Lipid A and Related Compounds. XXXII.[1] Synthesis of Biologically Active *N*-Acylated L-Homoserine-Containing D-Glucosamine-4-phosphate Derivatives Structurally Related to Lipid A

Keisuke MIYAJIMA and Kazuo ACHIWA*

School of Pharmaceutical Sciences, University of Shizuoka, Yada 52–1, Shizuoka 422, Japan.
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New *N*-acylated L-homoserine-containing non-phosphorylated and phosphorylated D-glucosamine derivatives were synthesized as mimicks of lipid A disaccharide. Some of the synthesized compounds exhibited mitogenic activity and nitric oxide (NO) productivity.

Key words *N*-acylated L-homoserine; D-glucosamine-4-phosphate; lipid A analog; mitogenic activity; nitric oxide productivity

Lipid A is well known to be responsible for the expression of many of the biological activities, such as endotoxicity, adjuvanticity, antitumor activity and so on, of lipopolysaccharide (LPS) of gram-negative bacteria.[2] Lipid A consists of α-D-glucosamyl-(1—6)-β-D-glucosamine carrying two phosphates and several fatty acid residues,[3] as indicated in Chart 1. Among the various synthetic lipid A analogs, D-glucosamine-4-phosphate analogs corresponding to the non-reducing unit of lipid A show many of the biological activities of LPS.[4] Recently, various acyclic analogs related to lipid A partial structure have been synthesized.[5] We have already reported that *N*-acylated L-serine-containing D-glucosamine 4-phosphate derivatives structurally similar to the lipid A disaccharide backbone show remarkable mitogenetic activity.[6] However, the synthesis of *O*-linked glycopeptides is complicated by the acid-lability of glycosides in general and the base-sensitivity (retro-Michael reaction) of the *O*-serinyl glycosides in particular.[7] Therefore, we designed new lipid A analogs containing the acyclic L-homoserine residue instead of the L-serine one, as mimicks of the cyclic reducing part of lipid A. The homoserinyl glycosides seem to be more stable than the serinyl glycosides. We also expected that they might have interesting biological activities.

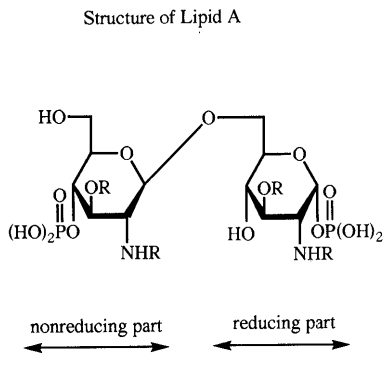
In this paper, we describe the synthesis of *N*-acylated L-homoserine-containing non-phosphorylated D-glucosamine derivatives (**1**—**7**) and a phosphorylated D-glucosamine derivative (**8**) structurally similar to the lipid A disaccharide backbone, and their biological effects.

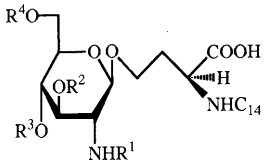
As our strategy to prepare compounds **1**—**8**, we employed the thiophenylglycosides (**13**, **33**) and the glycosyl bromide (**23**) as a key intermediate for the formation of β-*O*-homoserinyl glycosides.[8] The *N*-tetradecanoyl L-homoserine derivative (**11**) was easily prepared from L-homoserine (**9**) as shown in Chart 2.

Acylation of **9** with tetradecanoyl chloride using potassium hydrogen carbonate ($KHCO_3$) in ether–H_2O gave crude **10** in 85% yield. Reaction of **10** with potassium hydroxide (KOH) in EtOH–H_2O, followed by esterification of the resulting potassium salt with benzyl bromide in the presence of sodium iodide (NaI) in dimethyl sulfoxide (DMSO) gave **11** in 81% yield.

First, we synthesized the non-phosphorylated D-glucosamine-derived lipid A analogs (**1**—**7**). The synthetic sequence for compounds **1**—**5** is shown in Chart 3.

Treatment of **12**[9] with thiophenol (PhSH) in the presence of boron trifluoride etherate (BF_3OEt_2) in CH_2Cl_2 gave phenyl 1-thio-β-D-glucopyranoside (**13**) in 89% yield. Coupling of **11** and the key intermediate (**13**) with *N*-bromosuccinimide (NBS),[10] iodine, tetrabutylammonium trifluoromethanesulfonate (TBAOTf) as a promoter, and molecular sieves 4 Å in CH_2Cl_2 at −20 °C gave the β-glycoside (**14**) in 64% yield.[8a] The β-con-





1 : $R^1 = C_{14}$, $R^2 = R^3 = R^4 = Ac$
2 : $R^1 = C_{14}OC_{14}$, $R^2 = R^3 = R^4 = Ac$
3 : $R^1 = Ph(CH_2)_7C(O)$, $R^2 = R^3 = R^4 = Ac$
4 : $R^1 = GlyC_{12}$, $R^2 = R^3 = R^4 = Ac$
5 : $R^1 = C_{14}OC_{14}$, $R^2 = R^3 = R^4 = H$
6 : $R^1 = R^2 = C_{14}OC_{14}$, $R^3 = R^4 = H$
7 : $R^1 = C_{14}OC_{14}$, $R^2 = C_{14}$, $R^3 = R^4 = H$
8 : $R^1 = R^2 = C_{14}OC_{14}$, $R^3 = (HO)_2P(O)$, $R^4 = H$

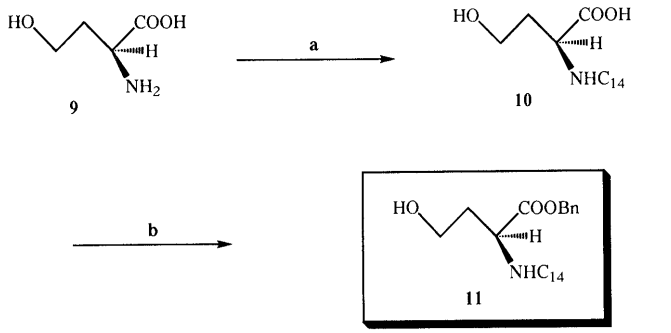
C_{14}: $CH_3(CH_2)_{12}C(O)$-
$C_{14}OC_{14}$: $CH_3(CH_2)_{10}\underset{(R)}{CH}CH_2C(O)$-
$CH_3(CH_2)_{12}C(O)O$
$GlyC_{12}$: $CH_3(CH_2)_{10}C(O)NHCH_2C(O)$-

Chart 1

* To whom correspondence should be addressed.

figuration of **14** was determined from the coupling constant value (8.3 Hz) of the signal due to the anomeric proton in the proton magnetic resonance (^{1}H-NMR) spectrum of **14**. The 2,2,2-trichloroethoxycarbonyl (Troc) group of **14** was cleaved by treatment with activated zinc powder in acetic acid (AcOH) to give the amine (**15**) in 64% yield. Acylation of **15** with tetradecanoic acid, optically active (*R*)-3-tetradecanoyloxytetradecanoic acid,[11] 8-phenyloctanoic acid, or *N*-dodecanoylglycine[12] in the presence of diethylphosphorocyanidate (DEPC) and triethylamine (TEA) in dimethylformamide (DMF) gave **16a**, **16b**, **16c**, and **16d** in yields of 72, 61, 64, and 32%, respectively. The benzyl groups of **16a**—**16d** were removed by hydrogenolysis over palladium-black at room temperature in MeOH–THF to afford the desired compounds **1**, **2**, **3**, and **4** in yields of 61, 88, 93, and 65%, respectively. Removal of acetyl groups in **2** by treatment with sodium methoxide (NaOMe) in MeOH gave the alcohol (**5**) in 68% yield.

