

Synthesis of Ganglioside G_{M3} and G_{M4} Analogs Having Mimics of Ceramide Moieties and Their Binding Activities with Influenza Virus A

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Ganglioside G_{M4} (1) and G_{M3} (2) analogs, which contain mimics of the ceramide moieties of gangliosides, were synthesized. The syntheses of 1 and 2 feature stereoselective glycosylation of methyl (phenyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio- β -D-galacto-2-nonulopyranosid)onate (10) as the sialosyl donor with suitably protected galactose and lactose acceptors catalyzed by *N*-bromosuccinimide (NBS), iodine, and tetrabutylammonium trifluoromethanesulfonate (TBAOTf) as the glycosyl promoter in acetonitrile under kinetically controlled conditions. Compound 2 exhibited binding activity towards influenza virus A.

Key words ganglioside G_{M4} analog; ganglioside G_{M3} analog; ceramide analog; L-serine diamide derivative; influenza virus A binding activity

Gangliosides, sialic acid-bearing glycosphingolipids, have received much attention in recent years because of their numerous biological roles in cellular recognition, differentiation, oncogenesis, and so on.¹⁾ Various gangliosides²⁾ and their analogs³⁾ have been synthesized. In order to study the structure–function relationship of gangliosides, a facile synthesis of ganglioside analogs containing modified ceramides seems to be of importance. In the preceding paper,⁴⁾ we reported the synthesis of sulfated cerebroside analogs having mimics of ceramide moieties of gangliosides and their anti-human immunodeficiency virus (HIV)-1 activities.

Here we describe an efficient regio- and stereo-selective synthesis of a sialosylcerebroside G_{M4} analog (1) and a sialosyllactosylceramide G_{M3} analog (2) bearing L-serine diamide derivatives to mimic the ceramide moieties of gangliosides.

We designed L-serine diamide derivatives carrying two fatty acyl groups as mimics of ceramides, as shown in Chart 1. In planning a synthetic route to the sialosyl-conjugates (1, 2), condensation of *N*-trichloroethoxycarbonyl-L-serine benzyl ester (7) with a suitably protected thioglycoside (6, 17), then glycosylation of the sialosyl donor (10) with the sialosyl acceptor (9, 19) were chosen, as summarized in Chart 1.

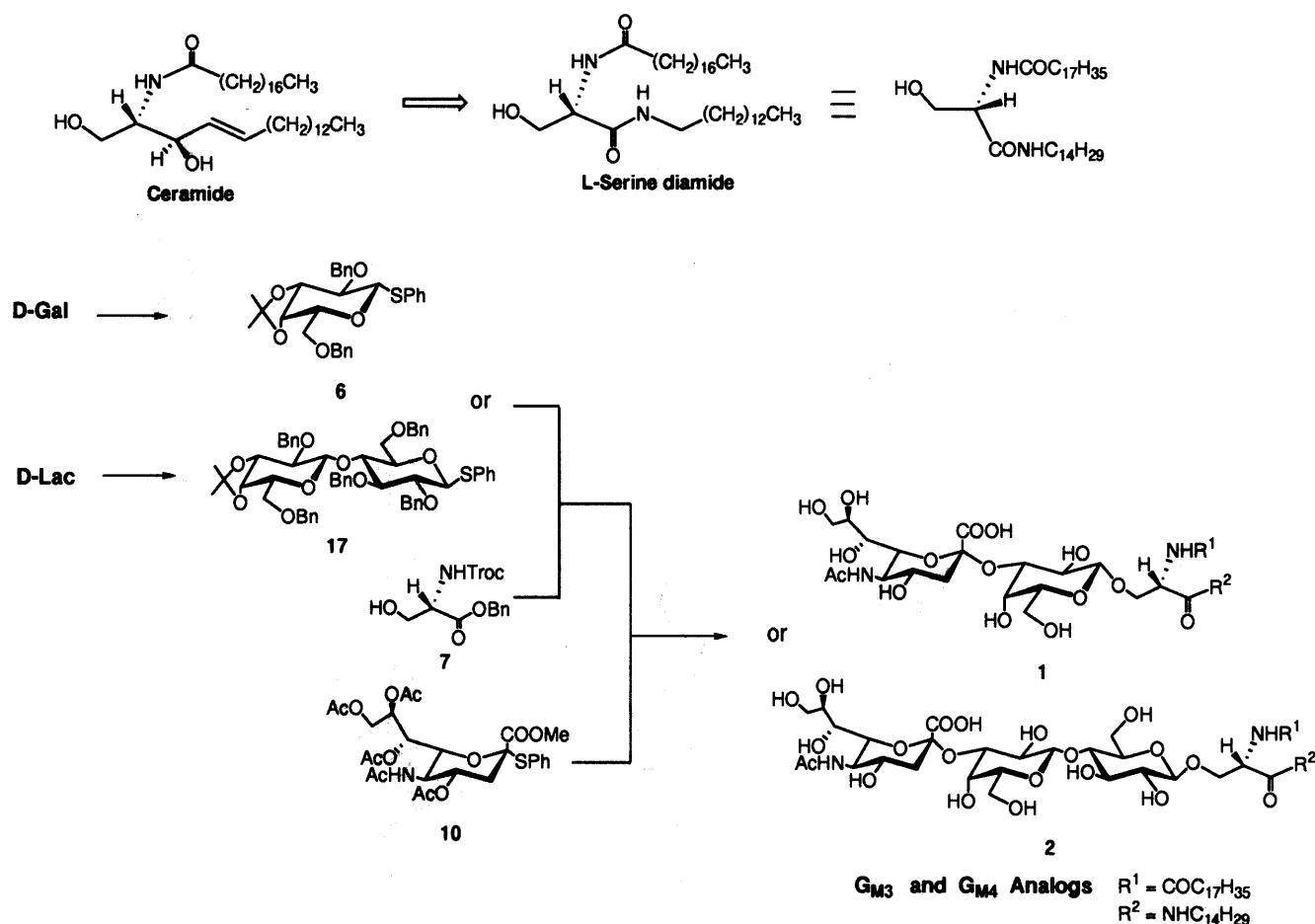
For the synthesis of compound 1, treatment of 1,2,3,4,6-penta-*O*-acetyl-D-galactose with thiophenol in the presence of boron trifluoride etherate (BF₃OEt₂) in CH₂Cl₂ gave phenyl 1-thio- β -D-glycoside (3) in 91% yield. Zemplén deacetylation of 3 with NaOMe in MeOH gave the tetraol 4 in quantitative yield. Compound 4 was converted into the 3,4-*O*-isopropylidene derivative (5) with 2,2-dimethoxypropane and a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) in dimethylformamide (DMF)–acetone in 72% yield. The remaining hydroxyl groups of 5 were benzylated with benzyl bromide and NaH in DMF to give compound 6 in 92% yield. Coupling of 6 and 7 with *N*-bromosuccinimide (NBS),⁵⁾ iodine, and tetrabutylammonium trifluoromethanesulfonate (TBAOTf) as the promoter in CH₃CN at –40 °C gave the β -glycoside (8) in 48% yield. The β -configuration of 8 was determined from the coupling constant value (7.9 Hz) of the signal due to anomeric protons in the proton magnetic resonance

