Neuraminic Acid and Related Compounds. V. Syntheses of Biologically Active Sialosyl-Glycerol Derivatives and Galactosyl-Glycerol Derivative

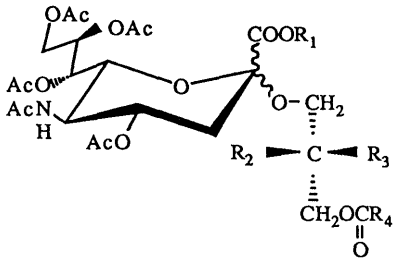
Chikako SHIMIZU, Naoki OHTA, and Kazuo ACHIWA*

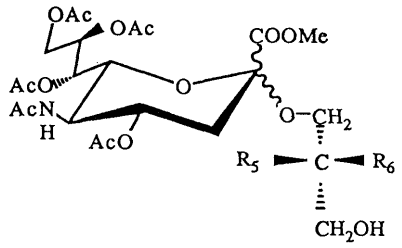
School of Pharmaceutical Sciences, University of Shizuoka, 395 Yada, Shizuoka 422, Japan. *Received March 19, 1990*

New 1-acyl-sialosyl-glycerol derivatives (1a—dα, 1a—dβ, 2α, 2β, which mimic the structure of the capusular polysaccharide of group C meningococcal were synthesized by the use of a chiral glycerol derivative, and were found to have phospholipases A_2 and C inhibitory activities. Furthermore, syntheses of 2-palmitoyl-sialosyl-glycerol derivative (4α, 4β, 5α, 5β), galactosyl-glycerol derivative (6), and sialosyl-galactosyl-glycerol derivative (7) were carried out to examine the difference between these activities. Among these sialosyl derivatives, 3-palmitoyl-sialosyl-glycerol derivatives (1—3α, 1—3β) demonstrated the most potent inhibitory activities.

Keywords sialosyl-glycerol derivative; phospholipase A_2 inhibitor; phospholipase C inhibitor; galactosyl-glycerol derivative; sialosyl-galactosyl-glycerol derivative

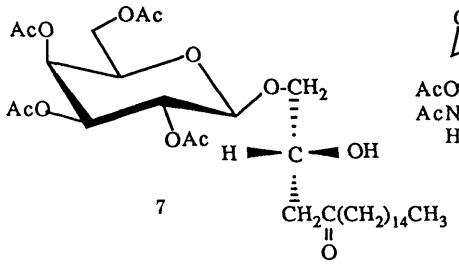
Capsular polysaccharides are located on the surface of the bacterial cell wall. Therefore, they are important agents in bacterial pathogenesis, and they also interact directly with the host's immune system. The capusular polysaccharide of group C meningococcal, whose structure was determined by Gotshlich and coworkers,[1] includes an α (2→9) linked homopolymer of sialic acid and phosphoglycerolipid. We conducted synthesis studies on biologically active new compounds by modifying the cell wall structures of gram negative bacteria.[2] As an extension of these studies, we have focused our attention on a polysaccharide involving sialic acid which plays important roles in various phenomena in living organisms. We synthesized sialosyl derivatives to search into a lead compound for medicines. In a recent communication, we described the novel syntheses of (*S*)- and (*R*)-3-*O*-acyl-1-*O*-sialosyl glycerol derivatives (**1a—dα**, **1a—dβ**, **2α**, **2β**, **3α**, **3β**: Fig. 1) which were expected to produce phospholipases A_2 and C inhibitory activities.[3] This paper describes these results in detail, as well as the syntheses of new compounds, (*S*)- and (*R*)-2-*O*-palmitoyl-1-*O*-sialosyl-glycerol (**4α**, **4β**, **5α**, **5β**: Fig. 1), (*S*)-1-*O*-galactosyl-3-*O*-palmitoyl-glycerol (**6**: Fig. 1) and





1aα, 1aβ : R_1=Me, R_2=H, R_3=OH, R_4=-$(CH_2)_{14}CH_3$
1bα, 1bβ : R_1=Me, R_2=H, R_3=OH, R_4=-$(CH_2)_{10}CH_3$
1cα, 1cβ : R_1=Me, R_2=H, R_3=OH, R_4=-$(CH_2)_6CH_3$
1dα, 1dβ : R_1=Me, R_2=H, R_3=OH, R_4=-$C(CH_2)_3CH_3$ (CH_2CH_3)
2α, 2β : R_1=Me, R_2=OH, R_3=H, R_4=-$(CH_2)_{14}CH_3$
3α, 3β : R_1=H, R_2=H, R_3=OH, R_4=-$(CH_2)_{14}CH_3$

4α, 4β : R_5=-$C(CH_2)_{14}CH_3$ (O), R_6=H
5a, 5b : R_6=H, R_6=-$C(CH_2)_{14}CH_3$ (O)



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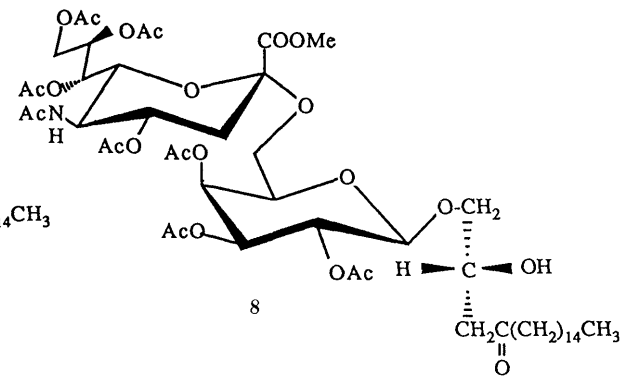

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Fig. 1

(*S*)-3-*O*-palmitoyl-1-*O*-sialosylgalactosyl-glycerl derivatives (**7**: Fig. 1) in order to clarify the influence of such structural changes.

Synthesis of glycosyl acceptors, glycerol derivatives, was carried out in Chart 1. (*S*)-1-*O*-Acetyl-2-*O*-benzylglycerol (**8**), used as a starting material,[4] was treated with trityl chloride and pyridine at 80 °C to produce a tritylated compound (**9**) in 72.5% yield. Deacetylation of **9** was carried out with NH_4OH–MeOH (1 : 10) at room temperature to afford the 1-hydroxyl compound (**10**), as the intermediate of (*S*)- and (*R*)-glycosyl acceptor, in 77.4% yield. Acylation of **9** with a variety of acyl groups proceeded smoothly. Compound (**9**) was acylated with hexadecanoyl chloride, dodecanoyl chloride, octanoyl chloride, and α-ethylhexanoyl chloride in the presence of triethylamine at room temperature to produce **11a** (85.0%), **11b** (93.7%), **11c** (88.8%), and **11d** (86.0%) respectively. The protective trityl groups of **11a—d** were removed by 80% AcOH at 80 °C to obtain glycosyl acceptors of (*S*)-3-acyl-sialosyl-(galactosyl)-glycerol derivatives (**1a—dα**, **1a—dβ**, **3α**, **3β**, **6**, **7**), **12a** (74.6%), **12b** (80.3%), **12c** (85.8%), and **12d** (73.9%), respectively. The glycosyl acceptors of (*R*)-sialosyl-glycerol derivatives (**2α**, **2β**, **4α**, **4β**) were synthesized as follows. The 1-hydroxyl group of **10** was protected with monochloroacetyl chloride and triethylamine at room temperature to afford **13** in a 91.5% yield. The trityl group of **13** was removed with 80% AcOH to produce the 3-hydroxyl compound (**14**), glycosyl acceptor of (*R*)-2-acyl-sialosyl-glycerol derivatives (**4α**, **4β**) in a 69.0% yield. Treatment of **14** with hexadecanoyl chloride and triethylamine afforded the acylated compound (**15**) in a 70.1% yield. Demonochloroacetylation was carried out with diisopropylethylamine and thiourea in tetrahydrofuran (THF) to give the (*R*)-glycosyl acceptor (**16**) of **2α** and **2β** in a 92.7% yield. The glycosyl acceptor of (*S*)-2-acyl-sialosyl-glycerol derivatives (**5α**, **5β**) was obtained in two steps from the starting material (**8**). The 3-hydroxyl group of **8** was protected with a *tert*-butyldimethylsilyl group by use of *tert*-butyldimethylsilyl chloride and triethylamine to obtain the silylated compound (**17**) in an 84.0% yield. The 1-acetyl group of **17** was removed by KOH–MeOH (1 : 10) to give the 1-hydroxyl derivative (**18**), glycosyl acceptor of **5α** and **5β**.

As a glycosyl donor, 5-acetamido-2-chloro-4,7,8,9-tetra-*O*-acetyl-D-*glycero*-D-*galacto*-2-nonulosonic acid methyl ester (**19**), prepared from *N*-acetylneuraminic acid in three steps,[5] was used for glycosylation of all sialosyl-glycerol derivatives except **3α** and **3β**. The glycosyl donor of **3α** and **3β** was compound (**22**), the benzyl ester type of **19** which could be removed by hydrogenolysis in the latter step of the synthetic route.

