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Studies on Sialic Acids. XV. Synthesis of α- and β-*O*-Glycosides of 3-Deoxy-D-*glycero*-D-*galacto*-2-nonulopyranosonic Acid (KDN)

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3-Deoxy-D-*glycero*-D-*galacto*-2-nonulopyranosonic acid (KDN) was synthesized by base-catalyzed condensation in good yield. Furthermore, benzyl (methyl 3-deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate and sodium 2-(5-cholesten-3β-yloxy)-3-deoxy-D-*glycero*-α- and β-D-*galacto*-2-nonulopyranosonate were synthesized under Koenigs–Knorr-like reaction conditions, using benzyl (4,5,7,8,9-penta-*O*-acetyl-3-deoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl bromid)-onate as a glycosyl donor. The structure and the stereochemistry of glycosylation products were determined by proton nuclear magnetic resonance and circular dichroism spectral analysis.

Keywords——sialic acid; 3-deoxy-D-*glycero*-D-*galacto*-2-nonulopyranosonic acid; bromination; glycosylation; ^{1}H-NMR; aldol condensation

A deaminated sialic acid, 3-deoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosonic acid (**1**, KDN) was isolated from polysialoglycoprotein (PSGP) of rainbow trout egg.[1] KDN (**1**) is exclusively located at the non-reducing end of the sialyl chains, and therefore may be involved in egg activation of salmoid fishes by protecting these chains against sialidases.

There have been a few publications concerning the synthesis of **1**. Inoue *et al.* synthesized protected **1** by converting the amino group of the *N*-deacylated sialic acid derivative to a hydroxy group in low yield *via* the diazonium intermidiate.[1] Furthermore, Auge and Gautheron achieved the synthesis of **1** by enzymatic condensation with D-mannose and pyruvate.[2] Recently, we also reported the synthesis of **1** by thermal rearrangement of the *N*-acetyl-*N*-nitrosoneuraminic acid derivative, although the yield was poor.[3] In this paper, we wish to report an improved chemical synthesis of **1** by base-catalyzed condensation of oxalacetic acid with D-mannose as employed in the synthesis of 3-deoxy-D-*manno*-octulosonic acid (KDO).[4] Furthermore, we succeeded in the synthesis of several α- and β-*O*-glycosyl derivatives of **1** under Koenigs–Knorr-like reaction conditions. The stereochemistry of *O*-glycosyl products was determined by proton nuclear magnetic resonance (^{1}H-NMR) and circular dichroism (CD) spectral analyses on the basis of earlier studies on *N*-acetyl-D-neuraminic acid derivatives.[5–12]

We found a facile method for the synthesis of **1** by the treatment of oxalacetic acid with D-mannose under slightly basic conditions without epimerization. The procedure was simplified when sodium carbonate buffer was used, and pure **1** was isolated with an average yield of 40% by using a column of Dowex-1 (formate) resin. The physical properties of ammonium 3-deoxy-D-*glycero*-D-*galacto*-2-nonulopyranosonate (**2**) were in good agreement with published values.[2]

As a first attempt to synthesize the glycoside derivative of **1**, we examined the Koenigs–Knorr-like reaction, using benzyl (4,5,7,8,9-penta-*O*-acetyl-3-deoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl bromid)onate (**4**) as a glycosyl donor.