Next, compounds **6** and **7** were synthesized by the route shown in Chart 4.



reagents: a) $C_{14}Cl$, $KHCO_3$ in ether-H_2O ; b) 1) KOH in EtOH-H_2O ; 2) $PhCH_2Br$, NaI in DMSO

Chart 2

Compound **17**[8c] was converted into the 4,6-*O*-*p*-methoxybenzylidene derivative (**18**) with *p*-methoxybenzaldehyde dimethylacetal and a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) in DMF in 94% yield. Treatment of **18** with Troc-Cl and pyridine–4-dimethylaminopyridine (DMAP) in CH_2Cl_2 afforded a 3-*O*-Troc derivative (**19**) in 75% yield. Compound **19** was treated with 68% AcOH to give the diol (**20**) in 94% yield. The diol (**20**) was benzylated with benzyl trichloroacetoimidate in the presence of a catalytic amount of trifluoromethanesulfonic acid (CF_3SO_3H) in CH_2Cl_2–cyclohexane to give the dibenzyl ether (**21**) in 98% yield. Removal of the *O*-allyl group with iridium catalyst, followed by hydrolysis with I_2–H_2O–pyridine gave the alcohol (**22**) in 85% yield. Bromination of **22** with the Vilsmeier reagent, generated *in situ* by the use of thionyl bromide and DMF,[13] gave the bromide (**23**) in quantitative yield. Condensation of the key intermediate (**23**) and the L-homoserine derivative (**11**) with $HgBr_2$ as a promoter and molecular sieves 4 Å in CH_2Cl_2 gave the β-glycoside (**24**) in 40% yield; the configuration of the glycosidic linkage was assigned as β form on the basis of the ^{1}H-NMR data ($J_{1,2}$ = 8.2 Hz), as in the case of **14**.[8c] Treatment of **24** with activated zinc powder in AcOH gave the amino alcohol (**25**) in 65% yield. Compound **25** thus obtained was acylated with optically active (*R*)-3-tetradecanoyloxy-tetradecanoic acid in the presence of dicyclohexylcarbodiimide (DCC) and DMAP in CH_2Cl_2 to give **26a** in 35% yield. Finally, catalytic hydrogenolysis using palladium-black in MeOH–THF removed the benzyl groups to give the desired compound **6** in 84% yield after purification followed by lyophilization from dioxane. Similarly, compound **7**, bearing the (*R*)-3-tetradecanoyloxytetradecanoyl group at *N*-2 and the tetradecanoyl group at *O*-3 of the D-

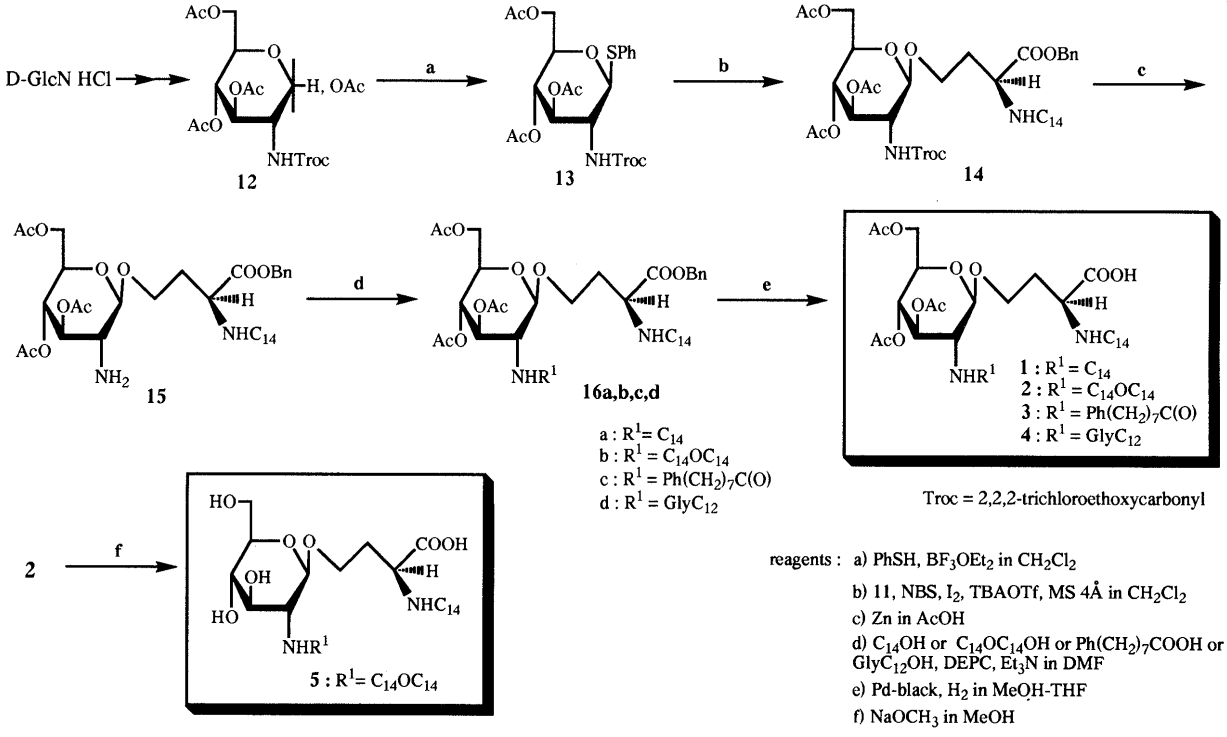
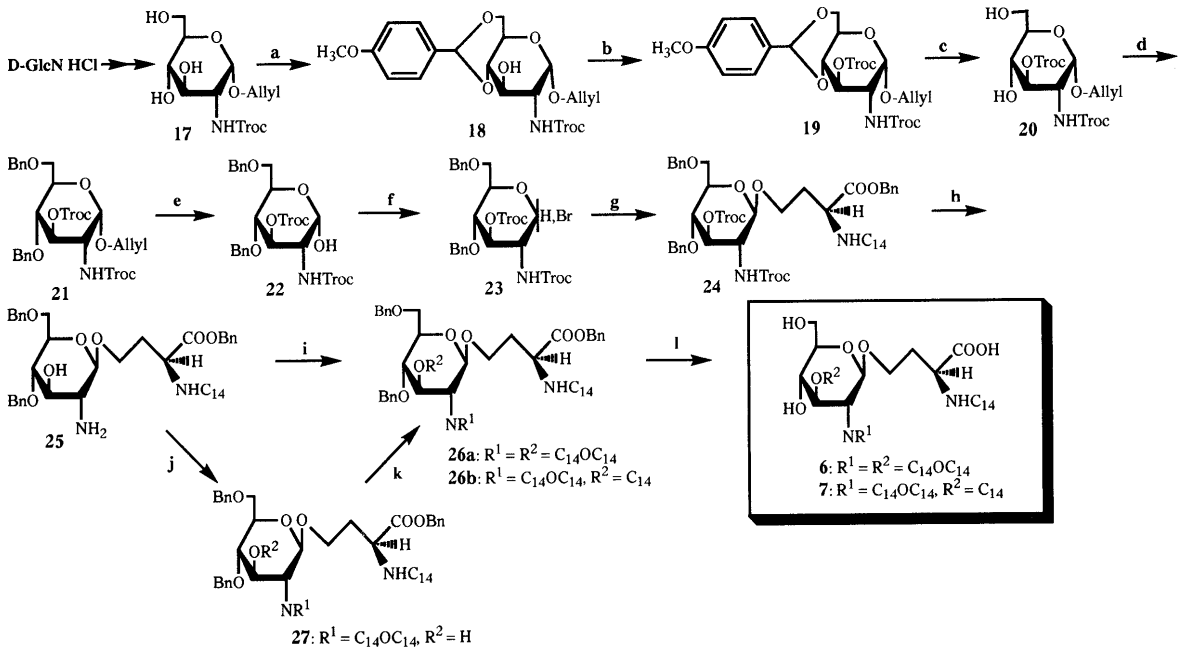


