Synthesis of *N*-Acetylglucosaminyl- and *N*-Acetylgalactosaminylceramides as Cerebroside Analogs and Their Anti-human Immunodeficiency Virus Type 1 Activities

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Monoglycosylceramide derivatives containing mimicks of ceramide were synthesized as cerebroside analogs from D-glucosamine or D-galactosamine derivatives and *N*-benzyloxycarbonyl-L-serine myristylamide by using trimethylsilyl trifluoromethanesulfonate (TMSOTf) as a promoter. The synthesized sulfated glycolipids show moderate anti-HIV-1 activities.

Key words sulfated glycosylceramide; cerebroside analog; anti-HIV-1 activity

Galactosylceramide is an essential component of neural receptor for type 1 human immunodeficiency virus (HIV) surface glycoprotein gp120.[1] Various galactosylceramide analogs have been synthesized and their biological activities were examined.[2] In preceding papers, we reported the synthesis of sulfated gangliosides[3] and sulfated cerebroside analogs[4] containing L-serine diamide derivatives as mimicks of the ceramide moieties of gangliosides showing anti-influenza virus activities and anti-HIV type 1 activities. *N*-Acetyl D-glucosamine and *N*-acetyl D-galactosamine are often found as constituents of glycoconjugates,[5] and they have various biological activities and functions.

As a part of our synthetic studies on biologically active new compounds designed by modifying natural glycoconjugates, we describe here the synthesis of sulfated monoglycosylceramides, as indicated in Chart 1, together with some results of biological testing.

Chart 2 shows the synthetic route to **5a** and **5b**. First, the neighboring-group-assisted coupling of 2-chloroacetamido-2-deoxy-1,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose and 2-chloroacetamido-2-deoxy-1,3,4,6-tetra-*O*-acetyl-β-D-galactopyranose with an *N*-benzyloxycarbonyl-L-serine myristylamide derivative in the presence of $Me_3SiOSO_2CF_3$ (TMSOTf) and molecular sieves 4 Å in $ClCH_2CH_2Cl$ gave the desired glycosides (**1a** and **1b**) in yields of 69 and 74%, respectively. The ^{1}H-NMR data for the anomeric proton H-1 [δ4.71 ($J_{1,2}$=6.8 Hz) in **1a**, δ4.69 ($J_{1,2}$=7.0 Hz) in **1b**] indicated the stereochemistry of the newly formed glycosidic bond to be β. Reduction of the benzyloxycarbonyl and chloroacetyl groups in **1a** and **1b** by hydrogenolysis over Pd–C in MeOH gave the alcohols **2a** and **2b** (quantitative and 93% yield, respectively). De-*O*-acetylation of **2a** and **2b** had to be done under mild conditions, due to base-sensitivity (*retro*-Michael reaction) of the *O*-serinyl glycosyl portion in particular.[6] The best results were achieved by treatment of **2a** and **2b** with triethylamine (TEA)–MeOH (1 : 10)[7] at room temperature to give the triols **3a** and **3b** (quantitative and 88% yield, respectively). During the de-*O*-acetylation, no β-elimination product was detected. Acylation of the free amino groups of **3a** and **3b** with stearoyl chloride and aqueous $NaHCO_3$ gave diacylated compounds **4a** and **4b** (87% yield and quantitative, respectively). Finally, *O*-sulfation of **4a** and **4b** was achieved with sulfur trioxide-tripyridine complex in *N*,*N*-dimethylformamide (DMF). Removal of pyridine was readily accomplished by brief treatment with trifluoromethanesulfonic acid (TFA) in dichloromethane and the products were purified by chromatography on Sephadex LH-20 ($CHCl_3$: MeOH : H_2O = 6 : 6 : 1) and lyophilized to afford the 3,4,6-tri-*O*-sulfated glycosides **5a** and **5b** (42 and 46% yields, respectively). Absorptions at 1215—1268 cm^{-1} (due to S=O stretching) and 756—834 cm^{-1} (due to C–O–S vibration) were observed in the infrared (IR) spectra of **5a** and **5b**, indicating the presence of sulfate esters. Furthermore, **5a** and **5b** gave a positive test with a specific spray-reagent (azure A reagent) for sulfated glycolipids.[8]

The structures of all compounds were characterized by ^{1}H-NMR spectroscopy, as well as IR spectroscopy, elemental analyses, and positive FAB-mass spectrometry.