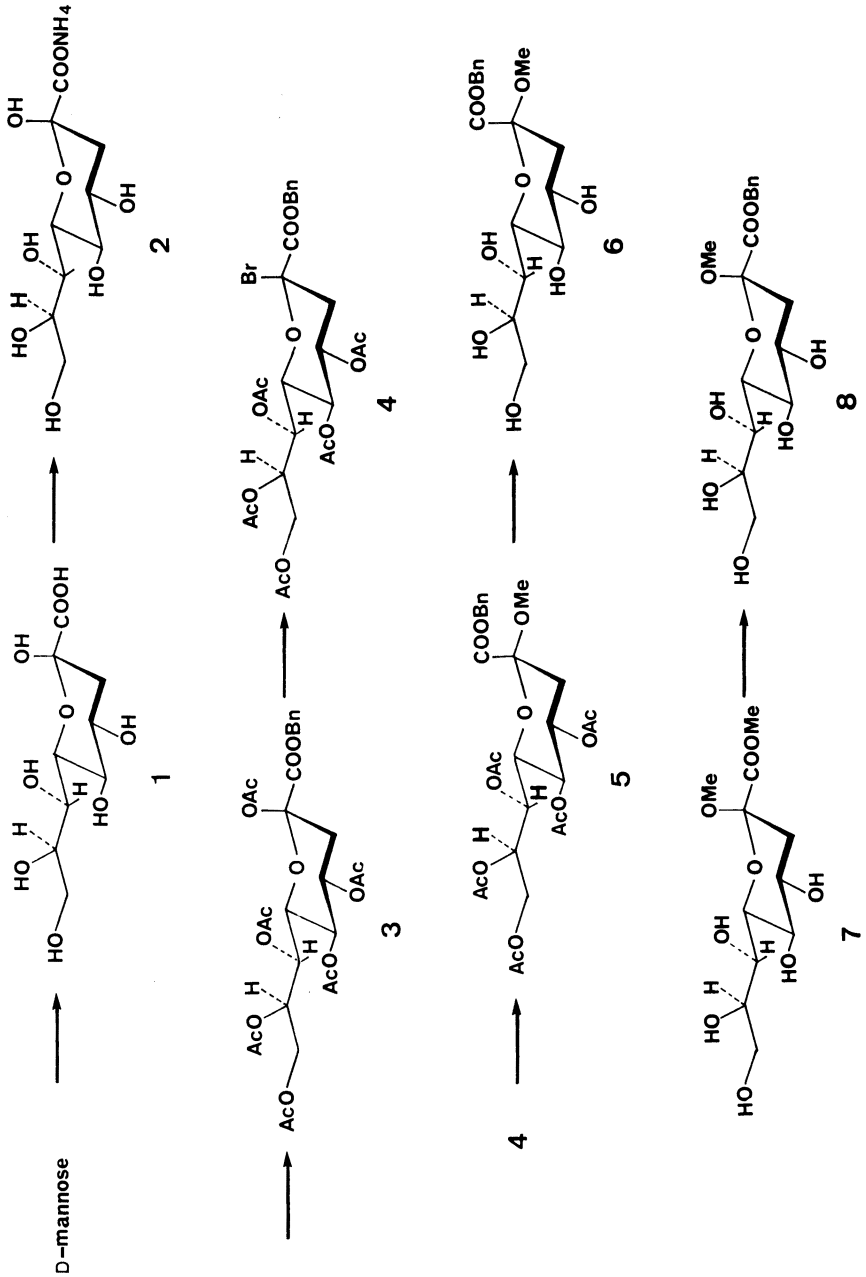

Chart 1

The key compound **4** for glycosylation was synthesized by the following process. Hydroxy groups of **1** were protected by acetylation with acetic anhydride in the presence of 4-dimethylaminopyridine to give the hexa-*O*-acetate of **1**, and protection of the carboxyl group was carried out by esterification with benzyl bromide to afford benzyl 2,4,5,7,8,9-hexa-*O*-acetyl-3-deoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosonate (**3**) in 47% yield. Subsequent bromination at the C-2 position of **3** was accomplished by using titanium (IV) bromide in dichloromethane at room temperature to give **4** in almost quantitative yield as a syrup, which was submitted to the next glycosylation without purification because of its instability. The structure of **4** was elucidated by ^{1}H-NMR comparison with methyl (3-acetamide-4,7,8,9-tetra-*O*-acetyl-2,3-deoxy-D-*glycero*-β-D-*galacto*-nonulopyranosyl bromid)onate.[5]