Chart 3

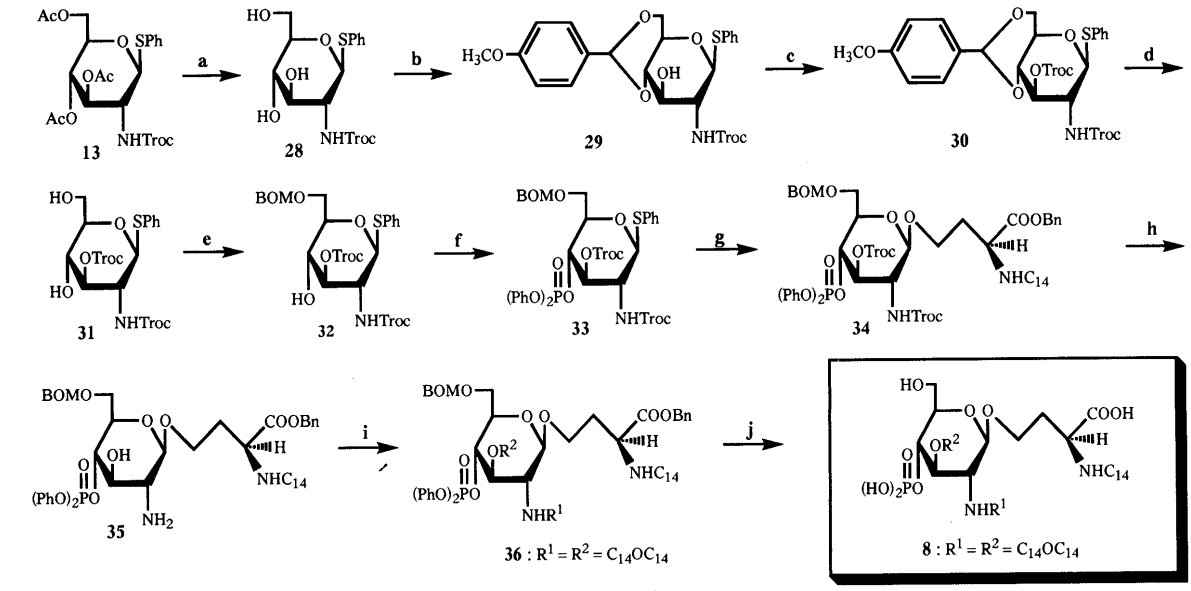


C_{14}: $CH_3(CH_2)_{12}C(O)$-

$C_{14}OC_{14}$: $CH_3(CH_2)_{10}\underset{(R)}{CH}CH_2C(O)$-
$CH_3(CH_2)_{12}C(O)O$

reagents : a) *p*-$MeOC_6H_4CH(OMe)_2$, *p*-TsOH in DMF ; b) Troc-Cl, pyridine-DMAP in CH_2Cl_2 ; c) 68 % AcOH ; d) $Cl_3CC(OBn)=NH$, CF_3SO_3H in CH_2Cl_2-cyclohexane (1:2) ; e) 1) $[CODIr(PMePh_2)_2]PF_6$ in THF ; 2) I_2, pyridine in THF-H_2O ;f) $SOBr_2$ in CH_2Cl_2-DMF (10:1) ; g) **11**, $HgBr_2$, MS 4Å in CH_2Cl_2 ; h) Zn in AcOH ; i) $C_{14}OC_{14}OH$, DCC-DMAP in CH_2Cl_2 ; j) $C_{14}OC_{14}OH$, DCC in CH_2Cl_2 ; k) $C_{14}Cl$, pyridine-DMAP in CH_2Cl_2 ; l) Pd-black, H_2 in MeOH-THF (2:1).

Chart 4



reagents : a) $NaOCH_3$ in MeOH ; b) *p*-$MeOC_6H_4CH(OMe)_2$, *p*-TsOH in DMF ; c) Troc-Cl, pyridine-DMAP in CH_2Cl_2 ; d) 83 % AcOH ; e) BOM-Cl, TMU in CH_2Cl_2 ; f) $(PhO)_2P(O)Cl$, pyridine-DMAP in CH_2Cl_2 g) **11**, NBS, I_2, TBAOTf, MS 4Å in CH_2Cl_2 ; h) Zn in AcOH ; i) $C_{14}OC_{14}OH$, DCC-DMAP in CH_2Cl_2 ; j) 1) Pd-black, H_2 in MeOH-THF (1:1) ; 2) PtO_2, H_2 in MeOH-THF (1:1)

BOM = $BnOCH_2$-

C_{14}: $CH_3(CH_2)_{12}C(O)$-

$C_{14}OC_{14}$: $CH_3(CH_2)_{10}\underset{(R)}{CH}CH_2C(O)$-
$CH_3(CH_2)_{12}C(O)O$

Chart 5

glucosamine skeleton of the GLA-27 type,[14] was synthesized stepwise by successive acylation of the amino and hydroxy groups of **25**. Compound **25** was first acylated at the amino group with (*R*)-3-tetradecanoyloxytetradecanoic acid and DCC to give **27** in 71% yield. The remaining hydroxy group of **27** was acylated with tetradecanoyl chloride in pyridine–DMAP to give **26b** in 74% yield. Finally, deprotection of **26b** as described for the preparation of **6** gave the desired product **7** in 50% yield after purification followed by lyophilization from dioxane.

Next, the synthesis of phosphorylated D-glucosamine-derived lipid A analog (**8**) was carried out as follows (Chart 5).

Methanolysis of **13** in the presence of NaOMe gave the

triol (**28**) in 88% yield. The same procedure as described for the preparation of **20** from **17** provided **31** from **28** in three steps in 74% yield. The 6-hydroxy group of **31** was selectively protected with benzyloxymethyl chloride and 1,1,3,3-tetramethylurea (TMU) in CH_2Cl_2 to give **32** in 71% yield. The phosphorylation of **32** with diphenyl phosphorochloridate in the presence of pyridine–DMAP in CH_2Cl_2 gave compound **33** in 93% yield. Condensation of **11** and the key intermediate (**33**) as described for the preparation of **14** gave compound **34** in 60% yield. The β-configuration of **34** was determined from the J_{C-H} value of 158.7 Hz in the carbon magnetic resonance (^{13}C-NMR) spectrum of **34**.[15] Deprotection of Troc groups of **34** with activated zinc powder in AcOH gave the crude amino alcohol (**35**) in almost quantitative yield. The simultaneous acylation of the amino and hydroxy groups of **35** with (*R*)-3-tetradecanoyloxytetradecanoic acid and DCC–DMAP gave **36** in 46% yield. Finally, the benzyl and phenyl protective groups of **36** were removed by stepwise hydrogenolysis catalyzed by Pd-black and then platinum oxide in MeOH–THF to give the expected compound **8** in 77% yield after purification followed by lyophilization from dioxane.

In the synthesis of **1**—**5** and **8**, glycosylation of the thiophenylglycosides (**13**, **33**) and *N*-tetradecanoyl homoserine derivative (**11**) with NBS, iodine, and TBAOTf as a promoter gave the desired β-*O*-homoserinyl glycosides (**14**, **34**) in satisfactory yields (60%, 64%) with high stereoselectivities. These results proved the thiophenylglycosides to be chemically stable and efficient glycosyl donors which are only activated under specific conditions, and allow efficient stereoselective glycosylations.

The structures of all compounds were characterized by ^{1}H-NMR spectroscopy as well as infrared (IR) and fast-atom bombardment (FAB) mass spectroscopy.

In a preliminary examination of the biological activities of the synthetic analogs (**1**—**8**), compound **8** was mitogenic to splenocytes of C3H/He mice[16] and its activity was similar to those of the original acyl-derivatives of D-glucosamine-4-phosphate,[17] while the other compounds exhibited only weak activity. On the other hand, compounds **6** and **7** showed NO-inducing activity[6c] about twice as potently as the original compounds.

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. FAB-MS were recorded on a JEOL JMS-SX 102 spectrometer. ^{1}H-NMR spectra were taken on a JEOL JNM-GX 270 (270 MHz) spectrometer. ^{13}C-NMR spectra were recorded with a JEOL JNM-GX 270 (67.5 MHz) spectrometer. ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to Me_4Si ($\delta=0$) in $CDCl_3$ or CD_3OD 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). 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.

***N*-Tetradecanoyl-L-homoserine (10)** Tetradecanoyl chloride (2.74 g, 12 mmol) was added to a solution of L-homoserine **9** (1.19 g, 10 mmol) and potassium hydrogen carbonate (5.0 g, 50 mmol) in ether–H_2O (1 : 1) (60 ml) at 0 °C. The reaction mixture was stirred at room temperature for 20 h and then extracted with ether. The aqueous phase was ice-cooled, carefully acidified to pH 2—3 with 2 N HCl, and extracted with AcOEt. The extract was dried ($MgSO_4$), and evaporated *in vacuo*. The resulting white solid (2.82 g, 85%) was used without further purification.

