

# Synthesis of Sulfated Cerebroside Analogs Having Mimicks of Ceramide and Their Anti-human Immunodeficiency Virus Type 1 Activities

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Various sulfated cerebroside analogs, which are mimicks of cerebroside, have been prepared from per-*O*-acetylated D-glucose, per-*O*-acetylated D-galactose, and per-*O*-acetylated D-lactose with ethyleneglycol dodecyl ether, 3-docosyloxy-1-propanol, 2-hydroxymethyl-1,3-*O*-dimyristyl-1,3-propanediol, and L-serine diamide derivatives as ceramide moieties. The synthesized sulfated glycolipids showed anti-HIV-1 activities.

**Key words** sulfated cerebroside analog; ganglioside analog; anti-HIV-1 activity; L-serine diamide derivative

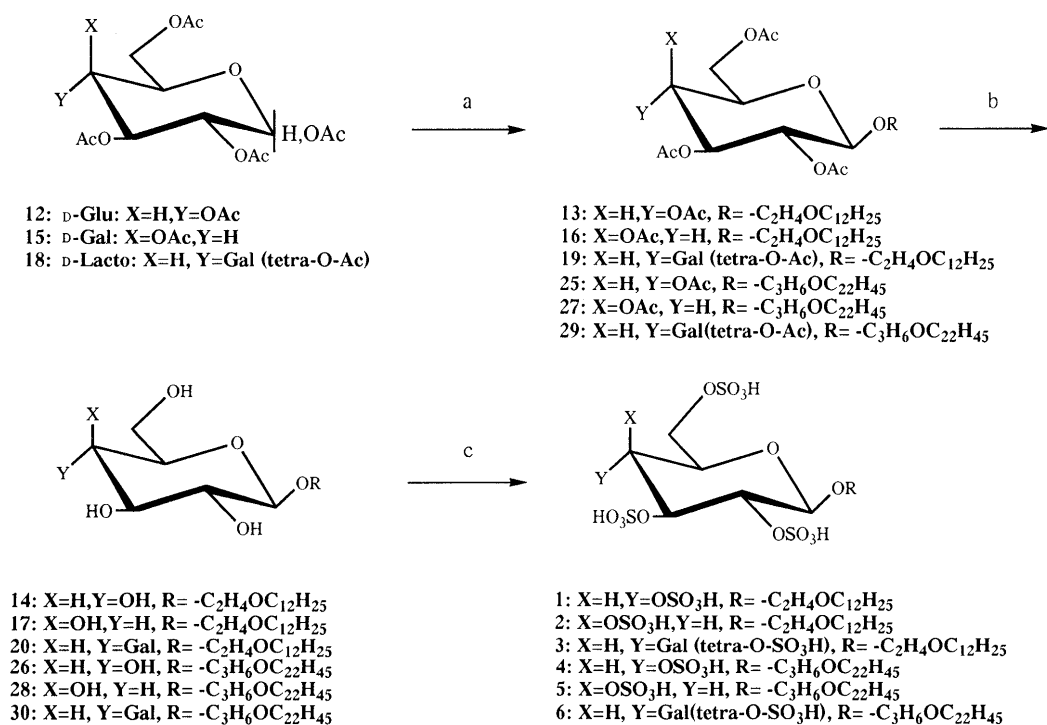
The glycoconjugates located on cell surface glycoprotein and glycolipids serve as recognition markers for the immune system and also play critical roles in the binding of lectins, hormones, and enzymes, the targeting of viruses and bacteria to the cell, and cell-cell recognition and development.<sup>1)</sup> It has been reported that dextran sulfate, heparin, and other sulfated polysaccharides are highly selective inhibitors of human immunodeficiency virus (HIV) replication.<sup>2)</sup> Sulfation is assumed to play a critical role in the anti-HIV activity of these polysaccharide.<sup>3)</sup>

We have recently reported that sulfated gangliosides have potent anti-HIV activities.<sup>4)</sup> However, gangliosides are usually available from natural sources in only limited quantities and are sialic acid-containing glycolipids, the

*O*-glycosidic linkage of which is fairly unstable to acids and bases. Therefore, versatile synthesis of cerebroside analogs as mimicks of gangliosides seems to be of importance.

As part of our synthetic studies<sup>5)</sup> on biologically active new compounds designed on the basis of the chemical structure of glycoconjugates, including some found in nature, we planned to develop practical syntheses of biologically active cerebroside analogs containing modified ceramides as ganglioside analogs. We describe herein the synthesis of biologically active cerebroside analogs as mimicks of the ceramide moieties of gangliosides and the results of evaluation of their biological activities.

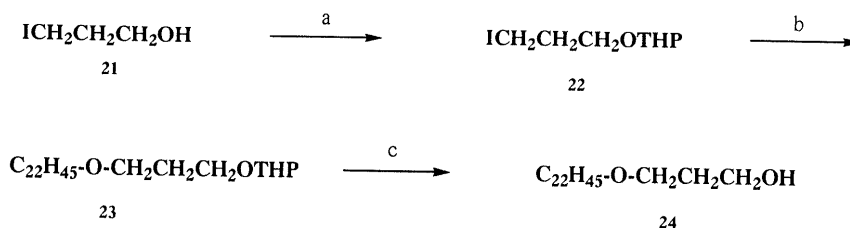
We chose the ethylene glycol dodecyl ether (**11**), 3-



reagents and conditions : a) TMSOTf, **11** (in the case of **1**, **2**, **3**), **24** (in the case of **4**, **5**, **6**); b) NH<sub>4</sub>OH-MeOH (1:20)  
c) i) SO<sub>3</sub>NMe<sub>3</sub>, ii) CF<sub>3</sub>CO<sub>2</sub>H

Chart 1

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reagents and conditions : a) 3,4-dihydro-2*H*-pyran, PPTS; b)  $\text{C}_{22}\text{H}_{45}\text{OH}$ , NaH; c) PPTS, EtOH

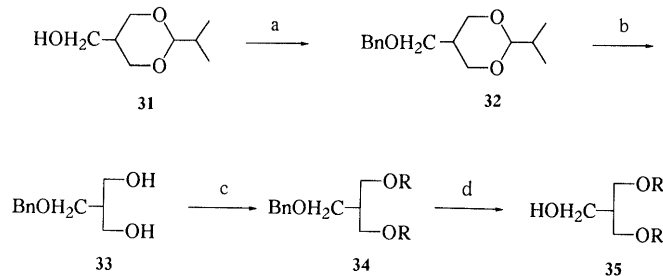
Chart 2

docosyloxy-1-propanol (**24**) and 2-hydroxymethyl-1,3-*O*-dimyristyl-1,3-propanediol (**35**) as ceramide moieties for the derivatives. First, for preparing **1**, **2**, and **3**, the neighboring-group-assisted coupling of per-*O*-acetylated D-glucose (**12**), per-*O*-acetylated D-galactose (**15**), and per-*O*-acetylated D-lactose (**18**) with ethylene glycol dodecyl ether (**11**) in the presence of trimethylsilyl trifluoromethanesulfonate (TMSOTf) and molecular sieves 4 Å in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  gave the desired glycosides **13**, **16**, and **19** in yields of 25, 42 and 59%, respectively, as shown in Chart 1.

Compounds **25**, **27**, and **29** were also obtained by the condensation of **12**, **15**, and **18** with 3-docosyloxy-1-propanol (**24**), readily prepared from 3-iodo-1-propanol (**21**) in 3 steps, according to Chart 2, in yields of 15, 20, and 72%, respectively.

The  $^1\text{H-NMR}$  signal of the anomeric proton H-1 at  $\delta$  4.62 ( $J_{1,2}=8.3$  Hz) in **13**,  $\delta$  4.58 ( $J_{1,2}=7.9$  Hz) in **16**,  $\delta$  4.50 ( $J_{1,2}=8.3$  Hz) in **19**,  $\delta$  4.48 ( $J_{1,2}=8.3$  Hz) in **25**,  $\delta$  4.46 ( $J_{1,2}=8.2$  Hz) in **27**, and  $\delta$  4.46 ( $J_{1,2}=7.8$  Hz) in **29** indicated the stereochemistry of the newly formed glycosidic bond to be  $\beta$ . Removal of acetyl groups in **13**, **16**, **19**, **25**, **27**, and **29** by treatment with  $\text{NH}_4\text{OH-MeOH}$  (1 : 10) gave the alcohols **14**, **17**, **20**, **26**, **28**, and **30** in yields of 31, 20, 46, 46, 53, and 29%, respectively. *O*-Sulfation of **14**, **17**, **20**, **26**, **28**, and **30** was achieved with sulfur trioxide-trimethylamine complex in *N,N*-dimethylformamide<sup>6)</sup> (DMF). Removal of trimethylamine was readily accomplished by brief treatment with trifluoromethanesulfonic acid in dichloromethane, and purification by chromatography on Sephadex LH-20 ( $\text{CHCl}_3$  :  $\text{MeOH}$  :  $\text{H}_2\text{O}$  = 20 : 20 : 1) followed by lyophilization of the aqueous solution afforded the sulfated glycosides **1**, **2**, **3**, **4**, **5**, and **6** in yields of 34, 31, 61, 33, 42, and 28%, respectively. Absorptions at  $1215\text{--}1268\text{ cm}^{-1}$  (due to S=O stretching) and  $756\text{--}834\text{ cm}^{-1}$  (due to C-O-S vibration) were observed in the infrared (IR) spectra of **1**, **2**, **3**, **4**, **5**, and **6**, indicating the presence of sulfate esters. Furthermore, these compounds gave a positive test with the specific spray-reagent (azure A reagent) for sulfated glycolipids.<sup>7)</sup>

Secondly, for the synthesis of **7** and **8**, we prepared 2-hydroxymethyl-1,3-*O*-dimyristyl-1,3-propanediol (**35**) as the aglycone (Chart 3). Treatment of 2-isopropyl-5-hydroxymethyl-1,3-dioxane (**31**)<sup>8)</sup> with benzyl bromide in DMF in the presence of sodium hydride gave, after chromatography, a monobenzyl ether (**32**) in 94% yield. Hydrolysis of **32** with 1 *N* HCl in MeOH gave the diol **33** in 50% yield. Then treatment of **33** with myristyl



reagents and conditions : a)  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ , NaH, *n*- $\text{Bu}_4\text{NI}$ ; b) 1 *N* HCl; c) NaH,  $\text{C}_{14}\text{H}_{29}\text{Br}$ , *n*- $\text{Bu}_4\text{NI}$ ; d) Pd-C,  $\text{H}_2$

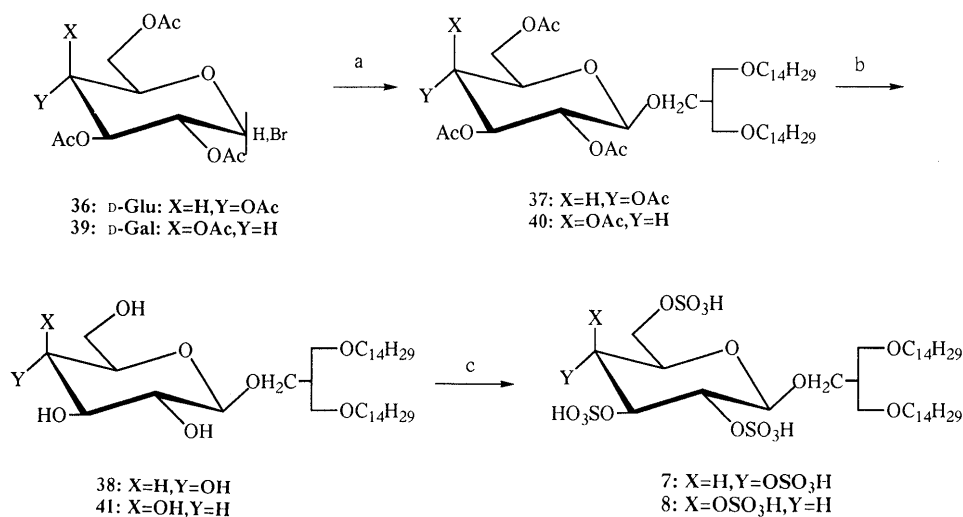
Chart 3

bromide in DMF in the presence of sodium hydride and *n*-tetrabutylammonium iodide, followed by hydrogenolysis over Pd-C with  $\text{H}_2$  gave the alcohol **35** in 61% yield in two steps.

Condensation of **36** and **39** with **35** in the presence of  $\text{HgBr}_2$  in 1,2-dichloroethane gave the expected glycosides **37** and **40**, in yields of 52 and 65%, respectively, as illustrated in Chart 4.  $^1\text{H-NMR}$  spectra revealed a doublet due to H-1 at  $\delta$  4.47 ( $J_{1,2}=8.3$  Hz) for **37** and  $\delta$  4.44 ( $J_{1,2}=7.8$  Hz) for **40**, indicating the stereochemistry of the glycosidic bond formed to be  $\beta$  in both **37** and **40**. Subsequent saponification of **37** and **40** with  $\text{NH}_4\text{OH-MeOH}$  (1 : 10) gave the  $\beta$ -linked glycosides **38** and **41** in quantitative yields. Compounds **38** and **41** were then per-*O*-sulfated in the same manner to afford the sulfated glycosides **7** and **8**, in yields of 43 and 30%, respectively.

