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Synthesis of 2-(5-Cholesten-3β-yloxy) Glycosides of *N*-Acetyl-D-neuraminic Acid Derivatives[1)]

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2-(5-Cholesten-3β-yloxy) α- and β-glycosides of *N*-acetyl-D-neuraminic acid were prepared under various conditions through a Koenigs–Knorr-like reaction. The stereochemistry of the products was confirmed by analysis of the nuclear magnetic resonance and circular dichroism spectra.

Keywords——*N*-acetylneuraminic acid; *O*-glycoside; cholesterol; NMR; CD; stereochemistry

N-Acetyl-D-neuraminic acid is widely distributed in membrane glycoprotein and glycolipids. Recently, we reported the stereochemistry,[2,3)] syntheses,[4)] and some biological activities[5,6)] of 2-*O*-glycosyl-[7)] and 2-*N*-substituted derivatives of *N*-acetyl-D-neuraminic acid.[8)] The stereochemistry of these compounds was studied by comparing the chemical shifts of 3-H (eq) in the nuclear magnetic resonance (NMR) spectra, and measuring the circular dichroism (CD) spectra, and the rate of hydrolysis of the glycosidic bonds with water.[7,8)]

In this paper, we wish to report the synthesis of cholesterol glycosides of *N*-acetyl-D-neuraminic acid derivatives for examination of neuritogenesis.[9)] Some cholesteryl glycosides have previously been prepared for studies on the effects of external carbohydrate determinants on liposome distribution[10)]: for example, 5-acetamido-2-*S*-[6-(5-cholesten-3β-yloxy)-hexyl]-3,5-dideoxy-2-thio-D-*glycero*-β-D-*galacto*-2-nonulopyranosonic acid was synthesized from methyl 5-acetamido-2,4,7,8,9-penta-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosonate and 6-(5-cholesten-3β-yloxy)-1-thiohexane in the presence of boron trifluoride etherate.

Koenigs–Knorr-like reaction of methyl *N*-acetyl-4,7,8,9-tetra-*O*-acetyl-2-chloro-β-D-neuraminate[11)] (**1**) and cholesterol (**2**) under various conditions (Table I) gave α- and β-

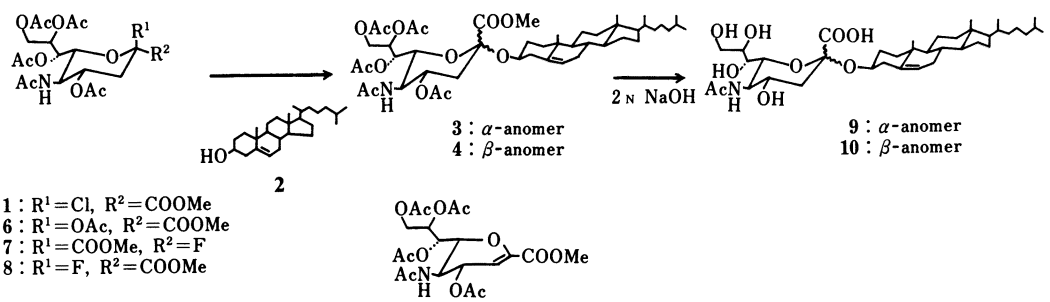

Chart 1

TABLE I. Isolated Yields of Cholest-5-en-3-yloxy Glycoside of *N*-Acetyl-D-neuraminic Acid Tetra-*O*-acetate after Koenigs–Knorr Reaction at 20—25 °C