***N*-Tetradecanoyl-L-homoserine Benzyl Ester (11)** Compound **10** obtained above (1.27 g, 3.86 mmol) was dissolved in EtOH (60 ml)–H_2O (1 ml) and KOH (0.24 g, 4.3 mmol) was added. The solution was stirred at room temperature for 16 h, and the reaction mixture was evaporated *in vacuo*. The residue was dissolved in DMSO (50 ml), and benzyl bromide (0.66 g, 3.86 mmol) and sodium iodide (0.58 g, 3.86 mmol) were added to the solution at 5—10 °C. The mixture was stirred at room temperature for 20 h, then ice water was added. The insoluble materials were collected by filtration, washed with H_2O, and dried under vacuum. The resulting precipitate was purified by silica gel column chromatography using hexane–AcOEt (3 : 1) to give **11** (1.32 g, 81%) as a white solid, mp 62—64 °C. $[\alpha]_D$ −12.8° ($c=1.07$, $CHCl_3$). IR (Nujol): 3492, 3330, 1756, 1628, 1537 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, $J=6.9$ Hz, $-CH_3$), 1.25 (20H, br s, $-CH_2-$), 1.53—1.64 (3H, m, $HOCH_2CH_2CHNH$, $COCH_2CH_2C_{11}H_{23}$), 2.17—2.30 (4H, m, $HOCH_2CH_2CHNH$, $COCH_2C_{12}H_{25}$), 3.49—3.67 (2H, m, $HOCH_2CH_2CHNH$), 4.76—4.84 (1H, m, $HOCH_2CH_2CHNH$), 5.19 (2H, br s, CH_2Ph), 6.34 (1H, d, $J=7.6$ Hz, NH), 7.36 (5H, s, Ph). Positive FAB-MS *m/z*: 420 $(M+H)^+$.

Phenyl 3,4,6-Tri-*O*-acetyl-2-deoxy-1-thio-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (13) Boron trifluoride etherate (2.04 g, 14.35 mmol) was added dropwise to a solution of **12** (3.0 g, 5.74 mmol) and thiophenol (633 mg, 5.74 mmol) in CH_2Cl_2 at 0 °C. The mixture was stirred at room temperature for 24 h, diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was purified by silica gel column chromatography using hexane–AcOEt (3 : 1) to give **13** (2.93 g, 89%) as a white solid, mp 141—143 °C. $[\alpha]_D$ −0.9° ($c=0.74$, $CHCl_3$). IR (Nujol): 1747, 1700, 1558 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.96, 2.02, 2.09 (each 3H, s, $OCOCH_3$), 3.69—3.79 (2H, m, H-2, 5), 4.07—4.27 (2H, m, H-6), 4.72, 4.80 (each 1H, d, $J=12.2$ Hz, CH_2CCl_3), 4.88 (1H, d, $J=10.2$ Hz, H-1), 5.02 (1H, t, $J=9.6$ Hz, H-4), 5.30 (1H, t, $J=9.6$ Hz, H-3), 5.69 (1H, d, $J=9.2$ Hz, NH), 7.26—7.53 (5H, m, Ph).

***N*-Tetradecanoyl-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl]-L-homoserine Benzyl Ester (14)** A solution of compound **13** (458 mg, 0.8 mmol) and *N*-tetradecanoyl-L-homoserine benzyl ester **11** (420 mg, 1.0 mmol) in anhydrous CH_2Cl_2 (15 ml) was stirred for 1 h at room temperature under argon in the presence of 4 Å powdered molecular sieves (700 mg). The mixture was cooled to −20 °C, then NBS (570 mg, 3.2 mmol), iodine (812 mg, 3.2 mmol), and TBAOTf (61 mg, 0.4 mmol) were added. Stirring was continued at the same temperature for 1 h. After removal of the insoluble materials by filtration, the filtrate was washed successively with 10% aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by silica gel column chromatography using hexane–AcOEt (2 : 1) to give **14** (450 mg, 64%) as an amorphous powder. $[\alpha]_D$ +1.9° ($c=1.28$, $CHCl_3$). IR (Nujol): 3316, 1742, 1727, 1712, 1642, 1552 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, $J=6.9$ Hz, $-CH_3$), 1.25 (20H, br s, $-CH_2-$), 1.56—1.65 (2H, m, $COCH_2CH_2C_{11}H_{23}$), 2.02, 2.03, 2.06 (each 3H, s, $OCOCH_3$), 1.97—2.18 (2H, m, OCH_2CH_2CHNH), 2.24 (2H, t, $J=7.3$ Hz, $COCH_2C_{12}H_{25}$), 3.47—3.55 (2H, m, H-2, OCH_2CH_2CHNH), 3.59—3.66 (1H, m, H-5), 3.89—3.94 (1H, m, OCH_2CH_2CHNH), 4.09 (1H, dd, $J=2.3$, 12.2 Hz, H-6), 4.23 (1H, dd, $J=4.6$, 12.2 Hz, H-6), 4.46 (1H, d, $J=8.3$ Hz, H-1), 4.66—4.78 (3H, m, CH_2CCl_3, OCH_2CH_2CHNH), 5.00 (1H, t, $J=9.9$ Hz, H-4), 5.09—5.26 (3H, m, H-3, CH_2Ph), 5.46 (1H, d, $J=8.6$ Hz, NH), 6.38 (1H, d, $J=7.6$ Hz, NH), 7.36 (5H, s, Ph). ^{13}C-NMR ($CDCl_3$) δ: 14.3 (q, $-CH_3$), 20.8, 20.9 (q, $OCOCH_3$), 22.9, 25.8, 29.5, 29.6, 29.7, 29.9 (t, CH_2), 31.5 (t, OCH_2CH_2), 32.1, 36.4 (t, CH_2), 50.3 (d, OCH_2CH_2CHNH), 56.2 (d, C-2), 62.1 (t, C-6), 66.3 (t, OCH_2CH_2CHNH), 67.3 (t, CH_2Ph), 68.8 (d, C-4), 71.9 (d, C-5), 72.0 (d, C-3), 74.6 (t, CH_2CCl_3), 95.7 (s, CH_2CCl_3), 101.0 (d, C-1), 128.6, 128.7, 128.8 (d, Ph), 135.6 (s, Ph), 154.5, 169.7, 170.8, 170.9, 173.2, 173.4 (s, C=O). Positive FAB-MS *m/z*: 883 $(M+3)^+$.

***N*-Tetradecanoyl-*O*-(3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranosyl)-L-homoserine Benzyl Ester (15)** Activated zinc powder (450 mg, 6.9 mmol) was added to a solution of **14** (449 mg, 0.51 mmol) in AcOH (25 ml), and the mixture was vigorously stirred at 40—50 °C for 20 h. After removal of the insoluble materials by filtration, the solvent was evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2, and this solution was washed with saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by silica gel column chromatography using CH_2Cl_2–MeOH (50 : 1) to give **15**

(230 mg, 64%) as a white solid, mp 118—121 °C. $[\alpha]_D$ +19.9° (c=0.80, $CHCl_3$). IR (Nujol): 3348, 1742, 1648, 1552 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.9 Hz, $-CH_3$), 1.25 (20H, br s, $-CH_2-$), 1.38—1.60 (2H, m, $COCH_2CH_2C_{11}H_{23}$), 2.02, 2.03, 2.07 (each 3H, s, $OCOCH_3$), 2.13—2.31 (4H, m, OCH_2CH_2CHNH, $COCH_2C_{12}H_{25}$), 2.63—2.73 (1H, m, H-2), 3.53—3.66 (2H, m, H-5, OCH_2CH_2CHNH), 3.95—4.02 (1H, m, OCH_2CH_2CHNH), 4.08 (1H, dd, J=2.0, 12.2 Hz, H-6), 4.14 (1H, d, J=8.3 Hz, H-1), 4.28 (1H, dd, J=4.9, 12.2 Hz, H-6), 4.74—4.88 (1H, m, OCH_2CH_2CHNH), 4.92—4.99 (2H, m, H-3, H-4), 5.16 (2H, br s, CH_2Ph), 6.57 (1H, d, J=7.3 Hz, NH), 7.37 (5H, s, Ph). ^{13}C-NMR ($CDCl_3$) δ: 14.5 (q, $-CH_3$), 21.1, 21.2 (q, $OCOCH_3$), 23.1, 26.1, 29.8, 29.9, 30.1 (t, CH_2), 31.6 (t, OCH_2CH_2), 32.3, 36.9 (t, CH_2), 50.2 (d, OCH_2CH_2CHNH), 56.1 (d, C-2), 62.6 (t, C-6), 66.4 (t, OCH_2CH_2CHNH), 67.7 (t, CH_2Ph), 69.1 (d, C-4), 72.3 (d, C-5), 75.7 (d, C-3), 104.6 (d, C-1), 128.7, 128.9, 129.1 (d, Ph), 135.7 (s, Ph), 169.8, 170.2, 171.1, 173.2, 173.5 (s, C=O). Positive FAB-MS m/z: 707 $(M+H)^+$.