The synthetic route of 3-acyl-sialosyl-glycerol derivatives is shown in Chart 2. Glycosilation of the glycosyl acceptor (**12a—d**) with the glycosyl donor (**19**) in the presence of $Hg(CN)_2$–$HgBr_2$–Molecular Sieves 4A (MS4A) in CH_2Cl_2 at room temperature for 4 d produced the sialosyl-glycerol derivatives (**20aα—dβ**) as a mixture of anomers. Separation by preparative thin layer chromatography ($CHCl_3$: MeOH =

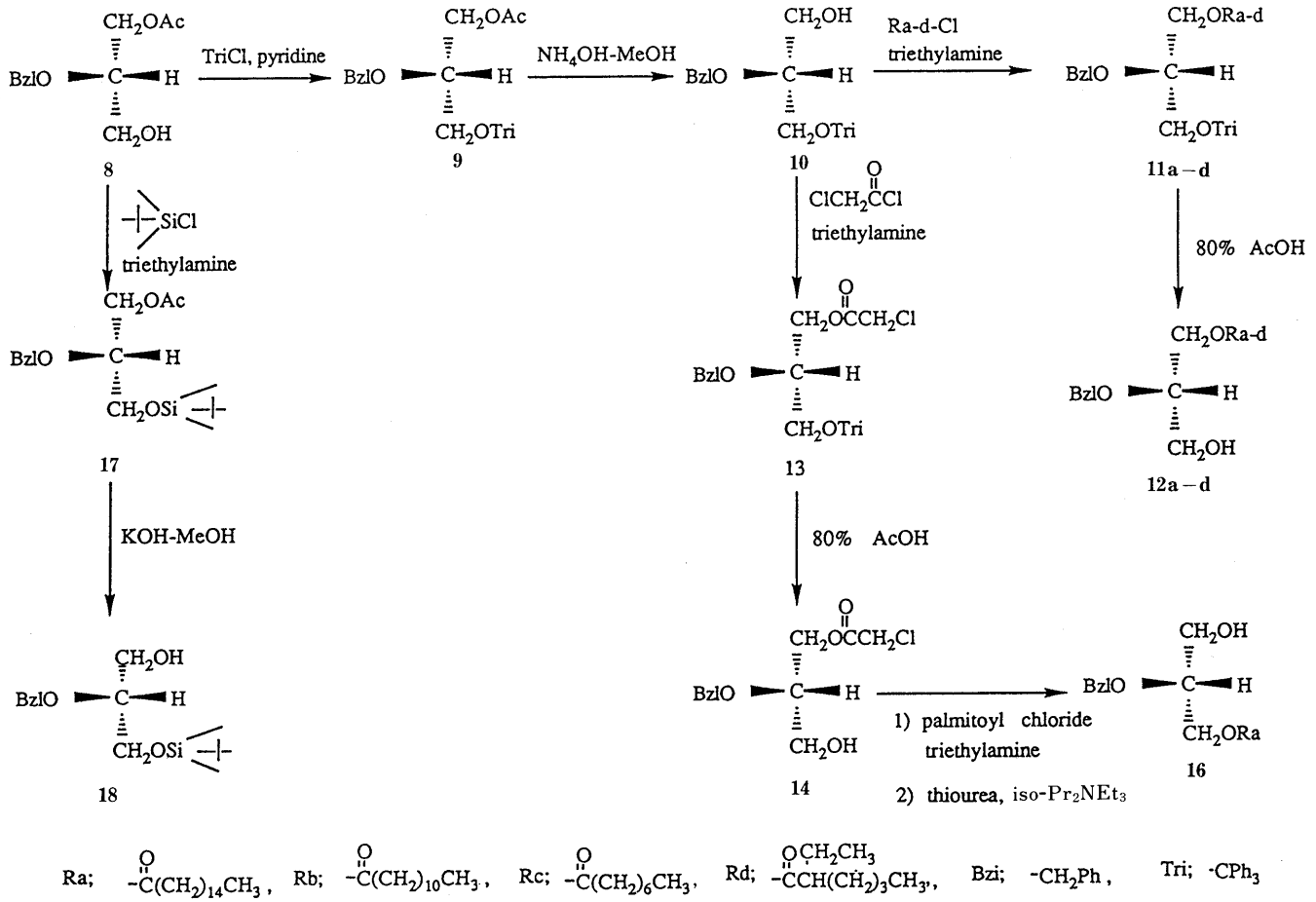
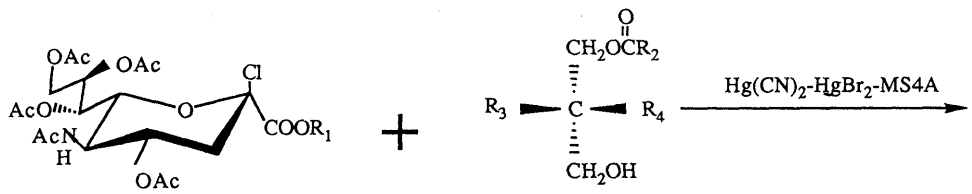
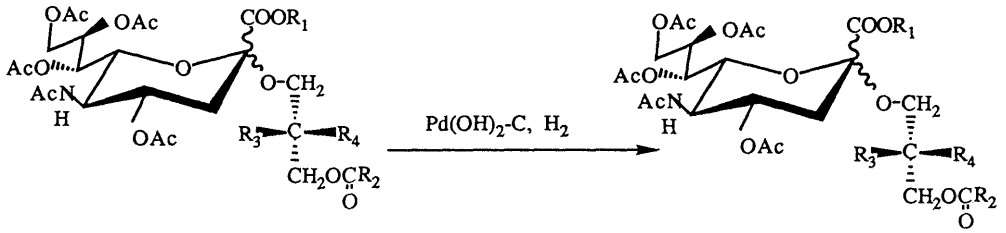


Chart 1



19 : R_1=Me
22 : R_1=-CH_2Ph

12a : R_2=-$(CH_2)_{14}CH_3$, R_3=-OCH_2Ph, R_4=H
12b : R_2=-$(CH_2)_{10}CH_3$, R_3=-OCH_2Ph, R_4=H
12c : R_2=-$(CH_2)_6CH_3$, R_3=-OCH_2Ph, R_4=H
12d : R_2=-CH($(CH_2)_3CH_3$)CH_2CH_3, R_3=-OCH_2Ph, R_4=H
16 : R_2=-$(CH_2)_{14}CH_3$, R_3=H, R_4=-OCH_2Ph



20aα, 20aβ : R_1=Me, R_2=-$(CH_2)_{14}CH_3$, R_3=H, R_4=-OCH_2Ph
20bα, 20bβ : R_1=Me, R_2=-$(CH_2)_{10}CH_3$, R_3=H, R_4=-OCH_2Ph
20cα, 20cβ : R_1=Me, R_2=-$(CH_2)_6CH_3$, R_3=H, R_4=-OCH_2Ph
20dα, 20dβ : R_1=Me, R_2=-CH($(CH_2)_3CH_3$)CH_2CH_3, R_3=H, R_4=-OCH_2Ph
21α , 21β : R_1=Me, R_2=-$(CH_2)_{14}CH_3$, R_3=-OCH_2Ph, R_4=H
23α , 23β : R_1=-CH_2Ph, R_2=-$(CH_2)_{14}CH_3$, R_3=H, R_4=-OCH_2Ph

1aα, 1aβ : R_1=Me, R_2=-$(CH_2)_{14}CH_3$, R_3=H, R_4=-OH
1bα, 1bβ : R_1=Me, R_2=-$(CH_2)_{10}CH_3$, R_3=H, R_4=-OH
1cα, 1cβ : R_1=Me, R_2=-$(CH_2)_6CH_3$, R_3=H, R_4=-OH
1dα, 1dβ : R_1=Me, R_2=-CH($(CH_2)_3CH_3$)CH_2CH_3, R_3=H, R_4=-OH
2α , 2β : R_1=Me, R_2=-$(CH_2)_{14}CH_3$, R_3=-OH, R_4=H
3α , 3β : R_1=H, R_2=-$(CH_2)_{14}CH_3$, R_3=H, R_4=-OH

Chart 2

20 : 1) afforded **20a—dα** (**20aα**, 26.9%; **20bα**, 10.8%; **20cα**, 15.6%; **20dα**, 27.0%) and **20a—dβ** (**20aβ**, 32.4%; **20bβ**, 11.5%; **20cβ**, 17.1%; **20dβ**, 23.5%). The anomeric stereochemistry of **20a—dα** and **20a—dβ** was determined by chemical shifts of 3-H_{eq} of the proton nuclear magnetic resonance (^{1}H-NMR) spectrum. It is known that for α anomers the chemical shift of 3-H_{eq} varies between δ 2.6—2.8, while for β anomers that of 3-H_{eq} are δ 2.1—2.5.[6] 3-H_{eq} signals of **20a—dα** were 2.62, 2.61, 2.61, 2.62 ppm, respectively (ranges of α glycoside). In the case of **20a—dβ**, these signals overlapped with the methylene proton signals of fatty acids in ^{1}H-NMR spectrum. Therefore, the anomeric configuration of **20a—dβ** as determined by the fact that the 3-H_{eq} signals of **20a—dβ** were not observed downfield from 2.6 ppm, and their other signals supported the structure of **20a—dβ**. The protective benzyl group of **20a—dα** and **20a—dβ** was cleaved by hydrogenation in the presence of 30% $Pd(OH)_2$–C in MeOH to yield (*S*)-sialosyl-glycerol derivatives, **1a—dα** (**1aα**, 71.2%, **1bα**, 95%; **1cα**, 95%; **1dα**, 82%) and **1a—dβ** (**1aβ**, 74.2%; **1bβ**, 87%; **1cβ**, 96%; **1dβ**, 85%).

Glycosilation of the (*R*)-glycosyl acceptor (**16**) and the chloride (**19**) was carried out as described for **20a—dαβ** to afford (*R*)-sialosyl-glycerol derivatives (**21α**, 24.6%; **21β**, 20.9%). Each of **21α** and **21β** were converted to debenzylated compounds (**2α** and **2β**) by usual hydrogenolysis with yields of 86.2% and 84.8%, respectively.

Similarly, the glycerol derivative (**12a**) was glycosylated with the benzyl ester donor (**22**) to obtain **23α** and **23β** (**23α**, 22.2%; **23β**, 17.7%). The two protective benzyl groups of **23α** and **23β** were removed by hydrogenolysis in the presence of 30% $Pd(OH)_2$–C to afford the free carboxylic acid derivatives (**3α**, quant.; **3β**, 96.2%).

Syntheses of 2-acyl-sialosyl-glycerol derivatives (**4α**, **4β**, **5α**, **5β**) were shown in Chart 3. Glycosylation of the silyl derivative (**18**) with the chloride (**19**) in the presence of $Hg(CN)_2$–$HgBr_2$–MS4A afforded the sialosyl-silylglycerol derivatives (**24α**, 11.2%; **24β**, 8.8%). The benzyl groups of **24α** and **24β** were smoothly removed by hydrogenolysis with 30% $Pd(OH)_2$. Chemical yields of the debenzylated compounds (**25α**, **25β**) were 77.0% and 85.5%, respectively. The 2-hydroxyl groups of **25α** and **25β** were acylated with palmitic acid, 1,3-dicyclohexylcarbodiimide (DCC), and 4-dimethylaminopyridine (DMAP), and then the *tert*-butyldimethylsilyl group was selectively removed by aqueous hydrogen fluoride in CH_3CN–$CHCl_3$ to **4α** and **4β** (**4α**, 24.7%; **4β**, 22.5%), respectively.

