetra-O-acetyl-2-chloro-2,3,5-trideoxy-D-glycero-β-D-galacto-2-nonulopyranosonate[19] (1; 10.2 g, 20 mmol) and molecular sieves 4A (4 g) in dichloromethane (50 mL) was stirred for 5 h and the suspension was added into the stirred suspension of the glycosyl acceptor. The stirring was continued overnight at room temperature, and the precipitates were filtered off on celite 545 pad and washed with dichloromethane. The filtrate and washings were combined, and concentrated to a syrup. The product was chromatographed on a column of silica gel (500 g) with dichloromethane and 150:1 dichloromethane-methanol. The latter eluant gave compound 2 (10.5 g, 89%) as crystals. Recrystallization from ether-hexane gave needles: mp 84-86 °C, $[\alpha]_D$ − 10.9° (c 0.2, chloroform); IR (KBr) 3280 (NH), 1750 and 1230 (ester), 1660 and 1550 (amide), and 1250, 860, and 840 cm^{-1} (TMS); ^{1}H NMR ($CDCl_3$) δ 0.88 (m, 2H, $Me_3SiCH_2CH_2$-), 1.88 (s, 3H, AcN), 2.02, 2.03, 2.13, 2.14 (4s, 12H, 4AcO), 2.57 (dd, 1H, $J_{3a,3e}$ = 12.7 Hz, $J_{3e,4}$ = 4.4 Hz, H-3e), 3.79 (s, 3H, MeO), 3.31, 3.88 (2dd, 2H, J_{gem} = 7.1 Hz, $J_{OCH,SiCH}$ = 9.0 Hz, $Me_3SiCH_2CH_2O$-), 4.05 (q, 1H, $J_{4,5} = J_{5,6} = J_{5,NH}$ = 9.3 Hz, H-5), 4.09 (dd, 1H, $J_{8,9}$ = 2.7 Hz, $J_{9,9'}$ = 12.5 Hz, H-9), 4.30 (dd, 1H, H-9'), 4.83 (ddd, 1H, $J_{3a,4}$ = 12.7 Hz, H-4), 5.15 (dd, 1H, NH), 5.32 (dd, 1H, $J_{6,7}$ = 1.7 Hz, $J_{7,8}$ = 8.3 Hz, H-7), and 5.39 (ddd, 1H, H-8).

Anal. Calcd for $C_{25}H_{41}NO_{13}Si$: C, 50.74; H, 6.98; N, 2.37. Found: C, 50.71; H, 7.05; N, 2.33.

Methyl [2-(Trimethylsilyl)ethyl 5-Acetamido-3,5-dideoxy-D-glycero-α-D-galacto-2-nonulopyranosid]onate (3). To a solution of 2 (10.5 g, 17.7 mmol) in methanol (100 mL) was added 1M sodium methoxide (5 mL), and the mixture

was kept for 3 h, 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 to a syrup, whereupon the residue crystallized. Recrystallization from ether gave compound 3 (6.9 g, 92%) as needles: mp 170-172 °C; $[\alpha]_D$ − 0.95° (c 0.21, methanol); IR (KBr) 3450 (OH), 3350 (NH), 1740 and 1230 (ester), 1670 and 1550 (amide), and 840 cm^{-1} (TMS); ^1H NMR (1:1 $CDCl_3$-CD_3OD) δ 0.84 (t, 2H, $J_{gem} = J_{OCH,SiCH} = 7.7$ Hz, $Me_3Si\underline{CH_2}CH_2O$-), 1.76 (dd, 1H, $J_{3a,3e} = 12.8$ Hz, $J_{3a,4} = 11.7$ Hz, H-3a), 2.20 (s, 3H, AcN), 2.67 (dd, 1H, $J_{3e,4} = 4.4$ Hz, H-3e), 3.39 (m, 1H, H-8), 3.48 (dd, 1H, $J_{5,6} = 10.3$ Hz, H-6), 3.53 (ddd, 1H, $J_{4,5} = 10.3$ Hz, H-4), 3.64-3.72 (m, 2H, H-5,7), 3.80 (m, 2H, H-9,9'), 3.83 (s, 3H, MeO), and 3.87, 3.88 (2q, 2H, $J_{gem} = J_{SiCH,OCH} = 7.7$ Hz, $Me_3SiCH_2\underline{CH_2}O$-).

Anal. Calcd for $C_{17}H_{33}NO_9Si$: C, 48.20; H, 7.85; N, 3.31. Found: C, 48.31; H, 7.85; N, 3.26.