***N*-Tetradecanoyl-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-tetradecanoylamino-*β*-D-glucopyranosyl)-L-homoserine Benzyl Ester (16a)** Compound **15** (66 mg, 0.094 mmol) and tetradecanoic acid (28 mg, 0.12 mmol) were dissolved in DMF (10 ml), and DEPC (20 mg, 0.12 mmol) and TEA (12 mg, 0.12 mmol) were added to the solution with ice cooling under argon. The reaction mixture was stirred for 16 h, then diluted with CH_2Cl_2, washed successively with saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by silica gel column chromatography using CH_2Cl_2–CH_3COCH_3 (20 : 1) to give **16a** (62 mg, 72%) as a white solid, mp 122—126 °C. $[\alpha]_D$ −1.1° (c=0.92, $CHCl_3$). IR (Nujol): 3288, 1744, 1643, 1552 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (6H, t, J=6.9 Hz, $-CH_3$), 1.25 (40H, br s, $-CH_2-$), 1.43—1.62 (4H, m, $COCH_2CH_2C_{11}H_{23}\times 2$), 2.02, 2.05, 2.07 (each 3H, s, $OCOCH_3$), 1.89—2.30 (6H, m, OCH_2CH_2CHNH, $COCH_2C_{12}H_{25}\times 2$), 3.45—3.53 (1H, m, OCH_2CH_2CHN) 3.63—3.71 (2H, m, H-2, H-5), 3.87—3.96 (1H, m, OCH_2CH_2CHN), 4.08 (1H, dd, J=2.3, 12.2 Hz, H-6), 4.23 (1H, dd, J=4.6, 12.2 Hz, H-6), 4.56 (1H, d, J=8.3 Hz, H-1), 4.67—4.74 (1H, m, OCH_2CH_2CHNH), 5.00 (1H, t, J=9.6 Hz, H-4), 5.15 (2H, br s, CH_2Ph), 5.25 (1H, d, J=9.6 Hz, H-3), 5.49 (1H, d, J=8.3 Hz, NH), 6.46 (1H, d, J=7.9 Hz, NH), 7.37 (5H, s, Ph). ^{13}C-NMR ($CDCl_3$) δ: 14.1 (q, $-CH_3$), 20.5, 20.6, 20.7 (q, $OCOCH_3$), 22.6, 25.5, 25.6, 29.1, 29.3, 29.4, 29.5, 29.6 (t, CH_2), 31.1 (t, OCH_2CH_2), 31.9, 36.2, 36.7 (t, CH_2), 50.0 (d, OCH_2CH_2CHNH), 54.5 (d, C-2), 62.0 (t, C-6), 65.5 (t, OCH_2CH_2CHNH), 67.0 (t, CH_2Ph), 68.5 (d, C-4), 71.8 (d, C-5), 72.0 (d, C-3), 100.8 (d, C-1), 128.2, 128.4, 128.6 (d, Ph), 135.6 (s, Ph), 169.4, 170.6, 170.7, 171.8, 173.4, 173.6 (s, C=O). Positive FAB-MS m/z: 917 $(M+H)^+$.

***N*-Tetradecanoyl-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-*β*-D-glucopyranosyl]-L-homoserine Benzyl Ester (16b)** As described for **16a**, compound **15** (85 mg, 0.12 mmol) was treated with (*R*)-3-tetradecanoyloxytetradecanoic acid (73 mg, 0.16 mmol) in the presence of DEPC (26 mg, 0.16 mmol) and TEA (16 mg, 0.16 mmol) to give **16b** (84 mg, 61%) as a white solid, mp 129—132 °C. $[\alpha]_D$ +2.4° (c=1.40, $CHCl_3$). IR (Nujol): 3280, 1741, 1656, 1552 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (9H, t, J=6.9 Hz, $-CH_3$), 1.25 (58H, br s, $-CH_2-$), 1.60—1.89 (6H, m, $-CH_2-$), 2.01, 2.02, 2.06 (each 3H, s, $OCOCH_3$), 2.14—2.39 (7H, m, $-CH_2-$, OCH_2CH_2CHNH), 2.47 (1H, dd, J=6.6, 14.5 Hz, $NHCOCH_2CH(OCO)-$), 3.38—3.54 (2H, m, H-2, OCH_2CH_2CHN), 3.61—3.66 (1H, m, H-5), 3.90—3.95 (1H, m, OCH_2CH_2CHN), 4.07 (1H, dd, J=2.3, 12.2 Hz, H-6), 4.24 (1H, dd, J=5.0, 12.2 Hz, H-6), 4.62 (1H, d, J=8.6 Hz, H-1), 4.71—4.76 (1H, m, OCH_2CH_2CHNH), 4.97 (1H, t, J=9.9 Hz, H-4), 5.03—5.10 (1H, m, $NHCOCH_2CH(OCO)-$), 5.15 (2H, br s, CH_2Ph), 5.32 (1H, t, J=9.2 Hz, H-3), 5.90 (1H, d, J=7.9 Hz, NH), 6.63 (1H, d, J=7.9 Hz, NH), 7.37 (5H, s, Ph). ^{13}C-NMR ($CDCl_3$) δ: 14.3 (q, $-CH_3$), 20.8, 20.9 (q, $OCOCH_3$), 22.9, 25.2, 25.5, 25.9, 29.2, 29.4, 29.5, 29.6, 29.7, 29.8, 30.0 (t, CH_2), 31.4 (t, OCH_2CH_2), 32.1, 34.6, 34.7, 36.4, 42.4 (t, CH_2), 50.0 (d, OCH_2CH_2CHNH), 55.2 (d, C-2), 62.3 (t, C-6), 65.6 (t, OCH_2CH_2), 67.2 (t, CH_2Ph), 68.9 (d, C-4), 71.5 (d, $NHCOCH_2CH(OCO)$), 72.0 (d, C-3), 72.1 (d, C-5), 100.6 (d, C-1), 128.4, 128.6, 128.8 (d, Ph), 135.9 (s, Ph), 169.7, 170.6, 170.7, 170.8, 172.2, 173.6, 174.2 (s, C=O). Positive FAB-MS m/z: 1144 $(M+H)^+$.

***N*-Tetradecanoyl-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(8-phenyloctanoylamino)-*β*-D-glucopyranosyl]-L-homoserine Benzyl Ester (16c)** As described for **16a**, compound **15** (50 mg, 0.071 mmol) was treated with 8-phenyloctanoic acid (21 mg, 0.092 mmol) in the presence of DEPC (15 mg, 0.092 mmol) and TEA (10 mg, 0.092 mmol) to give **15c** (41 mg, 64%) as an amorphous powder. $[\alpha]_D$ −9.8° (c=0.79, $CHCl_3$). IR (Nujol): 3316, 1744, 1654, 1551 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.9 Hz, $-CH_3$), 1.25 (28H, br s, $-CH_2-$), 1.55—1.85 (4H, m, $-CH_2-$), 2.01, 2.02, 2.06 (each 3H, s, $OCOCH_3$), 1.93—2.25 (6H, m, $NHCOCH_2CH_2\times 2$, OCH_2CH_2CHNH), 2.55—2.63 (2H, m, CH_2CH_2Ph), 3.41—3.49 (1H, m, OCH_2CH_2CHN), 3.51—3.68 (2H, m, H-2, H-5), 3.83—3.95 (1H, m, OCH_2CH_2CHN), 4.07—4.10 (1H, m, H-6), 4.23 (1H, d, J=4.3, 12.2 Hz, H-6), 4.55 (1H, d, J=8.6 Hz, H-1), 4.65—4.78 (1H, m, OCH_2CH_2CHNH), 4.99 (1H, t, J=9.9 Hz, H-4), 5.09—5.26 (3H, m, H-3, CH_2Ph), 5.37 (1H, br s, NH), 6.45 (1H, d, J=7.6 Hz, NH), 7.13—7.42 (10H, m, Ph). ^{13}C-NMR ($CDCl_3$) δ: 14.1 (q, $-CH_3$), 20.6, 20.7 (q, $OCOCH_3$), 22.7, 25.6, 29.1, 29.2, 29.3, 29.4, 29.5, 29.7 (t, CH_2), 31.2 (t, OCH_2CH_2), 31.4, 31.9 (t, CH_2), 35.9 (t, CH_2CH_2Ph), 36.2, 36.7 (t, CH_2), 50.0 (d, OCH_2CH_2CHNH), 54.5 (d, C-2), 62.0 (t, C-6), 65.5 (t, OCH_2CH_2CHNH), 67.0 (t, CH_2Ph), 68.5 (d, C-4), 71.9 (d, C-5), 72.0 (d, C-3), 100.8 (d, C-1), 128.2, 128.3, 128.4, 128.6, 128.7, 128.8 (d, Ph), 135.9 (s, Ph), 147.9 (s, Ph), 169.4, 170.6, 170.7, 171.8, 173.4, 173.6 (s, C=O). Positive FAB-MS m/z: 910 $(M+H)^+$.