Run	Compound No.	R^1	R^2	Catalyst	Solvent	Reaction time (d)	Total yield (%)[a]	Ratio of products 3	4	By-product 5 (%)[b]
1	**1**	Cl	COOMe	Ag_2CO_3	Benzene	3	20	4	1	19
2	**1**	Cl	COOMe	Ag_2CO_3/I_2	Benzene	3	22	11.5	1	21
3	**1**	Cl	COOMe	Ag salicylate	Benzene	1	27	7.2	1	35
							(34	12	1	42)[c]
4	**1**	Cl	COOMe	$AgClO_4$	CH_2Cl_2	1	58	1	1.5	10
5	**1**	Cl	COOMe	$AgOSO_2CF_3$	CH_2Cl_2	1	60	1	1	10
6	**1**	Cl	COOMe	$AgOCOCF_3$	CH_2Cl_2	1	21	2	1	10
7	**1**	Cl	COOMe	$Hg(CN)_2/HgBr_2$	CH_3NO_2	1	12	1	1	50
8	**8**	F	COOMe	$AgClO_4/SnCl_2$	Ether	1	8	1	1.3	—
9	**8**	F	COOMe	$BF_3 \cdot Et_2O$	CH_2Cl_2	1 (h)	56	0	1	42
10	**7**	COOMe	F	$BF_3 \cdot Et_2O$	CH_2Cl_2	1 (h)	16	1	6	10
11	**7**	COOMe	F	$AgOSO_2CF_3/SnCl_2$	Benzene	1	42	1	1.3	33
12	**6**	OAc	COOMe	$TMSOSO_2CF_3$	CH_2Cl_2	1	5	0	1	—

a) Isolated yield calculated from cholesterol. *b*) Isolated yield calculated from *N*-acetylneuraminic acid derivatives. *c*) Data of the best run.

anomers of methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-2-(5-cholesten-3β-yloxy)-3,5-dideoxy-D-*glycero*-D-*galacto*-nonulopyranosonate (**3** and **4**).

As can be seen from Table I, when silver perchlorate or silver trifluoromethanesulfonate was used as a catalyst, the yield was about 60% after chromatographic separation. When silver trifluoroacetate was used, the yield was low (21%), but the α-anomer (**3**) was obtained in 2 : 1 ratio. When a sparingly soluble catalyst, silver carbonate, was used, the α-anomer (**3**) was formed in about 16% yield with 4% of the β-anomer (**4**) after 3 d. When iodine was added to this reaction mixture, the α-anomer (**3**) was obtained in 11.5 : 1 ratio. In a case of silver salicylate catalyst, the α-anomer (**3**) was obtained in 7.2 : 1 ratio. Mercury salts were not good catalysts, because the anomeric mixture (1 : 1) was formed in 12% yield together with a large amount of the 2,3-dehydro derivative[11] (**5**; 50%).

Koenigs–Knorr-like reaction of methyl *N*-acetyl-4,7,8,9-tetra-*O*-acetyl-2-fluoro-α- (and -β-)-D-neuraminate[12,13] (**7**, **8**) and cholesterol (**2**) gave α- and β-anomeric mixture (**3**, **4**) as shown in Table I. This is very different from the known sugar chemistry.[14] On the other hand, the reaction of methyl *N*-acetyl-2,4,7,8,9-penta-*O*-acetyl-β-D-neuraminate[8] (**6**) with trimethylsilyl trifluoromethanesulfonate or that of methyl *N*-acetyl-4,7,8,9-tetra-*O*-acetyl-2-fluoro-β-D-neuraminate (**8**) with boron trifluoride etherate or tin(II) chloride–silver perchlorate gave only the β-anomer. In the latter reactions, methyl *N*-acetyl-4,7,8,9-tetra-*O*-acetyl-2,3-dehydro-2-deoxyneuraminate (**5**) was formed in 10—40% yield.

In conclusion, in view of the 1C conformational structure of *N*-acetylneuraminic acid, the β-anomer is more stable than the α-anomer. For this reason, formation of a β-glycosidic linkage is easier (for example, only the β-glycoside was formed from **8** by using boron trifluoride etherate *via* formation of an intimate ion pair). However, α-glycosidic linkage could be formed with high selectivity by using an insoluble catalyst, such as silver carbonate or silver salicylate, *via* a S_N2-like reaction mechanism.

Saponification of these acetates (**3**, **4**) with 2 N sodium hydroxide afforded the α- and β-anomers of *N*-acetyl-2-(5-cholesten-3β-yloxy)-D-neuraminic acid (**9**, **10**) in fair yields, and their sodium salts (**11**, **12**) were prepared with an equimolar amount of sodium hydroxide.