(¹H-NMR) spectrum of 8. Compound 8 was treated with 90% AcOH to give the diol 9 in 82% yield. The stereoselective coupling of 9 with 10 was performed at –40 °C, by using 1.5 eq of phenyl 2-thioglycoside (10)⁶⁾ in CH₃CN with NBS, I₂, and TBAOTf as the promoter, to give exclusively the desired α -glycoside (11) in 49% yield [in the case of using dimethyl(methylthio)sulfonium triflate (DMTST)⁷⁾ as the promoter, in 34% yield]. The observed signals of 11 included six singlets, each integrating for three protons, which demonstrated the presence of one *N*-acetyl (δ 1.88), four *O*-acetyl (δ 1.97–2.10), and one methyl ester (δ 3.78) groups; H-3_{eq} appeared at δ 2.54 ($J_{3ax,3eq}$ = 12.9, $J_{3eq,4}$ = 4.5 Hz; Neu5Ac unit) and the $\Delta\delta$ (H-9a–H-9b) value (0.36 ppm) and the $J_{7,8}$ coupling constant (8.2 Hz) (Neu5Ac unit) indicated α -configuration⁸⁾ of the newly formed glycosidic linkage; H-3 (Gal unit) appeared at δ 4.17 as a doublet of doublets ($J_{3,4}$ = 3.2, $J_{3,2}$ = 9.5 Hz), showing the glycosidic position. Treatment of 11 with activated Zn-dust in AcOH followed by acylation of the free amino group with stearoyl chloride and NaHCO₃ gave the monoacylated compound (12) in 63% yield in two steps. Catalytic hydrogenolysis of benzyl groups in 12 over Pd-black in 6:1 EtOH–AcOH for 2 d at 45 °C, followed by introduction of tetradecylamine, diethylphosphorocyanidate (DEPC), and NEt₃ afforded compound 13 in 32% yield in two steps. Finally, *O*-deacylation and saponification of acetyl groups and the methyl ester group of 13 with 0.1 N aqueous KOH in MeOH (1:1), followed by purification on a silica gel column and gel filtration (LH-20) and lyophilization from H₂O gave the expected compound 1 in 73% yield. Compound 1 gave a positive test with the specific spray-reagent (resorcinol reagent) for sialosyl compounds.⁹⁾

Next, we planned to synthesize the G_{M3} analog (2) bearing mimics of ceramide as indicated in Chart 3.

The starting material for 2 was 1-thio- β -lactoside (14) which was prepared from per-*O*-acetyl lactose, thiophenol and BF₃OEt₂ in CH₂Cl₂ in 88% yield. In essentially the same way as described for 1, transesterification of 14 with NaOMe in MeOH, followed by 2,2-dimethoxypropane and *p*-TsOH gave compound 16 in 67% yield in two steps. Benzoylation of 16 with benzyl bromide and NaH in DMF gave compound 17 in 83% yield. Condensation of

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17 and 7 with NBS and I₂ and TBAOTf in CH₃CN gave β -glycoside 18 in 44% yield. The ¹H-NMR spectrum of 18 revealed the signal assignable to H-1 at δ 4.69 as a doublet with $J_{1,2}$ = 8.8 Hz, indicating that the newly formed glycosidic bond had the β -configuration. Compound 18 was treated with 90% AcOH to give the diol 19 in 83% yield. Stereoselective condensation between 19 and 10 was performed in CH₃CN, employing NBS and I₂ and TBAOTf, to afford the expected α -sialosyl compound (20) (δ 2.50, $J_{3ax,3eq}$ = 12.7, $J_{3eq,4}$ = 4.5 Hz, H-3_{eq} of Neu5Ac moiety) in 45% yield. After treatment of 20 with activated Zn-dust in AcOH, the resulting free amino group was acylated with stearoyl chloride and NaHCO₃ to give compound 21 in 43% yield. Catalytic hydrogenolysis of the benzyl groups in 21 over Pd-black in 6:1 EtOH-AcOH for 3 d at 45°C, followed by treatment with tetradecylamine, DEPC, and NEt₃ afforded compound 22 in 28% yield. Finally, saponification of 22 with 0.1 N aqueous KOH in MeOH, followed by purification on a silica gel column and gel filtration (LH-20) and lyophilization from H₂O gave the title compound 2 in 72% yield.

The structures of all compounds were characterized by ¹H- and ¹³C-NMR spectroscopies, as well as infrared (IR) spectroscopy, elemental analyses and positive FAB-mass spectrometry.

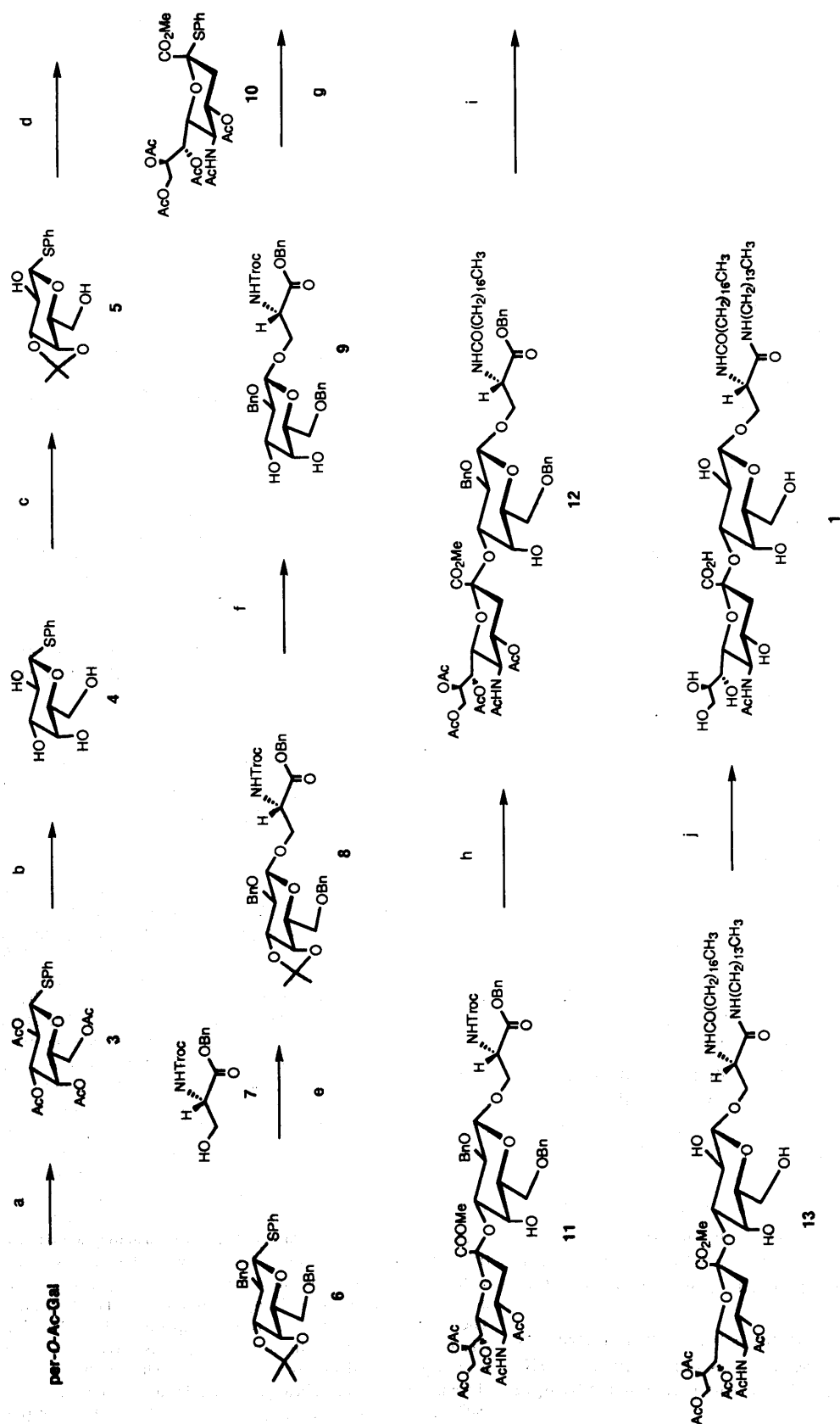
Preliminary examination of the biological activity¹⁰⁾ of the two chemically synthesized compounds showed that compound 1 had only weak binding activity with influenza

virus A/WSN/33, while compound 2 exhibited the same level of binding activity towards influenza virus A/PR/8/34 as did naturally occurring G_{M3}.