***N*-Tetradecanoyl-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(*N*-dodecanoylglycylamino)-*β*-D-glucopyranosyl]-L-homoserine Benzyl Ester (16d)** As described for **16a**, compound **15** (60 mg, 0.085 mmol) was treated with *N*-dodecanoylglycine (29 mg, 0.11 mmol) in the presence of DEPC (18 mg, 0.11 mmol) and TEA (11 mg, 0.11 mmol) to give **16d** (26 mg, 32%). $[\alpha]_D$ +0.5° (c=0.56, $CHCl_3$). IR (Nujol): 3292, 1743, 1653, 1542 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (6H, t, J=6.9 Hz, $-CH_3$), 1.25 (36H, br s, $-CH_2-$), 1.60—1.89 (4H, m, $-CH_2-$), 2.01, 2.02, 2.06 (each 3H, s, $OCOCH_3$), 2.08—2.38 (6H, m, $-CH_2-$, OCH_2CH_2CHNH), 3.48—3.92 (6H, m, H-2, H-5, OCH_2CH_2CHN, $NHCOCH_2NHCO$), 4.04—4.26 (2H, m, H-6), 4.56 (1H, d, J=8.3 Hz, H-1), 4.69—4.72 (1H, m, OCH_2CH_2CHNH), 4.99 (1H, t, J=9.6 Hz, H-4), 5.10—5.21 (4H, m, H-3, NH, CH_2Ph), 5.56 (1H, d, J=8.2 Hz, NH), 6.47 (1H, d, J=7.6 Hz, NH), 7.36 (5H, s, Ph). ^{13}C-NMR ($CDCl_3$) δ: 14.3 (q, CH_3), 20.7, 20.8, 20.9 (q, $OCOCH_3$), 22.9, 25.8, 25.9, 29.4, 29.5, 29.6, 29.7, 29.8, 29.9 (t, CH_2), 31.5 (t, OCH_2CH_2), 32.1, 36.5, 37.0 (t, CH_2), 50.3 (d, OCH_2CH_2CHNH), 54.1 (d, C-2), 54.8 (t, $NHCOCH_2NHCO$), 64.0 (t, C-6), 64.1 (t, OCH_2CH_2CHNH), 67.3 (t, CH_2Ph), 68.8 (d, C-4), 72.1 (d, C-5), 72.3 (d, C-3), 101.1 (d, C-1), 128.5, 128.7, 128.8 (d, Ph), 135.8 (s, Ph), 169.2, 170.9, 171.0, 172.1, 173.6, 173.9, 174.0 (s, C=O). Positive FAB-MS m/z: 947 $(M+H)^+$.

***N*-Tetradecanoyl-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-tetradecanoylamino-*β*-D-glucopyranosyl)-L-homoserine (1)** Palladium-black (70 mg) was added to a solution of **16a** (67 mg, 0.073 mmol) in THF–MeOH (1 : 1) (8 ml), and the mixture was stirred under a hydrogen atmosphere for 12 h at room temperature. The catalyst was filtered off and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2–CH_3COCH_3 (10 : 1) to give **1** (37 mg, 61%) as a white solid, mp 190—196 °C. $[\alpha]_D$ −7.8° (c=0.75, $CHCl_3$: MeOH = 1 : 1). IR (Nujol): 3280, 1745 1659, 1552 cm^{-1}. ^{1}H-NMR ($CDCl_3$: CD_3OD) δ: 0.88 (6H, t, J=6.9 Hz, $-CH_3$), 1.25 (40H, br s, $-CH_2-$), 1.43—1.55 (4H, m, $COCH_2CH_2C_{11}H_{23}\times 2$), 2.01, 2.03, 2.09 (each 3H, s, $OCOCH_3$), 1.95—2.30 (6H, m, OCH_2CH_2CHNH, $COCH_2C_{12}H_{25}\times 2$), 3.49—3.60 (1H, m, OCH_2CH_2CHN), 3.85—3.91 (3H, m, H-2, H-5, OCH_2CH_2CHN), 4.11—4.20 (2H, m, H-6, OCH_2CH_2CHN), 4.28 (1H, dd, J=4.3, 12.2 Hz, H-6), 4.68 (1H, d, J=8.3 Hz, H-1), 5.03 (1H, t, J=9.6 Hz, H-4), 5.27 (1H, d, J=9.9 Hz, H-3). ^{13}C-NMR ($CDCl_3$–CD_3OD) δ: 14.0 (q, $-CH_3$), 20.5, 20.6 (q, $OCOCH_3$), 22.6, 25.6, 25.8, 29.1, 29.2, 29.4, 29.5, 29.6, 29.7 (t, CH_2), 31.6 (t, OCH_2CH_2), 31.8, 36.2, 36.5 (t, CH_2), 51.8 (d, OCH_2CH_2CHNH), 53.9 (d, C-2), 62.0 (t, C-6), 66.8 (t, OCH_2CH_2CHNH), 68.8 (d, C-4), 71.4 (d, C-5), 72.4 (d, C-3), 100.6 (d, C-1)), 169.7, 170.6, 171.1, 174.5, 175.2, 178.6 (s, C=O). Positive FAB-MS m/z: 828 $(M+H)^+$, 850 $(M+Na)^+$.

***N*-Tetradecanoyl-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-*β*-D-glucopyranosyl]-L-homoserine (2)** As described for **1**, compound **16b** (65 mg, 0.057 mmol) was treated with palladium-black (30 mg) to give **2** (53 mg, 88%) as a white solid, mp 172—176 °C. $[\alpha]_D$ +5.3° (c=1.07, $CHCl_3$: MeOH = 1 : 1). IR (Nujol): 3280, 1744, 1656, 1544 cm^{-1}. ^{1}H-NMR ($CDCl_3$–CD_3OD) δ: 0.88 (9H, t, J=6.9 Hz, $-CH_3$), 1.25 (58H, br s, $-CH_2-$), 1.43—1.65 (6H, m, $-CH_2-$), 1.91—2.09 (2H, m, OCH_2CH_2CHNH), 1.96, 2.02, 2.08 (each 3H, s, $OCOCH_3$), 2.14—2.42 (5H, m, $-CH_2-$), 2.54 (1H, dd, J=6.3, 14.5 Hz, $NHCOCH_2CH(OCO)-$), 3.38—3.57 (1H, m, OCH_2CH_2CHN), 3.74—3.87 (3H, m, H-2, H-5, OCH_2CH_2CHN), 4.03—4.09 (1H, m, H-6), 4.10—4.31 (2H, m, H-6, OCH_2CH_2CHNH), 4.68 (1H, d, J=8.3 Hz, H-1), 5.01 (1H, t, J=9.6 Hz, H-4), 5.08—5.13 (1H, m, $NHCOCH_2CH-$

(OCO)–), 5.28 (1H, t, J=9.6 Hz, H-3). ^{13}C-NMR ($CDCl_3$–CD_3OD) δ: 14.1 (q, –CH_3), 20.6, 20.7 (q, $OCOCH_3$), 22.8, 25.1, 25.3, 25.8, 29.3, 29.4, 29.5, 29.6, 29.7, 30.2, 30.4 (t, CH_2), 31.7 (t, OCH_2CH_2), 32.0, 33.9, 34.6, 36.4, 41.3 (t, CH_2), 51.8 (d, OCH_2CH_2CHNH), 54.3 (d, C-2), 62.2 (t, C-6), 66.6 (t, OCH_2CH_2CHNH), 69.1 (d, C-4), 71.3 (d, $NHCOCH_2CH(OCO)$), 71.6 (d, C-5), 72.4 (d, C-3), 100.6 (d, C-1), 169.9, 170.7, 171.3, 171.4, 174.2, 174.4, 177.6 (s, C=O). Positive FAB-MS m/z: 1054 $(M+H)^+$.