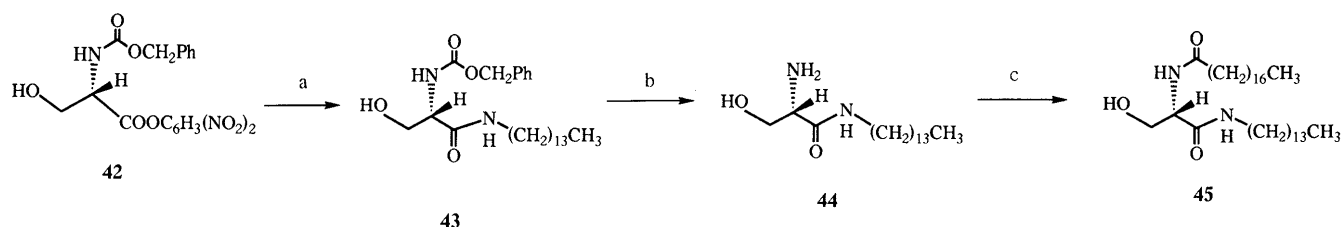
Thirdly, to obtain more effective compounds, we tried further structural modifications of the ceramide unit. We designed the L-serine diamide derivatives (**45**) bearing two amide functions as complicated mimicks of ceramides, as shown in Fig. 1.

That is, the (*S*)-configuration of the *N*-stearoyl group of **45** at the carbon of attachment is the same as that of natural sphingosines. In addition, the native allyl group has been replaced by an isosteric amide group consisting of a saturated fourteen-carbon fatty acid residue. For the preparation of **45**, *N*-carbobenzoxy-L-serine-2,4-dinitrophenol (**42**) was treated with myristylamine in the presence of triethylamine to give the amide **43** in 65% yield. Deprotection of the benzyloxycarbonyl group of **43** was carried out with Pd-C and  $\text{H}_2$ , followed by acylation with stearoyl chloride and  $\text{NaHCO}_3$  to give the diamide **45** in almost quantitative yield in 2 steps, as illustrated in



reagents and conditions : a) HgBr<sub>2</sub>, 35; b) NH<sub>4</sub>OH-MeOH (1:10); c) i) SO<sub>3</sub>NMe<sub>3</sub>, ii) CF<sub>3</sub>CO<sub>2</sub>H

Chart 4



reagents and conditions : a) C<sub>14</sub>H<sub>29</sub>NH<sub>2</sub>, Et<sub>3</sub>N; b) Pd-C, H<sub>2</sub>; c) C<sub>17</sub>H<sub>35</sub>COCl, NaHCO<sub>3</sub>

Chart 5

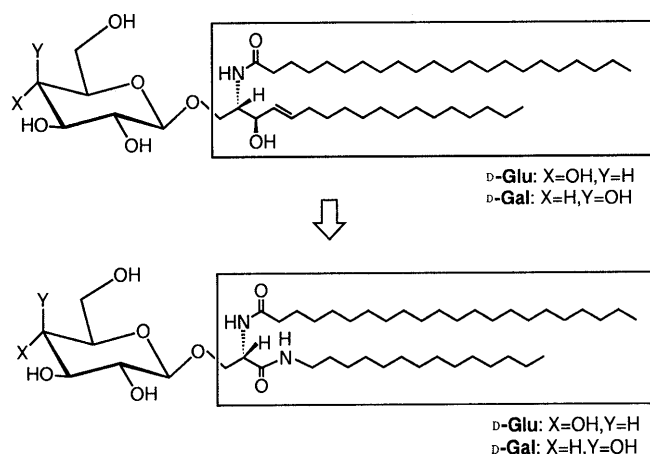
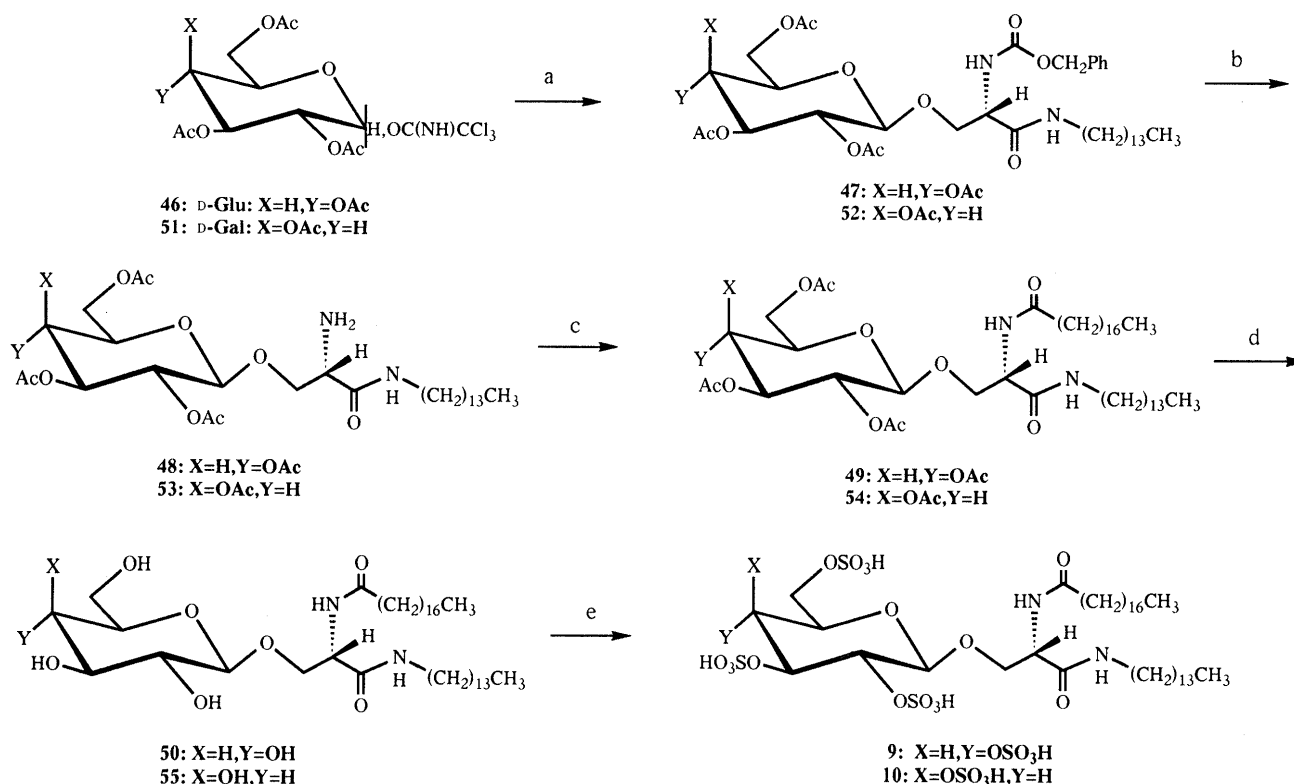


Fig. 1

Chart 5. Our attempts to prepare the glycoside **49** from **45** proceeded as follows. Glycosylation of **45** with glycosyl acetate (**12**), glycosyl bromide (**36**), and glycosyl trichloroacetimidate (**46**)<sup>9</sup> did not proceed using TMSOTf, HgBr<sub>2</sub>, and BF<sub>3</sub>-Et<sub>2</sub>O as promoters, probably due to the low reactivity of **45** and its low solubility in both organic solvents and water. We searched for an alternative method for the preparation of **9** and **10**. We examined the amide **43** instead of **45**. However, no reaction of **43** with glycosyl acetate (**12**) or glycosyl bromide (**36**) could be observed.

We turned our attention to the corresponding fluoride in place of **36**. The reaction of glycosyl fluoride and **43** gave the desired compound **47** in the presence of SnCl<sub>2</sub>-AgClO<sub>4</sub><sup>10</sup> in a low yield (6%). The problem was overcome by the use of glycosyl imidate (**46**) as the glycosyl donor. That is, coupling of **43** and **46** using BF<sub>3</sub>-Et<sub>2</sub>O as the promoter afforded the β-glycoside **47** exclusively, in 77% yield. Using the same methodology, coupling of **51** and **43** proceeded to give **52** in 33% yield using the same method. In the <sup>13</sup>C-NMR spectra of **47** and **52**, the <sup>13</sup>C-<sup>1</sup>H coupling constants observed for the anomeric carbon signals, 161.2 Hz in **47** and 159.5 Hz in **52**, suggested the stereochemistry of the glycosidic bond formed to be β<sup>11</sup> in both **47** and **52**. Subsequent hydrogenation of **47** and **52** with 10% Pd-on-carbon and H<sub>2</sub> in MeOH gave the amino compounds **48** and **53** in quantitative yields. The acylation of **48** and **53** was carried out with stearoyl chloride and NaHCO<sub>3</sub> to give the amides **49** and **54** in yields of 67 and 100%, respectively. Next, several attempts to remove the acetyl groups of **49** and **54** using usual mild de-O-acetylating reagents such as NH<sub>4</sub>OH-MeOH, H<sub>2</sub>NNH<sub>2</sub>H<sub>2</sub>O in EtOH,<sup>12</sup> and H<sub>2</sub>NNH<sub>2</sub>H<sub>2</sub>O in AcOH-pyridine (1:4)<sup>13</sup> resulted in β-elimination of the glycosides, because the reaction is complicated by the acid-lability of glycosides in general and the base-sensitivity (retro-Michael reaction) of the O-serinyl glycosides in particular.<sup>14</sup> The best result was obtained as follows. Basic



reagents and conditions : a) BF<sub>3</sub>·EtO<sub>2</sub>, **43**; b) Pd-C, H<sub>2</sub>; c) C<sub>17</sub>H<sub>35</sub>COCl, NaHCO<sub>3</sub>; d) NEt<sub>3</sub>-MeOH; e) i) SO<sub>3</sub>NMe<sub>3</sub>, ii) CF<sub>3</sub>CO<sub>2</sub>H

Chart 6

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

| Compd. No. | HIV-1 infection (IC <sub>50</sub> )<br>(μg/ml) <sup>a)</sup> | CT <sup>b)</sup> |
|------------|--------------------------------------------------------------|------------------|
| 1          | > 100                                                        | (-)              |
| 2          | > 100                                                        | (-)              |
| 3          | > 100                                                        | (-)              |
| 4          | 30                                                           | (-)              |
| 5          | 30—100                                                       | (-)              |
| 6          | 30—100                                                       | (-)              |
| 7          | 30—100                                                       | (-)              |
| 8          | > 100                                                        | (-)              |
| 9          | > 100                                                        | (++)             |
| 10         | > 100                                                        | (++)             |

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

hydrolysis of **49** and **54** was smoothly accomplished by stirring in 10% NEt<sub>3</sub>-MeOH<sup>15)</sup> at 45 °C to give the alcohols **50** and **55** in 89 and 70% yields, respectively. During the de-*O*-acetylation, no β-elimination product was detected. Finally, *O*-sulfation of **50** and **55** was achieved with sulfur trioxide-pyridine complex in DMF, followed by treatment with CF<sub>3</sub>CO<sub>2</sub>H, purification by chromatography on Sephadex LH-20 and lyophilization of the aqueous solution to afford the sulfated glycosides **9** and **10**, in yields of 28 and 43%, respectively.

The structures of all compounds were characterized by <sup>1</sup>H- and <sup>13</sup>C-NMR spectral methods, as well as IR spectroscopy, elemental analyses and positive FAB-mass spectrometry.

The anti-HIV-1 activities of the ten sulfated glycolipids are shown in Table 1. The anti-HIV-1 activity was tested by the syncytium-formation assay method using MT-4 cells according to our previously reported procedure.<sup>4)</sup> Among the synthesized compounds, **4**, **5**, **6**, **7** showed moderate activity with 50%-inhibitory concentration (IC<sub>50</sub>) value of 30 μM, 30—100 μM, 30—100 μM, and 30—100 μM, respectively. Compound **1**, **2**, **3**, **8**, **9**, **10** were found to be practically inactive (IC<sub>50</sub> > 100 μM) against HIV-1 and noncytotoxic, except for compounds **9** and **10**.

#### 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. <sup>1</sup>H-NMR spectra were taken on a JEOL JNM-GX270 (270 MHz) spectrometer. <sup>13</sup>C-NMR spectra were recorded with a JEOL JNM-GX270 (67.5 MHz) spectrometer. <sup>1</sup>H and <sup>13</sup>C chemical shifts (δ) are given in ppm relative to that of Me<sub>4</sub>Si (δ=0) in CDCl<sub>3</sub> or CD<sub>3</sub>OD, or sodium 4,4-dimethyl-4-silapentane-1-sulfonate hydrate (DSS, δ=0 in D<sub>2</sub>O) 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 60F<sub>254</sub> (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.