The monochloroacetyl glycosyl acceptor (**14**) and the chloride (**19**) were converted to sialosyl-glycerol derivatives (**27α** and **27β**) *via* **26α** and **26β** exactly as described for **18**+**19**→**25α**+**25β** (**14**+**19**→**26α**+**26β**: **26α**, 2.8%; **26β**, 16.4%; **26**→**27**: **26α**, 34.0%; **26β**, 50.4%), respectively. The glycerol-2-hydroxyl group of **27α** and **27β** was acylated with palmitic acid, DCC, and DMAP, and then the monochloroacetyl group was selectively removed with diisopropylethylamine and thiourea to yield **5α** and **5β** (**5α**, 16.9%; **5β**, 14.9%; **26**→**5**).

The synthetic routes of the galactosyl-glycerol derivative (**6**) and the sialosyl-galactosyl-glycerol derivative (**7**) are shown in Chart 4. Glycosylation was achieved by use of

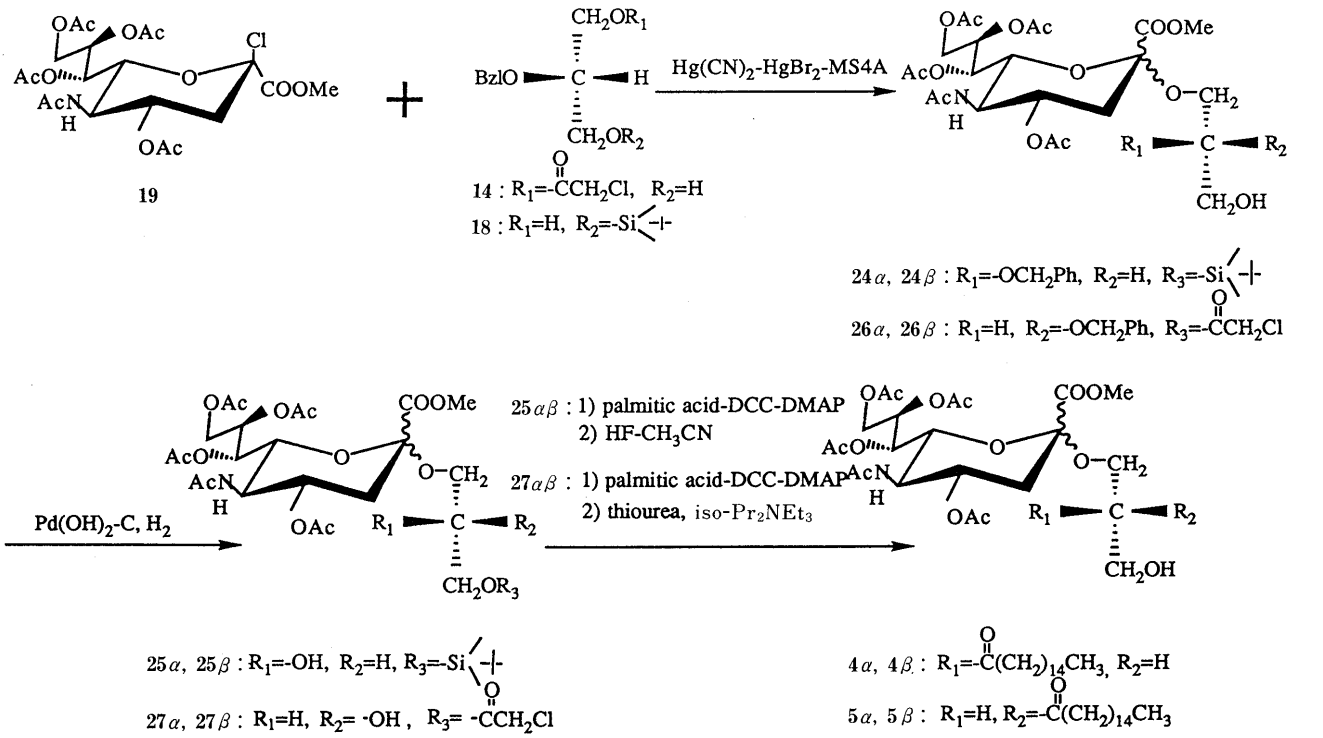


Chart 3

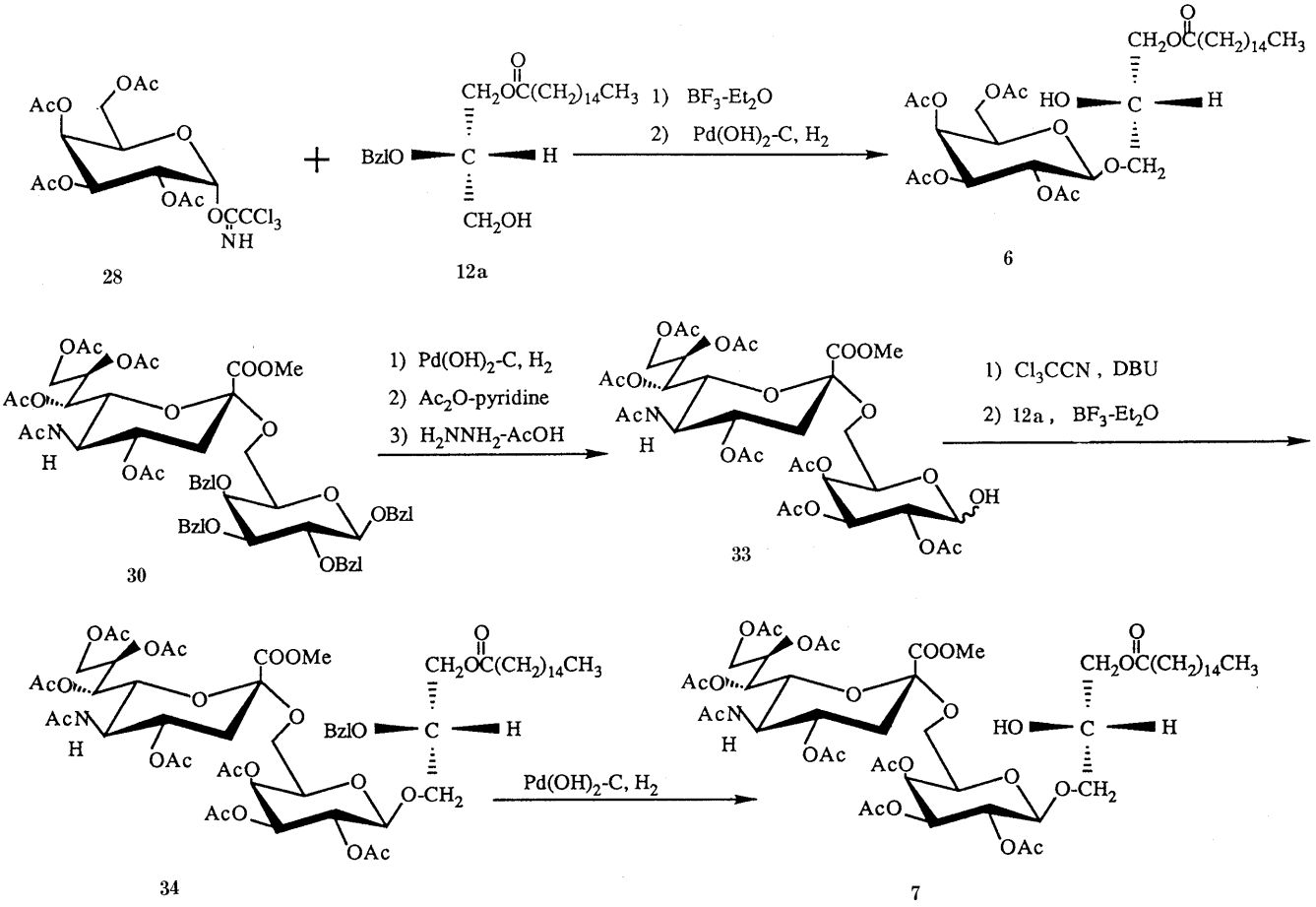


Chart 4

the imidate method. With the glycosyl donor, the galactosyl imidate (**28**), prepared from D-galactose in three steps, was glycosylated from the glycerol derivative (**12a**) in the presence of BF_3–Et_2O to give the galacto-glycerol derivative (**29**) in a 53.9% yield. Hydrogenolysis of **29** was performed with a catalyst of $Pd(OH)_2$–C to obtain **6** in

93.6% yield. An α (2→6)-linked sialosyl-galactosyl derivative (**30**) was obtained by glycosylation of 1,2,3,4-*tetra*-*O*-benzyl-D-galactose, prepared efficiently from D-galactose with chloride (**19**). The disaccharide was hydrogenated in the presence of $Pd(OH)_2$–C to afford the tetrahydroxyl compound (**31**), and then acetylated with acetic anhydride and pyridine to produce a nonaacetyl compound (**32**). Selective deacetylation at the anomeric position of the compound (**32**) was achieved with hydrazine acetate to produce the 1-hydroxyl compound (**33**). Compound (**33**) was transformed into the imidate (**34**) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU)–trichloroacetonitril as a glycosyl acceptor. Glycosilation of the glycerol derivative (**12a**) with **34** was performed by treatment of BF_3–Et_2O to yield the sialosyl-galactosyl-glycerol derivative (**35**) in a 14% yield (**33**→**35**). Hydrogenolysis of **35** was carried out with $Pd(OH)_2$–C to produce **7** in 81% yield. The structures of all compounds were characterized by ^{1}H-NMR spectroscopy, as well as infrared (IR) spectroscopy, elemental analyses, and fast-atom bombardment (FAB) mass spectroscopy.

The biological effects[7] (phospholipases A_2 and C inhibitions) of all compounds (**1a**—**dα**, **1a**—**dβ**, **2**—**5α**, **2**—**5β**, **6**, **7**) were tested. 3-Palmitoyl-sialosyl-glycerol derivatives (**1**—**3α**, **1**—**3β**) and 2-palmitoyl derivative (**4α**) possessed the strongest activities, while the 2-palmitoyl derivatives (**4β**, **5α**, **5β**), the galactosyl-glycerol derivative (**6**), and the sialosyl-galactosyl-glycerol derivative (**7**) showed little or no inhibitory activity.