Experimental

All melting points are uncorrected. Optical rotations were measured with a JASCO DIP-140 digital polarimeter. IR spectra were recorded on a JASCO A-202 IR spectrophotometer. ¹H-NMR spectra were taken on a JEOL JNM-GX270 (270 MHz) spectrometer. ¹³C-NMR spectra were recorded with a JEOL JNM-GX270 (67.5 MHz) spectrometer. ¹H and ¹³C chemical shifts (δ) are given in ppm relative to that of Me₄Si (δ = 0) in CDCl₃ or CD₃OD as an internal standard. The abbreviations of signal patterns are as follows: s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Column chromatography was carried out on Silica gel 60 (70–230 mesh, Merck). Gel filtration was performed on Sephadex LH-20 (Pharmacia). Thin-layer chromatography (TLC) on Silica gel 60-F₂₅₄ (Merck) was used to monitor the reaction and to ascertain the purity of the reaction products. The spots were visualized by spraying the plates with 5% aqueous sulfuric acid and then heating. Glycolipids containing sialic acid were visualized with resorcinol reagent. The bands of lipids containing sialic acid were stained blue.

Phenyl 2,3,4,6-Tetra-O-acetyl-1-thio- β -D-galactopyranoside (3) Boron trifluoride etherate (710 mg, 5.0 mmol) was added dropwise to a stirred solution of 1,2,3,4,6-penta-O-acetyl- β -D-galactopyranose (781 mg, 2.0 mmol) and thiophenol (242 mg, 2.2 mmol) in CH₂Cl₂ (20 ml) at 0°C. The mixture was stirred at room temperature for 24 h, diluted with CH₂Cl₂, and washed with saturated aqueous NaHCO₃ and brine, dried over MgSO₄, and evaporated *in vacuo*. The residue was purified by chromatography on silica gel using hexane-AcOEt (5:1) to give 3 (802 mg, 91%) as a syrup. [α]_D + 3.7° (c = 1.00, CHCl₃). IR (neat): 1750, 695 cm⁻¹. ¹H-NMR (CDCl₃) δ : 1.977, 2.045, 2.098, 2.123 (each 3H, s, OAc), 3.945 (1H, ddd, $J_{5,6a}$ = 6.1, $J_{5,6b}$ = 7.0 Hz, H-5), 4.120 (H, dd, $J_{6a,5}$ = 6.1, $J_{6a,6b}$ = 11.3 Hz, H-6a), 4.193 (2H, dd, $J_{5,6b}$ = 7.0, $J_{6a,6b}$ = 11.3 Hz, H-6b), 4.723 (1H, d, $J_{1,2}$ = 10.1 Hz, H-1), 3.944 (1H, dd,



Reagents: a) PhSH, BF₃·OEt₂ in CH₂Cl₂; b) NaOMe in MeOH; c) (MeO)₂CMe₂, p-TSA in DMF-acetone; d) BnBr, NaH in DMF; e) 7, NBS, I₂, TBAOTf in CH₃CN; f) 90% AcOH; g) 10, NBS, I₂, TBAOTf in CH₃CN; h) 1) Zn, AcOH, 2) CH₃(CH₂)₁₆COCl, NaHCO₃; i) 1) Pd-black, H₂ in EtOH-AcOH (6:1), 2) CH₃(CH₂)₁₃NH₂, DEPC, NEt₃ in THF; j) 0.1N KOH in MeOH(1:1)