The anti-HIV-1 activities of the two nonsulfated glycosylceramides (**4a** and **4b**) and the two sulfated glycosylceramides (**5a** and **5b**) are shown in Table 1. The anti-HIV-1 activity was tested by the syncytium-formation

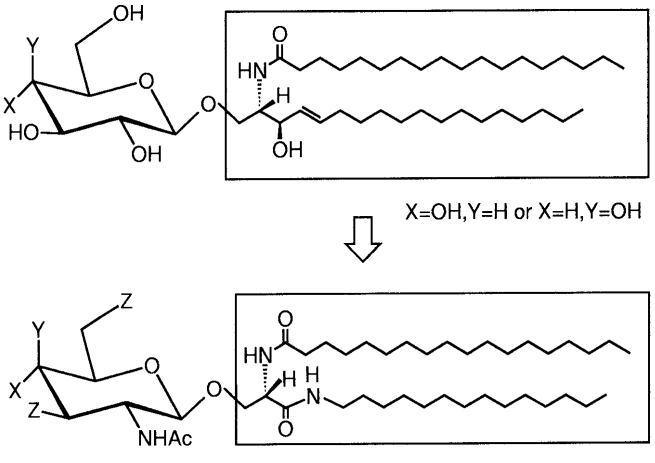

Chart 1

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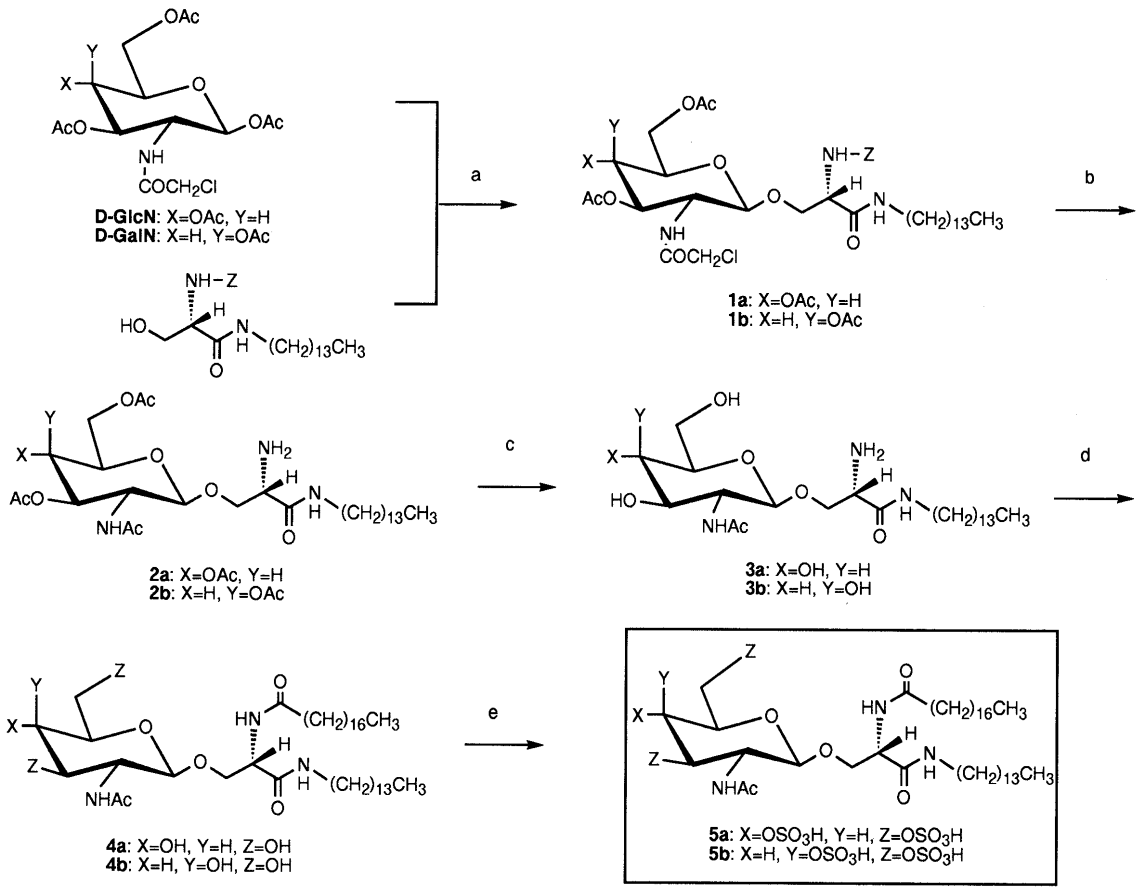