Glycosylation of **4** with methanol as a glycosyl acceptor (primary hydroxy group) in the presence of silver carbonate afforded benzyl (methyl 4,5,7,8,9-penta-*O*-acetyl-3-deoxy-D-*glycero*-α-D-*galacto*-nonulopyranosid)onate (**5**), which was converted into benzyl (methyl 3-deoxy-D-*glycero*-α-D-*galacto*-nonulopyranosid)onate (**6**) by deacetylation in 57% yield. The anomeric configuration of **6** was elucidated by ^{1}H-NMR comparison with an anomeric isomer of **6**, benzyl (methyl 3-deoxy-D-*glycero*-β-D-*galacto*-nonulopyranosid)onate (**8**), which was prepared from methyl (methyl 3-deoxy-D-*glycero*-β-D-*galacto*-nonulopyranosid)onate (**7**). The structure of **7** had been elucidated by X-ray crystallographic analysis.[3]

Cholesterol as a glycosyl acceptor was reacted with **4** in the presence of silver trifluoromethanesulfonate as a promoter and molecular sieves 4A in dry dichloromethane. After chromatographic separation, benzyl 4,5,7,8,9-penta-*O*-acetyl-2-(5-cholesten-3β-yloxy)-3-deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosonate (**9**) and the corresponding β-anomer (**10**) were obtained in 2 : 1 ratio (total yield 12%) with a large amount (37% yield) of the 2,3-dehydro derivative, benzyl 4,5,7,8,9-penta-*O*-acetyl-2,6-anhydro-2,3-dideoxy-D-*glycero*-D-*galacto*-non-2-enonate (**13**). Compounds **9** and **10** were deprotected with 1 N sodium hydroxide to give **11** and **12** in quantitative yield, respectively. The structures of **9**, **10**, and **13** were deduced from a comparison of the ^{1}H-NMR spectral data with those of corresponding *N*-acetyl-D-neuraminic acid derivatives.[6,7,10]

The stereochemistry of these compounds was elucidated by consideration of the ^{1}H-

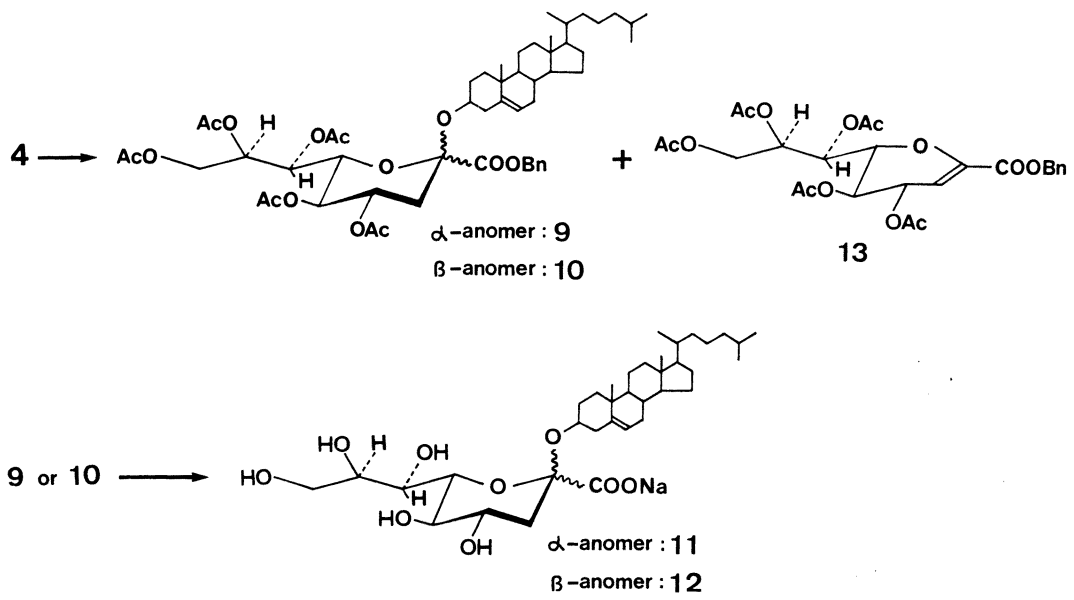

Chart 2

TABLE I. Proton Chemical-Shift and Spin-Coupling Data at 300 MHz for **6**,[a] **8**,[a] **9**,[b] **10**,[b] **11**,[c] and **12**[c]