Chart 2

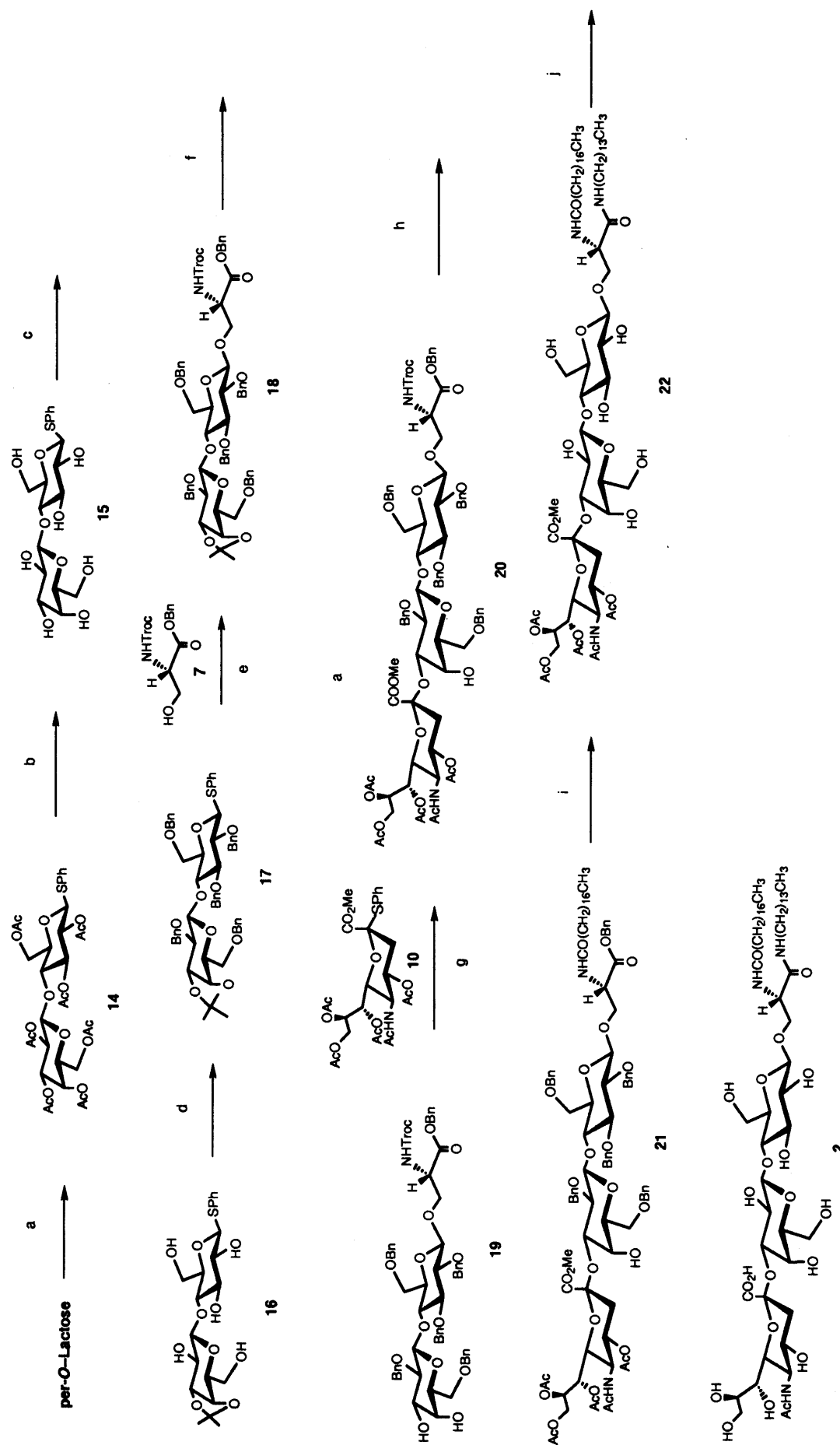


Chart 3

$J_{2,3}=9.8$, $J_{3,4}=3.4$ Hz, H-3), 5.242 (1H, dd, $J_{1,2}=10.1$, $J_{2,3}=9.8$ Hz, H-2), 5.421 (1H, brt, $J_{3,4}=J_{4,5}=3.4$ Hz, H-4), 7.30–7.32 (3H, m, Ph), 7.51–7.53 (2H, m, Ph). $^{13}\text{C-NMR}$ (CDCl_3) δ : 86.4 (d, C-1 β), 169.3, 169.9, 170.0, 170.2 (s, CO). Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_9\cdot 3/2\text{H}_2\text{O}$: C, 51.38; H, 5.82. Found: C, 51.50; H, 5.76.

Phenyl 1-Thio- β -D-galactopyranoside (4) A mixture of **3** (1.32 g, 3.0 mmol), MeOH (50 ml), and NaOMe (120 mg, 3.0 mmol) was stirred at room temperature for 12 h. The reaction mixture was acidified to pH 6 with IRC-50 (2.0 g), and stirred for 5 min, then the resin was filtered off, and the filtrate was stripped of the solvent. Chromatography of the residue using CH_2Cl_2 -MeOH (5:1) gave **4** (817 mg, quantitative), mp 123–124°C. $[\alpha]_D -44.6^\circ$ ($c=0.88$, MeOH). IR (KBr): 3340, 695 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 4.589 (1H, d, $J=9.6$ Hz, H-1), 7.29–7.40 (3H, m, Ph), 7.53–7.56 (2H, m, Ph). $^{13}\text{C-NMR}$ (CDCl_3) δ : 89.0 (d, C-1 β). Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_5\cdot 1/2\text{H}_2\text{O}$: C, 51.23; H, 6.09. Found: C, 51.74; H, 6.03.

Phenyl 3,4-O-Isopropylidene-1-thio- β -D-galactopyranoside (5) A mixture of **4** (817 mg, 3 mmol), acetone (20 ml), DMF (10 ml), and *p*-TsOH acid monohydrate (57 mg, 0.3 mmol) was stirred at 40°C for 48 h. The reaction mixture was neutralized with ion exchange resin (Amberlite IRA-94S), and stirred for 5 min, then the resin was filtered off, and the filtrate was evaporated to dryness. Chromatography of the residue using CH_2Cl_2 -MeOH (20:1) gave **5** (675 mg, 72%) as white prisms, mp 42–43°C. $[\alpha]_D -6.8^\circ$ ($c=0.52$, MeOH). IR (KBr): 3400, 870, 690 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 1.339, 1.433 (each 3H, s, Me_2C), 4.527 (1H, d, $J_{1,2}=10.2$ Hz, H-1), 7.29–7.33 (3H, m, Ph), 7.53–7.56 (2H, m, Ph). $^{13}\text{C-NMR}$ (CDCl_3) δ : 26.3, 28.0 (q, Me_2C), 87.8 (d, C-1 β), 110.5 (s, Me_2C). Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_5\cdot 2\text{H}_2\text{O}$: C, 51.71; H, 6.94. Found: C, 51.64; H, 6.10.

Phenyl 2,6-Di-O-benzyl-3,4-O-isopropylidene-1-thio- β -D-galactopyranoside (6) Sodium hydride (340 mg, 8.4 mmol) was added portionwise to a stirred mixture of compound **5** (656 mg, 2.1 mmol), benzyl bromide (1.43 g, 8.4 mmol), and *n*-Bu₄NBr (67 mg, 0.2 mmol) in DMF (15 ml) at 0°C. The mixture was stirred at 0°C for 1 h, then at room temperature for 12 h and methanol was added to destroy the excess NaH. The mixture was diluted with AcOEt, washed with water and brine, dried (MgSO_4), and evaporated *in vacuo*. The residue was chromatographed on silica gel using hexane-ethyl acetate (50:1) to give **6** (952 mg, 92%). $[\alpha]_D -20^\circ$ ($c=1.06$, CHCl_3). IR (neat): 3400, 870 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 1.339, 1.433 (each 3H, s, Me_2C), 4.522, 4.599 (each 1H, d, $J=11.9$ Hz, PhCH_2O), 4.661 (1H, d, $J_{1,2}=9.5$ Hz, H-1), 4.687, 4.824 (each 1H, d, $J=11.3$ Hz, PhCH_2O), 7.29–7.33 (13H, m, Ph), 7.53–7.56 (2H, m, Ph). $^{13}\text{C-NMR}$ (CDCl_3) δ : 26.3, 28.0 (q, Me_2C), 87.8 (d, C-1), 110.5 (s, Me_2C). Anal. Calcd for $\text{C}_{29}\text{H}_{32}\text{O}_5\text{S}$: C, 70.71; H, 6.55. Found: C, 71.05; H, 6.71.

***N*-Trichloroethoxycarbonyl-O-(2,6-di-O-benzyl-3,4-isopropylidene- β -D-galactopyranosyl)-L-serine Benzyl Ester (8)** NBS (356 mg, 2.0 mmol), iodine (508 mg, 2.0 mmol), and TBAOTf (63 mg, 0.16 mmol) were added to a solution of **6** (296 mg, 0.60 mmol), *N*-trichloroethoxy-L-serine benzyl ester (**7**) (74 mg, 0.20 mmol) and Molecular Sieves 3Å (1.0 g) in dry CH_3CN (20 ml) at -40°C under an argon atmosphere. The mixture was stirred at the same temperature for 15 h. Dichloromethane was added and insoluble materials were removed by filtration. The filtrate was washed with 10% aqueous $\text{Na}_2\text{S}_2\text{O}_3$, saturated aqueous NaHCO_3 and brine, dried over MgSO_4 , and concentrated *in vacuo*. The residue was purified by silica-gel column chromatography using hexane-AcOEt (10:1) to give **8** (73 mg, 48%), as white prisms. $[\alpha]_D +11.1^\circ$ ($c=1.22$, CHCl_3). IR (KBr): 1740, 1500, 700 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 1.331, 1.353 (each 3H, s, Me_2C), 3.32–3.39 (1H, m, H-2), 3.70–3.78 (3H, m, H-5, H-6a, Ser β -H), 3.84–3.91 (2H, m, H-6b, Ser β -H), 4.15–4.19 (2H, m, H-3, H-4), 4.307 (1H, d, $J=7.9$ Hz, H-1), 4.39–4.44 (1H, m, Ser α -H), 4.514, 4.602 (each 1H, d, $J=11.9$ Hz, PhCH_2O), 4.714 (2H, br s, Cl_3CCH_2), 4.718, 4.766 (each 1H, d, $J=11.6$ Hz, PhCH_2O), 5.185, 5.254 (each 1H, d, $J=12.4$ Hz, PhCH_2O), 6.24 (1H, brd, $J=8.3$ Hz, N-H), 7.24–7.38 (15H, m, Ph). $^{13}\text{C-NMR}$ (CDCl_3) δ : 26.3, 27.7 (q, Me_2C), 95.3 (s, Cl_3CCH_2), 103.2 (d, $J_{\text{C-H}}=157.5$ Hz, C-1 β), 110.0 (s, Me_2C), 135.2, 137.7, 138.0 (d, Ph), 154.4, 169.3 (s, CO). Positive FAB-MS (NBA): $(\text{M}+\text{H})^+$ m/z 752.