**2-(Dodecyloxy)ethyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside (**13**)**  
A solution of 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranose (**12**) (210 mg, 0.54 mmol) and ethyleneglycol dodecyl ether (186 mg, 0.81 mmol) in

anhydrous  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (10 ml) was stirred for 1 h at room temperature under argon in the presence of 4 Å powdered molecular sieves. The mixture was cooled to 0 °C, then  $\text{Me}_3\text{SiOSO}_2\text{CF}_3$  (TMSOTf) (132 mg, 0.59 mmol) was added. Stirring was continued for 3 h at room temperature, then the solution was poured into ice-water, and extracted with  $\text{CHCl}_3$ . The extract was successively washed with aqueous  $\text{NaHCO}_3$  and  $\text{H}_2\text{O}$ , dried ( $\text{MgSO}_4$ ), and evaporated *in vacuo*. The residual product was chromatographed on  $\text{SiO}_2$  with 10:1  $\text{CHCl}_3$ – $\text{CH}_3\text{COCH}_3$  to give **13** (75 mg, 25%) as an amorphous powder.  $[\alpha]_D^{25} -24.9^\circ$  ( $c=0.18$ ,  $\text{CHCl}_3$ ). IR (neat): 1752, 1375, 1113  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=6.4$  Hz,  $\text{OC}_{11}\text{H}_{22}\text{CH}_3$ ), 1.26 (18H, s,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.54 (2H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{10}\text{H}_{21}$ ), 2.01, 2.02, 2.04, 2.09 (each 3H, s,  $\text{OCOCH}_3 \times 4$ ), 3.43 (2H, t,  $J=6.4$  Hz,  $\text{OCH}_2\text{C}_{11}\text{H}_{23}$ ), 3.57 (2H, t,  $J=4.9$  Hz,  $\text{CH}_2\text{OC}_{12}\text{H}_{25}$ ), 3.66–3.77 (2H, m, Glu-H5,  $\text{OCH}_a\text{H}_b\text{CH}_2\text{O}$ ), 3.93 (1H, dt,  $J=4.4$ , 10.7 Hz,  $\text{OCH}_a\text{H}_b\text{CH}_2\text{O}$ ), 4.14 (1H, dd,  $J=12.3$ , 2.5 Hz, Glu-H6<sub>a</sub>), 4.27 (1H, dd,  $J=12.3$ , 4.9 Hz, Glu-H6<sub>b</sub>), 4.62 (1H, d,  $J=8.3$  Hz, Glu-H1), 5.00 (1H, dd,  $J=8.3$ , 9.3 Hz, Glu-H2), 5.09 (1H, t,  $J=9.3$  Hz, Glu-H4), 5.21 (1H, t,  $J=9.3$  Hz, Glu-H3). Positive FAB-MS  $m/z$ : 561 ( $\text{M}+\text{H}$ )<sup>+</sup>, 583 ( $\text{M}+\text{Na}$ )<sup>+</sup>.

**2-(Dodecyloxy)ethyl  $\beta$ -D-Glucopyranoside (14)** A mixture of **13** (75 mg, 0.13 mmol) and  $\text{NH}_4\text{OH}$ –MeOH (1:20) (10 ml) was stirred at room temperature for 15 h, and evaporated *in vacuo*. The residue was chromatographed on  $\text{SiO}_2$  in  $\text{CHCl}_3$ –MeOH (5:1) to give **14** (16 mg, 31%), mp 62–64 °C.  $[\alpha]_D^{25} +25.2^\circ$  ( $c=0.22$ , MeOH). IR (KBr): 3383, 1115  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=7.3$  Hz,  $\text{OC}_{11}\text{H}_{22}\text{CH}_3$ ), 1.26 (18H, s,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.56 (2H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{10}\text{H}_{21}$ ), 3.45 (2H, t,  $J=6.7$  Hz,  $\text{OCH}_2\text{C}_{11}\text{H}_{23}$ ), 3.55 (2H, m,  $\text{OCH}_2\text{CH}_2\text{OC}_{12}\text{H}_{25}$ ), 3.73 (2H, m,  $\text{OCH}_2\text{CH}_2\text{OC}_{12}\text{H}_{25}$ ), 4.34 (1H, d,  $J=7.6$  Hz, H-1). Positive FAB-MS  $m/z$ : 393 ( $\text{M}+\text{H}$ )<sup>+</sup>, 415 ( $\text{M}+\text{Na}$ )<sup>+</sup>.

**2-(Dodecyloxy)ethyl 2,3,4,6-Tetra-O-sulfo- $\beta$ -D-glucopyranoside (1)** A solution of **14** (16 mg, 0.041 mmol) in DMF (2 ml) was stirred for 20 h at 45–50 °C in the presence of sulfur trioxide–trimethylamine complex (46 mg, 0.33 mmol). The mixture was cooled and chromatographed on a column of Sephadex LH-20 equilibrated in 20:20:1 (v/v/v)  $\text{CHCl}_3$ –MeOH– $\text{H}_2\text{O}$ . Elution with the same solvent gave a residue that was dissolved in  $\text{CH}_2\text{Cl}_2$  (2 ml). The solution was treated with  $\text{CF}_3\text{SO}_3\text{H}$  (37 mg, 0.33 mmol) for 2 h under ice-cooling, then evaporated *in vacuo*. The residue was dissolved in  $\text{H}_2\text{O}$  (1 ml) and chromatographed on a column of Sephadex LH-20. Elution with 20:20:1 (v/v/v) in  $\text{CHCl}_3$ –MeOH– $\text{H}_2\text{O}$  afforded **1** (10 mg, 34%) as an amorphous powder, after lyophilization from  $\text{H}_2\text{O}$ .  $[\alpha]_D^{25} +51.4^\circ$  ( $c=0.22$ , MeOH). IR (KBr): 1255, 1109, 803  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{D}_2\text{O}$ )  $\delta$ : 0.90 (3H, t,  $J=6.9$  Hz,  $\text{OC}_{11}\text{H}_{22}\text{CH}_3$ ), 1.29 (18H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{20}\text{H}_{40}\text{O}_{19}\text{S}_4 \cdot \text{N}(\text{CH}_3)_3$ : C, 35.79; H, 6.40; N, 1.81. Found: C, 35.14; H, 6.68; N, 1.97.

**2-(Dodecyloxy)ethyl 2,3,4,6-Tetra-O-acetyl- $\beta$ -D-galactopyranoside (16)** The same procedure as described for the preparation of **13** provided a crude product from 1,2,3,4,6-penta-O-acetyl-D-galactopyranose (**15**) (119 mg, 0.31 mmol), ethylene glycol dodecyl ether (105 mg, 0.46 mmol) and TMSOTf (75 mg, 0.34 mmol), and this was purified by column chromatography with 10:1  $\text{CHCl}_3$ – $\text{CH}_3\text{COCH}_3$  to give **16** (72 mg, 42%) as an amorphous powder.  $[\alpha]_D^{25} -24.8^\circ$  ( $c=0.22$ ,  $\text{CHCl}_3$ ). IR (neat): 1752, 1369, 1120  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=7.0$  Hz,  $\text{OC}_{11}\text{H}_{22}\text{CH}_3$ ), 1.26 (18H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.54 (2H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{10}\text{H}_{21}$ ), 1.96, 2.05, 2.06, 2.15 (each 3H, s,  $\text{OCOCH}_3 \times 4$ ), 3.43 (2H, t,  $J=6.7$  Hz,  $\text{OCH}_2\text{C}_{11}\text{H}_{23}$ ), 3.58 (2H, t,  $J=4.6$  Hz,  $\text{CH}_2\text{OC}_{12}\text{H}_{25}$ ), 3.71–3.76 (1H, m,  $\text{OCH}_a\text{H}_b\text{CH}_2\text{OC}_{12}\text{H}_{25}$ ), 3.89–3.93 (2H, m, H-5,  $\text{OCH}_a\text{H}_b\text{CH}_2\text{OC}_{12}\text{H}_{25}$ ), 4.13 (1H, dd,  $J=6.7$ , 11.2 Hz, H-6<sub>a</sub>), 4.18 (1H, dd,  $J=6.4$ , 11.2 Hz, H-6<sub>b</sub>), 4.58 (1H, d,  $J=7.9$  Hz, H-1), 5.02 (1H, dd,  $J=3.3$ , 10.7 Hz, H-3), 5.22 (1H, t,  $J=7.9$ , 10.7 Hz, H-2), 5.39 (1H, d,  $J=3.3$  Hz, H-4).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 14.1 (q,  $\text{C}_{11}\text{H}_{22}\text{CH}_3$ ), 20.6, 20.7, 20.8 (q,  $\text{OCOCH}_3 \times 4$ ), 22.7, 26.1, 29.4, 29.5, 29.6, 29.8, 31.9 (t,  $\text{OCH}_2(\text{CH}_2)_{10}\text{CH}_3$ ), 61.3 (t, C-6), 67.1 (d, C-4), 68.9 (t,  $\text{OCH}_2\text{CH}_2\text{OC}_{12}\text{H}_{25}$ ), 69.0 (d, t,  $\text{OCH}_2\text{CH}_2\text{OC}_{12}\text{H}_{25}$ ), 69.8 (t,  $\text{OCH}_2\text{C}_{11}\text{H}_{23}$ ), 70.7 (d, C-5), 71.0 (d, C-3), 71.7 (d, C-2), 101.4 (d, C-1), 169.5, 170.2, 170.3, 170.4 (s,  $\text{OCOCH}_3 \times 4$ ). Positive FAB-MS  $m/z$ : 561 ( $\text{M}+\text{H}$ )<sup>+</sup>, 583 ( $\text{M}+\text{Na}$ )<sup>+</sup>.

**2-(Dodecyloxy)ethyl  $\beta$ -D-Galactopyranoside (17)** The same procedure as described for the preparation of **14** provided a crude product from **16** (72 mg, 0.13 mmol), and this was purified by column chromatography with 5:1  $\text{CHCl}_3$ –MeOH to give **17** (21 mg, 20%) as an amorphous powder.  $[\alpha]_D^{25} -23.1^\circ$  ( $c=0.30$ , MeOH). IR (KBr): 3382, 1118  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=7.0$  Hz,  $\text{OC}_{11}\text{H}_{22}\text{CH}_3$ ), 1.26 (18H, brs,  $\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.57 (2H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{10}\text{H}_{21}$ ), 3.46 (2H, t,

$J=6.7$  Hz,  $\text{OCH}_2\text{C}_{11}\text{H}_{23}$ ). Positive FAB-MS  $m/z$ : 393 ( $\text{M}+\text{H}$ )<sup>+</sup>, 415 ( $\text{M}+\text{Na}$ )<sup>+</sup>, 431 ( $\text{M}+\text{K}$ )<sup>+</sup>.

**2-(Dodecyloxy)ethyl 2,3,4,6-Tetra-O-sulfo- $\beta$ -D-galactopyranoside (2)** The same procedure as described for the preparation of **1** provided a crude product from **17** (21 mg, 0.054 mmol) and sulfur trioxide–trimethylamine complex (30 mg, 0.22 mmol), followed by trifluoroacetic acid (TFA, 24 mg, 0.22 mmol), and this was purified on a column of Sephadex LH-20 equilibrated in and eluted with 20:20:1 (v/v/v)  $\text{CHCl}_3$ –MeOH– $\text{H}_2\text{O}$  to give **9** (12 mg, 31%) as an amorphous powder.  $[\alpha]_D^{25} -121.4^\circ$  ( $c=0.05$ , MeOH). IR (KBr): 1255, 1109, 834  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{D}_2\text{O}$ )  $\delta$ : 0.90 (3H, t,  $J=7.3$  Hz,  $\text{OC}_{11}\text{H}_{22}\text{CH}_3$ ), 1.29 (18H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{20}\text{H}_{40}\text{O}_{19}\text{S}_4 \cdot 2 \times \text{N}(\text{CH}_3)_3$ : C, 37.58; H, 7.04; N, 3.37. Found: C, 37.74; H, 7.68; N, 3.97.

**2-(Dodecyloxy)ethyl 2,3,6-Tri-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- $\beta$ -D-galactopyranosyl)- $\beta$ -D-glucopyranoside (19)** The same procedure as described for the preparation of **13** provided a crude product from 1,2,3,6-tetra-O-acetyl-4-O-(2,3,4,6-tetra-O-acetyl- $\beta$ -D-galactopyranosyl)- $\beta$ -D-glucopyranose (**18**) (192 mg, 0.28 mmol), ethylene glycol dodecyl ether (98 mg, 0.43 mmol) and TMSOTf (69 mg, 0.31 mmol), and this was purified by column chromatography with 10:1  $\text{CHCl}_3$ – $\text{CH}_3\text{COCH}_3$  to give **7** (141 mg, 59%) as an amorphous powder.  $[\alpha]_D^{25} +7.0^\circ$  ( $c=0.27$ ,  $\text{CHCl}_3$ ). IR (neat): 1751, 1113  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=6.9$  Hz,  $\text{OC}_{11}\text{H}_{22}\text{CH}_3$ ), 1.26 (18H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.54 (2H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{10}\text{H}_{21}$ ), 1.96, 2.04, 2.05, 2.06, 2.12, 2.15 (2H, s,  $\text{OCOCH}_3 \times 7$ ), 3.41 (2H, t,  $J=6.3$  Hz,  $\text{OCH}_2\text{C}_{11}\text{H}_{23}$ ), 4.11 (4H, m, Gal-H6, Glu-H6), 4.50 (1H, d,  $J=8.3$  Hz, H-1), 4.57 (1H, d,  $J=7.8$  Hz, Gal-H1), 4.90 (1H, dd,  $J=8.3$ , 9.3 Hz, Glu-H2), 4.96 (1H, dd,  $J=3.4$ , 10.7 Hz, Gal-H3), 5.11 (1H, dd,  $J=7.8$ , 10.7 Hz, Gal-H2), 5.20 (1H, t,  $J=9.3$  Hz, Glu-H3). Anal. Calcd for  $\text{C}_{40}\text{H}_{58}\text{O}_{19} \cdot \text{H}_2\text{O}$ : C, 55.81; H, 7.02. Found: C, 55.89; H, 7.68.