Methyl [2-(Trimethylsilyl)ethyl 5-Acetamido-4,7-di-O-acetyl-3,5-dideoxy-β-L-arabino-2-heptulopyranosid]onate (4). To a solution of 3 (1.1 g, 2.6 mmol) in dry methanol (8 mL) was added sodium metaperiodate (1.5 g), and the mixture was stirred for 3 h at room temperature. The precipitates were filtered off, and washed with 5 mL of methanol. To this stirred solution was gradually added sodium borohydride (100 mg) at 0 °C. After completion of the reaction, acetic acid (0.2 mL) was added to the mixture in order to decompose the reagent, and the mixture was concentrated. The residue was treated with acetic anhydride (3 mL)-pyridine (5 mL) overnight at room temperature. The mixture was concentrated, the residue extracted with chloroform, and the extract successively washed with 2M hydrochloric acid, M sodium carbonate, and water, dried (sodium sulfate), and the solvent was evaporated to leave a syrup. The residue was chromatographed on a column of silica gel (100 g) with dichloromethane, and 1:1 dichloromethane-methanol. The latter eluant gave compound 4 (620 mg, 53%). Recrystallization from ether-hexane gave needles: mp 46 °C; $[\alpha]_D$ − 51.8° (c 1.2, chloroform); IR (KBr) 3270 (NH), 1750 and 1230 (ester), 1660 and 1560 (amide), and 860 and 840 cm^{-1} (TMS); ^1H NMR ($CDCl_3$) δ 0.90 (t, 2H, $J_{gem} = J_{SiCH,OCH} = 8.4$ Hz, $Me_3Si\underline{CH_2}CH_2O$-), 1.93 (s, 3H, AcN), 2.06, 2.11, (2s, 6H, 2AcO), 2.56 (dd, 1H, $J_{3a,3e} = 12.4$ Hz, $J_{3e,4} = 4.4$ Hz, H-3e), 3.82 (s, 3H, MeO), 3.44, 3.88 (2q, 2H, $Me_3SiCH_2\underline{CH_2}O$-), 4.04 (q, 1H, $J_{4,5} = J_{5,6} = J_{NH,5} = 10.3$ Hz, H-5), 4.19 (dd, $J_{6,7'} = 5.5$ Hz, $J_{7,7'} = 12.5$ Hz, H-7'), 4.26 (dd, 1H, $J_{6,7} = 2.2$ Hz, H-7), 4.87 (ddd, 1H, $J_{3a,4} = 12.1$ Hz, $J_{3e,4} = 4.4$ Hz, $J_{4,5} = 10.3$ Hz, H-4), and 6.19 (d, 1H, $J_{NH,5} = 10.3$ Hz, NH).

Anal. Calcd for $C_{19}H_{33}NO_9Si$: C, 50.98; H, 7.43; N, 3.13. Found: C, 50.79; H, 7.50; N,3.15.

Methyl [2-(Trimethylsilyl)ethyl 5-Acetamido-3,5-dideoxy-ß-D-arabino-2-heptulopyranosid]onate (5). To a solution of 4 (100 mg, 0.22 mmol) in dry methanol (10 mL) was added sodium methoxide (10 mg), and the mixture was stirred for one h at room temperature, and then treated with Amberlite IR-120 (H^+) resin to remove the base. The solvent was evaporated to give crystalline 5 in quantitative yield. Recrystallization from ether gave needles: mp 145-146 °C, $[\alpha]_D$ − 13.0° (c 0.2, chloroform); IR (KBr) 3470 (OH), 3280 (NH), 1740 and 1250 (ester), 1650 and 1600 (amide), and 860 and 850 cm^{-1} (TMS); ^1H NMR (1:1 $CDCl_3$-CD_3OD) δ 0.86 (t, 2H, J_{gem} = $J_{SiCH,OCH}$ = 8.1 Hz, $Me_3SiCH_2CH_2O$-), 1.71 (dd, 1H, $J_{3a,3e}$ = 12.5 Hz, $J_{3a,4}$ = 11.7 Hz, H-3a), 1.97 (s, 3H, AcN), 2.59 (dd, 1H, $J_{3e,4}$ = 4.4 Hz, H-3e), 3.39 (dd, 1H, $J_{5,6}$ = 10.1 Hz, $H_{6,7}$ = 2.2 Hz, H-6), 3.47 (ddd, 1H, $J_{3a,4}$ = 11.7 Hz, $J_{3e,4}$ = 4.4 Hz, $J_{4,5}$ = 10.1 Hz, H-4), 3.59 (t, 1H, $J_{4,5}$ = $J_{5,6}$ = 10.1 Hz, H-5), 3.68 (dd, 1H, $J_{6,7}$ = 2.2 Hz, $J_{7,7'}$ = 12.8 Hz, H-7), 3.78 (s, 3H, MeO), and 3.38 and 3.87 (q, 2H, J_{gem} = $J_{SiCH,OCH}$ = 8.1 Hz, $Me_3SiCH_2CH_2O$-).