Experimental

All melting points were determined with a micro-melting point apparatus (Yanagimoto) and are uncorrected. Optical rotations were measured on a JASCO-DIP-140 digital polarimeter. IR spectra were measured on JASCO A-202 and JASCO IR-810 infrared spectrophotometers. ^{1}H-NMR spectra were recorded on JEOL JNM-FX90Q (90 MHz), JEOL JNM-270GX (270 MHz), and JEOL JNM-500GX (500 MHz) spectrophotometers using tetramethylsilane (TMS) as an internal standard. Chemical shifts were recorded in values (δ) downfield from TMS, and the abbreviations of signal patterns are as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Thin layer chromatography (TLC) was performed on silica gel (Kieselgel $60F_{254}$ on aluminium sheet, Merck). All compounds were located by spraying with sulfuric acid and heating on a hot plate. Preparative TLC was performed on the preparative layer chromatography plate (Kieselgel $60F_{254}$ 2 and 0.5 mm, Merck). Column chromatography was performed on silica gel (Kieselgel 60, 70—230 mesh, Merck).

(*S*)-1-*O*-Acetyl-2-*O*-benzyl-3-*O*-tritylglycerol (9) Trityl chloride (8.76 g, 3.14×10^{-2} mol) was added to a solution of (*S*)-1-*O*-acetyl-2-*O*-benzylglycerol (**8**, 4.70 g, 2.09×10^{-3} mol) in dry pyridine (50 ml). The mixture was heated at 80 °C for 3 h, diluted with $CHCl_3$ (200 ml), and washed with saturated aqueous $CuSO_4$ and brine. The organic phase was concentrated to dryness and the residue was purified on a column of silica gel ($CHCl_3$: *n*-hexane = 10 : 1) to produced **9** (7.09 g, 72.5%) as colorless oil. $[\alpha]_D$ +11.3° (c = 1.98, $CHCl_3$). IR (neat): 1740, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.97 (3H, s, $-COCH_3$), 4.60 (2H, s, $-CH_2Ph$), 7.20—7.53 (20H, m, phenyl × 4).

(*R*)-2-*O*-Benzyl-1-*O*-tritylglycerol (10) **9** (753 mg, 1.61×10^{-3} mol) in NH_4OH–MeOH (1 : 10) (50 ml) was stirred at room temperature for 15 h. The resulting mixture was evaporated to dryness and subjected to column chromatography on silica gel ($CHCl_3$) to afford **10** (530 mg, 77.4%) as a colorless solid. $[\alpha]_D$ +22.5° (c = 0.58). IR (neat): 3450, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.24—3.28 (2H, s, $-CH_2OH$), 4.57 (2H, d, J = 4.4 Hz, $-CH_2Ph$), 7.06—7.54 (20H, m, phenyl × 4).

General Procedure for Syntheses of (*S*)-1-*O*-Acyl-2-*O*-benzyl-3-*O*-tritylglycerol (11a—d) Acyl chloride (8.69×10^{-2} mol) was added to a solution of **10** (30.8 g, 7.25×10^{-2} mol) and triethylamine (11.0 g, 1.09×10^{-1} mol) in dry CH_2Cl_2 (200 ml) at 0 °C, and then stirred at room temperature for 15 h. The solution was washed with brine, dried ($MgSO_4$), and purified on silica gel ($CHCl_3$: *n*-hexane = 10 : 1) to produce **11a**—**d** (**11a**, 85.0%; **11b**, 93.8%; **11c**, 88.8%; **11d**, 86.0%) as colorless oils.

11a: $[\alpha]_D$ +12.6° (c = 0.66, $CHCl_3$). IR (neat): 1740, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J = 6.1 Hz, $-CO(CH_2)_{14}\underline{CH_3}$), 1.26 (26H, s, $-COCH_2(\underline{CH_2})_{13}CH_3$), 2.22 (2H, t, J = 7.3 Hz, $-COCH_2(\underline{CH_2})_{13}CH_3$), 7.14—7.52 (20H, m, phenyl × 4).

11b: $[\alpha]_D$ +11.6° (c = 1.16, $CHCl_3$). IR (neat): 1740, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.87 (3H, t, J = 6.1 Hz, $-CO(CH_2)_{10}\underline{CH_3}$), 1.25 (18H, br s, $-COCH_2(\underline{CH_2})_9CH_3$), 2.23 (2H, t, J = 7.3 Hz, $-COCH_2(\underline{CH_2})_9CH_3$), 7.12—7.53 (20H, m, phenyl × 4).

11c: $[\alpha]_D$ +4.7° (c = 1.28, $CHCl_3$). IR (neat): 1740, 700 cm^{-1}). ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J = 6.6 Hz, $-CO(CH_2)_6\underline{CH_3}$), 1.26 (10H, br s, $-COCH_2(\underline{CH_2})_5CH_3$), 2.24 (2H, t, J = 7.3 Hz, $-COCH_2(\underline{CH_2})_5CH_3$), 7.16—7.55 (20H, m, phenyl × 4).

11d: $[\alpha]_D$ +9.3° (c = 0.74, $CHCl_3$). IR (neat): 1735, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.89 (6H, br t, J = 6.8 Hz, $-CH_2\underline{CH_3}$ × 2), 1.09—1.15 (8H, $-CHCH_2\underline{CH_3}$, $-CH(CH_2)_3\underline{CH_3}$), 7.04—7.55 (20H, m, phenyl × 4).

General Procedure for Syntheses of (*S*)-1-*O*-Acyl-2-*O*-benzylglycerol (12a—d) A solution of **11a**—**d** (6.17×10^{-2} mol) in 80% acetic acid (300 ml) was heated at 80 °C for 1 h, evaporated to dryness, and purified on a column of silica gel ($CHCl_3$) to afford **12a**—**d** (**12a**, 74.6%; **12b**, 80.3%; **12c**, 85.8%; **12d**, 73.9%) as colorless oils.

12a: $[\alpha]_D$ −4.8° (c = 1.16, $CHCl_3$). IR (neat): 3470, 1740, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J = 6.1 Hz, $-CO(CH_2)_{14}\underline{CH_3}$), 1.25 (26H, s, $-COCH_2(\underline{CH_2})_{13}CH_3$), 2.32 (2H, t, J = 7.6 Hz, $-COCH_2(\underline{CH_2})_{13}CH_3$), 7.34 (5H, s, phenyl).

12b: $[\alpha]_D$ −5.7° (c = 0.58, $CHCl_3$). IR (neat): 3450, 1740, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J = 6.3 Hz, $-CO(CH_2)_{10}\underline{CH_3}$), 1.25 (18H, $-COCH_2(\underline{CH_2})_9CH_3$), 2.30 (2H, t, J = 8.6 Hz, $-COCH_2(\underline{CH_2})_9CH_3$), 4.62 (2H, s, $-CH_2Ph$), 7.30 (5H, s, phenyl).

12c: $[\alpha]_D$ −6.4° (c = 0.28, $CHCl_3$). IR (neat): 3450, 1730, 690 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J = 6.3 Hz, $-CO(CH_2)_6\underline{CH_3}$), 1.27 (10H, s, $-COCH_2(\underline{CH_2})_6CH_3$), 2.32 (2H, t, J = 7.6 Hz, $COCH_2(\underline{CH_2})_6CH_3$), 7.33 (5H, s, phenyl).

12d: $[\alpha]_D$ −8.0° (c = 1.00, $CHCl_3$). IR (neat): 3450, 1740, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 0.89 (6H, t, J = 6.8 Hz, $-CH_2\underline{CH_3}$ × 2), 1.10—1.16 (10H, m, $-CH(CH_2)_3\underline{CH_3}$, $-CHCH_2\underline{CH_3}$). 7.35 (5H, s, phenyl).

(*S*)-2-*O*-Benzyl-1-*O*-monochloroacetyl-3-*O*-tritylglycerol (13) To **10** (990 mg, 2.33×10^{-3} mol) and triethylamine (354 mg, 3.50×10^{-3} mol) in dry CH_2Cl_2 (30 ml), monochloroacetyl chloride (316 mg, 2.80×10^{-3} mol) was added at 0 °C under argon. The mixture was stirred at room temperature for 3 h, washed with brine, and dried ($MgSO_4$). The residue was chromatographed on silica gel ($CHCl_3$) to produce **13** as a colorless oil (1.07 g, 91.5%). $[\alpha]_D$ +10.7° (c = 2.26, $CHCl_3$). IR (neat): 1740, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.92 (2H, s, $-COCH_2Cl$), 4.58 (2H, s, $-CH_2Ph$), 7.22—7.45 (20H, m, phenyl × 4).

(*S*)-2-*O*-Benzyl-1-*O*-monochloroacetylglycerol (14) **13** (1.00 g, 2.00×10^{-3} mol) in 80% acetic acid (10 ml) was heated at 80 °C for 1 h, evaporated to dryness, and purified on a column of silica gel ($CHCl_3$) to afford **14** (356 mg, 69.0%) as a colorless oil. $[\alpha]_D$ −3.1° (c = 1.56, $CHCl_3$). IR (neat): 3450, 1750, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.99 (2H, s, $-COCH_2Cl$), 4.62 (2H, $-CH_2Ph$), 7.27 (5H, s, phenyl).

(*S*)-2-*O*-Benzyl-3-*O*-hexadecanoyl-1-*O*-monochloroacetylglycerol (15) Palmitoyl chloride was added to a solution of **14** (1.34 g, 5.18×10^{-3} mol) and triethylamine (1.05 g, 1.04×10^{-2} mol) in dry CH_2Cl_2 (30 ml) at 0 °C under argon. The resulting mixture was stirred at room temperature for 15 h, washed with brine, and dried. Purification by the residue was achieved with a column of silica gel ($CHCl_3$: *n*-hexane = 10 : 1) to yield **15** (1.81 g, 70.1%) as a colorless oil. $[\alpha]_D$ +2.8° (c = 1.60, $CHCl_3$). IR (neat): 1740, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J = 6.1 Hz, $-CO(CH_2)_{14}\underline{CH_3}$), 1.25 (26H, s, $-COCH_2(\underline{CH_2})_{13}CH_3$), 3.99 (2H, s, $-COCH_2Cl$), 4.64 (2H, s, $-CH_2Ph$), 7.26 (5H, s, phenyl).

(*R*)-2-*O*-Benzyl-1-*O*-hexadecanoylglycerol (16) A mixture of **15** (1.72 g, 3.47×10^{-3} mol), diisopropylethylamine (538 mg, 4.16×10^{-3} mol), and thiourea (317 mg, 4.16×10^{-3} mol) in dry THF (30 ml) was refluxed for 2 h. The resulting mixture was filtered and the filtrate was concentrated to dryness. The residue was chromatographed on silica gel ($CHCl_3$) to produce **16** (1.35 g, 92.7%) as a colorless oil. $[\alpha]_D$ +4.7° (c = 4.13, $CHCl_3$). IR (neat): 3445, 1740, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J = 6.1 Hz, $-CO(CH_2)_{14}\underline{CH_3}$), 1.25 (26H, s, $-CO(CH_2)_{14}CH_3$), 2.32 (2H, t, J = 7.6 Hz, $-COCH_2(\underline{CH_2})_{13}CH_3$), 7.34 (5H, s, phenyl).