**2-(Dodecyloxy)ethyl 4-O-( $\beta$ -D-Galactopyranosyl)- $\beta$ -D-glucopyranoside (20)** The same procedure as described for the preparation of **14** provided a crude product from **19** (141 mg, 0.17 mmol), and this was purified by column chromatography with 5:1  $\text{CHCl}_3$ –MeOH to give **20** (42 mg, 46%), mp 133–137 °C.  $[\alpha]_D^{25} +2.4^\circ$  ( $c=0.36$ , MeOH). IR (KBr): 3395, 1110  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=7.0$  Hz,  $\text{OC}_{11}\text{H}_{22}\text{CH}_3$ ), 1.26 (18H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.60 (2H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{10}\text{H}_{21}$ ), 4.32 (1H, d,  $J=7.9$  Hz, Glu-H1), 4.37 (1H, d,  $J=8.0$  Hz, Gal-H1). Positive FAB-MS  $m/z$ : 555 ( $\text{M}+\text{H}$ )<sup>+</sup>, 577 ( $\text{M}+\text{Na}$ )<sup>+</sup>, 593 ( $\text{M}+\text{K}$ )<sup>+</sup>.

**2-(Dodecyloxy)ethyl 2,3,6-Tri-O-sulfo-4-O-(2,3,4,6-tetra-O-sulfo- $\beta$ -D-galactopyranosyl)- $\beta$ -D-glucopyranoside (3)** The same procedure as described for the preparation of **1** provided a crude product from **20** (42 mg, 0.076 mmol) and sulfur trioxide–trimethylamine complex (149 mg, 1.07 mmol), followed by TFA (122 mg, 1.07 mmol), and this was purified on a column of Sephadex LH-20 equilibrated in and eluted with 20:20:1 (v/v/v)  $\text{CHCl}_3$ –MeOH– $\text{H}_2\text{O}$  to give **3** (52 mg, 61%) as a colorless amorphous solid after lyophilization from  $\text{H}_2\text{O}$ .  $[\alpha]_D^{25} +16.7^\circ$  ( $c=0.24$ , MeOH). IR (KBr): 1218, 1132, 812  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=6.3$  Hz,  $\text{OC}_{11}\text{H}_{22}\text{CH}_3$ ), 1.26 (18H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ). Anal. Calcd for  $\text{C}_{26}\text{H}_{30}\text{O}_{33}\text{S}_7 \cdot 6 \times \text{N}(\text{CH}_3)_3$ : C, 35.96; H, 7.13; N, 5.72. Found: C, 35.55; H, 8.01; N, 5.92.

**3-Iodo-1-O-tetrahydropyranylpropanol (22)** 3,4-Dihydro-2H-pyran (THP) (9.76 g, 116 mmol) was added dropwise to a stirred mixture of 3-iodo-1-propanol (**21**) (10.8 g, 58.2 mmol) and pyridinium toluene-*p*-sulfonic acid (PPTS) (0.73 g, 29.1 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (100 ml) at 0 °C and was kept at 0 °C overnight, after which it was washed with saturated aqueous  $\text{NaHCO}_3$  and saturated aqueous  $\text{NaCl}$ , dried ( $\text{MgSO}_4$ ), and evaporated to dryness. Chromatography of the residual oil on a column of  $\text{SiO}_2$  with 2:1 hexane–EtOAc gave **22** (14.8 g, 94%). IR (neat): 1182, 1131, 1644  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 2.10 (2H, m,  $-\text{CH}_2-$ ), 1.50–1.92 (6H, m, THP), 3.30 (2H, t,  $J=6.8$  Hz,  $-\text{CH}_2\text{I}$ ), 3.43 (2H, t,  $J=5.9$  Hz, THP), 3.79 (2H, t,  $J=5.9$  Hz,  $\text{CH}_2\text{OTHP}$ ), 4.61 (1H, t,  $J=3.4$  Hz, THP).

**1-O-Tetrahydropyranyl-3-O-docosylpropanediol (23)** A solution of 1-docosanol (17.9 g, 54.8 mmol) in dry tetrahydrofuran (THF, 30 ml) was added to an ice-cooled solution of NaH (1.97 g, 82.2 mmol, 60% dispersion in oil) in DMF (100 ml) under an argon atmosphere. The mixture was stirred for 1 h at room temperature, then **22** (14.8 g, 54.8 mmol) was added dropwise and stirring was continued for 4 d at 60 °C. After being cooled to room temperature, the mixture was partitioned between  $\text{CH}_2\text{Cl}_2$  and water. The organic phase was washed with water, dried ( $\text{MgSO}_4$ ), and evaporated to dryness. Chromatography of the residual oil on a column of  $\text{SiO}_2$  with 10:1 hexane–EtOAc gave **23** (3.08 g, 12%) as an oil. IR (neat): 1647, 1118, 1057  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=5.4$  Hz,  $\text{O}(\text{CH}_2)_{21}\text{CH}_3$ ), 1.25 (38H, s,

$\text{OCH}_2\text{CH}_2(\text{CH}_2)_{19}\text{CH}_3$ ), 1.43–1.82 (8H, m, THP,  $\text{OCH}_2\text{CH}_2\text{C}_{20}\text{H}_{41}$ ), 1.87 (2H, m,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 3.40 (2H, t,  $J=6.3$  Hz,  $\text{OCH}_2\text{C}_{21}\text{H}_{43}$ ), 3.50 (2H, t,  $J=6.3$  Hz,  $\text{CH}_2\text{OC}_{22}\text{H}_{45}$ ), 3.51 (2H, t,  $J=6.6$  Hz, THP), 3.84 (2H, t,  $J=6.4$  Hz,  $-\text{CH}_2\text{O}-$ ), 4.59 (1H, t,  $J=2.5$  Hz, THP).

**3-(Docosyloxy)propyl 24** A mixture of **23** (3.08 g, 6.57 mmol) and PPTS (0.165 g, 0.66 mmol) in ethanol (30 ml) was heated at 55 °C for 3 h. The solution was cooled, then saturated aqueous  $\text{NaHCO}_3$  was added and the whole was extracted with ether. The extract was washed with water, dried ( $\text{MgSO}_4$ ) and evaporated to dryness. Chromatography of the residue on a column of  $\text{SiO}_2$  with 10:1 hexane–EtOAc gave **24** (1.07 g, 43%), mp 57–61 °C. IR (KBr): 3382, 1024  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=6.8$  Hz,  $\text{O}(\text{CH}_2)_{21}\text{CH}_3$ ), 1.25 (38H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{19}\text{CH}_3$ ), 1.55 (2H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{19}\text{H}_{39}$ ), 1.83 (2H, m,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 3.43 (2H, t,  $J=6.4$  Hz,  $\text{OCH}_2\text{C}_{21}\text{H}_{43}$ ), 3.62 (2H, t,  $J=5.4$  Hz,  $\text{CH}_2\text{OC}_{22}\text{H}_{45}$ ), 3.78 (2H, t,  $J=5.5$  Hz,  $-\text{CH}_2\text{OH}$ ). Positive FAB-MS  $m/z$ : 385 ( $\text{M}+\text{H}$ )<sup>+</sup>.

**3-(Docosyloxy)propyl 2,3,4,6-Tetra-O-acetyl- $\beta$ -D-glucopyranoside (25)** The same procedure as described for the preparation of **13** provided a crude product from 1,2,3,4,6-penta-O-acetyl- $\beta$ -D-glucopyranose (**12**) (201 mg, 0.52 mmol), **24** (298 mg, 0.77 mmol) and TMSOTf (126 mg, 0.57 mmol), and this was purified by column chromatography with 10:1  $\text{CHCl}_3$ – $\text{CH}_3\text{COCH}_3$  to give **17** (55 mg, 15%) as white prisms, mp 63–65 °C.  $[\alpha]_D + 44.1^\circ$  ( $c=0.03$ ,  $\text{CHCl}_3$ ). IR (KBr): 1744, 1059  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=7.3$  Hz,  $\text{O}(\text{CH}_2)_{21}\text{CH}_3$ ), 1.25 (38H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{19}\text{CH}_3$ ), 1.58 (2H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{20}\text{H}_{41}$ ), 1.83 (2H, m,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 2.00, 2.02, 2.04, 2.09 (each 3H, s,  $\text{OCOCH}_3 \times 4$ ), 3.38 (2H, t,  $J=7.8$  Hz,  $\text{OCH}_2\text{C}_{21}\text{H}_{43}$ ), 3.44 (2H, t,  $J=6.4$  Hz,  $\text{CH}_2\text{OC}_{22}\text{H}_{45}$ ), 4.13 (1H, dd,  $J=2.4$ , 14.4 Hz, H-6a), 4.27 (1H, dd,  $J=4.8$ , 14.4 Hz, H-6b), 4.48 (1H, d,  $J=8.3$  Hz, H-1), 4.98 (1H, dd,  $J=8.3$ , 9.2 Hz, H-2), 5.08 (1H, t,  $J=9.2$  Hz, H-4), 5.20 (1H, t,  $J=9.2$  Hz, H-3).

**3-(Docosyloxy)propyl  $\beta$ -D-Glucopyranoside (26)** The same procedure as described for the preparation of **14** provided a crude product from **25** (55 mg, 0.077 mmol) and  $\text{NH}_4\text{OH}$ –MeOH (1:20), and this was purified by column chromatography with 5:1  $\text{CHCl}_3$ –MeOH to give **26** (19 mg, 46%) as a white powder, mp 67–69 °C.  $[\alpha]_D + 47.5^\circ$  ( $c=0.10$ , MeOH). IR (KBr): 3384, 1038  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=6.8$  Hz,  $\text{O}(\text{CH}_2)_{21}\text{CH}_3$ ), 1.25 (38H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{19}\text{CH}_3$ ), 1.55 (2H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{20}\text{H}_{41}$ ), 1.88 (2H, m,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 3.39 (2H, t,  $J=6.8$  Hz,  $\text{OCH}_2\text{C}_{21}\text{H}_{43}$ ), 3.52 (2H, t,  $J=5.9$  Hz,  $\text{CH}_2\text{OC}_{22}\text{H}_{45}$ ), 4.32 (1H, d,  $J=7.3$  Hz, Glu-H1).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 14.1 (q,  $\text{OC}_{21}\text{H}_{42}\text{CH}_3$ ), 22.7, 26.2, 29.4, 29.6, 29.7, 31.9 (t,  $\text{OCH}_2(\text{CH}_2)_{20}\text{CH}_3$ ), 29.7 (t,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 61.6 (t, C-6), 67.6 (t,  $\text{CH}_2\text{OC}_{22}\text{H}_{45}$ ), 69.7 (d, C-4), 71.2 (t,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{OC}_{22}\text{H}_{45}$ ), 73.5 (d, C-2), 75.6 (d, C-3), 77.2 (d, C-5), 102.9 (d, C-1). Positive FAB-MS  $m/z$ : 547 ( $\text{M}+\text{H}$ )<sup>+</sup>, 569 ( $\text{M}+\text{Na}$ )<sup>+</sup>, 585 ( $\text{M}+\text{K}$ )<sup>+</sup>.

**3-(Docosyloxy)propyl 2,3,4,6-Tetra-O-sulfo- $\beta$ -D-glucopyranoside (4)** The same procedure as described for the preparation of **1** provided a crude product from **26** (19 mg, 0.036 mmol) and sulfur trioxide–trimethylamine complex (40 mg, 0.029 mmol), followed by treatment with  $\text{CF}_3\text{CO}_2\text{H}$  (25 mg, 0.22 mmol), and this was purified on a column of Sephadex LH-20 equilibrated in and eluted with 20:20:1 (v/v/v)  $\text{CHCl}_3$ –MeOH– $\text{H}_2\text{O}$  to give **4** (13 mg, 33%) as an amorphous solid.  $[\alpha]_D + 0.3^\circ$  ( $c=0.37$ , MeOH). IR (KBr): 1250, 1109, 812  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=6.9$  Hz,  $\text{OC}_{21}\text{H}_{42}\text{CH}_3$ ), 1.25 (38H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{19}\text{CH}_3$ ), 1.53 (2H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{20}\text{H}_{41}$ ), 1.86 (2H, m,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 2.04, 2.05, 2.06, 2.15 (each 3H, s,  $\text{OCOCH}_3 \times 4$ ), 3.38 (2H, t,  $J=6.0$  Hz,  $\text{OCH}_2\text{C}_{21}\text{H}_{43}$ ), 3.44 (2H, t,  $J=7.9$  Hz,  $\text{CH}_2\text{OC}_{22}\text{H}_{45}$ ), 3.61 (1H, d,  $J=8.7$  Hz,  $\text{OCH}_2\text{H}_6\text{CH}_2\text{CH}_2\text{O}$ ), 3.90 (1H, d,  $J=7.4$  Hz,  $\text{OCH}_2\text{H}_6\text{CH}_2\text{CH}_2\text{O}$ ), 4.46 (1H, d,  $J=8.2$  Hz, H-1), 5.02 (1H, dd,  $J=5.9$ , 15.6 Hz, H-3), 5.20 (1H, dd,  $J=5.9$ , 8.2 Hz, H-2), 5.39 (1H, d,  $J=3.6$  Hz, H-4).