***N*-Trichloroethoxycarbonyl-O-(2,6-di-O-benzyl- β -D-galactopyranosyl)-L-serine Benzyl Ester (9)** A solution of **7** (120 mg, 0.16 mmol) in 90% AcOH (10 ml) was heated at 90°C for 1 h. After evaporation of the solvent, the residue was purified by silica gel column chromatography (hexane-AcOEt, 2:1) to give **9** (93 mg, 82%) as an amorphous powder. $[\alpha]_D +10.2^\circ$ ($c=1.49$, CHCl_3). IR (KBr): 1740, 1500, 700 cm^{-1} .

$^1\text{H-NMR}$ (CDCl_3) δ : 3.449 (1H, dd, $J_{1,2}=7.6$, $J_{2,3}=10.4$ Hz, H-2), 3.54–3.58 (2H, m, Ser β -H), 3.703 (1H, dd, $J_{6a,6b}=5.5$, $J_{5,6a}=10.1$ Hz, H-6a), 3.761 (1H, dd, $J_{6a,6b}=5.5$, $J_{5,6b}=10.1$ Hz, H-6b), 3.923 (1H, dd, $J_{2,3}=10.4$, $J_{3,4}=3.5$ Hz, H-3), 3.984 (1H, brt, $J_{4,3}=J_{4,5}=3.5$ Hz, H-4), 4.338 (1H, d, $J_{1,2}=7.6$ Hz, H-1), 4.382 (1H, dd, $J_{5,6a}=10.1$, $J_{5,6b}=5.5$ Hz, H-5), 4.554 (2H, s, Cl_3CCH_2), 4.56–4.59 (3H, m, Ser α -H, PhCH_2O), 4.693, 4.726 (each 1H, d, $J=12.0$ Hz, PhCH_2O), 5.232, 5.199 (each 1H, d, $J=12.0$ Hz, PhCH_2O), 6.046 (1H, d, $J=7.9$ Hz, NH), 7.30–7.36 (15H, m, Ph). $^{13}\text{C-NMR}$ (CDCl_3) δ : 95.2 (s, Cl_3CCH_2), 103.6 (d, C-1 β), 134.9, 137.6, 38.0 (d, Ph), 154.0, 169.2 (s, CO). Positive FAB-MS (NBA): $(\text{M}+\text{H})^+$ m/z 712.

***N*-Trichloroethoxycarbonyl-2-(methyl 5-acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-2-nonulopyranosyl)onate-(α 2 $\rightarrow$ 3)-O-(2,6-di-O-benzyl- β -D-galactopyranosyl)-L-serine Benzyl Ester (11)** NBS (267 mg, 1.5 mmol), iodine (381 mg, 1.5 mmol), and TBAOTf (47 mg, 0.12 mmol) were added to a mixture of **9** (213 mg, 0.30 mmol), methyl (5-acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-2-thiophenyl-D-glycero- α -D-galacto-2-nonulopyranosyl)onate (**10**) (263 mg, 0.45 mmol), and Molecular Sieves 3Å (1.0 g) in dry CH_3CN (15 ml) at -40°C under an argon atmosphere. The mixture was stirred at the same temperature for 18 h. Dichloromethane was added and insoluble materials were removed by filtration. The filtrate was washed with 10% aqueous $\text{Na}_2\text{S}_2\text{O}_3$, saturated aqueous NaHCO_3 and brine, dried over MgSO_4 , and concentrated *in vacuo*. The residue was purified by silica-gel column chromatography using acetone:AcOEt (1:10) to give **11** (174 mg, 49%) as an amorphous powder. $[\alpha]_D -5.7^\circ$ ($c=0.89$, CHCl_3). IR (KBr): 1740, 1500, 700 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 1.877 (3H, s, NAc), 1.968, 2.010, 2.025, 2.103 (each 3H, s, OAc), 2.542 (1H, dd, $J_{3a,3e}=12.9$, $J_{3e,4}=4.5$ Hz, H-3'e), 3.524 (1H, dd, $J_{1,2}=7.6$, $J_{2,3}=9.6$ Hz, H-2), 3.778 (3H, s, CH_3OCO), 3.973 (1H, dd, $J_{8,9a}=5.7$, $J_{9a,9b}=12.5$, H-9a'), 4.044 (1H, brs, H-4), 4.168 (1H, $J_{3,2}=9.5$, $J_{3,4}=3.2$ Hz, H-3), 4.328 (1H, dd, $J_{9a,9b}=12.5$, $J_{8,9b}=2.3$ Hz, H-9b'), 4.429 (1H, d, $J_{1,2}=7.6$ Hz, H-1), 4.55 (2H, brs, Cl_3CCH_2), 4.695, 4.729 (each 1H, d, $J=12.0$ Hz, PhCH_2O), 4.85 (1H, m, H-4'), 5.19 (2H, brs, PhCH_2O), 5.315 (1H, dd, $J_{6,7}=1.6$, $J_{7,8}=8.2$ Hz, H-7'), 5.40 (1H, m, H-8'), 7.28–7.36 (15H, m, Ph). $^{13}\text{C-NMR}$ (CDCl_3) δ : 95.3 (s, Cl_3CCH_2), 98.4 (d, C-1' α), 103.5 (d, C-1 β), 135.1, 137.9, 138.0 (d, Ph), 154.2, 168.5, 169.3, 169.9, 170.1, 170.3, 170.6, 170.8 (s, CO). Positive FAB-MS (NBA): $(\text{M}+\text{H})^+$ m/z 1186 and $(\text{M}+\text{Na})^+$ 1208.