Reagents: a) TMSOTf, $ClCH_2CH_2Cl$; b) H_2, Pd-C, MeOH; c) TEA-MeOH (1:10); d) $CH_3(CH_2)_{16}COCl$, $NaHCO_3$, ether-H_2O; e) i) SO_3-pyridine, DMF-pyridine (1:1) ; ii) TFA , CH_2Cl_2, then LH-20 ($CHCl_3$-MeOH-H_2O= 6:6:1)

Chart 2

Table 1. Results of Anti-HIV Assay by IFA Using MT-4 Cells

Compd. No.	HIV-1 infection (IC_{50}) (μg/ml)[a]	CT[b]
4a	>100	(++)
4b	>100	(++)
5a	30—100	(−)
5b	30—100	(−)

a) Concentrations (μg/ml) of compounds at which 50% of MT-4 cells expressed HIV-1 antigens. *b*) CT: cytotoxic (− to ++).

assay method using MT-4 cells according to our previously reported method.[3b] Among the synthesized compounds, the sulfated compounds (**5a** and **5b**) showed moderate activities with 50%-inhibitory concentration (IC_{50}) values of 30—100 μM, and they were noncytotoxic. The non-sulfated compounds (**4a** and **4b**) were practically inactive (IC_{50} > 100 μM) against HIV-1 and were cytotoxic.

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 infrared spectrophotometer ^{1}H-NMR spectra were taken on a JEOL JNM-GX 270 (270 MHz) spectrometer with tetramethylsilane (in $CDCl_3$) as an internal standard, and the chemical shifts are given in δ values. The abbreviations of signal patterns are as follows: s, singlet; brs, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra (MS) were recorded on a JEOL JMS-SX102 spectrometer. Column chromatography was carried out on Silica gel 60 (70—230 mesh, Merck). Thin-layer chromatography (TLC) on silica gel 60-F_{254} (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. Sulfated glycolipids were visualized with azure A reagent. The bands of lipids containing sulfate esters were stained blue.

***N*-Benzyloxycarbonyl-*O*-(3,4,6-tri-*O*-acetyl 2-chloroacetylamino-2-deoxy-β-D-glucopyranosyl)-L-serine Myristylamide (1a)** A solution of 2-chloroacetamido-2-deoxy-1,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose (0.85 g, 2 mmol) and *N*-benzyloxycarbonyl-L-serine myristylamide (0.90 g, 2 mmol) in anhydrous $ClCH_2CH_2Cl$ (20 ml) was stirred for 1 h at room temperature under argon in the presence of powdered molecular sieves 4 Å. The mixture was cooled to 0 °C, then TMSOTf (0.45 g, 2 mmol) was added. The mixture was stirred for 15 h at room temperature, and the reaction mixture was filtered through Celite 545. The filtrate was washed with aqueous $NaHCO_3$ and H_2O, dried ($MgSO_4$), and concentrated *in vacuo*. The residual product was chromatographed on SiO_2 with CH_2Cl_2–CH_3COCH_3 (20:1) to give **1a** (1.10 g, 69%) as an amorphous powder. $[\alpha]_D$ +1.1° (*c*=0.90, $CHCl_3$). IR (Nujol): 1744 (ester), 1657, 1535 (amide) cm^{-1}.