**3-(Docosyloxy)propyl 2,3,4,6-Tetra-O-acetyl- $\beta$ -D-galactopyranoside (27)** The same procedure as described for the preparation of **13** provided a crude product from 1,2,3,4,6-penta-O-acetyl- $\beta$ -D-galactopyranose (**15**) (212 mg, 0.55 mmol), **24** (314 mg, 0.82 mmol) and TMSOTf (200 mg, 0.90 mmol), and this was purified by column chromatography with 10:1  $\text{CHCl}_3$ – $\text{CH}_3\text{COCH}_3$  to give **27** (79 mg, 20%) as an amorphous solid.  $[\alpha]_D + 41.5^\circ$  ( $c=0.12$ ,  $\text{CHCl}_3$ ). IR (neat): 1754, 1055  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=6.8$  Hz,  $\text{O}(\text{CH}_2)_{21}\text{CH}_3$ ), 1.26 (38H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{19}\text{CH}_3$ ), 1.58 (2H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{20}\text{H}_{41}$ ), 1.84 (2H, m,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 2.04, 2.05, 2.06, 2.15 (each 3H, s,  $\text{OCOCH}_3 \times 4$ ), 3.38 (2H, t,  $J=6.0$  Hz,  $\text{OCH}_2\text{C}_{21}\text{H}_{43}$ ), 3.44 (2H, t,  $J=7.9$  Hz,  $\text{CH}_2\text{OC}_{22}\text{H}_{45}$ ), 3.61 (1H, d,  $J=8.7$  Hz,  $\text{OCH}_2\text{H}_6\text{CH}_2\text{CH}_2\text{O}$ ), 3.90 (1H, d,  $J=7.4$  Hz,  $\text{OCH}_2\text{H}_6\text{CH}_2\text{CH}_2\text{O}$ ), 4.46 (1H, d,  $J=8.2$  Hz, H-1), 5.02 (1H, dd,  $J=5.9$ , 15.6 Hz, H-3), 5.20 (1H, dd,  $J=5.9$ , 8.2 Hz, H-2), 5.39 (1H, d,  $J=3.6$  Hz, H-4).

**3-(Docosyloxy)propyl  $\beta$ -D-Galactopyranoside (28)** The same procedure as described for the preparation of **14** provided a crude product from **27** (79 mg, 0.11 mol) and  $\text{NH}_4\text{OH}$ –MeOH (1:20), and this was purified by column chromatography with 5:1  $\text{CHCl}_3$ –MeOH to give **28** (32 mg, 53%).  $[\alpha]_D + 19.3^\circ$  ( $c=0.13$ , MeOH). IR (neat): 3418, 1055  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=7.3$  Hz,  $\text{O}(\text{CH}_2)_{21}\text{CH}_3$ ), 1.26 (38H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{19}\text{CH}_3$ ), 1.56 (2H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{20}\text{H}_{41}$ ), 1.88 (2H, m,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 14.2 (q,  $\text{OC}_{21}\text{H}_{42}\text{CH}_3$ ), 18.1, 19.8, 22.8, 26.2, 27.2, 29.5, 29.7, 29.8, 30.2, 32.1, 32.9, 37.2 (t,  $\text{OCH}_2(\text{CH}_2)_{20}\text{CH}_3$ ), 29.8 (t,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 61.6 (t, C-6), 67.4 (t,  $\text{CH}_2\text{OC}_{22}\text{H}_{45}$ ), 67.8 (d, C-2), 69.2 (d, C-4), 71.6 (t,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}-\text{C}_{22}\text{H}_{45}$ ), 73.8 (d, C-3), 74.9 (d, C-5), 103.6 (d, C-1). Positive FAB-MS  $m/z$ : 547 ( $\text{M}+\text{H}$ )<sup>+</sup>, 569 ( $\text{M}+\text{Na}$ )<sup>+</sup>, 585 ( $\text{M}+\text{K}$ )<sup>+</sup>.

**3-(Docosyloxy)propyl 2,3,4,6-Tetra-O-sulfo- $\beta$ -D-galactopyranoside (5)** The same procedure as described for the preparation of **1** provided a crude product from **28** (32 mg, 0.058 mmol) and sulfur trioxide–trimethylamine complex (65 mg, 0.47 mmol), followed by treatment with  $\text{CF}_3\text{CO}_2\text{H}$  (40 mg, 0.35 mmol), and this was purified on a column of Sephadex LH-20 equilibrated in and eluted with 20:20:1 (v/v/v)  $\text{CHCl}_3$ –MeOH– $\text{H}_2\text{O}$  to give **5** (27 mg, 42%) as an amorphous solid.  $[\alpha]_D + 14.7^\circ$  ( $c=0.24$ , MeOH). IR (KBr): 1268, 1055, 756  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=6.8$  Hz,  $\text{OC}_{21}\text{H}_{42}\text{CH}_3$ ), 1.25 (38H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{19}\text{CH}_3$ ), 1.55 (2H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{20}\text{H}_{41}$ ), 1.87 (2H, m,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 14.1 (q,  $\text{OC}_{21}\text{H}_{42}\text{CH}_3$ ), 22.7, 29.4, 29.7, 29.8, 31.9 (t,  $\text{OCH}_2(\text{CH}_2)_{20}\text{CH}_3$ ), 107.3 (d, C-1).

**3-(Dodecyloxy)propyl 4-O-(2,3,4,6-Tetra-O-acetyl- $\beta$ -D-galactopyranosyl)-2,3,6-tri-O-acetyl- $\beta$ -D-glucopyranoside (29)** The same procedure as described for the preparation of **13** provided a crude product from **18** (119 mg, 0.18 mmol), **24** (73 mg, 0.19 mmol) and TMSOTf (43 mg, 0.19 mmol), and this was purified by column chromatography with 10:1  $\text{CHCl}_3$ – $\text{CH}_3\text{COCH}_3$  to give **29** (126 mg, 72%) as an amorphous solid, mp 44–45 °C.  $[\alpha]_D + 16.7^\circ$  ( $c=0.19$ ,  $\text{CHCl}_3$ ). IR (KBr): 1751, 1370, 1052, 1637  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=6.9$  Hz,  $\text{O}(\text{CH}_2)_{21}\text{CH}_3$ ), 1.25 (38H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{19}\text{CH}_3$ ), 1.54 (2H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{20}\text{H}_{41}$ ), 1.83 (2H, m,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 1.97, 2.04, 2.05, 2.06, 2.12, 2.15 (21H, s,  $\text{OCOCH}_3 \times 7$ ), 3.43 (2H, dd,  $J=4.5$ , 6.0 Hz,  $\text{OCH}_2\text{C}_{21}\text{H}_{43}$ ), 3.60 (2H, t,  $J=7.4$  Hz,  $\text{CH}_2\text{OC}_{22}\text{H}_{45}$ ), 3.79 (1H, t,  $J=9.6$  Hz, Glu-H5), 3.86–3.92 (2H, m, Gal-H5, Glu-H4), 4.46 (1H, d,  $J=7.8$  Hz, Glu-H1), 4.49 (1H, d,  $J=7.8$  Hz, Gal-H1), 4.89 (1H, t,  $J=7.8$  Hz, Glu-H2), 4.96 (1H, dd,  $J=3.3$ , 10.1 Hz, Gal-H3), 5.11 (1H, dd,  $J=7.8$ , 10.1 Hz, Gal-H2), 5.19 (1H, t,  $J=7.8$  Hz, Glu-H3), 5.33 (1H, dd,  $J=3.3$ , 14.2 Hz, Gal-H4). Anal. Calcd for  $\text{C}_{51}\text{H}_{80}\text{O}_{19} \cdot 5\text{H}_2\text{O}$ : C, 56.34; H, 8.34. Found: C, 55.98; H, 8.11.

**3-(Dodecyloxy)propyl 4-O-( $\beta$ -D-Galactopyranosyl)- $\beta$ -D-glucopyranoside (30)** The same procedure as described for the preparation of **14** provided a crude product from **29** (126 mg, 0.13 mmol) and  $\text{NH}_4\text{OH}$ –MeOH (1:20), and this was purified by column chromatography with 5:1  $\text{CHCl}_3$ –MeOH to give **30** (26 mg, 29%) as a white powder, mp 153–156 °C.  $[\alpha]_D + 6.8^\circ$  ( $c=0.96$ , MeOH). IR (KBr): 1114, 1639  $\text{cm}^{-1}$ .  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 14.2 (q,  $\text{OC}_{21}\text{H}_{42}\text{CH}_3$ ), 19.9, 23.0, 25.8, 26.5, 29.7, 29.8, 29.9, 30.0, 30.1, 30.3, 32.3, 34.8, 39.2 (t,  $\text{OCH}_2(\text{CH}_2)_{20}\text{CH}_3$ ), 32.3 (t,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 61.6 (t, Gal-C6), 62.0 (t, Glu-C6), 68.0 (d, Gal-C4), 69.5 (d, Gal-C2), 71.5 (t,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ), 73.7 (d, Glu-C2), 73.9 (d, Gal-C3), 75.3 (d, Glu-C5), 75.9 (d, Glu-C3), 78.0 (d, Gal-C5), 80.4 (d, Glu-C4), 103.3 (d, Glu-C1), 104.2 (d, Gal-C1). Positive FAB-MS  $m/z$ : 732 ( $\text{M}+\text{Na}$ )<sup>+</sup>.

**3-(Dodecyloxy)propyl 4-O-(2,3,4,6-Tetra-O-sulfo- $\beta$ -D-galactopyranosyl)-2,3,6-tri-O-sulfo- $\beta$ -D-glucopyranoside (6)** The same procedure as described for the preparation of **1** provided a crude product from **30** (26 mg, 0.037 mmol) and sulfur trioxide–trimethylamine complex (71 mg, 0.051 mmol), followed by treatment with  $\text{CF}_3\text{CO}_2\text{H}$  (44 mg, 0.38 mmol), and this was purified on a column of Sephadex LH-20 equilibrated in and eluted with 20:20:1 (v/v/v)  $\text{CHCl}_3$ –MeOH– $\text{H}_2\text{O}$  to give **6** (17 mg, 28%) as an amorphous solid.  $[\alpha]_D - 23.7^\circ$  ( $c=0.13$ , MeOH). IR (KBr): 1215, 1051, 757  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=6.9$  Hz,  $\text{OC}_{21}\text{H}_{42}\text{CH}_3$ ), 1.25 (38H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{19}\text{CH}_3$ ), 1.54 (2H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{20}\text{H}_{41}$ ), 1.85 (2H, m,  $\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}$ ).

**2-Isopropyl-5-benzoyloxymethyl-1,3-dioxane (31)** A solution of 2-isopropyl-5-hydroxymethyl-1,3-dioxane (*cis, trans* mixture) (**31**) (8.20 g, 0.052 mol) in dry THF (50 ml) was added portionwise to an ice-cooled solution of sodium hydride (2.00 g, 0.082 mol, 60% dispersion in oil) and *n*-tetrabutylammonium iodide (6.10 g, 0.016 mol) in dry THF (100 ml) under argon. The mixture was stirred at room temperature for 1 h, then benzyl bromide (18.8 g, 0.11 mol) was added dropwise to it at 0 °C and

the whole was left overnight at room temperature. The reaction was quenched with MeOH and the mixture was concentrated under reduced pressure. The residue was extracted with ether, and the ethereal layer was washed with brine. The organic layer was dried over  $\text{MgSO}_4$ , and concentrated to an oil, which was applied to a column of silica gel and eluted with 5:1 *n*-hexane–EtOAc to give **32** (12.6 g, 94%) as an oil. IR (neat): 2958, 2918, 2852, 1039, 1112, 736, 698  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.91 (6H, d,  $J=6.9$  Hz,  $\text{CHCH}(\text{CH}_3)_2$ ), 1.62 (1H, m,  $\text{CHCH}_2\text{OCH}_2\text{Ph}$ ), 1.76 (1H, m,  $\text{CHCH}(\text{CH}_3)_2$ ), 3.77 (2H, d,  $J=7.8$  Hz,  $\text{CHCH}_2\text{OCH}_2\text{Ph}$ ), 3.82 (2H, m,  $\text{CHCH}_2\text{H}_6\text{OCH}$ ), 4.07 (2H, dd,  $J=1.5, 11.7$  Hz,  $\text{CHCH}_2\text{H}_6\text{OCH}$ ), 4.24 (1H, d,  $J=4.4$  Hz,  $\text{CHCH}(\text{CH}_3)_2$ ), 4.54 (2H, s,  $\text{OCH}_2\text{Ph}$ ), 7.28 (5H, m, Ph). *Anal.* Calcd for  $\text{C}_{14}\text{H}_{20}\text{O}_3$ : C, 71.58; H, 8.53. Found: C, 71.77; H, 9.06.