***N*-Tetradecanoyl-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(8-phenyloctanoylamino)-β-D-glucopyranosyl]-L-homoserine (3)** As described for **1**, compound **16c** (37 mg, 0.041 mmol) was treated with palladium-black (25 mg) to give **3** (31 mg, 93%) as a white solid, mp 201—203 °C. $[\alpha]_D$ −7.6° (c=0.65, $CHCl_3$: MeOH = 1 : 1). IR (Nujol): 3280, 1744, 1643, 1553 cm^{-1}. ^{1}H-NMR ($CDCl_3$–CD_3OD) δ: 0.88 (3H, t, J=6.9 Hz, –CH_3), 1.25 (28H, br s, –CH_2–), 1.55—1.85 (4H, m, –CH_2–), 2.01, 2.02, 2.06 (each 3H, s, $OCOCH_3$), 1.93—2.39 (6H, m, –CH_2–, OCH_2CH_2CHNH), 2.61—2.80 (2H, m, CH_2CH_2Ph), 3.61—3.77 (1H, m, OCH_2CH_2CHN), 3.79—3.85 (1H, m, H-5), 3.86—3.97 (2H, m, H-2, OCH_2CH_2CHN), 4.05—4.40 (3H, m, H-6, OCH_2CH_2CHNH), 4.75 (1H, d, J=8.3 Hz, H-1), 5.09 (1H, t, J=9.6 Hz, H-4), 5.29—5.39 (1H, m, H-3), 7.26—7.52 (5H, m, Ph). ^{13}C-NMR ($CDCl_3$–CD_3OD) δ: 13.9 (q, –CH_3), 20.3, 20.5 (q, $OCOCH_3$), 22.6, 25.6, 29.1, 29.2, 29.3, 29.4, 29.5, 29.7 (t, CH_2), 31.1 (t, OCH_2CH_2), 31.6, 31.9 (t, CH_2), 35.6 (t, CH_2CH_2Ph), 35.9, 36.1 (t, CH_2), 51.8 (d, OCH_2CH_2CHNH), 53.6 (d, C-2), 61.9 (t, C-6), 66.3 (t, OCH_2CH_2CHNH), 68.6 (d, C-4), 71.2 (d, C-5), 72.3 (d, C-3), 100.6 (d, C-1), 126.9, 128.2, 128.3 (d, Ph), 144.5 (s, Ph), 169.6, 169.7, 170.4, 171.0, 174.3, 175.2 (s, C=O). Positive FAB-MS m/z: 842 $(M+Na)^+$.

***N*-Tetradecanoyl-*O*-[3,4,6-tri-*O*-acetyl-2-deoxy-2-(*N*-dodecanoylglycylamino)-β-D-glucopyranosyl]-L-homoserine (4)** As described for **1**, compound **16d** (26 mg, 0.027 mmol) was treated with palladium-black (20 mg) to give **4** (15 mg, 65%) as an amorphous powder. $[\alpha]_D$ −19.2° (c=0.10, $CHCl_3$: MeOH = 1 : 1). IR (Nujol): 3285, 1740, 1651, 1539 cm^{-1}. ^{1}H-NMR ($CDCl_3$–CD_3OD) δ: 0.88 (6H, t, J=6.9 Hz, –CH_3), 1.25 (36H, br s, –CH_2–), 1.45—1.80 (4H, m, –CH_2–), 2.01, 2.02, 2.07 (each 3H, s, $OCOCH_3$), 1.97—2.40 (6H, m, –CH_2–, OCH_2CH_2CHNH), 3.35—4.51 (9H, m, H-1, 2, 5, 6, OCH_2CH_2CHN, $NHCOCH_2NHCO$), 4.65—4.74 (1H, m, OCH_2CH_2CHNH), 4.98—5.32 (2H, m, H-3, H-4). ^{13}C-NMR ($CDCl_3$–CD_3OD) δ: 14.1 (q, –CH_3), 20.5, 20.6 (q, $OCOCH_3$), 22.6, 25.7, 25.9, 29.4, 29.5, 29.6, 29.7, 29.8, 30.1 (t, CH_2), 31.7 (t, OCH_2CH_2), 32.0, 36.3, 36.9 (t, CH_2), 51.7 (d, OCH_2CH_2CHNH), 54.1 (d, C-2), 56.8 (t, $NHCOCH_2NHCO$), 62.5 (t, C-6), 66.2 (t, OCH_2CH_2CHNH), 68.8 (d, C-4), 72.3 (d, C-5), 72.5 (d, C-3), 96.8 (d, C-1), 169.1, 169.8, 171.2, 172.4, 173.6, 174.9, 176.3 (s, C=O). Positive FAB-MS m/z: 879 $(M+Na)^+$.

***N*-Tetradecanoyl-*O*-[2-deoxy-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-β-D-glucopyranosyl]-L-homoserine (5)** $NaOCH_3$–MeOH (0.01 ml, 5 N, 0.05 mmol) was added to a solution of compound **2** (20 mg, 0.019 mmol) in MeOH (3 ml) at 0 °C. The mixture was stirred for 3 h, then the solvent was removed by evaporation. The residue was purified by silica gel column chromatography using CH_2Cl_2–MeOH (4 : 1) to give **5** (12 mg, 68%) as a powder. $[\alpha]_D$ −20.8° (c=0.30, $CHCl_3$: MeOH = 1 : 2). IR (Nujol): 3280, 1735, 1636 cm^{-1}. ^{1}H-NMR ($CDCl_3$–CD_3OD) δ: 0.88 (9H, t, J=6.9 Hz, –CH_3), 1.25 (58H, br s, –CH_2–), 1.67—2.58 (14H, m, –CH_2–), 3.27—4.41 (10H, m, H-1, 2, 3, 4, 5, 6, OCH_2CH_2CH), 5.08—5.14 (1H, m, $NHCOCH_2CH(OCO)$–). ^{13}C-NMR ($CDCl_3$–CD_3OD) δ: 13.7 (q, –CH_3), 22.4, 25.4, 25.5, 26.1, 28.7, 29.0, 29.1, 29.2, 29.4, 29.8, 30.1, 31.6 (t, CH_2), 31.9 (t, OCH_2CH_2), 32.4, 35.9, 36.0, 39.8 (t, CH_2), 51.8 (d, OCH_2CH_2CHNH), 54.4 (d, C-2), 59.5 (t, C-6), 69.0 (t, OCH_2CH_2CHNH), 69.9 (d, C-4), 70.4 (d, $NHCOCH_2CH(OCO)$), 71.5 (d, C-5), 73.3 (d, C-3), 100.9 (d, C-1), 170.5, 171.1, 174.2, 174.5 (s, C=O). Positive FAB-MS m/z: 950 $(M+Na)^+$.

Allyl 2-Deoxy-4,6-*O*-*p*-methoxybenzylidene-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranoside (18) *p*-Methoxybenzaldehyde dimethylacetal (10.9 g, 60 mmol) was added to a solution of compound **17** (7.9 g, 20 mmol) and *p*-toluenesulfonic acid (1.9 g, 10 mmol) in DMF (30 ml) at 0 °C under argon, and the mixture was stirred for 18 h at room temperature. It was diluted with AcOEt, and the solution was washed with saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by silica gel column chromatography using hexane–AcOEt (3 : 1) to give **18** (9.65 g, 94%) as a white powder, mp 138—140 °C. $[\alpha]_D$ +39.7° (c=1.56, $CHCl_3$). IR (Nujol): 3330, 1702, 1643 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.56 (1H, t, J=9.2 Hz, H-3), 3.71—4.06 (5H, m, H-2, 4, 5, 6), 3.81 (3H, s, OCH_3), 4.18—4.29 (2H, m, $OCH_2CH=CH_2$), 4.69, 4.82 (each 1H, d, J=12.2 Hz, CH_2CCl_3), 4.93 (1H, d, J=2.6 Hz, H-1), 5.23—5.35 (3H, m, $OCH_2CH=CH_2$, NH), 5.52 (1H, s, CHPh), 5.83—5.98 (1H, m, $OCH_2CH=CH_2$), 6.90 (2H, d, J=8.6 Hz, Ph), 7.42 (2H, d, J=8.6 Hz, Ph). Positive FAB-MS m/z: 512 $(M+H)^+$.