^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, *J*=7.0 Hz, $-CH_3$), 1.26 (22H, brs, $-CH_2-$), 1.42—1.49 (2H, m, $NCH_2C\underline{H}_2$), 2.03, 2.04, 2.06 (each 3H, s, OAc), 3.23 (2H, t, *J*=6.5 Hz, $NC\underline{H}_2CH_2$), 3.77 (1H, dd, *J*=10.5, 7.3 Hz, $OC\underline{H}_aH_bCHN$), 3.86—3.98 (2H, m, H-2,5), 3.94 (2H, brs, $NHCOC\underline{H}_2Cl$), 4.08 (1H, dd, *J*=10.5, 4.3 Hz, $OCH_a\underline{H}_bCHN$), 4.15 (1H, dd, *J*=11.7, 2.2 Hz, H-6b), 4.24 (1H, dd, *J*=11.7, 4.9 Hz, H-6a), 4.34—4.36 (1H, m, $OCH_2C\underline{H}N$), 4.71 (1H, d, *J*=6.8 Hz, H-1), 5.05 (1H, dd, *J*=9.5 Hz, H-4), 5.11 (2H, brs, CH_2Ph), 5.25 (1H, t, *J*=9.5 Hz, H-3), 5.68 (1H, brs, $OCH_2CHN\underline{H}$), 6.37 (1H, brs, CONH), 6.61 (1H, d, *J*=8.9 Hz, $N\underline{H}COCH_2Cl$), 7.36 (5H, brs, Ph). *Anal.* Calcd for $C_{39}H_{60}ClN_3O_{12}$: C, 58.67;H, 7.58; N, 5.26. Found: C, 58.32; H, 7.61; N, 5.05.

***O*-(3,4,6-Tri-*O*-acetyl-2-acetylamino-2-deoxy-β-D-glucopyranosyl)-L-serine Myristylamide (2a)** A mixture of **1a** (0.98 g, 0.84 mmol) and 10% Pd–C (0.24 g) in MeOH (40 ml) was stirred under H_2 overnight at room temperature. The catalyst was removed by filtration and the filtrate was concentrated to dryness. The residue was chromatographed on SiO_2 with CH_2Cl_2–MeOH (10 : 1) to give **2a** (0.529 g, quant.), mp 125—128 °C. $[\alpha]_D$ −14.3° (c = 0.46, MeOH). IR (KBr): 3300 (NH), 1744 (ester), 1657, 1535 (amide) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J = 7.3 Hz, –CH_3), 1.26 (22H, br s, –CH_2–), 1.50 (2H, br s, $NCH_2C\underline{H}_2$), 1.95, 2.03, 2.09 (12H, s, OAc, NAc), 3.18—3.26 (2H, m, $NC\underline{H}_2CH_2$), 3.54 (1H, dd, J = 7.6, 4.9 Hz, $OCH_2C\underline{H}N$), 3.64—3.70 (1H, m, H-5), 3.82 (1H, dd, J = 10.3, 7.6 Hz, $OC\underline{H}_aH_bCHN$), 3.90 (1H, dd, J = 10.3, 4.9 Hz, $OCH_a\underline{H}_bCHN$), 3.98 (1H, dd, J = 8.4, 8.9 Hz, H-2), 4.13 (1H, dd, J = 12.2, 2.2 Hz, H-6a), 4.25 (1H, dd, J = 12.2, 4.6 Hz, H-6b), 4.59 (1H, d, J = 8.4 Hz, H-1), 5.07 (1H, t, J = 9.2 Hz, H-4), 5.17 (1H, t, J = 9.2 Hz, H-3), 5.71 (1H, d, J = 8.9 Hz, AcNH). *Anal.* Calcd for $C_{31}H_{55}N_3O_{10}$: C, 59.12; H, 8.80; N, 6.67. Found: C, 59.10; H, 8.90; N, 6.70.