**2-Benzoyloxymethyl-1,3-propanediol (33)** Compound **32** (12.6 g, 0.05 mol) was dissolved in 1 N HCl (90 ml) and MeOH (180 ml). The mixture was refluxed for 3 h, neutralized with 1 N NaOH, diluted with  $\text{CH}_2\text{Cl}_2$ , and washed with brine. The organic phase was dried over  $\text{MgSO}_4$ , and concentrated under reduced pressure. The residual oily product was applied to a column of silica gel and eluted with 5:1 *n*-hexane–AcOEt to give **32** (4.50 g, 50%) as an oil. IR (neat): 3384, 1029, 1074, 738, 697  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 2.00 (1H, m,  $\text{CH}_2\text{CH}(\text{CH}_2\text{OH})$ ), 3.40 (2H, brs,  $\text{CH}(\text{CH}_2\text{OH})_2$ ), 3.55 (2H, d,  $J=6.0$  Hz,  $\text{CHCH}_2\text{OCH}_2\text{Ph}$ ), 3.72 (4H, d,  $J=6.0$  Hz,  $\text{CH}(\text{CH}_2\text{OH})_2$ ), 4.47 (2H, s,  $\text{OCH}_2\text{Ph}$ ), 7.29 (5H, m, Ph). *Anal.* Calcd for  $\text{C}_{11}\text{H}_{16}\text{O}_3 \cdot 1/3\text{H}_2\text{O}$ : C, 65.33; H, 8.31. Found: C, 65.65; H, 8.41.

**2-Benzoyloxymethyl-1,3-dimyristylpropanediol (34)** A solution of **33** (1.20 g, 6.59 mmol) in dry THF (10 ml) was added to an ice-cooled solution of sodium hydride (0.63 g, 26.4 mmol) and *n*-tetrabutylammonium iodide (1.46 g, 3.95 mmol) in dry THF (50 ml) under argon. The mixture was stirred at room temperature for 1 h, then myristyl bromide (5.48 g, 19.8 mmol) was added dropwise at  $0^\circ\text{C}$  and the reaction mixture was left overnight at room temperature. The reaction was quenched with MeOH and the mixture was concentrated under reduced pressure. The residue was extracted with ether, and the ethereal layer was washed with brine. The organic layer was dried over  $\text{MgSO}_4$ , and concentrated to an oil, which was applied to a column of silica gel and eluted with 5:1 *n*-hexane–EtOAc to give **34** (2.70 g, 69%) as an oil. IR (neat): 1027, 1109, 733, 697  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (6H, t,  $J=6.6$  Hz,  $\text{OC}_{13}\text{H}_{26}\text{CH}_3 \times 2$ ), 1.25 (44H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{11}\text{CH}_3 \times 2$ ), 1.53 (4H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{12}\text{H}_{25} \times 2$ ), 2.20 (1H, m,  $\text{OCH}_2\text{CH}(\text{CH}_2\text{OC}_{14}\text{H}_{29})_2$ ), 3.38 (4H, t,  $J=6.6$  Hz,  $\text{OCH}_2\text{C}_{13}\text{H}_{27} \times 2$ ), 3.47 (4H, d,  $J=5.9$  Hz,  $\text{OCH}_2\text{CH}(\text{CH}_2\text{OC}_{14}\text{H}_{29})_2 \times 2$ ), 3.53 (2H, d,  $J=5.9$  Hz,  $\text{OCH}_2\text{CH}(\text{CH}_2\text{OC}_{14}\text{H}_{29})_2$ ), 4.49 (2H, s,  $\text{OCH}_2\text{C}_6\text{H}_5$ ), 7.31 (5H, m,  $\text{OCH}_2\text{C}_6\text{H}_5$ ). *Anal.* Calcd for  $\text{C}_{39}\text{H}_{72}\text{O}_3$ : C, 79.53; H, 12.32. Found: C, 79.61; H, 12.19.

**2-Hydroxymethyl-1,3-O-dimyristyl-1,3-propanediol (35)** A mixture of **34** (2.70 g, 4.70 mmol) and 10% Pd-on-charcol (0.27 g) suspended in EtOH (30 ml) was hydrogenated for 3 h at room temperature under atmospheric pressure, then filtered, and the filtrate was concentrated to dryness. The residue was column-chromatographed with *n*-hexane–EtOAc (5:1) to give **35** (2.00 g, 88%) as a white powder, mp  $52\text{--}54^\circ\text{C}$ . IR (KBr): 3342, 1036  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (6H, t,  $J=6.6$  Hz,  $\text{OC}_{13}\text{H}_{26}\text{CH}_3 \times 2$ ), 1.26 (44H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{11}\text{CH}_3 \times 2$ ), 1.56 (4H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{12}\text{H}_{25} \times 2$ ), 2.10 (1H, m,  $\text{HOCH}_2\text{CH}(\text{CH}_2\text{OC}_{14}\text{H}_{29})_2$ ), 2.94 (1H, br,  $\text{CH}_2\text{OH}$ ), 3.41 (4H, t,  $J=6.6$  Hz,  $\text{OCH}_2\text{C}_{13}\text{H}_{27} \times 2$ ), 3.76 (2H, t,  $J=5.2$  Hz,  $\text{CH}_2\text{OH}$ ). *Anal.* Calcd for  $\text{C}_{32}\text{H}_{66}\text{O}_3$ : C, 77.04; H, 13.33. Found: C, 77.40; H, 13.51. Positive FAB-MS  $m/z$ : 500 ( $\text{M}+\text{H}$ ) $^+$ .

**2-O-(2,3,4,6-Tetra-O-acetyl- $\beta$ -D-glucopyranosyl)methyl-1,3-O-dimyristylpropanediol (37)** A solution of 2,3,4,6-tetra-O-acetyl-D-glucopyranosyl bromide (**36**) (111 mg, 0.29 mmol) in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (1 ml) was added to a suspension of **35** (71 mg, 0.15 mmol),  $\text{HgBr}_2$  (106 mg, 0.29 mmol) and  $\text{MS4 \AA}$  in  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (5 ml). The mixture was stirred overnight at room temperature, then filtered, and the filtrate was diluted with  $\text{ClCH}_2\text{CH}_2\text{Cl}$ . The mixture was successively washed with 10% aqueous KI and brine, then dried ( $\text{MgSO}_4$ ) and concentrated to a syrup. This was column-chromatographed with *n*-hexane–EtOAc (5:1) to give **37** (63 mg, 52%) as an oil.  $[\alpha]_D -9.1^\circ$  ( $c=0.21$ ,  $\text{CHCl}_3$ ). IR (neat): 1742, 1107  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (6H, t,  $J=6.8$  Hz,  $\text{OC}_{13}\text{H}_{26}\text{CH}_3 \times 2$ ), 1.26 (44H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{11}\text{CH}_3 \times 2$ ), 1.53 (4H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{12}\text{H}_{25} \times 2$ ), 2.00, 2.02, 2.04, 2.09 (each 3H, s,  $\text{OCOCH}_3 \times 4$ ), 2.10 (1H, m,  $\text{OCH}_2\text{CH}(\text{CH}_2\text{OC}_{14}\text{H}_{29})_2$ ), 3.68 (1H, m, H-5), 4.12 (1H, dd,  $J=2.5, 12.2$  Hz, H-6 $_{\text{a}}$ ), 4.28 (1H, dd,  $J=4.9, 12.2$  Hz, H-6 $_{\text{b}}$ ), 4.47 (1H, d,  $J=8.3$  Hz, H-1), 4.99 (1H, dd,  $J=8.3, 9.7$  Hz, H-2), 5.08 (1H, t,

$J=9.3$  Hz, H-4), 5.19 (1H, dd,  $J=9.3, 9.7$  Hz, H-3). Positive FAB-MS  $m/z$ : 830 ( $\text{M}+\text{H}$ ) $^+$ , 852 ( $\text{M}+\text{Na}$ ) $^+$ .

**2-O-( $\beta$ -D-Glucopyranosyl)methyl-1,3-dimyristylpropanediol (38)** A solution of **37** (63 mg, 0.076 mmol) in  $\text{NH}_4\text{OH}$ –MeOH (1:10) (10 ml) was stirred at room temperature overnight. It was concentrated to dryness under reduced pressure and the residual product was purified by column chromatography with *n*-hexane–EtOAc 2:1 to give **38** (50 mg, quant.) as a white powder, mp  $60\text{--}63^\circ\text{C}$ .  $[\alpha]_D -18.8^\circ$  ( $c=0.40$ , MeOH). IR (KBr): 3392, 1102  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (6H,  $J=6.8$  Hz,  $\text{OC}_{13}\text{H}_{26}\text{CH}_3 \times 2$ ), 1.26 (44H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{11}\text{CH}_3 \times 2$ ), 1.55 (4H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{12}\text{H}_{25} \times 2$ ), 2.20 (1H, m,  $\text{OCH}_2\text{CH}(\text{CH}_2\text{OC}_{14}\text{H}_{29})_2$ ), 4.28 (1H, d,  $J=7.8$  Hz, Glu-H1).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 14.1 (q,  $\text{OC}_{13}\text{H}_{26}\text{CH}_3 \times 2$ ), 22.7, 26.2, 29.4, 29.6, 29.7, 29.8, 32.0 (t,  $\text{OCH}_2(\text{CH}_2)_{12}\text{CH}_3 \times 2$ ), 40.2 (d,  $\text{OCH}_2\text{CH}(\text{CH}_2\text{OC}_{14}\text{H}_{29})_2$ ), 62.0 (t, C-6), 69.2 (t,  $\text{OCH}_2\text{CH}(\text{CH}_2\text{OC}_{14}\text{H}_{29})_2$ ), 69.4 (t,  $\text{OCH}_2\text{CH}(\text{CH}_2\text{OC}_{14}\text{H}_{29})_2$ ), 70.2 (d, C-4), 71.6 (t,  $\text{OCH}_2\text{C}_{13}\text{H}_{27} \times 2$ ), 73.7 (d, C-2), 75.9 (d, C-5), 76.4 (d, C-3), 103.3 (d, C-1). Positive FAB-MS  $m/z$ : 662 ( $\text{M}+\text{H}$ ) $^+$ , 684 ( $\text{M}+\text{Na}$ ) $^+$ .

**2-O-(2,3,4,6-Tetra-O-sulfo- $\beta$ -D-glucopyranosyl)methyl-1,3-dimyristylpropanediol (7)** The same procedure described for the preparation of **1** provided a crude product from **38** (50 mg, 0.076 mmol) and sulfur trioxide–trimethylamine complex (96 mg, 0.61 mmol), followed by TFA (69 mg, 0.61 mmol), and this was purified on a column of Sephadex LH-20 equilibrated in and eluted with 20:20:1 (v/v/v)  $\text{CHCl}_3$ –MeOH– $\text{H}_2\text{O}$  to give **7** (32 mg, 43%) as an amorphous solid.  $[\alpha]_D +1.6^\circ$  ( $c=0.81$ , MeOH). IR (neat): 1205, 1107, 799  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (6H, brs,  $\text{OC}_{13}\text{H}_{26}\text{CH}_3 \times 2$ ), 1.25 (44H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{11}\text{CH}_3 \times 2$ ), 1.50 (4H, br,  $\text{OCH}_2\text{CH}_2\text{C}_{12}\text{H}_{25} \times 2$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 14.1 (q,  $\text{OC}_{13}\text{H}_{26}\text{CH}_3 \times 2$ ), 22.7, 26.2, 29.4, 29.5, 29.6, 29.7, 31.9 (t,  $\text{OCH}_2(\text{CH}_2)_{12}\text{CH}_3 \times 2$ ), 68.7 (t,  $\text{OCH}_2\text{CH}(\text{CH}_2\text{OC}_{14}\text{H}_{29})_2$ ), 71.0 (t,  $\text{OCH}_2\text{CH}(\text{CH}_2\text{OC}_{14}\text{H}_{29})_2$ ), 71.4, 71.6 (t,  $\text{OCH}_2\text{C}_{13}\text{H}_{27} \times 2$ ). Positive FAB-MS  $m/z$ : 923 ( $\text{M}+\text{Na}-\text{SO}_3$ ) $^+$ . *Anal.* Calcd for  $\text{C}_{38}\text{H}_{76}\text{O}_{20}\text{S}_4 \cdot 1/3\text{H}_2\text{O}$ : C, 46.23; H, 8.36. Found: C, 46.51; H, 7.81.

**2-O-(2,3,4,6-Tetra-O-acetyl- $\beta$ -D-galactopyranosyl)-1,3-dimyristylpropanediol (40)** The same procedure described for the preparation of **37** provided a crude product from **40** (59 mg, 0.12 mmol), and 2,3,4,6-tetra-O-acetyl-D-galactopyranosyl bromide (**39**) (89 mg, 0.24 mmol) and  $\text{HgBr}_2$  (85 mg, 0.24 mmol), and this was purified by column chromatography with *n*-hexane–EtOAc 5:1 to give **40** (62 mg, 65%) as a syrup.  $[\alpha]_D +7.4^\circ$  ( $c=0.39$ ,  $\text{CHCl}_3$ ). IR (neat): 1752, 1076  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (6H, t,  $J=6.9$  Hz,  $\text{OC}_{13}\text{H}_{26}\text{CH}_3 \times 2$ ), 1.26 (44H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{11}\text{CH}_3 \times 2$ ), 1.56 (4H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{12}\text{H}_{25} \times 2$ ), 1.98, 2.04, 2.05, 2.15 (each 3H, s,  $\text{OCOCH}_3 \times 4$ ), 3.57 (1H, dd,  $J=6.4, 10.0$  Hz, H-5), 3.90 (1H, m, H-6 $_{\text{a}}$ ), 4.14 (1H, m, H-6 $_{\text{b}}$ ), 4.44 (1H, d,  $J=7.8$  Hz, H-1), 4.50 (1H, dd,  $J=3.7, 10.6$  Hz, H-3), 5.19 (1H, dd,  $J=7.8, 10.6$  Hz, H-2), 5.38 (1H, d,  $J=2.3$  Hz, H-4). Positive FAB-MS  $m/z$ : 830 ( $\text{M}+\text{H}$ ) $^+$ .