Compound No.	Chemical shifts (δ)								
	KDN moiety								
	H-3ax	H-3eq	H-4	H-5	H-6	H-7	H-8	H-9	H-9′
6	1.64	2.53	—	—	—	—	—	—	—
8	1.61	2.23	3.85	3.45	3.75	3.69	3.75	3.58	3.74
9	1.90	2.72	4.89	4.84	4.13	5.31	5.35	4.18	4.30
10	1.79	2.59	5.30	4.86	4.24	5.37	5.16	4.21	4.72
11	—	2.62	—	—	—	—	—	—	—
12	—	2.37	—	3.47	—	—	—	—	—

Compound No.	Chemical shifts (δ)						
	CH_2Ph	Aromatic	OCH_3	OAc	Cholesterol moiety		
					H-3	H-18	H-19
6	5.26	7.37	3.21				
8	5.18, 5.25	7.35	3.10				
9	5.17, 5.24	7.35		1.98—2.14	3.51	0.65	0.95
10	5.15, 5.26	7.35		1.79—2.09	3.52	0.66	0.96
11					3.07	0.70	1.00
12					3.07	0.70	1.00

Compound No.	Spin couplings (Hz)									
	$J_{3ax,3eq}$	$J_{3ax,4}$	$J_{3eq,4}$	$J_{4,5}$	$J_{5,6}$	$J_{6,7}$	$J_{7,8}$	$J_{8,9}$	$J_{8,9'}$	$J_{9,9'}$
6	13.7	11.0	4.0	—	—	—	—	—	—	—
8	13.0	11.4	5.0	9.5	9.5	1.0	10.0	5.4	—	12.0
9	13.0	11.6	4.5	9.5	10.0	1.9	8.0	4.6	2.2	12.5
10	13.0	11.6	5.2	9.5	10.0	2.2	3.5	7.4	2.1	12.5
11	12.7	—	4.2	9.5	—	—	—	—	—	—
12	12.9	—	4.8	—	—	—	—	—	—	—

a) Recorded for solution in D_2O. *b*) Recorded for solution in $CDCl_3$. *c*) Recorded for solution in CD_3OD.

NMR and CD spectra. In the ^{1}H-NMR spectra, the differences between the chemical shifts at the H-3′′ (eq) double-doublet resonance of the α-anomer (**6**, **9**, **11**) and those of the β-anomer (**8**, **10**, **12**) were +0.30, +0.13, and +0.25 ppm, respectively, as shown in Table I. Empirical studies of *N*-acetyl-D-neuraminic acid derivatives indicated that the H-3′′ (eq) signal of the α-anomer is usually observed at lower field than that of the β-anomer.[8-10]

Figure 1 shows the CD spectra of the α-anomer (**6**, **11**) and β-anomer (**8**, **12**). According to studies on the CD spectra of *N*-acetyl-D-neuraminic acid derivatives, the peak around 220 nm is assigned to the n-π* Cotton effect of the carboxyl group and the negative sign of the Cotton effect was assigned to the α-anomer and the positive sign to the β-anomer.[10-12] Our results are consistent with those reports.

In conclusion, we have developed a stereoselective synthesis of **1** by base-catalyzed condensation, and we have synthesized α- and β-*O*-glycosides of **1** under Koenigs–Knorr-like reaction conditions. The stereochemistry at the anomeric position of the glycosyl derivatives