The stereochemistry of these compounds was evaluated from the proton nuclear

TABLE II. Selected ^{1}H-NMR Chemical Shifts of Sialic Acid Derivatives ($CDCl_3$; δ ppm)

Anomeric configuration	Methyl *N*-acetyl-2,4,7,8,9-penta-*O*-acetyl-D-neuraminate			**3**	**4**	*Δ*	**9**	**10**	*Δ*	**11**	**12**	*Δ*
	α	β	*Δ* (α−β)	α	β	α−β	α	β	α−β	α	β	α−β
3-H_{ax}	1.930	—	—	—	—	—	—	—	—	—	—	—
3-H_{eq}	2.718	2.550	+0.168	2.596	2.525	+0.071	2.43	2.39	+0.04	2.839	2.482	+0.357
4-H	4.924	5.258	−0.334	4.854	—	—	—	—	—	—	—	—

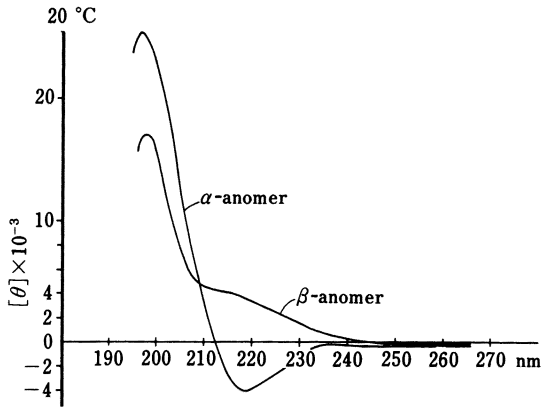

Fig. 1. CD Curves of 5-Acetamido-2-(5-cholesten-3β-yl)-3,5-dideoxy-D-*glycero*-α- and -β-D-*galacto*-nonulopyranosonic Acid (**9** and **10**) in Methanol

magnetic resonance (^{1}H-NMR) spectra and the CD spectra. The differences of the chemical shifts of the 3-H (eq) double-doublet of α-anomers (**3**, **9**, **11**) and β-anomers (**4**, **10**, **12**) are +0.07, +0.04 and +0.36 ppm, respectively, as shown in Table II. The anomeric configuration of *N*-acetylneuraminic acid derivatives can be inferred from the lower chemical shifts of 3-H (eq) in the range from δ 2.5 to 2.8. In conclusion, the stereochemistry at the anomeric position could be assessed from the NMR data.

We have already reported the CD spectra of a number of *N*-acetylneuraminic acid derivatives, and the peak at *ca.* 220 nm was assigned to the n–π* Cotton effect of the carboxyl group. The negative sign of the Cotton effect is attributed to α-glycoside and the positive sign is attributed to β-glycoside.[2] Figure 1 shows the CD spectra of the α- and β-anomer of *N*-acetyl-2-(5-cholesten-3β-yloxy)-D-neuraminic acid (**9**, **10**). The α-anomer (**9**) shows a negative n–π* Cotton effect around 220 nm, whereas the β-anomer (**10**) shows a positive n–π* Cotton effect.

In conclusion, the stereochemistry at the C-2 position of the *N*-acetylneuraminic acid moiety was confirmed on the basis of the NMR and CD spectra.

Experimental

All temperatures are uncorrected. Infrared (IR) spectra were recorded with a JASCO A-2 spectrometer and NMR spectra on a Varian XL-400 spectrometer. Tetramethylsilane (TMS) in $CDCl_3$ or sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS) in D_2O was used as an internal reference. Field desorption (FD) mass spectra (MS) were obtained on a JEOL JMS-DX 300 spectrometer. Optical rotations were measured in a 50 mm cell with a JASCO DIP-181 automatic polarimeter, and CD data were obtained with a JASCO J-20 recording polarimeter.