***O*-(2-Acetylamino-2-deoxy-β-D-glucopyranosyl)-L-serine Myristylamide (3a)** A solution of **1b** (0.55 g, 0.87 mmol) in NEt_3–MeOH (1 : 10) (30 ml) was stirred at room temperature for 5 h, then concentrated to dryness under reduced pressure. The residue was purified by column chromatography with CH_2Cl_2–MeOH (3 : 1) to give **3a** (0.44 g, quant.), mp 188—191 °C. $[\alpha]_D$ −14.5° (c = 0.36, $CHCl_3$–MeOH (1 : 1)). IR (KBr): 3300 (NH), 1646, 1557 (amide) cm^{-1}. ^{1}H-NMR ($CDCl_3$: CD_3OD = 10 : 1) δ: 0.88 (3H, t, J = 7.0 Hz, –CH_3), 1.26 (22H, br s, –CH_2–), 1.44—1.51 (2H, m, $NCH_2C\underline{H}_2$), 2.01 (3H, s, AcN), 3.20 (2H, t, J = 6.8 Hz, $NC\underline{H}_2CH_2$), 3.29—3.41 (4H, m, $NCH_2C\underline{H}N$, H-5, 6), 3.44 (1H, t, J = 8.4 Hz, H-3), 3.61 (1H, t, J = 8.4 Hz, H-2), 3.73 (1H, dd, J = 10.3, 4.9 Hz, $OC\underline{H}_aH_bCHN$), 3.87 (1H, dd, J = 10.3, 2.7 Hz, $OCH_a\underline{H}_bCHN$), 4.40 (1H, d, J = 8.4 Hz, H-1). *Anal.* Calcd for $C_{25}H_{49}N_3O_7 \cdot H_2O$: C, 57.56; H, 9.85; N, 8.05. Found: C, 58.04; H, 9.58; N, 7.55. Positive FAB-MS m/z: 503 $(M+1)^+$.

***N*-Stearoyl-*O*-(2-acetylamino-2-deoxy-β-D-glucopyranosyl)-L-serine Myristylamide (4a)** A solution of stearoyl chloride (0.112 g, 0.36 mmol) in ether (10 ml) was added to a solution of **3a** (0.171 g, 0.36 mmol) and saturated aqueous $NaHCO_3$ (50 ml) at 0 °C. The mixture was stirred for 4 h. The resulting precipitates was washed with ether and dried *in vacuo* to give **4a** (0.24 g, 87%), mp 229—231 °C, as an amorphous powder. IR (KBr): 3280 (OH, NH), 1654, 1542 (amide) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 0.86 (6H, t, J = 6.5 Hz, –CH_3), 1.24 (52H, br s, –CH_2–), 1.40 (2H, br s, $COCH_2C\underline{H}_2$), 1.49 (2H, br s, $NCH_2C\underline{H}_2$), 1.83 (3H, s, AcNH), 4.34 (1H, d, J = 7.3 Hz, H-1), 4.48 (1H, br s, NH), 4.89 (1H, br s, NH). *Anal.* Calcd for $C_{43}H_{83}N_3O_8 \cdot 5H_2O$: C, 60.04; H, 10.90; N, 4.88. Found: C, 60.20; H, 10.96; N, 4.11. Positive FAB-MS m/z: 771 $(M+1)^+$, 793 $(M+Na)^+$.

***N*-Stearoyl-*O*-(2-acetylamino-2-deoxy-3,4,6-tri-*O*-sulfo-β-D-glucopyranosyl)-L-serine Myristylamide (5a)** A solution of **4a** (0.093 g, 0.12 mmol) in DMF (4 ml) was stirred for 20 h at 40—50 °C in the presence of sulfur trioxide–pyridine complex (0.086 g, 0.54 mmol). The mixture was cooled and chromatographed on a column of Sephadex LH-20 equilibrated in 1 : 1 (v/v) $CHCl_3$–MeOH. Elution with the same solvent gave a residue that was dissolved in CH_2Cl_2 (4 ml). The solution was treated with CF_3SO_3H (0.062 g, 0.54 mmol) for 3 h under ice-cooling, then the solvent was evaporated *in vacuo*. The residue was dissolved in H_2O (1 ml) and chromatographed on a column of Sephadex LH-20. Elution with 6 : 6 : 1 (v/v/) $CHCl_3$–MeOH–H_2O afforded **5a** (0.052 g, 42%) as an amorphous powder, after lyophilization from H_2O, mp 165—167 °C. IR (KBr): 1652, 1542 (amide), 1251 (S=O), 816 cm^{-1} (C–O–S). *Anal.* Calcd for $C_{48}H_{83}N_3O_{17}S_3 \cdot 2H_2O$: C, 52.11; H, 7.93; N, 3.80. Found: C, 52.33; H, 7.71; N, 3.75.