***N*-Stearoyl 2-(Methyl 5-acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-2-nonulopyranosyl)onate-(α 2 $\rightarrow$ 3)-O-(2,6-di-O-benzyl- β -D-galactopyranosyl)-L-serine Benzyl Ester (12)** Activated zinc powder (87 mg) was added to a solution of **11** (158 mg, 0.13 mmol) in AcOH (5 ml), and the mixture was vigorously stirred for 24 h at room temperature. The reaction mixture was filtered and the filtrate was concentrated *in vacuo* to give an oil. This was dissolved in AcOEt, then the solution was washed with saturated aqueous NaHCO_3 and brine, and dried. After removal of the solvent, the residue was dissolved in H_2O (5 ml) containing NaHCO_3 (89 mg, 1.06 mmol) and to this mixture was added a solution of stearoyl chloride (81 mg, 0.13 mmol) in ether (1 ml). The reaction mixture was held at room temperature for 16 h, then extracted with ether. The ethereal layer was washed with saturated aqueous NaHCO_3 and brine, and dried. After evaporation of the solvent, the residue was purified by silica gel column chromatography (CH_2Cl_2 :MeOH=50:1) to give **12** (107 mg, 63%) as a white powder, mp 42–43°C. $[\alpha]_D -3.9^\circ$ ($c=0.74$, CHCl_3). IR (KBr): 1750, 1660, 700 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 0.88 (3H, t, $J=7.0$ Hz, -Me), 1.25 (28H, brs, - CH_2 -), 1.876 (3H, s, NAc), 1.945, 2.013, 2.022, 2.105 (each 3H, s, OAc), 2.575 (1H, dd, $J_{3a,3e}=12.9$, $J_{3e,4}=4.3$ Hz, H-3'e), 3.532 (1H, dd, $J_{1,2}=7.8$, $J_{2,3}=9.6$ Hz, H-2), 3.778 (3H, s, CH_3O), 4.316 (1H, dd, $J_{8,9a}=5.6$, $J_{9a,9b}=12.5$ Hz, H-9a'), 4.316 (1H, dd, $J_{9a,9b}=12.5$, $J_{8,9b}=2.6$ Hz, H-9b'), 4.392 (1H, d, H-1), 4.685, 4.742 (each 1H, d, $J=11.6$ Hz, PhCH_2O), 4.86 (1H, m, H-4'), 5.19 (2H, brs, PhCH_2OCO), 5.315 (1H, dd, $J_{6,7}=1.7$, $J_{7,8}=8.3$ Hz, H-7'), 5.41 (1H, m, H-8'), 7.28–7.36 (15H, m, Ph). $^{13}\text{C-NMR}$ (CDCl_3) δ : 97.9 (s, C-1' α), 103.9 (d, C-1 β), 135.3, 137.9, 138.7 (d, Ph), 168.5, 169.8, 169.9, 170.2, 170.3, 170.6, 170.8, 173.2 (s, CO). Positive FAB-MS $(\text{M}+\text{Na})^+$ m/z 1300.

***N*-Stearoyl 2-(Methyl 5-acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-2-nonulopyranosyl)onate-(α 2 $\rightarrow$ 3)-O-(2,6-di-O-benzyl- β -D-galactopyranosyl)-L-serine Myristoylamide (13)** Palladium-black (100 mg) was added to a solution of **12** (100 mg, 0.078 mmol) in EtOH-AcOH (6:1) (14 ml), and the mixture was stirred under a hydrogen atmosphere for 3 d at 45°C. The catalyst was filtered off and the filtrate was concentrated under reduced pressure, then the

resulting oil was dissolved in tetrahydrofuran (THF) (4 ml) containing tetradecylamine (20 mg, 0.094 mmol). DEPC (17 mg, 0.10 mmol) and NEt_3 (12 mg, 0.12 mmol) were added to this mixture at 0°C and the whole was stirred for 15 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 and washed with saturated aqueous NaHCO_3 and brine, and dried. After evaporation of the solvent, the residue was purified by silica gel column chromatography (CH_2Cl_2 :MeOH=20:1) to give **13** (30 mg, 32%) as a white powder, mp 35–36°C. $[\alpha]_D^{20} + 22.0^\circ$ ($c=0.44$, CHCl_3). IR (KBr): 1750, 1660, 1550 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 0.88 (6H, t, $J=7.0$ Hz, –Me), 1.25 (52H, brs, $-\text{CH}_2-$), 1.903, 2.045, 2.133, 2.136 (15H, s, NHAc, OAc), 2.721 (1H, dd, $J_{3a,3e}=12.9$, $J_{3e,4}=4.30$ Hz, H-3'e), 3.67 (1H, m, H-2), 3.841 (3H, s, $\text{CH}_3\text{O}-$), 4.566 (1H, d, $J=7.4$ Hz, H-1), 5.20 (1H, m, H-4'), 5.312 (1H, dd, $J_{6,7}=1.8$, $J_{7,8}=8.8$ Hz, H-7'), 5.42 (1H, m, H-8'). $^{13}\text{C-NMR}$ (CDCl_3) δ : 97.6 (s, C-1' α), 104.2 (d, C-1 β), 168.1, 169.9, 170.0, 170.1, 170.4, 170.7, 170.8, 173.4 (s, CO). Positive FAB-MS (NBA): (M+Na) $^+$ m/z 1225.

N-Stearoyl 2-(N-Acetyl-3,5-dideoxy-D-glycero- α -D-galacto-2-nonulopyranosyl)-(α 2 $\rightarrow$ 3)-O-(β -D-galactopyranosyl)-L-serine Myristoylamide (1) Compound **13** (30 mg, 0.025 mmol) was dissolved in a solution of 0.1 N KOH and MeOH (1:1) (3.0 ml). The solution was stirred at room temperature for 20 h. It was adjusted to pH 3 with ion exchange resin (Amberlite IR-120) and then the resin was removed by filtration. The filtrate was evaporated to dryness and the residue was purified by silica gel column chromatography (CHCl_3 -MeOH- H_2O (60:60:5)) and gel filtration (LH-20) with CHCl_3 -MeOH- H_2O (60:60:10) to give **1** (19 mg, 73%), after lyophilization from H_2O as a white powder. $[\alpha]_D^{20} - 35.6^\circ$ ($c=0.26$, CHCl_3 :MeOH=1:1). IR (neat): 2919, 1730, 1639, 1552 cm^{-1} . Positive FAB-MS (NBA): (M) $^+$ m/z 1083.

Phenyl O-(2,3,4,6-Tetra-O-acetyl- β -D-galactopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-acetyl-1-thio- β -D-glucopyranoside (14) The same procedure as described for the preparation of **3** provided a crude product from per-O-Ac lactose (3.39 g, 5 mmol), thiophenol (0.61 g, 5.5 mmol) and boron trifluoride etherate (1.77 g, 12.5 mmol), and this was purified by column chromatography (elution with 1:1 hexane-AcOEt) to give **14** (3.21 g, 88%) as an amorphous powder, mp 68–72°C. $[\alpha]_D^{20} + 27.2^\circ$ ($c=1.00$, CHCl_3). IR: 1750, 695 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 1.963, 2.033, 2.040, 2.043, 2.089, 2.108, 2.148 (each 3H, s, OAc), 3.65 (1H, m, H-5), 3.751 (1H, t, $J_{3,4}=9.0$, $J_{4,5}=10.0$ Hz, H-4'), 3.87 (1H, m, H-5'), 4.10 (3H, m, H-6a,b, H-6'a), 4.471 (1H, d, $J_{7,8}=7.8$ Hz, H-1'), 4.530 (1H, dd, $J_{5,6b}=2.0$, $J_{6a,6b}=12.0$ Hz, H-6'b), 4.675 (1H, d, $J_{1,2}=10.2$ Hz, H-1), 4.901 (1H, t, $J_{2,3}=9.8$ Hz, H-2), 4.948 (1H, dd, $J_{2,3}=9.8$, $J_{3,4}=3.7$ Hz, H-3), 5.102 (1H, dd, $J_{2,1}=7.8$, $J_{2,3}=9.0$ Hz, H-2'), 5.215 (1H, t, $J_{3,4}=9.2$ Hz, H-3'), 5.344 (1H, brd, H-4), 7.30–7.32 (3H, m, Ph), 7.46–7.49 (2H, m, Ph). $^{13}\text{C-NMR}$ (CDCl_3) δ : 85.4 (d, C-1 β), 101.0 (d, C-1' β), 169.0, 169.5, 169.7, 170.0, 170.1, 170.2, 170.3 (s, CO). Positive FAB-MS (NBA): (M+H) $^+$ m/z 729.