Anal. Calcd for $C_{15}H_{29}NO_7Si$: C, 49.56; H, 8.04; N, 3.85. Found: C, 49.55; H, 8.18; N, 3.63.

Methyl [2-(Trimethylsilyl)ethyl 5-Acetamido-4-O-acetyl-7-bromo-3,5,7-trideoxy-β-L-arabino-2-heptulopyranosid]onate (7). To a solution of 5 (363.5 mg, 1.0 mmol) in N,N-dimethylformamide (6 mL) were added, with stirring, N-bromosuccinimide (268 mg) and triphenylphosphine (400 mg) at 0 °C, and the mixture was heated for 1.5 h at 50 °C. Methanol (3 mL) was added to the mixture, and concentrated. The residue was chromatographed on a column of silica gel (30 g) using (a) dichloromethane, (b) 150:1, and (c) 50:1 dichloromethane-methanol as the eluants. Eluant (c) gave compound 6 (260 mg, 61%) as a syrup. Compound 6 thus obtained was acetylated with acetic anhydride (1 mL) in pyridine (5 mL) overnight at room temperature. The product was obtained as a syrup in quantitative yield after purification by column chromatography: $[\alpha]_D$ − 41.0° (c 0.5, chloroform); IR (film) 3270 (NH), 1740 and 1230 (ester), 1660 and 1550 (amide), and 860 and 840 cm^{-1} (TMS); ^1H NMR ($CDCl_3$) δ 0.90 (t, 2H, J_{gem} = $J_{SiCH,OCH}$ = 8.8 Hz, $Me_3SiCH_2CH_2O$-), 1.94 (s, 3H, AcN), 2.04 (s, 3H, AcO), 2.57 (dd, 1H, $J_{3a,3e}$ = 12.8 Hz, $J_{3e,4}$ = 4.8 Hz, H-3e), 3.81 (s, 3H, MeO), 3.93 (m, 2H, H-7,7'), 3.95 (q, 1H, $J_{4,5}$ = $J_{5,6}$ = $J_{5,NH}$ = 9.9 Hz, H-5), 4.91(ddd, 1H, $J_{3a,4}$ = 12.1 Hz, $J_{3e,4}$ = 4.8 Hz, $J_{4,5}$ = 9.9 Hz, H-4), and 5.99 (d, 1H, $J_{NH,5}$ = 9.9 Hz, NH).

Anal. Calcd for $C_{17}H_{30}NO_7BrSi$: C, 43.59; H, 6.45; n, 2.99. Found: C, 43.63; H, 6.48; N, 3.10.

Methyl 5-Acetamido-4,7-di-O-acetyl-3,5-dideoxy-α-L-arabino-2-heptulopyranosonate (8). To a solution of 4 (420 mg, 0.94 mmol) in acetonitrile (10 mL) was added boron trifluoride etherate (0.23 mL), and the mixture was stirred for 3 h at room temperature, and then dichloromethane was added. The solution was washed with water, dried (sodium sulfate), and concentrated, whereupon the residue crystallized. Recrystallization from ether-hexane gave 8 (285 mg, 88%) as needles: mp 156-158 °C, $[\alpha]_D$ − 67.1° (c 0.33, chloroform); IR (KBr) 3500 (OH), 3320 (NH), 1730 and 1250 (ester), and 1660 and 1540 cm^{-1} (amide); ^1H NMR ($CDCl_3$) δ 1.95 (s, 3H, AcN), 2.04, 2.07 (2s, 6H, 2AcO), 3.86 (s, 3H, MeO), 4.09 (q, 1H, $J_{4,5} = J_{5,6} = J_{5,NH} =$ 9.8 Hz, H-5), 4.19 (d, 2H, $J_{6,7} = J_{6,7'} = 3.4$ Hz, H-7,7'), 5.28 (ddd, 1H, $J_{3a,4} = 11.5$ Hz, $J_{3e,4} = 5.1$ Hz, $J_{4,5} = 9.8$ Hz, H-4), and 5.69 (d, 1H, $J_{NH,5} = 9.8$ Hz, NH).

Anal. Calcd for $C_{14}H_{21}NO_9$: C, 48.41; H, 6.09; N, 4.03. Found: C, 48.55; H, 6.13; N, 4.02.