***N*-Benzyloxycarbonyl-*O*-(3,4,6-tri-*O*-acetyl-2-chloroacetylamino-2-deoxy-β-D-galactopyranosyl)-L-serine Myristylamide (1b)** The same procedure as described for the preparation of **1a** provided a crude product from 2-chloroacetamido-2-deoxy-1,3,4,6-tetra-*O*-acetyl-β-D-galactopyranose (0.425 g, 1.0 mmol), *N*-benzyloxycarbonyl-L-serine myristylamide (0.455 g, 1.0 mmol) and TMSOTf (0.222 g, 1.0 mmol) and this was purified by column chromatography (elution with 20 : 1 $CHCl_3$–CH_3COCH_3) to give **1b** (0.59 g, 74%) as an amorphous powder. $[\alpha]_D$ +2.3° (c = 1.30, $CHCl_3$). IR (KBr): 1744 (ester), 1657, 1535 (amide) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J = 6.8 Hz, –CH_3), 1.25 (22H, br s, –CH_2–), 1.42—1.49 (2H, m, $NCH_2C\underline{H}_2$), 2.03, 2.04, 2.14 (each 3H, s, AcO), 3.23 (2H, t, J = 5.9 Hz, $NC\underline{H}_2CH_2$), 3.78 (1H, dd, J = 10.5, 7.0 Hz, $OC\underline{H}_aH_bCHN$), 3.95 (2H, br s, $NHCOC\underline{H}_2Cl$), 4.01—4.18 (3H, m, H-2, 5, $OCH_a\underline{H}_bCHN$), 4.34 (1H, dd, J = 4.9, 7.0 Hz, $OCH_2C\underline{H}N$), 4.69 (1H, d, J = 7.0 Hz, H-1), 5.11 (2H, s, $OC\underline{H}_2Ph$), 5.20 (1H, dd, J = 3.0, 8.1 Hz, H-3), 5.36 (1H, br d, J = 3.0 Hz, H-4), 5.71 (1H, br s, $OCH_2CHN\underline{H}$), 6.38 (1H, br s, CONH), 6.54 (1H, d, J = 8.6 Hz, $N\underline{H}COCH_2Cl$), 7.35 (5H, br s, Ph). *Anal.* Calcd for $C_{39}H_{60}ClN_3O_{12}$: C, 58.67; H, 7.58; N, 5.26. Found: C, 58.75; H, 7.77; N, 5.06.

***O*-(3,4,6-Tri-*O*-acetyl-2-acetylamino-2-deoxy-β-D-glucopyranosyl)-L-serine Myristylamide (2b)** The same procedure as described for the preparation of **2a** provided a crude product from **1b** (0.59 g, 0.74 mmol), Pd-on-charcoal (0.25 g) and MeOH (15 ml), and this was purified by column chromatography (elution with 10 : 1 CH_2Cl_2–MeOH) to give **2b** (0.471 g, 93%) as an amorphous powder, mp 110—113 °C. $[\alpha]_D$ −12.0° (c = 0.99, MeOH). IR (KBr): 3354 (NH, OH), 1745 (ester), 1656, 1527 (amide) cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J = 7.0 Hz, –CH_3), 1.26 (22H, br s, –CH_2–), 1.51 (2H, br s, $NCH_2C\underline{H}_2$), 1.96, 2.01, 2.05, 2.15 (each 3H, s, OAc, NAc), 3.18—3.27 (2H, m, $NC\underline{H}_2CH_2$), 3.56 (1H, dd, J = 7.6, 4.6 Hz, $OCH_2C\underline{H}NH$), 3.83 (1H, dd, J = 10.0, 7.6 Hz, H-6a), 3.90 (1H, dd, J = 10.0, 4.9 Hz, H-6b), 4.04—4.08 (1H, m, H-5), 4.12—4.22 (1H, m, H-2), 4.62 (1H, d, J = 8.4 Hz, H-1), 5.15 (1H, dd, J = 11.3, 3.5 Hz, H-3), 5.35 (1H, br d, J = 3.5 Hz, H-4), 5.70 (1H, br d, J = 8.6 Hz, NHAc). *Anal.* Calcd for $C_{31}H_{55}N_3O_{10}$: C, 59.12; H, 8.80; N, 6.67. Found: C, 58.67; H, 8.78; N, 6.65.