Phenyl O-(β -D-Galactopyranosyl)-(1 $\rightarrow$ 4)-1-thio- β -D-glucopyranoside (15) The same procedure as described for the preparation of **4** provided a crude product from **14** (7.80 g, 10.7 mmol) and 0.1 M NaOMe (77 ml, 7.7 mmol), and this was purified by column chromatography (elution with 5:2 CH_2Cl_2 -MeOH) to give **15** (4.65 g, quantitative yield). $[\alpha]_D^{20} - 13.3^\circ$ ($c=0.69$, MeOH). IR: 3380, 690 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 4.403 (1H, d, $J=7.2$ Hz, H-1'), 4.617 (1H, d, $J=9.8$ Hz, H-1), 7.26–7.30 (3H, m, Ph), 7.48–7.52 (2H, m, Ph). $^{13}\text{C-NMR}$ (CDCl_3) δ : 87.7 (d, C-1 β), 103.3 (d, C-1' β). Positive FAB-MS (NBA): (M+Na) $^+$ m/z 457.

Phenyl O-(3,4-O-Isopropylidene- β -D-galactopyranosyl)-(1 $\rightarrow$ 4)-1-thio- β -D-glucopyranoside (16) The same procedure as described for the preparation of **5** provided a crude product from **15** (2.56 g, 5.9 mmol), *p*-TsOH monohydrate (112 mg, 0.59 mmol), acetone (40 ml) and DMF (20 ml), and this was purified by column chromatography (elution with 10:1 CH_2Cl_2 -MeOH) to give **16** (1.88 g, 67%), mp 102–104°C. $[\alpha]_D^{20} - 10.5^\circ$ ($c=0.37$, MeOH). IR: 870, 690 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 1.340, 1.510 (each 3H, s, Me_2C), 7.31–7.34 (3H, m, Ph), 7.51–7.58 (2H, m, Ph). $^{13}\text{C-NMR}$ (CDCl_3) δ : 26.0, 27.7 (q, Me_2C), 87.7 (d, C-1 β), 102.9 (d, C-1' β), 110.3 (s, Me_2C). Positive FAB-MS (NBA): (M+Na) $^+$ m/z 497.

Phenyl O-(2,6-Di-O-benzyl-3,4-O-isopropylidene- β -D-galactopyranosyl)-(1 $\rightarrow$ 4)-1-thio- β -D-glucopyranoside (17) The same procedure as described for the preparation of **6** provided a crude product from **16** (1.33 g, 2.8 mmol), sodium hydride (60% in oil) (0.45 g, 11.2 mmol), benzyl bromide (1.92 g, 11.2 mmol), *n*-Bu₄NBr (90 mg, 0.28 mmol) and DMF (20 ml), and this was purified by column chromatography (elution with 3:1 hexane-AcOEt) to give **17** (2.15 g, 83%). $[\alpha]_D^{20} + 4.8^\circ$ ($c=1.26$, CHCl_3). IR: 870 (isopropylidene), 695 (Ph) cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ :

1.354, 1.388 (each 3H, s, Me_2C), 3.357 (1H, dd, $J_{1,2}=8.0$, $J_{2,3}=6.6$ Hz, H-2'), 3.41 (2H, m, H-2, H-5), 3.54 (1H, m, H-6'a), 3.619 (1H, t, $J=8.9$ Hz, H-4), 3.69 (2H, m, H-5', H-6'b), 3.807 (2H, dd, $J_{3,6}=5.6$, $J_{6a,6b}=1.0$ Hz, H-6a,b), 3.991 (1H, m, H-3), 4.061 (1H, $J_{3,4}=5.7$ Hz, H-3'), 4.131 (1H, dd, $J_{4,5}=1.4$ Hz, H-4), 4.426 (1H, d, H-1'), 4.643 (1H, d, $J_{1,2}=9.8$ Hz, H-1), 4.28–5.00 (10H, m, PhCH_2-), 7.20–7.41 (28H, m, Ph), 7.54–7.57 (2H, m, Ph). $^{13}\text{C-NMR}$ (CDCl_3) δ : 26.3, 27.7 (q, Me_2C), 86.2 (d, $J_{C-H}=154.9$ Hz, C-1 β), 110.0 (s, Me_2C), 137.7, 138.2 (d, Ph). Positive FAB-MS (NBA): (M+H) $^+$ m/z 925.

N-Trichloroethoxycarbonyl O-(2,6-Di-O-benzyl-3,4-O-isopropylidene- β -D-galactopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- β -D-glucopyranosyl)-L-serine Benzyl Ester (18) The same procedure as described for the preparation of **8** provided a crude product from **17** (435 mg, 0.47 mmol), **7** (88 mg, 0.24 mmol), NBS (214 mg, 1.2 mmol), TBAOTf (38 mg, 0.096 mmol), iodine (305 mg, 1.2 mmol), and CH_3CN (20 ml), and this was purified by column chromatography (elution with 3:1 hexane-AcOEt) to give **18** (125 mg, 44%). $[\alpha]_D^{20} + 17.7^\circ$ ($c=1.01$, CHCl_3). IR: 1740, 1500, 700 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 1.349, 1.399 (each 3H, s, Me_2C), 4.307 (1H, d, $J=7.6$ Hz, H-1'), 4.65 (1H, m, Ser α -H), 4.692 (1H, d, $J=8.8$ Hz, H-1), 4.696 (2H, s, Cl_3CCH_2-), 4.70 (4H, m, PhCH_2-), 5.18 (2H, brs, PhCH_2-), 6.002 (1H, d, $J=8.2$ Hz, NH), 7.22–7.38 (30H, m, Ph). $^{13}\text{C-NMR}$ (CDCl_3) δ : 26.3, 27.9 (q, Me_2C), 95.3 (s, Cl_3CCH_2-), 101.7 (d, $J_{C-H}=160.4$ Hz, C-1 β), 103.7 (d, $J_{C-H}=159.5$ Hz, C-1' β), 109.7 (s, Me_2C), 135.1, 138.0, 138.2, 138.3, 138.4, 138.7 (d, Ph), 154.2, 169.2 (s, CO). Positive FAB-MS (NBA): (M+H) $^+$ m/z 1184.

N-Trichloroethoxycarbonyl O-(2,6-Di-O-benzyl- β -D-galactopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- β -D-glucopyranosyl)-L-serine Benzyl Ester (19) The same procedure as described for the preparation of **9** provided a crude product from **18** (439 mg, 0.37 mmol) and 90% AcOH (20 ml), and this was purified by column chromatography (elution with 1:1 hexane-AcOEt) to give **19** (352 mg, 83%). $[\alpha]_D^{20} + 27.8^\circ$ ($c=0.57$, CHCl_3). IR: 1740, 1500, 700 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 3.449 (1H, dd, $J_{1,2}=7.6$, $J_{2,3}=10.4$ Hz, H-2), 3.54–3.58 (2H, m, Ser β -H), 3.703 (1H, dd, $J_{6a,6b}=5.5$, $J_{5,6a}=10.1$ Hz, H-6a), 3.761 (1H, dd, $J_{6a,6b}=5.5$, $J_{5,6b}=10.1$ Hz, H-6b), 3.923 (1H, dd, $J_{3,4}=3.4$ Hz, H-3), 4.338 (1H, d, $J_{1,2}=7.6$ Hz, H-1), 4.382 (1H, brd, H-5), 4.554 (2H, s, Cl_3CCH_2-), 4.56–4.59 (1H, m, Ser-1), 4.692, 4.726 (each 1H, d, $J=11.9$, PhCH_2-), 4.834, 4.868 (each 1H, d, $J=11.6$ Hz, PhCH_2-), 5.199, 5.233 (2H, d, $J=12.2$, PhCH_2-), 6.046 (1H, d, $J=7.9$ Hz, NH), 7.30–7.36 (30H, m, Ph). $^{13}\text{C-NMR}$ (CDCl_3) δ : 95.3 (s, Cl_3CCH_2-), 99.4 (d, C-1' β), 102.7 (d, C-1 β), 135.0, 137.8, 138.1, 138.2, 139.2 (d, Ph), 154.5, 169.5 (s, CO). Positive FAB-MS (NBA): (M+H) $^+$ m/z 1144.