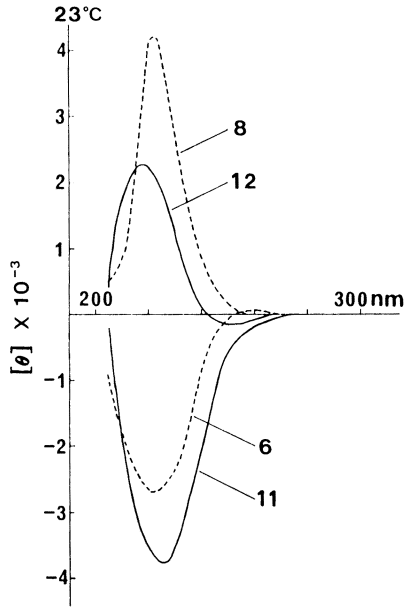

Fig. 1. CD Curves of **6** and **8** in D_2O and **11** and **12** in MeOH

of **1** could be confirmed on the basis of the ^{1}H-NMR and CD spectra. Moreover, we found that the conformations of **1** and its derivatives have many similarities with those of *N*-acetyl-D-neuraminic acid and its derivatives.

Experimental

Melting points were measured with a Yamato melting point apparatus and the results are uncorrected. Optical rotations were measured with a JASCO JIP-4 digital polarimeter. Thin layer chromatography (TLC) was performed on Silica gel GF254 (Merck) plates, and spots were detected by ultraviolet (UV) irradiation and by spraying with 5% sulfuric acid solution. Field desorption mass spectra (FDMS), and infrared (IR) spectra were measured with JEOL JMS-DX300 and JASCO IR-A2 instruments, respectively. CD spectra were measured in a 0.1 cm cell with a JASCO J-20 spectrometer. The ^{1}H-NMR spectra were measured with Varian VXR-300 spectrometers. Tetramethylsilane (TMS) in $CDCl_3$ or sodium 3-(trimethylsilyl)-1-propanesulfonate (DSS) in D_2O was used as an internal reference. Column chromatography was conducted on Silica gel 60 (70—230 mesh).

Ammonium 3-Deoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosonate (2)——D-Mannose (27.03 g, 150.03 mmol) was added to a solution of sodium carbonate (6.36 g, 60 mmol) in water (32 ml), followed by the slow addition of oxalacetic acid (6.61 g, 50 mmol). The solution was adjusted to pH 11 with 10 M sodium hydroxide, stirred for 2 h, then acidified (pH 1—2) with Dowex-50 (H^+) resin, filtered, and neutralized with ammonia. **1** was isolated by column chromatography, using a column of Dowex-1 (formate) resin which was washed with water (2 l) and then eluted with 0.3 M formic acid. The eluate was concentrated under reduced pressure, neutralized with ammonia, then freeze-dried to give **2** as an amorphous solid (5.6 g, 39%), which gave physicochemical data in accordance with published values. ^{1}H-NMR (300 MHz, D_2O): 1.70 (1H, dd, J=12.9 and 11.8 Hz, 3-H_{ax}), 2.09 (1H, dd, J=12.9, 5.0 Hz, 3-H_{eq}), 3.50 (1H, t, J=10.0 Hz, 5-H), 3.57 (1H, dd, J=11.5, 6.1 Hz, 9-H), 3.68 (1H, ddd, J=9.0, 6.1, 2.4 Hz, 8-H), 3.75 (1H, dd, J=9.0, 1.1 Hz, 7-H), 3.79 (1H, dd, J=11.5, 2.4 Hz, 9′-H), 3.84 (1H, dd, J=10.0, 1.1 Hz, 6-H), 3.89 (1H, ddd, J=11.8, 9.3, 5.0 Hz, 4-H).

Benzyl 2,4,5,7,8,9-Hexa-*O*-acetyl-3-deoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosonate (3)——A solution of **2** (3.9 g, 13.7 mmol) in pyridine (54 ml) and acetic anhydride (54 ml) was stirred at 5 °C, and then 4-dimethylaminopyridine (67 mg) was added. After 24 h, chloroform (390 ml) was added, and the reaction mixture was cooled to 5 °C and washed twice with 1 N HCl (140 ml + 140 ml). The chloroform solution was dried over anhydrous magnesium sulfate and filtered, and the filtrate was evaporated to dryness. Anhydrous cesium carbonate (1.53 g 4.7 mmol) was added to a solution of the residue in *N*,*N*-dimethylformamide (DMF) (5 ml) and water (5 ml) at room temperature. After being stirred for 30 min, the mixture was evaporated to dryness completely. The residue was dissolved in DMF (20 ml), benzyl bromide (1.9 g, 11.2 mmol) was added, and the whole was stirred at room temperature for 2 h. The reaction mixture was poured into water and extracted with ethyl acetate, then the extract was washed with sodium hydrogen carbonate solution, dried and concentrated. The residual syrup was purified on a column of silica gel to yield **3** (4.05 g, 47%) as an amorphous solid. $[\alpha]_D^{25}$ −17.4° (c=1, $CHCl_3$). EIMS m/z: 550 (M^+ − 59). *Anal.* Calcd for $C_{28}H_{34}O_{15}$: C,