***O*-(2-Acetylamino-2-deoxy-β-D-glucopyranosyl)-L-serine Myristylamide (3b)** The same procedure as described for the preparation of **3a** provided a crude product from **2b** (0.25 g, 0.50 mmol) and NEt_3–MeOH (1 : 10) (20 ml), and this was purified by column chromatography (elution with 3 : 1 CH_2Cl_2–MeOH) to give **3b** (0.15 g, 88%) as an amorphous powder, mp 160—162 °C. $[\alpha]_D$ − 7.6° (c = 1 : 1 $CHCl_3$–MeOH). IR (KBr): 3282 (NH, OH), 1648, 1560 (amide) cm^{-1}. ^{1}H-NMR ($CDCl_3$: CD_3OD = 10 : 1) δ: 0.88 (3H, t, J = 7.0 Hz, –CH_3), 1.27 (22H, br s, –CH_2–), 1.51 (2H, br s, $NCH_2C\underline{H}_2$), 2.02 (3H, s, AcN), 3.20 (2H, t, J = 7.0 Hz, $NC\underline{H}_2CH_2$), 3.49 (1H, dd, J = 11.3, 4.9 Hz, H-6a), 3.56 (1H, dd, J = 10.5, 3.5 Hz, H-3), 3.71—3.75 (1H, m, H-5), 3.77 (1H, dd, J = 4.6, 3.5 Hz, H-4), 3.85 (1H, t, J = 10.5 Hz, H-2), 3.84 (1H, dd, J = 11.3, 3.2 Hz, H-6b), 4.37 (1H, d, J = 8.1 Hz, H-1). *Anal.* Calcd for $C_{25}H_{49}N_3O_7$: C, 59.62; H, 9.81; N, 8.34. Found: C, 59.32; H, 9.81; N, 8.13.

***N*-Stearoyl-*O*-(2-acetylamino-2-deoxy-β-D-glucopyranosyl)-L-serine Myristylamide (4b)** The same procedure as described for the preparation of **4a** provided a crude product from **3b** (0.12 g, 0.25 mmol), stearoyl chloride (0.078 g, 0.25 mmol) and saturated aqueous $NaHCO_3$ (25 ml), and this was washed with ether to give **3b** (0.19 g, quant.) as an amorphous powder, mp 219—222 °C. IR (KBr): 3276 (OH), 1639, 1559 (amide) cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 0.86 (6H, t, J = 5.9 Hz, –CH_3), 1.24 (52H, br s, –CH_2–, 1.40 (2H, br s, $COCH_2C\underline{H}_2$), 1.49 (2H, br s, $NCH_2C\underline{H}_2$), 1.84 (3H, s, AcNH). *Anal.* Calcd for $C_{43}H_{83}N_3O_8 \cdot 5H_2O$: C, 60.04; H, 10.90; N, 4.88. Found: C, 60.07; H, 10.39; N, 4.23.

***N*-Stearoyl-*O*-(2-acetylamino-2-deoxy-3,4,6-tri-*O*-sulfo-β-D-glucopyranosyl)-L-serine Myristylamide (5b)** The same procedure as described for the preparation of **5a** provided a crude product from **4b** (0.070 g, 0.09 mmol) and sulfur trioxide–pyridine complex (0.065 g, 0.41 mmol), followed by TFA (0.047 g, 0.41 mmol), and this was purified on a column of Sephadex LH-20 equilibrated in $CHCl_3$–MeOH–H_2O (6 : 6 : 1, v/v) to give **9** (0.042 g, 46%) as an amorphous powder. mp 154—157 °C. IR (KBr): 1653, 1543 (amide), 1250 (S=O), 812 (C–O–C) cm^{-1}. *Anal.* Calcd for $C_{48}H_{83}N_3O_{17}S_3 \cdot H_2O$: C, 52.97; H, 7.87; N, 3.86. Found: C, 53.17; H, 8.26; N, 3.81.

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