Methyl 5-Acetamide-4,7,8,9-tetra-*O*-acetyl-2-(5-cholesten-3β-yl)-3,5-dideoxy-D-*glycero*-α- and -β-D-*galacto*-nonulopyranosonate (3, 4) from Methyl *N*-Acetyl-4,7,8,9-tetra-*O*-acetyl-2-chloro-β-D-neuraminate (1)—— Dichloromethane or benzene (10 ml), **1** (2 mmol) and silver salts (2.4 mmol) were added to a solution of cholesterol (**2**;

TABLE III. ^{1}H-NMR Data for **3** and **4** in $CDCl_3$ (400 MHz, δ ppm)

Compound	**3**		**4**	
Sialic acid moiety				
3-H_{ax}	—		—	
3-H_{eq}	2.596	1H, dd, J=5.2, 12.8 Hz	2.525	1H, dd, J=4.9, 13.1 Hz
4-H	4.853	1H, ddd, J=5.2, 9.8, 12.0 Hz	5.22—5.27	1H, m
5-H	4.02—4.09	2H, m	4.04—4.13	2H, m
6-H				
7-H	5.33—5.37	2H, m	5.34—5.38[a]	2H, m
8-H			5.07	1H, tt, J=2.0, 8.2 Hz
9-H^a	4.166	1H, dd, J=5.8, 12.5 Hz	4.146	1H, dd, J=7.6, 12.5 Hz
9-H^b	4.347	1H, dd, J=2.5, 12.8 Hz	4.880	1H, dd, J=1.8, 12.5 Hz
$NHCOCH_3$	1.883	3H, s	1.871	3H, s
$NHCOCH_3$	5.205	1H, d, J=10.1 Hz	5.34—5.38[a]	2H, m
$(COCH_3)_4$	2.026		2.021×2	
	2.031	3H×4, s×4	2.077	3H×4, s×3
	2.126		2.130	
	2.145			
$COOCH_3$	3.790	3H, s	3.798	3H, s
Cholesterol moiety				
18-CH_3	0.669	3H, s	0.670	3H, s
19-CH_3	0.985	3H, s	0.999	3H, s
3-H	3.650	1H, m	3.572	1H, m

a) Values may be interchanged.

2.4 mmol) in dried tetrahydrofuran (THF) under an argon atmosphere. The reaction mixture was stirred for 24 h at room temperature (20—25 °C), then filtered through Celite. The filtrate was evaporated to dryness under reduced pressure, and the residue was extracted with ethyl acetate. The extract was purified by silica gel column chromatography with chloroform–methanol to yield the α-anomer (**3**) and β-anomer (**4**), and methyl *N*-acetyl-4,7,8,9-tetra-*O*-acetyl-2,3-dehydro-2-deoxyneuraminate (**5**).[11] **5** was assigned from the ^{1}H-NMR spectrum (90 MHz, $CDCl_3$) δ_H (ppm): 1.87 (3H, s, NAc), 2.04, 2.08, 2.10, 2.15 (12H, s, OAc), 3.74 (1H, s, COOMe), 5.98 (1H, d, J=1.9 Hz, H-3). The data are summarized in Table I.

α-Anomer (**3**): Colorless needles, mp 113—115 °C (ether–pet. ether). IR ν_{max}^{film} cm^{-1}: 3250 (NH), 2940, 1745 (OAc), 1660 (NHCO), 1540. $[\alpha]_D^{25}$ −23.8° (c=1, $CHCl_3$). The NMR ($CDCl_3$) data are summarized in Table III. MS (EI; in-beam method) *m/z*: 860 (M^++1), 800 (M^+−59). *Anal.* Calcd for $C_{47}H_{73}NO_{13}$: C, 65.63; H, 8.55; N, 1.63. Found: C, 65.41; H, 8.61; N, 1.60.

β-Anomer (**4**): Colorless needles, mp 138—140 °C (ether–pet. ether). IR ν_{max}^{film} cm^{-1}: 3420, 3250 (NH), 2930, 1740, (OAc), 1660 (NHCO), 1540. $[\alpha]_D^{25}$ −40.2° (c=1, $CHCl_3$) data are summarized in Table III. MS (EI; in-beam method) *m/z: 860 (M^++1), 800 (M^+−59). Anal. Calcd for $C_{47}H_{73}NO_{13}$: C, 65.63; H, 8.55; N, 1.63. Found: C, 65.89; H, 8.58;* N, 1.66.

Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-2-(5-cholesten-3β-yl)-3,5-dideoxy-D-*glycero*-β-D-*galacto*-nonulopyranosonate (4)——Tetramethylsilyl trifluoromethanesulfonate (16 μl, 0.83 μmol) was added to a stirred mixture of methyl *N*-acetyl-penta-*O*-acetyl-D-neuraminate (**6**; 1.2 mmol),[8] cholesterol (**2**; 1.2 mmol), and molecular sieves (2 g) in dried dichloromethane (40 ml). After being stirred for 24 h at room temperature, the whole mixture was filtered through Celite. The filtrate was evaporated to dryness under reduced pressure, and the residue was chromatographed on silica gel, giving the β-anomer (**4**), 0.043 g (yield; 5%).

Methyl 5-Acetamido-4,7,8,9-tetra-*O*-acetyl-2-(5-cholesten-3β-yl)-3,5-dideoxy-D-*glycero*-α- and -β-D-*galacto*-nonulopyranosonate (3, 4) from Methyl *N*-Acetyl-4,7,8,9-tetra-*O*-acetyl-2-fluoro-α-and -β-D-neuraminate (7, 8)——a) A solution of cholesterol (**2**; 0.1 mmol) in dried dichloromethane (5 ml) was stirred with molecular sieves 4A (0.05 g) under an argon atmosphere. After 0.5 h, methyl *N*-acetyl-4,7,8,9-tetra-*O*-acetyl-2-fluoro-β-D-neuraminate[12] (**8**; 0.15 mmol) and boron trifluoride etherate (0.6 mmol) were added to the mixture. After 1 h, the whole was filtered through Celite, the filtrate was evaporated to dryness under reduced pressure, and the residue was purified by silica gel column chromatography to yield the α-anomer (**3**), β-anomer (**4**), and **5**. These data are summarized in Table I. In the case of run No. 9, methyl *N*-acetyl-4,7,8,9-tetra-*O*-acetyl-β-D-neuraminate[15] (10.3% from **8**) was separated.

b) A solution of cholesterol (**2**; 0.1 mmol) in dried benzene (5 ml) was stirred with molecular sieves 4A (0.05 g) under an argon atmosphere. After 1 h, methyl *N*-acetyl-4,7,8,9-tetra-*O*-acetyl-2-fluoro-α-D-neuraminate[12] (**7**;

TABLE IV. ^{1}H-NMR Data (400 MHz) and ^{13}C-NMR Data (100 MHz) for **11** and **12** in CD_3OD (δ ppm, TMS)

Compound	**11**		**12**	
Cholesterol moiety				
6-H	5.332	1H, d, J=5.5 Hz	5.282	1H, d, J=5.3 Hz
18-CH_3	0.704	3H, s	0.700	3H, s
19-CH_3	0.992	3H, s	0.991	3H, s
21-CH_3	0.936	3H, d, J=6.5 Hz	0.928	3H, d, J=6.5 Hz
26-CH_3	0.870	3H×2, d, J=1.7 Hz	0.861	3H×2, d, J=1.5 Hz
27-CH_3	0.885		0.880	
Sialic acid moiety				
2-H_{eq}	2.839	1H, dd, J=4.2, 12.0 Hz	2.482	1H, dd, J=4.5, 13.0 Hz
NAc	2.010	3H, s	1.972	3H, s
^{13}C-NMR (100 MHz, CD_3OD)				
C-3	70.50		72.37	
C-5	142.87		143.08	
C-6	122.59		122.46	
C-1′	102.57		101.37	
C-2′	41.00		43.82	
1′-COONa	175.26		174.51	
NAc	175.91		176.95	

0.12 mmol), tin(II) chloride (0.12 mmol), and silver triflate (0.12 mmol) were added to the mixture. After continued stirring for 1 d in the dark, the whole was filtered through Celite, the filtrate was evaporated to dryness under reduced pressure, and the residue was purified by silica gel column chromatography to yield the α-anomer (**3**), β-anomer (**4**) and **5** (Table I). In the case of run No. 11, methyl *N*-acetyl-4,7,8,9-tetra-*O*-acetyl-β-D-neuraminate[15] (13.6% from **7**) was separated.