55.08; H, 5.61. Found: C, 55.29; H, 5.78. IR ν_{max}^{KBr} cm^{-1}: 2960, 1745. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.99, 2.01, 2.02, 2.02, 2.09, 2.11 (18 H, s × 6), 2.08 (1H, dd, J = 13.5, 11.4 Hz, 3-H_{ax}), 2.62 (1H, dd, J = 13.5, 5.2 Hz, 3-H_{eq}), 4.15 (1H, dd, J = 12.5, 5.9 Hz, 9-H), 4.19 (1H, dd, J = 10.2, 2.2 Hz, 6-H), 4.40 (1H, dd, J = 12.5, 2.6 Hz, 9′-H), 4.96 (1H, t, J = 10.2, 9.8 Hz, 5-H), 5.16 (1H, m, 8-H), 5.15, 5.23 (2H, d × 2, J = 12.0 Hz, CH_2Ph), 5.26 (1H, m, 4-H), 5.39 (1H, dd, J = 6.1, 2.2 Hz, 7-H), 7.35 (5H, m, aromatic H).

Benzyl (4,5,7,8,9-Penta-*O*-acetyl-3-deoxy-D-*glycero*-β-D-*galacto*-2-nonulopyranosyl bromid)onate (4)——A solution of **3** (2.0 g, 3.27 mmol) in dichloromethane (103 ml) and ethyl acetate (10 ml) was stirred at room temperature. Then, molecular sieves 4A (2.0 g) was added to the solution and the whole was stirred for 1 h. The solution was cooled to 5 °C, titanium tetrabromide (4.85 g) was added, and the stirring was continued at room temperature with exclusion of moisture. After 16 h, acetonitrile (57 ml) and anhydrous sodium acetate (8.9 g) were added, and the stirring was continued at room temperature for 30 min. Toluene (268 ml) was added to the mixture with cooling, the whole was stirring for 30 min, and then the solids were filtered off and the filtrate was concentrated to give **4** as a syrup. This syrup was used for the following reaction without purification. $[\alpha]_D^{25}$ −59.0° (c = 0.6, $CHCl_3$). EIMS m/z: 631, 633 (M^+). IR ν_{max}^{KBr}cm^{-1}: 3480, 2970, 1750. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.02, 2.05, 2.06, 2.08, 2.09 (3H × 5, s × 5, $COCH_3$), 2.23 (1H, dd, J = 14.2, 11.2 Hz, 3-H_{ax}), 2.99 (1H, dd, J = 14.2, 5.0 Hz, 3-H_{eq}), 4.12 (1H, dd, J = 12.8, 4.9 Hz, 9-H), 4.36 (1H, dd, J = 12.8, 2.4 Hz, 9′-H), 4.44 (1H, dd, J = 10.4, 2.1 Hz, 6-H), 4.99 (1H, t, J = 10.0 Hz, 5-H), 5.23 (1H, m, 8-H), 5.26, 5.38 (2H, d × 2, J = 12.0 Hz, CH_2Ph), 5.50 (1H, m, 4-H), 5.51 (1H, dd, J = 8.4, 2.1 Hz, 7-H), 7.40 (5H, m, aromatic H).