(*R*)-1-*O*-Acetyl-2-*O*-benzyl-3-*O*-*tert*-butyldimethylsilylglycerol (17) *tert*-Butyldimethylsilyl chloride was added to a solution of **8** (6.04 g, 2.69×10^{-2} mol) and triethylamine (3.39 g, 3.35×10^{-2} mol) in dry CH_2Cl_2

(50 ml) at 0 °C under argon. The mixture was stirred at room temperature for 3 h, washed with brine, and dried ($MgSO_4$). The organic phase was evaporated to dryness and the residue was chromatographed on silica gel ($CHCl_3$) to afford **17** (7.65 g, 84.0%) as a colorless oil. $[\alpha]_D$ +15.6° (c=1.78, $CHCl_3$). IR (neat): 1745, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.075 (6H, s, $-Si(CH_3)_2$), 0.89 (9H, s, $-SiC(CH_3)_3$), 2.04 (3H, s, $-CH_2Ph$), 4.65 (2H, s, $-CH_2Ph$), 7.32—7.34 (5H, m, phenyl).

(*R*)-2-*O*-Benzyl-1-*O*-*tert*-butyldimethylsilylglycerol (18) **17** (6.93 g, 2.05×10^{-2} mol) as described for **10** gave **18** (5.62 g, 92.7%) as a colorless oil. $[\alpha]_D$ +17.3° (c=1.00, $CHCl_3$). IR (neat): 3465, 3400, 1750, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.090 (6H, s, $-Si(CH_3)_2$), 0.90 (9H, s, $-SiC(CH_3)_3$), 4.60, 4.68 (2H, d×2, J=11.9 Hz, $-CH_2Ph$), 7.29 (5H, s, phenyl).

General Procedure for the Syntheses of 2-*O*-Benzyl 3-*O*-acyl-1-*O*-[methyl(5-acetamido-4,7,8,9-*tert*-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]glycerols (20a—dα, 20a—dβ, 21α, 21β) Glycerol derivatives (**12a—d**, **16**), pulverized MS4A (3 g), $Hg(CN)_2$ (1.26 g, 4.99×10^{-3} mol), and $HgBr_2$ (771 mg, 2.14×10^{-3} mol) were dried by the use of a high vacuum-pump for 2 h. The mixture was dissolved in dry CH_2Cl_2 (30 ml) and stirred at room temperature for 1 h under argon. 5-Acetamido-2-chloro-4,7,8,9-tetra-*O*-acetyl-2,3,5-trideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosonic acid methyl ester (**19**, 3.64 g, 7.13×10^{-3} mol) in dry CH_2Cl_2 (20 ml) was added by drops to the mixture within 1 h at room temperature, and the suspension was then stirred for 4 d. The resulting mixture was diluted with CH_2Cl_2, filtered, and the filtrate was washed with aqueous 10% KI and brine. The organic phase was dried ($MgSO_4$), concentrated to dryness, and purified on a column of silica gel ($CHCl_3$: MeOH = 40 : 1) to yield **20a—dα**,**β** and **21α**,**β**. The anomeric mixture was further purified on preparative TLC ($CHCl_3$: MeOH = 20 : 1) to afford **20a—dα**, (**20a**α, 26.9%; **20b**α, 10.8%; **20c**α, 15.6%; **20d**α, 27.0%), **20a—dβ** (**20a**β, 32.4%; **20b**β, 11.5%; **20c**β, 17.1%; **20d**β, 23.5%), **21**α (24.6%), and **21**β (20.9%) as colorless, amorphous powders.

20aα: $[\alpha]_D$ −8.5° (c=1.16, $CHCl_3$). IR (neat): 3220, 1745, 1660, 1540, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=5.9 Hz, $-CO(CH_2)_{14}CH_3$), 1.25 (26H, s, $-COCH_2(CH_2)_{13}CH_3$), 1.88—2.14 (15H, m, $-COCH_3\times5$), 2.62 (1H, dd, J=4.6, 12.4 Hz, 3-H_{eq}), 3.76 (3H, s, $-COOCH_3$), 7.33 (5H, s, phenyl). Positive FAB-MS $(M+H)^+$ m/z: 894.

20bα: $[\alpha]_D$ −7.4° (c=1.24, $CHCl_3$). IR (neat): 3380, 1740, 1660, 1550, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.1 Hz, $-CO(CH_2)_{10}CH_3$), 1.25 (18H, s, $-CO(CH_2)_{10}CH_3$), 1.88—2.20 (15H, m, $-COCH_3\times5$), 2.61 (1H, dd, J=4.6, 12.4 Hz, 3-H_{eq}), 3.79 (3H, s, $-COOCH_3$), 7.29—7.51 (5H, m, phenyl). Positive FAB-MS $(M+H)^+$ m/z: 838.

20cα: $[\alpha]_D$ −18.2° (c=0.18, $CHCl_3$). IR (neat): 3395, 1745, 1660, 1540, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.87 (3H, t, J=6.1 Hz, $-CO(CH_2)_6CH_3$), 1.27 (10H, s, $-COCH_2(CH_2)_5CH_3$), 1.98—2.13 (15H, m, $-COCH_3\times5$), 2.20—2.48 (2H, m, $-COCH_2(CH_2)_5CH_3$), 2.61 (1H, dd, J=4.1, 13.1 Hz, 3-H_{eq}), 3.79 (3H, s, $COOCH_3$), 7.21—7.56 (5H, m, phenyl). Positive FAB-MS $(M+H)^+$ m/z: 782.

20dα: $[\alpha]_D$ −16.7° (c=0.06). IR (neat): 3270, 3360, 1750, 1660, 1540, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (6H, br t, J=6.8 Hz, $-CH_2CH_3\times2$), 1.26 (8H, br s, $-CHCH_2CH_3$, $-CH(CH_2)_3CH_3$), 1.98—2.13 (15H, m, $-COCH_3\times5$), 2.62 (1H, dd, J=4.6, 12.4 Hz, 3-H_{eq}), 3.79 (3H, s, $-COOCH_3$), 7.19—7.57 (5H, m, phenyl). Positive FAB-MS $(M+H)^+$ m/z: 782.

20aβ: $[\alpha]_D$ −5.5° (c=0.36, $CHCl_3$). IR (neat): 3390, 1750, 1660, 1540, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=5.9 Hz, $-CO(CH_2)_{14}CH_3$), 1.26 (26H, s, $-COCH_2(CH_2)_{13}CH_3$), 1.82—2.08 (15H, m, $-COCH_3\times5$), 3.80 (3H, s, $-COOCH_3$), 7.37—7.44 (5H, m, phenyl). Positive FAB-MS $(M+H)^+$ m/z: 894.

20bβ: $[\alpha]_D$ −6.6° (c=0.64, $CHCl_3$). IR (neat): 3395, 1750, 1670, 1590, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=5.6 Hz, $-CO(CH_2)_{10}CH_3$), 1.25 (18H, s, $-COCH_2(CH_2)_9CH_3$), 1.98—2.08 (15H, m, $-COCH_3\times5$), 3.79 (3H, s, $-COOCH_3$), 7.22—7.52 (5H, m, phenyl). Positive FAB-MS $(M+H)^+$ m/z: 838.

20cβ: $[\alpha]_D$ −10.7° (c=0.64, $CHCl_3$). IR (neat): 3400, 1750, 1670, 1540, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.87 (3H, t, J=6.1 Hz, $-CO(CH_2)_6CH_3$), 1.26 (10H, s, $-COCH_2(CH_2)_5CH_3$), 1.98—2.08 (15H, m, $-COCH_3\times5$), 3.80 (3H, s, $-COOCH_3$), 7.28—7.57 (5H, m, phenyl). Positive FAB-MS $(M+H)^+$ m/z: 782.

20dβ: $[\alpha]_D$ −8.2° (c=0.44, $CHCl_3$). IR (neat): 3390, 1740, 1680, 1520, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.89 (6H, br t, J=7.1 Hz, $-CH_2CH_3\times2$), 1.25 (8H, br s, $-CH(CH_2)_3CH_3$, $-CHCH_2CH_3$), 1.98—2.08 (15H, m, $-COCH_3\times5$), 3.79 (3H, s, $-COOCH_3$), 7.22—7.52 (5H, m, phenyl). Positive FAB-MS $(M+H)^+$ m/z: 782.

21α: $[\alpha]_D$ −10.8° (c=1.00, $CHCl_3$). IR (neat): 3205, 1740, 1660, 1540, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.1 Hz, $-CO(CH_2)_{14}CH_3$), 1.25 (26H, s, $-COCH_2(CH_2)_{13}CH_3$), 1.97—2.19 (15H, m, $-COCH_3\times5$), 2.61 (1H, dd, J=4.6, 12.7 Hz, 3-H_{eq}), 3.75 (3H, s, $-COCH_3$), 7.23—7.46 (5H, m, phenyl). Positive FAB-MS $(M+H)^+$ m/z: 894.

21β: $[\alpha]_D$ −7.0° (c=1.42, $CHCl_3$). IR (neat): 3260, 3350, 1740, 1662, 1540, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=5.9 Hz, $-CO(CH_2)_{14}CH_3$), 1.25 (26H, s, $-COCH_2(CH_2)_{13}CH_3$), 1.92—2.16 (15H, m, $-COCH_3\times5$), 2.34 (2H, t, J=5.6 Hz, $-COCH_2(CH_2)_{13}CH_3$), 3.75 (3H, s, $-COOCH_3$), 7.15—7.56 (5H, m, phenyl). Positive FAB-MS $(M+H)^+$ m/z: 894.