Methyl 5-Acetamido-4,7-di-O-acetyl-2-S-acetyl-3,5-dideoxy-2-thio-β-L-arabino-2-heptulopyranosonate (10). Compound 8 (320 mg, 0.92 mmol) was dissolved in dry dichloromethane (5 mL), and hydrogen chloride was bubbled through for 10 min at − 20 °C, and the mixture was kept for 24 h at room temperature. After completion of the reaction, the solvent and hydrogen chloride were removed by evaporation, to give compound 9 as an amorphous mass, which was dissolved in dry dichloromethane (2 mL) and dry acetone (2 mL). To this stirred solution were added potassium thioacetate (360 mg) and drierite (500 mg), and the mixture was stirred for 24 h at room temperature; TLC then showed the reaction to be complete. The mixture was filtered, and the solid was washed with dichloromethane. The filtrate and washings were combined, and concentrated to a syrup which was chromatographed on a column of silica gel (30 g) with 1:2, and 1:1 ethyl acetate-hexane as the eluants. The latter eluant gave compound 10 (318 mg, 85%) as a syrup: $[\alpha]_D$ + 4.6° (c 2.4, chloroform); IR (film) 3300 (NH), 1750 and 1230 (ester), and 1660 and 1550 cm^{-1} (amide); ^1H NMR ($CDCl_3$) δ 1.94 (s, 3H, AcN), 2.05, 2.10 (2s, 6H, 2AcO), 2.31 (s, 3H, AcS), 2.75 (dd, 1H, $J_{3a,3e} = 12.8$ Hz, $J_{3e,4} = 4.6$ Hz, H-3e), 3.82 (s, 3H, MeO), 4.13 (q, 1H, $J_{4,5} = J_{5,6} = J_{5,NH} = 10.3$ Hz, H-5), 4.99 (ddd, 1H, $J_{3a,4} = 11.5$ Hz, H-4), and 6.13 (d, 1H, NH).

Anal. Calcd for $C_{16}H_{23}NO_9S$: C, C, 47.40; H, 5.71; N, 3.50. Found: C, 47.31; H, 5.86; N, 3.50.

ACKNOWLEDGMENT

This work was supported in part by a Grant-in-Aid (No. 6360122) for the Scientific Research from Ministry of Education, Science and Culture of Japan.

REFERENCES AND FOOTNOTES

1. a) R. Schauer (ed.) "Sialic Acids, Chemistry, Metabolism, and Function" Cell Biology Monographs, Vol. 10, Spring-Verlag, Wien-New York, 1982; b) H. Wiegandt (ed.), "Glycolipids", New Comprehensive Biochemistry Vol. 10, Elsevier, Amsterdam, 1985.

2. a) A. K. Shukla, C. Schröder, U. Nöhle, and R. Schauer, Carbohydr. Res., 168, 199 (1987); b) A. P. Corfield, C. Ferreira do Amaral, M. Wember, and R. Schauer, Eur. J. Biochem., 68, 597 (1976).

3. M. Salunkhe, M. Hartmann, W. Schmid, and E. Zbiral, Ann. Chem., 187 (1988).

4. R. Brossmer and H. W. Hagedorn, Helv. Chim. Acta, 69, 2127 (1986).

5. F. Baumberger, A. Vasella, and R. Schauer, Helv. Chim. Acta, 69, 1927 (1986).

6. J. M. Beau and R. Schauer, Eur. J. Biochem., 106, 531 (1980).

7. E. Zbiral and H. H. Brandstetter, Monatsh. Chem., 116, 87 (1985).

8. R. Christian, G. Schulz, H. H. Brandstetter, and E. Zbiral, Carbohydr. Res., 162, 1 (1987).

9. E. Zbiral, H. H. Brandstetter, R. Christian, and R. Schauer, Ann. Chem., 781 (1987).

10. H. Ogura, K. Furuhata, S. Sato, K. Anazawa, M. Itoh, and Y. Shitori, Carbohydr. Res., 167, 77 (1987).

11. K. Clinch and A. Vasella, Tetrahedron Lett., 28, 6245 (1987).

12. M. Sharma, C. R. Petrie, and W. Korytnyk, Carbohydr. Res., 175, 25 (1988).

13. H. Paulsen, C. Krogmann, and U. von Deessen, Ann. Chem., 277 (1988).

14. T. Nakajima, H. Hori, H. Ohrui, H. Meguro, and T. Ido, Agric. Biol. Chem., 52, 1209 (1988).

15. F. Baumberger, A. Vasella, and R. Schauer, Helv. Chim. Acta, 71, 429 (1988).

16. A. Hasegawa, J. Nakamura, and M. Kiso, J. Carbohydr. Chem., 5, 11 (1986).

17. O. Kanie, J. Nakamura, M. Kiso, and A. Hasegawa, J. Carbohydr. Chem., 6, 105 (1987).

18. K. Okamoto, T. Kondo, and T. Goto, Tetrahedron Lett., 27, 5233 (1986).

19. R. Kuhn, P. Lutz, and D. L. MacDonald, Chem. Ber., 99, 611 (1966).

20. H. Paulsen and H. Tietz, Carbohydr. Res., 125, 47 (1984).

21. S. Hanessian, E. M. Ponpipom, and P. Lavallee, Carbohydr. Res., 24, 45 (1972).

22. K. Janssen, T. Frejd, J. Kihlberg, and G. Magnusson, Tetrahedron Lett., 27, 753 (1986).