Benzyl (Methyl 4,5,7,8,9-Penta-*O*-acetyl-3-deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (5)——Molecular sieves 4A (1.03 g) and silver carbonate (903 mg, 3.27 mmol) were added to a solution of **4** (1.03 g, 1.63 mmol) in dichloromethan at room temperature. After being stirred for 30 min, the reaction mixture was filtered and the filtrate was concentrated. The residue was purified on a column of silica gel with ether–hexane (3 : 1) to yield **5** (712 mg, 75%) as an amorphous solid. $[\alpha]_D^{25}$ −24.0° (c = 1, $CHCl_3$). EIMS m/z: 582 (M^+). *Anal.* Calcd for $C_{27}H_{34}O_{14}$: C, 55.67; H, 5.88. Found: C, 55.90; H, 5.93. IR ν_{max}^{KBr}cm^{-1}: 2980, 2950, 1750. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.89 (1H, t, J = 12.5 Hz, 3-H_{ax}), 1.99, 1.99, 2.02, 2.09, 2.16 (15H, s × 5, $COCH_3$), 2.70 (1H, dd, J = 12.7, 4.2 Hz, 3-H_{eq}), 3.23 (3H, s, CH_3), 4.12 (1H, dd, J = 12.5, 4.6 Hz, 9-H), 4.18 (1H, dd, J = 10.0, 2.2 Hz, 6-H), 4.26 (1H, dd, J = 12.5, 2.4 Hz, 9′-H), 4.86 (1H, t, J = 9.5 Hz, 5-H), 4.89 (1H, m, 4-H), 5.20, 5.25 (2H, d × 2, J = 12.0 Hz, CH_2Ph), 5.34 (1H, dd, J = 9.1, 2.2 Hz, 7-H), 5.42 (1H, m, 8-H).

Benzyl (Methyl 3-Deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (6)——A stirred solution of **5** (300 mg, 0.515 mmol) in methanol (15 ml) was treated with 0.01 N sodium hydroxide (15 ml) at room temperature. After being stirred for 2 h, water (30 ml) was added and the solution was neutralized with Dowex-50 (H^+), and filtered. The filtrate was evaporated to dryness under reduced pressure, and the residue was crystallized from methanol–ether to give **6** (130 mg, 67%) as colorless needles. mp 97—99 °C. $[\alpha]_D^{27}$ −38.4° (c = 0.17, MeOH). EIMS m/z: 341 (M^+ − 31). *Anal.* Calcd for $C_{17}H_{24}O_9 \cdot H_2O$: C, 52.30; H, 6.71. Found: C, 52.42; H, 6.49. IR ν_{max}^{KBr}cm^{-1}: 3510, 3330, 2950, 2900, 1720. ^{1}H-NMR data are summarized in Table I.

Benzyl (Methyl 3-Deoxy-D-*glycero*-α-D-*galacto*-2-nonulopyranosid)onate (8)——A solution of **7** in 1 N sodium hydroxide (5 ml) was stirred at room temperature. After 2 h, the solution was neutralized with Dowex-50 (H^+), filtered, and then evaporated to dryness completely. The residue was dissolved in DMF (5 ml), and benzyl bromide (57 mg, 0.336 mmol) was added at room temperature. After being stirred for 2 h, the reaction mixture was filtered and evaporated. The residual syrup was purified on a column of silica gel to yield the benzyl ester (**8**) (40 mg, 58%) as an amorphous solid. $[\alpha]_D^{26}$ −37.9° (c = 0.33, MeOH). EIMS m/z: 340 (M^+ − 32). *Anal.* Calcd for $C_{17}H_{24}O_9 \cdot H_2O$: C, 52.30; H, 6.71. Found: C, 52.71; H, 6.58. IR ν_{max}^{KBr}cm^{-1}: 3300, 2925, 1725. ^{1}H-NMR data are summarized in Table I.