N-Trichloroethoxycarbonyl O-(Methyl 5-acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-2-nonulopyranosyl)onate-(α 2 $\rightarrow$ 3)-O-(2,6-dibenzyl- β -D-galactopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- β -D-glucopyranosyl)-L-serine Benzyl Ester (20) The same procedure as described for the preparation of **11** provided a crude product from **19** (298 mg, 0.26 mmol), **10** (306 mg, 0.52 mmol), NBS (231 mg, 1.3 mmol), TBAOTf (407 mg, 0.10 mmol), iodine (330 mg, 1.3 mmol) and CH_3CN (20 ml), and this was purified by column chromatography (elution with 20:1 CH_2Cl_2 -MeOH) to give **20** (189 mg, 45%). $[\alpha]_D^{20} - 28.1^\circ$ ($c=0.62$, CHCl_3). IR: 1740, 1500, 700 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 1.877 (3H, s, NAc), 1.891, 1.981, 2.015, 2.089 (each 3H, s, OAc), 2.502 (1H, dd, $J_{3a,3e}=12.7$, $J_{3e,4}=4.5$ Hz, H-3'e), 3.762 (3H, s, CH_3O), 4.688 (2H, s, Cl_3CCH_2-), 5.173 (2H, brd, PhCH_2-), 7.28–7.36 (30H, m, Ph). $^{13}\text{C-NMR}$ (CDCl_3) δ : 95.3 (s, Cl_3CCH_2-), 98.4 (d, C-1' α), 102.3 (d, C-1' β), 135.1, 138.3, 138.4, 138.9, 139.0 (d, Ph), 154.3, 168.4, 169.3, 169.9, 170.0, 170.4, 170.6, 170.8 (s, CO). Positive FAB-MS (NBA): (M+Na) $^+$ m/z 1639.

N-Stearoyl O-(Methyl 5-acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-2-nonulopyranosyl)onate-(α 2 $\rightarrow$ 3)-O-(2,6-dibenzyl- β -D-galactopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- β -D-glucopyranosyl)-L-serine Benzyl Ester (21) The same procedure as described for the preparation of **12** provided a crude product from **20** (222 mg, 0.137 mmol), zinc (89 mg, 1.4 mmol) and AcOH (5.0 ml), followed by treatment with stearoyl chloride (83 mg, 0.27 mmol) and NaHCO_3 (92 mg, 1.1 mmol). This product was purified by column chromatography (elution with 20:1 CH_2Cl_2 -MeOH) to give **21** (101 mg, 43%). $[\alpha]_D^{20} + 7.5^\circ$ ($c=2.0$, CHCl_3). IR (neat): 2921, 1745, 1654, 1541, 735, 698 cm^{-1} . $^1\text{H-NMR}$ (CDCl_3) δ : 0.88 (3H, t, $J=7.0$ Hz, –Me), 1.25 (28H, brs, $-\text{CH}_2-$), 1.613 (2H, t, $J=7.3$ Hz, $\text{COCH}_2\text{CH}_2-$), 1.88 (3H, s, NAc), 1.976, 2.015, 2.041, 2.14, 2.083 (each 3H, s, OAc), 2.312 (2H, t, $J=7.6$ Hz, $\text{COCH}_2\text{CH}_2-$), 2.502 (1H, dd, $J_{3e,3a}=13.2$, $J_{3e,4}=4.6$ Hz, H-3_e), 3.755 (3H, s, CO_2Me), 5.169, 5.214 (each 1H, d, $J=10.5$ Hz, $\text{CO}_2\text{CH}_2\text{Ph}$), 7.23–7.39 (30H, m,

Ph). Positive FAB-MS (NBA): $(M+H)^+$ m/z 1710.

N-Stearoyl O-(Methyl 5-acetamido-4,7,8,9-tetra-O-acetyl-3,5-dideoxy-D-glycero- α -D-galacto-2-nonulopyranosyl)onate-(α 2 $\rightarrow$ 3)-O-(2,6-dibenzyl- β -D-galactopyranosyl)-(1 $\rightarrow$ 4)-2,3,6-tri-O-benzyl- β -D-glucopyranosyl)-L-serine Myristoylamide (22) The same procedure as described for the preparation of 13 provided a crude product from 21 (150 mg, 0.088 mmol), palladium-black (160 mg) and EtOH-AcOH (6:1) (14 ml), followed by treatment with tetradecanoylamine (23 mg, 0.11 mmol), DEPC (20 mg, 0.12 mmol) and NEt₃ (13 mg, 0.13 mmol). This product was purified by silica gel column chromatography (elution with 10:1 CH₂Cl₂-MeOH) to give 22 (33 mg, 28%) as a wax. $[\alpha]_D^{+5.9}$ ($c=0.68$, CHCl₃). IR (Nujol): 1737, 1647, 1536 cm⁻¹. ¹H-NMR (CDCl₃) δ : 0.88 (6H, t, $J=6.8$ Hz, -Me), 1.25 (52H, br s, -CH₂-), 1.48-1.59 (2H, m, COCH₂CH₂), 1.90 (3H, s, NAc), 2.04, 2.07, 2.14, 2.16 (each 3H, s, OAc), 2.70-2.73 (1H, m, H-3_{eq}), 3.84 (3H, s, CO₂Me). ¹³C-NMR (CDCl₃) δ : 97.7 (s, C-1' α), 103.6 (d, C-1 β), 168.2, 169.7, 170.1, 170.5, 170.7, 171.0, 171.1, 174.0 (s, CO). Positive FAB-MS (NBA): $(M+Na)^+$ m/z 1387.

N-Stearoyl O-(5-Acetamido-3,5-dideoxy-D-glycero- α -D-galacto-2-nonulopyranosyl)-(α 2 $\rightarrow$ 3)-O-(β -D-galactopyranosyl)-(1 $\rightarrow$ 4)- β -D-glucopyranosyl)-L-serine Myristoylamide (2) The same procedure as described for the preparation of 1 provided a crude product from 22 (35 mg, 0.026 mmol) and 0.1 N KOH-MeOH (3.0 ml, 1:1), and this was purified by silica gel column chromatography (elution with 60:60:5 CHCl₃-MeOH-H₂O) and LH-20 column chromatography (elution with 60:60:10 CHCl₃-MeOH-H₂O) to give 2 (22 mg, 72%) after lyophilization from H₂O, as a white amorphous powder. $[\alpha]_D^{+4.5}$ ($c=0.44$, CHCl₃-MeOH (1:1)). IR (Nujol): 1724, 1655, 1634, 1560, 1538 cm⁻¹. ¹H-NMR (CDCl₃-CD₃OD) δ : 0.88 (6H, t, $J=6.5$ Hz, -Me), 1.26 (52H, br s, -CH₂-), 1.49 (2H, m, COCH₂CH₂), 1.62 (2H, m,

NHCH₂CH₂), 2.04 (2H, m, COCH₂CH₂), 2.27 (2H, m, NHCH₂CH₂). Positive FAB-MS (NBA): $(M+K-H)^+$ m/z 1220.

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