5-Acetamido-2-(5-cholesten-3β-yl)-3,5-dideoxy-D-*glycero*-α- and -β-D-*galacto*-nonulopyranosonic Acid (9, 10)——A stirred solution of **3** or **4** (0.05 g) in methanol (2 ml) was treated with 1 N NaOH (3 ml). After continued stirring overnight at room temperature, water (2 ml) was added and the solution was neutralized with Dowex 50 (H^+), and filtered. The filtrate was evaporated to dryness under reduced pressure to give **9** (yield; 79.7%) or **10** (yield; 76.1%) as colorless needles from ethanol.

α-Anomer (**9**): mp 207—208.5 °C. IR ν_{max}^{KBr} cm^{-1}: 2750, 1575. $[\alpha]_D^{22}$ −12.58° (c=0.41, MeOH). ^{1}H-NMR (CD_3OD) δ (90 MHz): 0.71 (3H, s, 18-CH_3), 0.84, 0.91 (6H, 26- and 27-CH_3), 0.95 (3H, d, J=4.5 Hz, 21-CH_3), 1.00 (3H, s, 19-CH_3), 2.01 (3H, s, NAc), 2.43 (1H, dd, J=4.5, 12.6 Hz, 3-H_{eq}). *Anal.* Calcd for $C_{38}H_{63}NO_9$: C, 67.36; H, 9.31; N, 2.07. Found: C, 67.41; H, 9.53; N, 2.09.

β-Anomer (**10**): mp 269—271 °C. IR ν_{max}^{KBr} cm^{-1}: 2870, 1620, 1550. $[\alpha]_D^{20}$ −31.77° (c=0.78, MeOH). ^{1}H-NMR (CD_3OD) δ (90 MHz): 0.71 (3H, s, 18-CH_3), 0.86, 0.92 (6H, 26- and 27-CH_3), 0.95 (3H, d, J=4.5 Hz, 21-CH_3), 1.00 (3H, s, 19-CH_3), 2.00 (3H, s, NAc), 2.39 (1H, dd, J=4.5, 12.6 Hz, 3-H_{eq}). *Anal.* Calcd for $C_{38}H_{63}NO_9$: C, 67.36; H, 9.31; N, 2.07. Found: C, 67.62; H, 9.55; N, 1.87.

Sodium 5-Acetamido-2-(5-cholesten-3β-yl)-3,5-dideoxy-D-*glycero*-α- and -β-D-*galacto*-nonulopyranosonate (11, 12)——A stirred solution of **3** or **4** (0.05 g) in methanol (100 ml) was treated with 2 N NaOH (20 ml). After continued stirring for 24 h at room temperature, the solution was neutralized with Dowex 50 (H^+) and the filtrate was evaporated to dryness under reduced pressure. The resulting white powder was dissolved in 0.02 N NaOH, and chromatographed on Diaion HP 20 with 75% methanol. The eluate was evaporated under reduced pressure. Freeze-drying of the residue gave **11** (90%) and **12** (88%) as a white powder.

α-Anomer (**11**): IR ν_{max}^{KBr} cm^{-1}: 3250, 2940, 1605. $[\alpha]_D^{24}$ +2.2° (c=1, MeOH). The NMR (CD_3OD) data are summarized in Table IV. MS (FD) *m/z*: 722 (M^++Na), 700 (M^++1), 386, 336, 314. *Anal.* Calcd for $C_{38}H_{62}NNaO_9 \cdot 2H_2O$: C, 61.96, H, 8.42; N, 1.90. Found: C, 61.92; H, 8.71; N, 2.04.

β-Anomer (**12**): IR ν_{max}^{KBr} cm^{-1}: 3270, 2950, 1608. $[\alpha]_D^{24}$ −10.6° (c=1.0, MeOH). The NMR (CD_3OD) data are summarized in Table IV. MS (FD) *m/z*: 722 (M^++Na), 700 (M^++1), 386. *Anal.* Calcd for $C_{38}H_{62}NNaO_9 \cdot H_2O$: C, 63.52; H, 8.91; N, 1.95. Found: C, 63.81; H, 9.25; N, 2.13.

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1) This constitutes Part X in the series entitled "Studies on Sialic Acids."
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