Benzyl 4,5,7,8,9-Penta-*O*-acetyl-2-(5-cholesten-3β-yloxy)-3-deoxy-D-*glycero*-α- and β-D-*galacto*-2-nonulopyranosonate (9, 10)——A solution of cholesterol (0.77 g, 2.0 mmol) in dried dichloromethane was stirred with molecular sieves 4A (0.77 g). After 1 h, **4** (1.5 g, 2.38 mmol) and TfOAg (0.61 g, 2.38 mmol) were added to the solution, and the mixture was stirred for 1 h in the dark. The whole was filtered through Celite, the filtrate was evaporated to dryness, and the residue was chromatographed on a column of silica gel with ether–hexane (2 : 1) to give the α-anomer (**9**) (157 mg, 8%), β-anomer (**10**) (76 mg, 4%) and **13** (490 mg, 37%).

α-Anomer (**9**): $[\alpha]_D^{25}$ −37.4° (c = 1, $CHCl_3$). EIMS m/z: 859 (M^+ − 80). *Anal.* Calcd for $C_{53}H_{78}O_{14}$: C, 67.78; H, 8.37. Found: C, 67.82; H, 8.28. IR ν_{max}^{KBr}cm^{-1}: 2940, 1745. The ^{1}H-NMR data are summarized in Table I.

β-Anomer (**10**): $[\alpha]_D^{25}$ −35.6° (c = 1, $CHCl_3$). EIMS m/z: 937 (M^+). *Anal.* Calcd for $C_{53}H_{78}O_{14}$: C, 67.78; H, 8.37. Found: C, 67.67; H, 8.17. IR ν_{max}^{KBr}cm^{-1}: 1940, 1750. The ^{1}H-NMR data are summarized in Table I.

13: $[\alpha]_D^{26}$ −15.2° (c = 0.97, $CHCl_3$). EIMS m/z: 552 (M^+ + 1). *Anal.* Calcd for $C_{26}H_{30}O_{13}$: C, 56.73; H, 5.49. Found: C, 56.62; H, 5.59. IR ν_{max}^{KBr}cm^{-1}: 2970, 1740, 1660. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.99, 2.00, 2.01, 2.02, 2.04 (3H × 5, s × 5, $COCH_3$), 4.18 (1H, dd, J = 12.4, 6.3 Hz, 9-H), 4.33 (1H, dd, J = 9.4, 3.0 Hz, 4-H), 4.51 (1H, dd, J = 12.4, 2.8 Hz, 9′-H), 5.18 (1H, dd, J = 9.4, 7.0 Hz, 5-H), 5.20 (2H, d, CH_2Ph), 5.35 (1H, m, 8-H), 5.46 (1H, dd, J = 6.0, 3.0 Hz, 7-H), 5.54 (1H, dd, J = 7.0, 3.0 Hz, 6-H), 5.95 (1H, d, J = 3.0 Hz, 3-H), 7.34 (5H, m, aromatic).

Sodium 2-(5-Cholesten-3β-yloxy)-3-deoxy-D-*glycero*-α- and β-D-*galacto*-2-nonulopyranosonate (11, 12)——A stirred solution of **9** or **10** (50 mg) in methanol (10 ml) was treated with 1 N sodium hydroxide (10 ml) at room temperature. The mixture was stirred for 3 h, water (10 ml) was added and the solution was neutralized with Dowex-

50 (H^+), and filtered. The filtrate was evaporated to dryness to give **11** or **12** in quantitative yield as an amorphous powder.

α-Anomer (**11**): $[\alpha]_D^{27}$ −36.7° (c=0.42, MeOH). FDMS m/z: 659 (M^+). *Anal.* Calcd for $C_{36}H_{61}NaO_9$: C, 65.53; H, 9.16. Found: C, 65.42; H, 9.21. IR $\nu_{max}^{KBr}cm^{-1}$: 3400, 2940, 1720. The ^{1}H-NMR data are summarized in Table I.

β-Anomer (**12**): $[\alpha]_D^{25}$ −36.7° (c=0.42, MeOH). FDMS m/z: 659 (M^+). *Anal.* Calcd for $C_{36}H_{61}NaO_9$: C, 65.53; H, 9.16. Found: C, 65.05; H, 9.38. IR $\nu_{max}^{KBr}cm^{-1}$: 3400, 2940, 1720. The ^{1}H-NMR data are summarized in Table I.

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