General Procedure for the Syntheses of 3-*O*-Acyl-1-*O*-[methyl(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]glycerols (1a—dα, 1a—dβ, 2α, 2β) A solution of (**20a—dα**, **20a—dβ**, **21α**, **21β**, 7.16×10^{-5} mol) in methanol (1 ml) was hydrogenated in the presence of 30% $Pd(OH)_2$ on carbon at room temperature for 2 h. The catalyst was filtered off and the filtrate was concentrated to dryness. The residue was purified on a column of silica gel ($CHCl_3$: MeOH = 20 : 1) to give **1a—dα** (**1a**α, 71.2%; **1b**α, 95%; **1c**α, 95%; **1d**α, 82%), **1a—dβ** (**1a**β, 74.2%; **1b**β, 87%; **1c**β, 96%; **1d**β, 85%), **2**α (86.2%), and **2**β (84.8%) as colorless, amorphous powders.

1aα: $[\alpha]_D$ −11.3° (c=0.50, $CHCl_3$). IR (neat): 3400, 1750, 1660, 1560 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.4 Hz, $-CO(CH_2)_{14}CH_3$), 1.26 (26H, s, $-COCH_2(CH_2)_{13}CH_3$), 1.89—2.14 (15H, m, $-COCH_3\times5$), 2.59 (1H, dd, J=4.9, 12.9 Hz, 3-H_{eq}), 3.81 (3H, s, $-COOCH_3$). Positive FAB-MS $(M+H)^+$ m/z: 804.

1bα: $[\alpha]_D$ −8.0° (c=0.64, $CHCl_3$). IR (neat): 3350, 1740, 1660, 1550 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=5.6 Hz, $-CO(CH_2)_{10}CH_3$), 1.26 (18H, s, $-COCH_2(CH_2)_9CH_3$), 1.84—2.19 (15H, m, $-COCH_3\times5$), 2.61 (1H, dd, J=4.4, 12.4 Hz, 3-H_{eq}), 3.82 (3H, s, $-COOCH_3$). Positive FAB-MS $(M+H)^+$ m/z: 748.

1cα: $[\alpha]_D$ −7.8° (c=0.52, $CHCl_3$). IR (neat): 3400, 1740, 1645, 1550 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=5.6 Hz, $-CO(CH_2)_6CH_3$), 1.26 (18H, s, $-COCH_2(CH_2)_5CH_3$), 1.89—2.15 (15H, m, $-COCH_3\times5$), 2.61 (1H, dd, J=4.9, 12.4 Hz, 3-H_{eq}), 3.81 (3H, s, $-COOCH_3$). Positive FAB-MS $(M+H)^+$ m/z: 692.

1dα: $[\alpha]_D$ −4.9° (c=0.56, $CHCl_3$). IR (neat): 3350, 1740, 1665, 1550 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.89 (6H, br t, J=7.3 Hz, $-CH_2CH_3\times2$), 1.26 (8H, br s, J=7.3 Hz, $-CH(CH_2)_3CH$, $-CHCH_2CH_3$), 1.89—2.14 (15H, m, $-COCH_3\times5$), 2.61 (1H, dd, J=4.6, 12.4 Hz, 3-H_{eq}), 3.81 (3H, s, $-COOCH_3$). Positive FAB-MS $(M+H)^+$ m/z: 692.

1aβ: $[\alpha]_D$ −12.6° (c=0.18, $CHCl_3$). IR (neat): 3360, 1750, 1660, 1550 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.4 Hz, $-CO(CH_2)_{14}CH_3$), 1.26 (26H, s, $-COCH_2(CH_2)_{13}CH_3$), 1.90—2.16 (15H, m, $-COCH_3\times5$), 3.81 (3H, s, $-COOCH_3$). Positive FAB-MS $(M+H)^+$ m/z: 804.

1bβ: $[\alpha]_D$ −10.0° (c=0.52, $CHCl_3$). IR (neat): 3355, 1740, 1660, 1555 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=5.6 Hz, $-CO(CH_2)_{10}CH_3$), 1.26 (18H, s, $-COCH_2(CH_2)_9CH_3$), 1.85—2.22 (15H, m, $-COCH_3\times5$), 3.80 (3H, s, $-COOCH_3$). Positive FAB-MS $(M+H)^+$ m/z: 748.

1cβ: $[\alpha]_D$ −5.1° (c=1.94, $CHCl_3$). IR (neat): 3400, 1740, 1650, 1540 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.1 Hz, $-CO(CH_2)_6CH_3$), 1.26 (10H, s, $-COCH_2(CH_2)_5CH_3$), 1.90—2.16 (15H, m, $-COCH_3\times5$), 3.81 (3H, s, $-COOCH_3$). Positive FAB-MS $(M+H)^+$ m/z: 692.

1dβ: $[\alpha]_D$ −6.0° (c=1.68, $CHCl_3$). IR (neat): 0.89 (6H, br t, J=6.8 Hz, $-CH_2CH_3\times2$), 1.26 (8H, br s, $-CH(CH_2)_3CH_3$, $-CHCH_2CH_3$), 1.90—2.16 (15H, m, $-COCH_3\times5$), 2.51 (1H, dd, J=4.6, 12.4 Hz, 3-H_{eq}), 3.80 (3H, s, $-COOCH_3$). Positive FAB-MS $(M+H)^+$ m/z: 692.

2α: $[\alpha]_D$ −3.6° (c=0.52, $CHCl_3$). IR (neat): 3390, 1740, 1665, 1540 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.1 Hz, $-CO(CH_2)_{14}CH_3$), 1.25 (26H, s, $-COCH_2(CH_2)_{13}CH_3$), 1.86—2.20 (15H, m, $-COCH_3\times5$), 2.36 (2H, t, J=7.1 Hz, $-COCH_2(CH_2)_{13}CH_3$), 2.60 (1H, dd, J=4.4, 12.6 Hz, 3-H_{eq}), 3.81 (3H, s, $-COOCH_3$). Positive FAB-MS $(M+H)^+$ m/z: 804.

2β: $[\alpha]_D$ −4.8° (c=0.30, $CHCl_3$). IR (neat): 3360, 1740, 1660, 1545 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.87 (3H, t, J=4.4 Hz, $-CO(CH_2)_{14}CH_3$), 1.25 (26H, s, $-COCH_2(CH_2)_{13}CH_3$), 1.89—2.42 (15H, m, $-COCH_3\times5$), 3.80 (3H, s, $-COOCH_3$). Positive FAB-MS $(M+H)^+$ m/z: 804.

(*S*)-2-*O*-Benzyl-1-*O*-[benzyl(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-3-*O*-hexadecanoylglycerol (23α, 23β) **12a** (242 mg, 5.75×10^{-4} mol), $Hg(CN)_2$ (204 mg, 8.08×10^{-4} mol), $HgBr_2$ (124 mg, 3.44×10^{-4} mol), MS4A (1 g), and 5-acetamido-2-chloro-4,7,8,9-tetra-*O*-acetyl-2,3,5-trideoxy-D-*glycero*-D-*galacto*-2-nonulosonic acid benzyl ester (799 mg, 1.19×10^{-3} mol) described for **20**α afforded **23**α (124 mg, 22.2%) and **23**β (99 mg, 17.7%) as colorless, amorphous powders.

23α: $[\alpha]_D$ −4.1° (c=1.38, $CHCl_3$). IR (neat): 3255, 3350, 1740, 1640, 1550, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=5.9 Hz, $-CO(CH_2)_{14}CH_3$), 1.26 (26H, s, $-COCH_2(CH_2)_{13}CH_3$), 1.91—2.17 (15H, m, $-COCH_3\times5$),

2.67 (1H, dd, J=4.6 Hz, 3-H$_{eq}$), 5.18 (2H, s, –COOCH$_2$Ph), 7.31, 7.34 (10H, s×2, phenyl×2), positive FAB-MS (M+H)$^+$ m/z: 970.

23β: $[\alpha]_D$ −6.4° (c=1.00, $CHCl_3$). IR (neat): 3395, 1740, 1680, 1520, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=5.9 Hz, –CO(CH$_2$)$_{14}$CH$_3$), 1.26 (26H, s, –COCH$_2$(CH$_2$)$_{13}$CH$_3$), 1.91—2.17 (15H, m, –COCH$_3$×5), 5.22 (2H, s, –COOCH$_2$Ph), 7.22—7.54 (10H, m, phenyl×2), positive FAB-MS (M+H)$^+$ m/z: 970.

(*S*)-1-*O*-(5-Acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosyl)-3-*O*-hexadecanoyl-glycerol (3α, 3β) A solution of **23**α and **23**β (33 mg, 3.40×10^{-5} mol) in MeOH (1 ml) was hydrogenated in the presence of 30% Pd(OH)$_2$–C at room temperature. The catalyst was filtered off and the filtrate was concentrated to dryness. The residue was chromatographed on silica gel ($CHCl_3$: MeOH = 30 : 1) to give **3**α (27 mg, quant.) and **3**β (23 mg, 96.2%), respectively.

3α: $[\alpha]_D$ +13.8° (c=0.26, $CHCl_3$). IR (neat): 3480, 1740, 1660, 1560 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, –CO(CH$_2$)$_{14}$CH$_3$), 1.26 (26H, s, –COCH$_2$(CH$_2$)$_{13}$CH$_3$), 1.92—2.16 (15H, m, –COCH$_3$×5), 2.35 (2H, t, J=7.3 Hz, –COCH$_2$(CH$_2$)$_{13}$CH$_3$), 5.97 (1H, d, J=9.6 Hz, –NH–). Positive FAB-MS (M+H)$^+$ m/z: 790.

3β: $[\alpha]_D$ −13.3° (c=0.36, $CHCl_3$). IR (neat): 3480, 1740, 1660, 1560 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=5.9 Hz, –CO(CH$_2$)$_{14}$CH$_3$), 1.26 (26H, s, –COCH$_2$(CH$_2$)$_{13}$CH$_3$), 1.92—2.16 (15H, m, –COCH$_3$×5), 2.35 (2H, t, J=7.3 Hz, –COCH$_2$(CH$_2$)$_{13}$CH$_3$), 2.54 (1H, dd, J=4.8, 13.2 Hz, 3-H$_{eq}$), 5.97 (1H, d, J=9.7 Hz, –NH–).

(*R*)-2-*O*-Benzyl-3-*O*-*tert*-butyldimethylsilyl-1-*O*-[methyl(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-nonulopyranosyl)onate]glycerol (24α, 24β) Glycerol derivative (**18**, 1.76 g, 5.94×10^{-3} mol), Hg(CN)$_2$ (1.82 g, 7.21×10^{-3} mol), HgBr$_2$ (1.11 g, 3.09×10^{-3} mol), and MS4A (6 g) described for **20**α gave **24**α (513 mg, 11.2%) and **24**β (401 mg, 8.8%) as colorless, amorphous powders.