**2-O-( $\beta$ -D-Galactopyranosyl)methyl-1,3-O-dimyristylpropanediol (41)** The same procedure as described for the preparation of **38** provided a crude product from **40** (63 mg, 0.076 mmol), and this was purified by column chromatography with *n*-hexane–EtOAc 2:1 to give **41** (50 mg, quant.) as a white powder, mp  $69\text{--}71^\circ\text{C}$ .  $[\alpha]_D -7.3^\circ$  ( $c=0.37$ , MeOH). IR (KBr): 3392, 1074  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (6H,  $J=6.8$  Hz,  $\text{OC}_{13}\text{H}_{26}\text{CH}_3 \times 2$ ), 1.26 (44H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{11}\text{CH}_3 \times 2$ ), 1.55 (4H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{12}\text{H}_{25} \times 2$ ), 2.20 (1H, m,  $\text{OCH}_2\text{CH}(\text{CH}_2\text{OC}_{14}\text{H}_{29})_2$ ), 4.21 (1H, d,  $J=7.4$  Hz, H-1).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 14.1 (q,  $\text{OC}_{13}\text{H}_{26}\text{CH}_3 \times 2$ ), 22.8, 26.2, 29.4, 29.6, 29.8, 32.0 (t,  $\text{OCH}_2(\text{CH}_2)_{12}\text{CH}_3 \times 2$ ), 40.3 (d,  $\text{OCH}_2\text{CH}(\text{CH}_2\text{OC}_{14}\text{H}_{29})_2$ ), 61.8 (t, C-6), 69.1 (d, C-4), 69.2 (t,  $\text{OCH}_2\text{CH}(\text{CH}_2\text{OC}_{14}\text{H}_{29})_2$ ), 69.4 (t,  $\text{OCH}_2\text{CH}(\text{CH}_2\text{OC}_{14}\text{H}_{29})_2$ ), 71.6 (d, C-2), 73.6 (d, C-3), 74.8 (d, C-5), 103.9 (d, C-1). Positive FAB-MS  $m/z$ : 661 ( $\text{M}$ ) $^+$ , 662 ( $\text{M}+\text{H}$ ) $^+$ .

**2-O-(2,3,4,6-Tetra-O-sulfo- $\beta$ -D-galactopyranosyl)-1,3-dimyristylpropanediol (8)** The same procedure described for the preparation of **1** provided a crude product from **41** (50 mg, 0.076 mmol) and sulfur trioxide–trimethylamine complex (96 mg, 0.61 mmol), followed by TFA (69 mg, 0.61 mmol), and this was purified on a column of Sephadex LH-20 equilibrated in and eluted with 20:20:1 (v/v/v)  $\text{CHCl}_3$ –MeOH– $\text{H}_2\text{O}$  to give **8** (22 mg, 30%) as an amorphous solid.  $[\alpha]_D +6.8^\circ$  ( $c=0.68$ , MeOH). IR (neat): 1251, 1101, 818  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (6H, t,  $J=6.4$  Hz,  $\text{OC}_{13}\text{H}_{26}\text{CH}_3 \times 2$ ), 1.26 (44H, brs,  $\text{OCH}_2\text{CH}_2(\text{CH}_2)_{11}\text{CH}_3 \times 2$ ), 1.54 (4H, m,  $\text{OCH}_2\text{CH}_2\text{C}_{12}\text{H}_{25} \times 2$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 13.9 (q,  $\text{OC}_{13}\text{H}_{26}\text{CH}_3 \times 2$ ), 22.5, 23.6, 25.5, 28.9, 29.2, 29.5, 31.8 (t,  $\text{OCH}_2(\text{CH}_2)_{12}\text{CH}_3$ ). Positive FAB-MS  $m/z$ : 981 ( $\text{M}$ ) $^+$ , 923 ( $\text{M}+\text{Na}-\text{SO}_3$ ) $^+$ . *Anal.* Calcd for  $\text{C}_{38}\text{H}_{76}\text{O}_{20}\text{S}_4 \cdot 1/2\text{H}_2\text{O}$ : C, 46.09; H, 7.94. Found: C, 46.51; H, 7.81.

**N-Benzoyloxycarbonyl-L-serine Myristylamide (43)** *N*-Carbobenzoxyl-L-serine-2,4-dinitrophenol (**42**) (997 mg, 2.40 mmol) was added to a solution of myristylamine (614 mg, 2.88 mmol) and triethylamine (262 mg, 2.88 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) at room temperature under argon. The mixture was stirred for 5 h, washed with aqueous  $\text{NaHCO}_3$  and brine, dried ( $\text{MgSO}_4$ ), filtered and evaporated to dryness. The residue was crystallized from *n*-hexane to afford **43** (675 mg, 65%) as a white powder, mp 108–112 °C.  $[\alpha]_D -7.3^\circ$  ( $c=0.34$ ,  $\text{CHCl}_3$ ). IR (KBr): 3274, 1647, 1071, 720, 691  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=6.4$  Hz,  $\text{C}_{13}\text{H}_{26}\text{CH}_3$ ), 1.25 (22H, s,  $(\text{CH}_2)_{11}\text{CH}_3$ ), 1.47 (2H, m,  $\text{CH}_2\text{C}_{12}\text{H}_{25}$ ), 3.23 (2H, m,  $\text{CH}_2\text{C}_{13}\text{H}_{27}$ ), 3.65 (1H, m,  $\text{CHCH}_2\text{OH}$ ), 4.15 (2H, m,  $\text{CHCH}_2\text{OH}$ ), 5.14 (2H, s,  $\text{CH}_2\text{C}_6\text{H}_5$ ), 7.36 (5H, m,  $\text{CH}_2\text{C}_6\text{H}_5$ ). *Anal.* Calcd for  $\text{C}_{25}\text{H}_{42}\text{N}_2\text{O}_4$ : C, 69.09; H, 9.74; N, 6.45. Found: C, 69.32; H, 9.76; N, 6.34.

**L-Serine Myristylamide (44)** A mixture of **43** (323 mg, 0.74 mmol) and 10% Pd-C (0.10 g) in MeOH (10 ml) was stirred under  $\text{H}_2$  overnight at room temperature. The catalyst was removed by filtration and the filtrate was concentrated to dryness to give **44** (400 mg, quant.). Compound **44** was used for the subsequent acylation without further purification.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=6.4$  Hz,  $\text{C}_{13}\text{H}_{26}\text{CH}_3$ ), 1.26 (22H, brs,  $(\text{CH}_2)_{11}\text{CH}_3$ ), 1.51 (2H, m,  $\text{CH}_2\text{C}_{12}\text{H}_{25}$ ), 3.25 (2H, m,  $\text{CH}_2\text{C}_{13}\text{H}_{27}$ ), 3.42 (1H, t,  $J=5.5$  Hz,  $\text{CHCH}_2\text{OH}$ ), 3.69 (1H, dd,  $J=6.0$ , 10.6 Hz,  $\text{CHCH}_2\text{OH}$ ), 3.86 (1H, dd,  $J=5.1$ , 10.6 Hz,  $\text{CHCH}_2\text{OH}$ ).

**N-Stearoyl-L-serine Myristylamide (45)** A solution of stearoyl chloride (304 mg, 1.00 mmol) in ether (2 ml) was added to a stirred solution of **44** (232 mg, 0.77 mmol) and  $\text{NaHCO}_3$  (260 mg, 3.09 mmol) in  $\text{H}_2\text{O}$  (10 ml) at room temperature. Stirring was continued overnight, and the solid that separated was collected by filtration, washed with ether and water, and dried *in vacuo*. Crystallization from acetone gave **45** (546 mg, quant.) as an amorphous powder.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (6H, t,  $J=6.4$  Hz,  $\text{C}_{13}\text{H}_{26}\text{CH}_3$ ,  $\text{C}_{16}\text{H}_{32}\text{CH}_3$ ), 1.26 (50H, brs,  $(\text{CH}_2)_{11}\text{CH}_3$ ,  $(\text{CH}_2)_{14}\text{CH}_3$ ), 1.49 (2H, brs,  $\text{CH}_2\text{C}_{12}\text{H}_{25}$ ), 1.62 (2H, brs,  $\text{CH}_2(\text{CH}_2)_{14}\text{CH}_3$ ), 2.23 (2H, brs,  $\text{CH}_2\text{C}_{16}\text{H}_{33}$ ), 3.22 (2H, brs,  $\text{CH}_2\text{C}_{13}\text{H}_{27}$ ), 3.41 (1H, brs,  $\text{HOCH}_2\text{CH}-$ ), 3.56 (1H, m,  $\text{HOCH}_2\text{CH}-$ ), 3.94 (1H, d,  $J=8.9$  Hz,  $\text{HOCHCH}_2-$ ). Positive FAB-MS  $m/z$ : 568 ( $\text{M}+\text{H}^+$ ).

**N-Benzoyloxycarbonyl-O-(2,3,4,6-tetra-O-acetyl- $\beta$ -D-glucopyranosyl)-L-serine Myristylamide (47)** A stirred mixture of **46** (489 mg, 1.13 mmol), prepared from 2,3,4,6-tetra-O-acetyl- $\beta$ -D-glucopyranose and trichloroacetonitrile and 1,8-diazabicyclo[5.4.0]-7-undecene, was treated with  $\text{BF}_3 \cdot \text{OEt}_2$  (159 mg, 1.13 mmol) and powdered 4 Å molecular sieves in  $\text{CH}_2\text{Cl}_2$  (5 ml) at 0 °C under Ar. The mixture was stirred overnight at room temperature, diluted with  $\text{CH}_2\text{Cl}_2$ , and filtered through Celite. The filtrate was washed with saturated aqueous  $\text{NaHCO}_3$  and dried ( $\text{MgSO}_4$ ) and the solvent was evaporated *in vacuo*. The residue was chromatographed over  $\text{SiO}_2$  with 10:1  $\text{CHCl}_3$ -MeOH to give **47** (801 mg, 77%) as an amorphous powder.  $[\alpha]_D +8.4^\circ$  ( $c=1.15$ ,  $\text{CHCl}_3$ ). IR (neat): 1752, 1524, 1222, 1113  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=6.9$  Hz,  $\text{C}_{13}\text{H}_{26}\text{CH}_3$ ), 1.26 (22H, brs,  $(\text{CH}_2)_{11}\text{CH}_3$ ), 1.48 (2H, brs,  $\text{CH}_2\text{C}_{12}\text{H}_{25}$ ), 2.00, 2.02, 2.03, 2.05 (each 3H, s,  $\text{OCOCH}_3 \times 4$ ), 3.23 (2H, dd,  $J=6.3$ , 13.2 Hz,  $-\text{CH}_2\text{C}_{13}\text{H}_{27}$ ), 3.77 (1H, dd,  $J=8.3$ , 10.5 Hz,  $-\text{OCH}_2\text{CH}-$ ), 5.11 (2H, s,  $\text{OCH}_2\text{C}_6\text{H}_5$ ), 7.35 (5H, s,  $\text{OCH}_2\text{C}_6\text{H}_5$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 14.1 (q,  $\text{CONHC}_{13}\text{H}_{26}\text{CH}_3$ ), 20.6, 20.7 (q,  $\text{OCOCH}_3$ ), 22.7, 23.0, 26.9, 28.9, 29.3, 29.4, 29.6, 29.7, 30.4, 31.9, 38.7, 39.8 (t,  $\text{OCONHC}_{13}\text{H}_{26}\text{CH}_3$ ), 53.8 (t,  $\text{OCH}_2\text{CH}-$ ), 61.7 (t, C-6), 67.2 (t,  $\text{COOCH}_2\text{Ph}$ ), 68.2 (d, C-2), 70.5 (d,  $\text{OCH}_2\text{CH}$ ), 71.1 (d, C-5), 72.1 (d, C-3), 72.6 (d, C-4), 101.8 (d, C-1), 128.2, 128.6, 128.8, 130.9, 132.5, 136.1 (d, Ph), 156.0 (s,  $\text{NHCO}$ ), 167.8, 168.9, 169.4, 170.1 (s,  $\text{OCOCH}_3$ ), 170.6 (s,  $\text{CONH}$ ). *Anal.* Calcd for  $\text{C}_{39}\text{H}_{60}\text{N}_2\text{O}_{13}$ : C, 61.20; H, 7.91; N, 3.66. Found: C, 60.71; H, 7.79; N, 3.15. Positive FAB-MS  $m/z$ : 765 ( $\text{M}^+$ ).