24α: $[\alpha]_D$ −10.0° (c=0.60, $CHCl_3$). IR (neat); 3375, 1745, 1665, 1550, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.90 (9H, s, –SiC(CH$_3$)$_3$), 1.88—2.17 (15H, m, –COCH$_3$×2), 2.62 (1H, dd, J=4.4, 12.4 Hz, 3-H$_{eq}$). 3.75 (3H, s, –COOCH$_3$), 7.30—7.38 (5H, m, –CH$_2$Ph). Positive FAB-MS (M+H)$^+$ m/z: 770.

24β: $[\alpha]_D$ −6.1° (c=1.18, $CHCl_3$). IR (neat): 3400, 1740, 1660, 1550, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.90 (9H, s, –SiC(CH$_3$)$_3$), 1.86 (1H, t, J=12.8 Hz, 3-H$_{eq}$), 1.78—2.12 (15H, m, –COCH$_3$×5), 2.45 (1H, dd, J=4.8, 12.8 Hz, 3-H$_{eq}$), 3.78 (3H, s, –COOCH$_3$), 7.29—7.44 (5H, m, –CH$_2$Ph). Positive FAB-MS (M+H)$^+$ m/z: 770.

(*R*)-3-*O*-*tert*-Butyldimethylsilyl-1-*O*-[methyl(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-glycerol (25α, 25β) A solution of **24**α and **24**β (3.20×10^{-4} mol) in EtOH (3 ml) was hydrogenated in the presence of 30% Pd(OH)$_2$–C (25 mg) at room temperature, the reaction being monitored by TLC ($CHCl_3$: MeOH = 20 : 1, Rf=0.40). The catalyst was filtered off and concentrated to dryness. The residue was purified on a column of silica gel ($CHCl_3$: MeOH = 50 : 1) and further purified by preparative TLC ($CHCl_3$: MeOH = 20 : 1) to afford **25**α (167 mg, 77.0%) and **25**β (185 mg, 85.5%) as colorless, amorphous powders, respectively.

25α: $[\alpha]_D$ −10.0° (c=0.60, $CHCl_3$). IR (neat): 3430, 1740, 1660, 1540 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.08 (6H, s, –Si(CH$_3$)$_2$), 0.92 (9H, s, –SiC(CH$_3$)$_3$), 1.89—2.15 (15H, m, –COCH$_3$×5), 2.59 (1H, dd, J=4.4, 12.8 Hz, 3-H$_{eq}$), 3.82 (3H, s, –COOCH$_3$). Positive FAB-MS (M+H)$^+$ m/z: 680.

25β: $[\alpha]_D$ −4.5° (c=0.44, $CHCl_3$). IR (neat): 3400, 1740, 1660, 1560 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.10 (6H, s, –Si(CH$_3$)$_2$), 0.92 (9H, s, –SiC(CH$_3$)$_3$), 1.89—2.16 (15H, m, –COCH$_3$×5), 2.47 (1H, dd, J=5.1, 12.8 Hz, 3-H$_{eq}$), 3.82 (3H, s, –COOCH$_3$). Positive FAB-MS (M+H)$^+$ m/z: 680.

(*S*)-2-*O*-Hexadecanoyl-1-*O*-[methyl(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]glycerol (4α, 4β) DCC (63 mg, 3.07×10^{-4} mol) was added to a solution of **25**α (115 mg, 1.69×10^{-4} mol), palmitic acid (79 mg, 3.07×10^{-4} mol), and DMAP (6 mg, 4.91×10^{-5} mol) in dry CH_2Cl_2 (5 ml) at −15 °C under argon, and then stirred for 3 h. The mixture was warmed at room temperature, stirred for 15 h, and filtered on Celite. The filtrate was evaporated to dryness and the residue was purified on silica gel ($CHCl_3$: MeOH = 50 : 1) to produce a crude acylated compound, to which CH_3CN–$CHCl_3$ (3 : 1) involving trace aqueous 46.5% HF was added, and stirred for 1 h at room temperature. The resulting mixture was concentrated to dryness and chromatographed on silica gel ($CHCl_3$: MeOH = 20 : 1) to afford **4**α (33 mg, 24.7%) as a colorless, amorphous powder.

4α: $[\alpha]_D$ −15.5° (c=0.66, $CHCl_3$). IR (neat): 3400, 1740, 1670, 1560 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=7.0 Hz, –CO(CH$_2$)$_{14}$CH$_3$), 1.26 (26H, s, –COCH$_2$(CH$_2$)$_{13}$CH$_3$), 1.89—2.15 (15H, m, –COCH$_3$×5), 2.35 (2H, t, J=7.5 Hz, –COCH$_2$(CH$_2$)$_{13}$CH$_3$), 2.59 (1H, dd, J=4.5, 12.5 Hz, 3-H$_{eq}$), 3.81 (3H, s, –COOCH$_3$).

25β (92 mg, 1.35×10^{-4} mol), palmitic acid (67 mg, 2.46×10^{-4} mol), DMAP (8 mg, 6.12×10^{-5} mol), and DCC (54 mg, 2.46×10^{-4} mol) as described for **4**α gave **4**β (24 mg, 22.5%) as a colorless, amorphous powder.

4β: $[\alpha]_D$ −8.8° (c=0.48, $CHCl_3$). IR (neat): 3400, 1750, 1660, 1560 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=7.0 Hz, –CO(CH$_2$)$_{14}$CH$_3$), 1.26 (26H, s, –COCH$_2$(CH$_2$)$_{13}$CH$_3$), 1.89—2.08 (15H, m, –COCH$_3$×5), 2.35 (2H, t, J=7.7 Hz, –COCH$_2$(CH$_2$)$_{13}$CH$_3$), 2.47 (1H, dd, J=4.8, 12.8 Hz, 3-H$_{eq}$), 3.81 (3H, s, –COOCH$_3$).

(*S*)-2-*O*-Benzyl-1-*O*-[methyl(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-3-*O*-monochloroacetylglycerol (26α, 26β) Glycerol derivative (**14**, 493 mg, 1.91×10^{-3} mol), Hg(CN)$_2$ (1.01 g, 4.00×10^{-3} mol), HgBr$_2$ (1.11 g, 3.09×10^{-3} mol), MS4A (3 g), and the chloride (**19**) as described for **20**α afforded **26**α (41 mg, 2.8%) and **26**β (240 mg, 16.4%) as colorless, amorphous powders.

26α: $[\alpha]_D$ −8.6° (c=0.56, $CHCl_3$). IR (neat): 3360, 1740, 1660, 1540, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.95—2.08 (15H, m, –COCH$_3$×5), 2.61 (1H, dd, J=4.4, 12.4 Hz, 3-H$_{eq}$). 3.77 (3H, s, –COOCH$_3$), 4.14 (2H, s, –COCH$_2$Cl), 4.65 (2H, s, –CH$_2$Ph), 7.31—7.50 (5H, m, phenyl). Positive FAB-MS (M+H)$^+$ m/z: 732.

26β: $[\alpha]_D$ −10.8° (c=0.48). IR (neat): 3400, 1750, 1670, 1540, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.85—2.09 (15H, m, –COCH$_3$×5), 2.41 (1H, dd, J=4.9, 12.9 Hz, 3-H$_{eq}$), 3.77 (3H, s, –COOCH$_3$), 4.15 (2H, s, –COCH$_2$Cl), 7.31—7.50 (5H, m, phenyl). Positive FAB-MS (M+H)$^+$ m/z: 732.

(*S*)-1-*O*-[Methyl(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]-3-*O*-monochloroacetylglycerol (27α, 27β) A solution of **26**α (50 mg, 6.51×10^{-5} mol) in MeOH (1 ml) was hydrogenated in the presence of 30% Pd(OH)$_2$–C (5 mg) at room temperature. The catalyst was filtered off and the filtrate was concentrated to dryness. The residue was purified on a column of silica gel ($CHCl_3$: MeOH = 20 : 1) to give **27**α (15 mg, 34.0%) as a colorless, amorphous powder. $[\alpha]_D$ −2.7° (c=0.30, $CHCl_3$). IR (neat): 3325, 1710, 1660, 1510 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.89—2.14 (15H, m, –COCH$_3$×5), 2.63 (1H, dd, J=4.6, 12.4 Hz, 3-H$_{eq}$), 3.82 (3H, s, –COOCH$_3$). Positive FAB-MS (M+H)$^+$ m/z: 642.

26β (186 mg, 2.42×10^{-4} mol) and 30% Pd(OH)$_2$ (19 mg) as described for **27**α gave **27**β (83 mg, 50.4%) as a colorless, amorphous powder. $[\alpha]_D$ −4.5° (c=0.84, $CHCl_3$). IR (neat): 3325, 1740, 1660, 1545 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.97—2.17 (15H, m, –COCH$_3$×5), 2.48 (1H, dd, J=4.6, 12.7 Hz, 3-H$_{eq}$), 3.82 (3H, s, –COOCH$_3$), 4.18 (2H, s, –COCH$_2$Cl). Positive FAB-MS (M+H)$^+$ m/z: 642.

(*R*)-2-*O*-Hexadecanoyl-1-*O*-[methyl(5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosyl)onate]glycerol (5α, 5β) DCC (9 mg, 4.4×10^{-5} mol) was added to a solution of **27**α (15 mg, 2.2×10^{-5} mol), palmitic acid (11 mg, 4.4×10^{-5} mol), and DMAP (1.1 mg, 8.8×10^{-6} mol) in dry CH_2Cl_2 (2 ml) at −15 °C under argon, and then stirred for 3 h. The mixture was warmed at room temperature and stirred for 15 h. The suspension was filtered and the filtrate was washed with brine and dried ($MgSO_4$). After removal of the solvent, the residue was chromatographed on a flash column of silica gel ($CHCl_3$: MeOH = 20 : 1) to afford a crude acylated compound, to which thiourea (2.5 mg, 3.3×10^{-5} mol) and diisopropylethylamine (4.3 mg, 3.32×10^{-5} mol) in dry THF (0.5 ml) was added, and refluxed for 2 h. The resulting mixture was filtered off and the filtrate was concentrated to dryness. The residue was purified by preparative TLC ($CHCl_3$: MeOH = 20 : 1) to yield **5**α (3 mg, 16.9%) as a colorless, amorphous powder.

5α: $[\alpha]_D$ −17.0° (c=0.06, $CHCl_3$). IR (neat): 3400, 1740, 1660, 1540 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=7.5 Hz, –CO(CH$_2$)$_{14}$CH$_3$), 1.24—1.28 (26H, m, –COCH$_2$(CH$_2$)$_{13}$CH$_3$), 1.89—2.16 (15H, m, –COCH$_3$×5), 2.36 (2H, t, J=8.5 Hz, –COCH$_2$(CH$_2$)$_{13}$CH$_3$), 2.59 (1H, dd, J=4.5, 12.5 Hz, 3-H$_{eq}$). 3.79 (3H, s, –COOCH$_3$). Positive FAB-MS (M+H)$^+$ m/z: 804.

DCC (21 mg, 1.0×10^{-4} mol), **27**β (34 mg, 5.0×10^{-5} mol), palmitic acid (26 mg, 1.0×10^{-4} mol), DMAP (2.4 mg, 2.0×10^{-5} mol), thiourea (6 mg, 7.5×10^{-5} mol), and diisopropylethylamine (9.7 mg, 7.5×10^{-5} mol) as described for **5**α produced **5**β (6 mg, 14.9%) as a colorless, amorphous powder.

(*S*)-2-*O*-Benzyl-3-*O*-hexadecanoyl-1-*O*-(2,3,4,6-tetra-*O*-acetyl-D-galactopyranosyl)glycerol (29) 2,3,4,6-Tetra-*O*-acetyl-D-galactopyranosyl trichloroacetimidate (**28**, 420 mg, 8.52×10^{-4} mol), synthesized from D-galactose in three steps, the glycerol derivative (**12a**, 4.47×10^{-4} mol), and MS4A (5 g) were dried by a high vacuum-pump for 2 h. The mixture

was dissolved in dry CH_2Cl_2 (5 ml) and stirred at −20 °C under argon. BF_3–Et_2O (0.08 ml) was added to the mixture −20 °C, stirred for 3 h, and further stirred at room temperature for 15 h. The resulting mixture was filtered and the filtrate was washed with saturated aqueous $NaHCO_3$ and brine. The organic phase was dried ($MgSO_4$) and concentrated. The residue was purified on a column of silica gel ($CHCl_3$: MeOH = 50 : 1) to afford **29** (184 mg, 53.9%) as a colorless, amorphous powder. $[\alpha]_D$ +5.0° (c = 0.20, $CHCl_3$). IR (neat): 1740, 745, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J = 6.2 Hz, –$CO(CH_2)_{14}CH_3$), 1.25 (26H, s, –$COCH_2(CH_2)_{13}CH_3$), 1.98—2.16 (12H, m, –$COCH_3 \times 4$), 5.30 (2H, s, –CH_2Ph), 7.33—7.34 (5H, m, phenyl). Positive FAB-MS $(M+H)^+$ m/z: 751.

(*S*)-3-*O*-Hexadecanoyl-1-*O*-(2,3,4,6-tetra-*O*-acetyl-D-galactopyranosyl)glycerol (6) A solution of **29** (295 mg, 3.93×10^{-4} mol) in MeOH (2 ml) was hydrogenated in the presence of $Pd(OH)_2$–C (30 mg) at room temperature for 2 h. The catalyst was filtered off and the filtrate was chromatographed on a silica gel column to give **6** (248 mg, 93.6%) as a colorless, amorphous powder. $[\alpha]_D$ +18.3° (c = 0.24, $CHCl_3$). IR (neat): 3470, 1750 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 0.88 (3H, t, J = 6.2 Hz, –$CO(CH_2)_{14}CH_3$), 1.25 (26H, s, –$COCH_2(CH_2)_{13}CH_3$), 1.99—2.17 (12H, m, –$COCH_3 \times 4$), 2.34 (2H, t, J = 7.8 Hz, –$COCH_2(CH_2)_{13}CH_3$). Positive FAB-MS $(M+H)^+$ m/z: 661.

6-*O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosylonate)-D-galactopyranoside (31) A mixture of 6-*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosylonate)-1,2,3,4-tetra-*O*-benzyl-galactopyranoside (**30**, 500 mg, 4.93×10^{-4} mol) and $Pd(OH)_2$–C (50 mg) in MeOH (5 ml) was stirred for 3 h at room temperature under H_2. The mixture was filtered, the filtrate was evaporated to dryness, and the residue was purified on a column of silica gel ($CHCl_3$: MeOH = 10 : 1) to yield **31** (322 mg, quant.). mp 110—113 °C, $[\alpha]_D$ −0.01° (c = 0.67, $CHCl_3$). IR (KBr): 3400, 1745, 1660, 1560 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.88—2.15 (15H, m, –$COCH_3 \times 5$), 2.62 (1H, dd, J = 4.4, 12.9 Hz, 3-H_{eq}), 3.81 (3H, s, –$COOCH_3$), 5.64 (1H, d, J = 8.5 Hz, –NH–). *Anal.* Calcd for $C_{26}H_{39}NO_{18} \cdot H_2O$: C, 46.46; H, 6.15; N, 2.08. Found: C, 46.57; H, 5.90; N, 1.85.

6-*O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosylonate)-1,2,3,4-tetra-*O*-acetyl-D-galactopyranoside (32) Acetic anhydrate (94 mg, 9.21×10^{-4} mol) was added to a solution of **30** (60 mg, 9.18×10^{-5} mol) in dry pyridine (145 mg, 1.83×10^{-3} mol) at 0 °C under argon and stirred for 15 h at room temperature. The mixture was diluted with $CHCl_3$ (50 ml) and washed 1 N HCl and brine. The organic phase was dried ($MgSO_4$) and the residue was purified on a column of silica gel ($CHCl_3$: MeOH = 20 : 1) to afford **32** (**63** mg, 79.6%). mp 91—94 °C, $[\alpha]_D$ −0.5° (c = 0.76, $CHCl_3$). IR (KBr): 3360, 1740, 1660, 1540 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.88—2.20 (27H, m, –$COCH_3 \times 9$), 2.30—2.63 (1H, m, 3-H_{eq}). 3.77 (3H, s, –$COOCH_3$). *Anal.* Calcd for $C_{34}H_{47}NO_{22}$: C, 48.63; H, 5.88; N, 1.67. Found: C, 48.68; H, 5.64; N, 1.56.

6-*O*-(Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosylonate)-2,3,4-tri-*O*-acetyl-D-galactopyranoside (33) Hydrazine acetate (128 mg, 1.39×10^{-3} mol) was added to a solution of **32** (257 mg, 3.13×10^{-4} mol) in dry *N*,*N*-dimethylformamide (DMF) (1 ml) at 50 °C. The mixture was diluted with AcOEt (30 ml) and cooled to room temperature. The resulting mixture was washed with brine, dried and chromatographed on a silica gel column ($CHCl_3$: MeOH = 20 : 1) to give **33** (162 mg, 65.0%). mp 103—106 °C. $[\alpha]_D$ −0.5° (c = 0.42, $CHCl_3$). IR (KBr): 3260, 1740, 1660, 1550 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.89—2.22 (24H, m, –$COCH_3 \times 5$), 2.55 (1H, dd, J = 4.4, 13.2 Hz, 3-H_{eq}), 3.79 (3H, s, –$COOCH_3$). *Anal.* Calcd for $C_{32}H_{45}NO_{21} \cdot 2H_2O$: C, 47.11; H, 6.06; N, 1.72. Found: C, 47.37; H, 5.56; N, 1.99.

(*S*)-2-*O*-Benzyl-3-*O*-hexadecanoyl-1-*O*-[6-*O*-methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosylonate)-2,3,4-tri-*O*-acetyl-D-galactopyranosyl]glycerol (34) To a solution of **33** (62 mg, 7.79×10^{-5} mol) in dry (CH_2Cl_2 (5 ml) was added Cl_3CCN (86 mg, 9.35×10^{-4} mol) and DBU (6 mg, 3.9×10^{-5} mol) at −5 °C. This mixture was directly chromatographed on a column of silica gel (CH_2Cl_2 : AcOEt = 1 : 1) to afford the imidate of **33**. A mixture of the imidate, **12a** (98 mg, 2.34×10^{-4} mol), and MS4A (600 mg) in dry CH_2Cl_2 (2 ml) was treated with BF_3–Et_2O (11 μl) at −10 °C. The mixture was stirred for 2 h at −10 °C and for 15 h at room temperature. The resulting mixture was filtered and the filtrate was washed with saturated aqueous $NaHCO_3$ and brine, dried, and evaporated to dryness. The residue was purified on a column of silica gel ($CHCl_3$: MeOH = 20 : 1) to give **34** (13 mg, 14%, 2 steps) as a colorless, amorphous powder. $[\alpha]_D$ −7.4° (c = 0.72, $CHCl_3$). IR (neat): 1750, 1660, 1550, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J = 6.5 Hz, –$CO(CH_2)_{14}CH_3$), 1.25 (26H, s, –$COCH_2(CH_2)_{13}CH_3$), 1.88—2.13 (24H, m, –$COCH_3 \times 8$), 2.58 (1H, dd, J = 4.8, 12.8 Hz, 3-H_{eq}), 3.82 (3H, s, –$COOCH_3$), 7.29—7.37 (5H, m, phenyl). Positive FAB-MS $(M+H)^+$ m/z: 1182.

(*S*)-3-*O*-Hexadecanoyl-1-*O*-[6-*O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-D-*glycero*-D-*galacto*-2-nonulopyranosylonate)-2,3,4-tri-*O*-acetyl-D-galactopyranosyl]glycerol (7) A soluton of **34** (12 mg, 1.0×10^{-5} mol) in MeOH (0.5 ml) was hydrogenated with $Pd(OH)_2$–C (6 mg) and stirred for 1 h at room temperature. The catalyst was filtered off and evaporated to dryness. The residue was purified on PTLC ($CHCl_3$: MeOH = 20 : 1) to give **7** (9 mg, 81%) as a colorless, amorphous powder. $[\alpha]_D$ −5.2° (c = 0.48, $CHCl_3$). IR (neat): 3370, 1740, 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J = 6.5 Hz, –$CO(CH_2)_{14}CH_3$), 1.25 (26H, s, –$COCH_2(CH_2)_{13}CH_3$), 1.86—2.19 (24H, m, –$COCH_3 \times 8$), 2.58 (1H, dd, J = 4.5, 12.7 Hz, 3-H_{eq}), 3.81 (3H, s, –$COOCH_3$). Positive FAB-MS $(M+H)^+$ m/z: 1092.

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