**O-(2,3,4,6-Tetra-O-acetyl- $\beta$ -D-glucopyranosyl)-L-serine Myristylamide (48)** A mixture of **47** (133 mg, 0.17 mmol) and 10% Pd-C (50 mg) in MeOH (10 ml) was stirred under  $\text{H}_2$  overnight at room temperature. The catalyst was removed by filtration and the filtrate was concentrated to dryness to give **48** (67 mg, 61%). Compound **48** was used for the subsequent acylation without further purification.  $[\alpha]_D -22.7^\circ$  ( $c=0.47$ ,  $\text{CHCl}_3$ ). IR (neat): 1729, 1694, 1107  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=6.4$  Hz,  $\text{C}_{13}\text{H}_{26}\text{CH}_3$ ), 1.26 (22H, brs,  $\text{CH}_2(\text{CH}_2)_{11}\text{CH}_3$ ), 1.54 (2H, brs,  $\text{CH}_2\text{CH}_2\text{C}_{12}\text{H}_{25}$ ). Positive FAB-MS  $m/z$ : 631 ( $\text{M}^+$ ).

**N-Stearoyl-O-(2,3,4,6-tetra-O-acetyl- $\beta$ -D-glucopyranosyl)-L-serine Myristylamide (49)** A solution of stearoyl chloride (131 mg, 0.43 mmol) in ether (2 ml) was added to a solution of **48** (210 mg, 0.33 mmol) and  $\text{NaHCO}_3$  (111 mg 5.3 mmol) in  $\text{H}_2\text{O}$  (10 ml) at 0 °C. The mixture was

stirred for 5 h at room temperature, diluted with  $\text{CH}_2\text{Cl}_2$ , washed with aqueous  $\text{NaHCO}_3$  and brine, dried ( $\text{MgSO}_4$ ), and filtered. The filtrate was evaporated to dryness. The residue was chromatographed on a column of silica gel with 10:1  $\text{CH}_2\text{Cl}_2$ -MeOH to give **49** (201 mg, 67%) as an amorphous powder.  $[\alpha]_D -1.8^\circ$  ( $c=0.68$ ,  $\text{CHCl}_3$ ). IR (neat): 1749, 1639, 1552, 1228, 1062  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.86 (3H, t,  $J=7.0$  Hz,  $-\text{CH}_3$ ), 1.26 (52H, brs,  $-\text{CH}_2-$ ), 1.50, 1.59 (4H, brs,  $\text{NCH}_2\text{CH}_2$  and  $\text{C}(\text{O})\text{CH}_2\text{CH}_2$ ), 2.01, 2.05, 2.10 (12H, s,  $\text{OCOCH}_3$ ), 2.19 (2H, t,  $J=7.6$  Hz,  $\text{C}(\text{O})\text{CH}_2\text{CH}_2$ ), 3.20 (2H, t,  $J=6.5$  Hz,  $\text{NCH}_2\text{CH}_2$ ). *Anal.* Calcd for  $\text{C}_{49}\text{H}_{88}\text{N}_2\text{O}_{12}$ : C, 65.59; H, 9.89; N, 3.12. Found: C, 65.22; H, 9.75; N, 3.50. Positive FAB-MS  $m/z$ : 898 ( $\text{M}+1$ ) $^+$ .

**N-Stearoyl-O-( $\beta$ -D-glucopyranosyl)-L-serine Myristylamide (50)** A solution of **49** (62 mg, 0.069 mmol) in  $\text{NEt}_3$ -MeOH (1:9) (2 ml) was stirred at 45 °C overnight. The mixture was concentrated to dryness under reduced pressure and the residual product was purified by column chromatography with 5:1  $\text{CH}_2\text{Cl}_2$ -MeOH to give **50** (50 mg, 81%).  $[\alpha]_D -1.0^\circ$  ( $c=0.88$ ,  $\text{CHCl}_3$ ). IR (neat): 1749, 1639, 1522  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=7.0$  Hz,  $-\text{CH}_3$ ), 1.26 (52H, brs,  $-\text{CH}_2-$ ), 1.50 (2H, brs,  $\text{C}(\text{O})\text{CH}_2\text{CH}_2$ ), 2.20 (2H, t,  $J=8.1$  Hz,  $\text{C}(\text{O})\text{CH}_2\text{CH}_2$ ). *Anal.* Calcd for  $\text{C}_{41}\text{H}_{80}\text{N}_2\text{O}_8$ : C, 67.54; H, 11.06; N, 3.84. Found: C, 67.35; H, 11.25; N, 3.54. Positive FAB-MS  $m/z$ : 729 ( $\text{M}^+$ ) and 752 ( $\text{M}+\text{Na}$ ) $^+$ .

**N-Stearoyl-O-(2,3,4,6-penta-O-sulfo- $\beta$ -D-glucopyranosyl)-L-serine Myristylamide (9)** The same procedure described for the preparation of **1** provided a crude product from **50** (50 mg, 0.069 mmol) and sulfur trioxide-pyridine complex (66 mg, 0.41 mmol), followed by TFA (66 mg, 0.58 mmol), and this was purified on a column of Sephadex LH-20 equilibrated in and eluted with 20:20:1 (v/v)  $\text{CHCl}_3$ -MeOH- $\text{H}_2\text{O}$  to give **9** (20 mg, 28%) as an amorphous powder, followed by lyophilization from  $\text{H}_2\text{O}$ .  $[\alpha]_D -2.9^\circ$  ( $c=0.20$ , MeOH). IR (Nujol): 1654, 1546, 1227, 1047  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{41}\text{H}_{80}\text{N}_2\text{O}_{20}\text{S}_4 \cdot 1/2\text{C}_5\text{H}_5\text{N}$ : C, 47.98; H, 7.46; N, 3.22. Found: C, 48.57; H, 8.15; N, 3.84.

**N-Benzoyloxycarbonyl-O-(2,3,4,6-tetra-O-acetyl- $\beta$ -D-galactopyranosyl)-L-serine Myristylamide (52)** The same procedure described for the preparation of **47** provided a crude product from **51** (1.23 g, 2.48 mmol), itself prepared from 2,3,4,6-tetra-O-acetyl- $\beta$ -D-galactopyranose, trichloroacetonitrile, 1,8-diazabicyclo[5.4.0]-7-undecene, **43** (1.08 g, 2.48 mmol) and  $\text{BF}_3 \cdot \text{OEt}_2$  (0.35 g, 2.48 mmol), and this was purified on a column of silica gel with 10:1  $\text{CHCl}_3$ -MeOH to give **52** (0.62 g, 33%) as prisms, mp 98–100 °C.  $[\alpha]_D +9.6^\circ$  ( $c=0.80$ ,  $\text{CHCl}_3$ ). IR (neat): 1747, 1665, 1536, 737, 699  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.91 (3H, t,  $J=6.8$  Hz,  $\text{C}_{13}\text{H}_{26}\text{CH}_3$ ), 1.28 (22H, brs,  $\text{CH}_2(\text{CH}_2)_{11}\text{CH}_3$ ), 1.50 (2H, brs,  $\text{NCH}_2\text{CH}_2$ ), 2.02, 2.07, 2.12, 2.17 (each 3H, s,  $\text{OCOCH}_3 \times 4$ ), 3.24 (2H, m,  $\text{NHCH}_2\text{CH}_2$ ), 3.69 (1H, dd,  $J=5.4$ , 11.3 Hz,  $\text{OCH}_2\text{CHN}$ ), 5.15 (2H, s,  $\text{OCH}_2\text{C}_6\text{H}_5$ ), 5.99 (1H, brd,  $J=7.3$  Hz,  $\text{NHCO}$ ), 6.72 (1H, brs,  $\text{NHCH}_2$ ), 7.37 (5H, s,  $\text{OCH}_2\text{C}_6\text{H}_5$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 14.1 (q,  $\text{C}_{13}\text{H}_{26}\text{CH}_3$ ), 20.6, 20.7 (q,  $\text{OCOCH}_3$ ), 22.7, 26.8, 26.9, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 39.7, 39.9 (t,  $\text{C}_{13}\text{H}_{26}\text{CH}_3$ ), 55.4 (t,  $\text{OCH}_2\text{CH}$ ), 62.8 (t, C-6), 67.2 (t,  $\text{COOCH}_2\text{Ph}$ ), 68.2 (d, C-2), 70.5 (d,  $\text{OCH}_2\text{CH}$ ), 71.0 (d, C-5), 101.9 (d, C-1), 128.1, 128.3, 128.6, 136.0 (s, Ph), 156.0 (s,  $\text{NHCO}$ ), 170.1, 170.3, 170.4, 170.5, 170.6 (s, C=O). *Anal.* Calcd for  $\text{C}_{39}\text{H}_{60}\text{N}_2\text{O}_{13}$ : C, 61.20; H, 7.91; N, 3.66. Found: C, 61.57; H, 7.83; N, 3.15.

**O-(2,3,4,6-Tetra-O-acetyl- $\beta$ -D-galactopyranosyl)-L-serine Myristylamide (53)** The same procedure described for the preparation of **48** provided a crude product from **52** (622 mg, 0.81 mmol) and this was concentrated to dryness to give **53** (48 mg, 94%). Compound **53** was used for the subsequent acylation without further purification.  $[\alpha]_D +11.4^\circ$  ( $c=0.95$ ,  $\text{CHCl}_3$ ). IR (neat): 1748, 1674, 1538, 1226, 1071  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.87 (3H, t,  $J=6.4$  Hz,  $-\text{C}_{13}\text{H}_{26}\text{CH}_3$ ), 1.25 (22H, brs,  $\text{CH}_2(\text{CH}_2)_{11}\text{CH}_3$ ), 1.50 (2H, brs,  $\text{CH}_2\text{CH}_2\text{C}_{12}\text{H}_{25}$ ), 1.98, 2.03, 2.14 (12H, s,  $\text{COCH}_3$ ). Positive FAB-MS  $m/z$ : 731 ( $\text{M}^+$ ) $^+$ .

**N-Stearoyl-O-(2,3,4,6-tetra-O-acetyl- $\beta$ -D-galactopyranosyl)-L-serine Myristylamide (54)** The same procedure described for the preparation of **54** provided a crude product from **53** (483 mg, 0.77 mmol) and this was purified on a column of silica gel with 10:1  $\text{CHCl}_3$ -MeOH to give **54** (702 mg, quant.).  $[\alpha]_D +4.3^\circ$  ( $c=0.51$ , 1:1  $\text{CHCl}_3$ -MeOH). IR (KBr): 1747, 1641, 1555, 1223, 1059  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.86 (3H, t,  $J=7.3$  Hz,  $-\text{CH}_3$ ), 1.26 (52H, brs,  $-\text{CH}_2-$ ), 1.51–1.60 (4H, m,  $\text{NCH}_2\text{CH}_2$  and  $\text{C}(\text{O})\text{CH}_2\text{CH}_2$ ), 1.99, 2.06, 2.16 (12H, s,  $\text{OCOCH}_3$ ), 2.26 (2H, t,  $J=7.6$  Hz,  $\text{C}(\text{O})\text{CH}_2\text{CH}_2$ ), 3.21 (2H, t,  $J=6.5$  Hz,  $\text{NCH}_2\text{CH}_2$ ). *Anal.* Calcd for  $\text{C}_{49}\text{H}_{88}\text{N}_2\text{O}_{12}$ : C, 65.59; H, 9.89; N, 3.12. Found: C, 65.19; H, 9.77; N, 3.75. Positive FAB-MS  $m/z$ : 920 ( $\text{M}+\text{Na}$ ) $^+$ .

**N-Stearoyl-O-( $\beta$ -D-galactopyranosyl)-L-serine Myristylamide (55)** The same procedure described for the preparation of **50** provided a crude product from **54** (60 mg, 0.067 mmol), and this was purified on a column

of silica gel with 5:1  $\text{CHCl}_3$ -MeOH to give **55** (34 mg, 70%) as an amorphous powder.  $[\alpha]_D^{25} +1.2^\circ$  ( $c=0.29$ ,  $\text{CHCl}_3$ ). IR (neat): 3324, 2918, 1666, 1553  $\text{cm}^{-1}$ .  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$ : 0.88 (3H, t,  $J=7.0$  Hz,  $-\text{CH}_3$ ), 1.26 (52H, br s,  $-\text{CH}_2-$ ), 1.54–1.68 (4H, m,  $\text{C}(\text{O})\text{CH}_2\text{CH}_2$  and  $\text{NCH}_2\text{CH}_2$ ), 2.27 (2H, t,  $J=7.0$  Hz,  $\text{C}(\text{O})\text{CH}_2\text{CH}_2$ ). Positive FAB-MS  $m/z$ : 752 ( $\text{M} + \text{Na}$ ) $^+$ .

**N-Stearoyl-O-(2,3,4,6-penta-O-sulfo- $\beta$ -D-galactopyranosyl)-L-serine Myristylamide (10)** The same procedure described for the preparation of **1** provided a crude product from **55** (44 mg, 0.06 mmol) and sulfur trioxide-pyridine complex (57 mg, 0.36 mmol), followed by TFA (41 mg, 0.36 mmol), and this was purified by column of Sephadex LH-20 equilibrated in and eluted with 20:20:1 (v/v)  $\text{CHCl}_3$ -MeOH- $\text{H}_2\text{O}$  to give **10** (27 mg, 43%) as an amorphous powder, after lyophilization from  $\text{H}_2\text{O}$ .  $[\alpha]_D^{25} -10.4^\circ$  ( $c=0.36$ , MeOH). IR (Nujol): 1649, 1539, 1230  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{41}\text{H}_{80}\text{N}_2\text{O}_{20}\text{S}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ : C, 49.12; H, 7.27; N, 3.37. Found: C, 49.06; H, 7.74; N, 3.62.

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