Allyl 2-Deoxy-4,6-*O*-*p*-methoxybenzylidene-3-*O*-(2,2,2-trichloroethoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranoside (19) 2,2,2-Trichloroethyl chloroformate (6.0 g, 28.3 mmol) was added to a solution of **18** (9.7 g, 18.8 mmol) and DMAP (575 mg, 4.7 mmol) in pyridine–CH_2Cl_2 (2 : 1) (75 ml) at 0 °C under argon. The mixture was stirred at room temperature for 20 h, then diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and brine, and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by silica gel column chromatography using hexane–AcOEt (3 : 1) to give **19** (9.76 g, 75%) as a white powder, mp 65—68 °C. $[\alpha]_D$ +33.4° (c=0.98, $CHCl_3$). IR (Nujol): 3358, 1761, 1736 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.74—4.06 (7H, m, H-2, 4, 5, 6, $OCH_2CH=CH_2$), 3.80 (3H, s, OCH_3), 4.66—4.86 (4H, m, $CH_2CCl_3 \times 2$), 4.96 (1H, d, J=3.6 Hz, H-1), 5.17—5.40 (4H, m, H-3, $OCH_2CH=CH_2$, NH), 5.50 (1H, s, CHPh), 5.83—5.97 (1H, m, $OCH_2CH=CH_2$), 6.86 (2H, d, J=8.6 Hz, Ph), 7.36 (2H, d, J=8.6 Hz, Ph). Positive FAB-MS m/z: 688 $(M+3)^+$.

Allyl 2-Deoxy-3-*O*-(2,2,2-trichloroethoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranoside (20) A solution of **20** (4.7 g, 6.9 mmol) in 68% AcOH (50 ml) was stirred at room temperature for 5 h. After evaporation of the solvent, the residue was purified by silica gel column chromatography using hexane–AcOEt (3 : 1) to give **20** (3.67 g, 94%) as a white solid, mp 113—115 °C. $[\alpha]_D$ +60.3° (c=0.97, $CHCl_3$). IR (Nujol): 3428, 1759, 1733 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.29 (1H, t, J=5.9 Hz, CH_2OH), 3.17 (1H, d, J=5.3 Hz, OH), 3.72—3.78 (1H, m, H-4), 3.87—4.16 (5H, m, H-2, 5, 6, $OCH_2CH=CH_2$), 4.21 (1H, dd, J=5.3, 12.9 Hz, $OCH_2CH=CH_2$), 4.71—4.85 (4H, m, $CH_2CCl_3 \times 2$), 4.94 (1H, d, J=3.6 Hz, H-1), 5.05 (1H, dd, J=9.2, 10.6 Hz, H-3), 5.23—5.35 (2H, m, $OCH_2CH=CH_2$), 5.42 (1H, d, J=9.9 Hz, NH), 5.82—5.97 (1H, m, $OCH_2CH=CH_2$). Positive FAB-MS m/z: 570 $(M+3)^+$.

Allyl 4,6-Di-*O*-benzyl-2-deoxy-3-*O*-(2,2,2-trichloroethoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranoside (21) Trifluoromethanesulfonic acid (132 mg, 0.88 mmol) was added to a solution of compound **20** (2.50 g, 4.4 mmol) and benzyl 2,2,2-trichloroacetoimidate (3.33 g, 13.2 mmol) in CH_2Cl_2–cyclohexane (1 : 2) (30 ml) at 0 °C under argon, and the mixture was stirred for 20 h at room temperature. MeOH was added and the insoluble materials were removed by filtration. The filtrate was washed with saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by silica gel column chromatography using hexane–AcOEt (5 : 1) to give **21** (3.24 g, 98%) as a syrup. $[\alpha]_D$ +44.9° (c=2.36, $CHCl_3$). IR (Nujol): 3429, 1765, 1735 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.65—4.21 (7H, m, H-2, 4, 5, 6, $OCH_2CH=CH_2$), 4.49, 4.50 (each 1H, dd, J=11.9, 10.9 Hz, CH_2CCl_3), 4.60—4.77 (6H, m, $OCH_2Ph \times 2$, CH_2CCl_3), 4.95 (1H, d, J=3.6 Hz, H-1), 5.14—5.31 (3H, m, H-3, $OCH_2CH=CH_2$), 5.35 (1H, d, J=10.2 Hz, NH), 5.79—5.94 (1H, m, $OCH_2CH=CH_2$), 7.13—7.36 (10H, m, Ph). Positive FAB-MS m/z: 750 $(M+3)^+$.

4,6-Di-*O*-benzyl-2-deoxy-3-*O*-(2,2,2-trichloroethoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-α-D-glucopyranose (22) Compound **21** (530 mg, 0.7 mmol) was dissolved in THF (30 ml) and treated with 1,5-cyclooctadienebis(methyldiphenylphosphine)iridium hexafluorophosphate (30 mg, 0.035 mmol) under an argon atmosphere at 50 °C for 2 h after activation of the iridium catalyst with hydrogen. After cooling of the solution, iodine (360 mg, 1.42 mmol), pyridine (220 mg, 2.8 mmol) and H_2O (3.0 ml) were added, and the mixture was stirred for 30 min at room temperature. The solution was concentrated by evaporation. The residue was dissolved in CH_2Cl_2 and the solution was washed with 5% aqueous Na_2SO_3 and brine, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by silica gel column chromatography using CH_2Cl_2–CH_3COCH_3 (50 : 1) to give **22** (428 mg, 85%) as a white solid, mp 108—111 °C. $[\alpha]_D$ +24.0° (c=1.40, $CHCl_3$). IR (Nujol): 3310, 1753, 1717 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.65—3.67 (2H, m, H-6), 3.69—3.89 (1H, m, H-4), 4.02—4.13 (2H, m, H-2, 5), 4.41—4.79 (8H, m, $OCH_2Ph \times 2$, $CH_2CCl_3 \times 2$), 5.16—5.28 (2H, m, H-1, 3), 5.52 (1H, d, J=9.9 Hz, NH), 7.13—7.38 (10H, m, Ph). Positive FAB-MS m/z: 710 $(M+3)^+$.

***N*-Tetradecanoyl-*O*-[4,6-di-*O*-benzyl-2-deoxy-3-*O*-(2,2,2-trichloroethoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl]-L-homoserine Benzyl Ester (24)** Thionyl bromide (1.0 M solution in CH_2Cl_2) (0.89 ml, 0.89 mmol) was added to a solution of **22** (210 mg, 0.30 mmol) in CH_2Cl_2–DMF (10 : 1) (5.5 ml) at 0 °C under

argon, and the mixture was stirred at room temperature for 2 h. The mixture was diluted with Et_2O, washed with saturated aqueous $NaHCO_3$ and brine, and dried ($MgSO_4$). Evaporation of the solvent gave **23** as a syrup. A solution of this syrup and **11** (87 mg, 0.21 mmol) in anhydrous CH_2Cl_2 (5 ml) was stirred for 1 h at room temperature under argon in the presence of 4 Å powdered molecular sieves (300 mg), then cooled to 0 °C for 1 h, and $HgBr_2$ (75 mg, 0.21 mmol) was added. The mixture was stirred at room temperature for 20 h. The insoluble materials were filtered off, and the filtrate was washed successively with 10% aqueous KI, saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was chromatographed on silica gel using hexane–AcOEt (3 : 1) to give **24** (133 mg, 40%) as an amorphous powder. $[\alpha]_D$ −4.8° (c=1.80, $CHCl_3$). IR (Nujol): 3374, 1759, 1726, 1656, 1549 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.9 Hz, –CH_3), 1.25 (20H, br s, –CH_2–), 1.57—1.62 (2H, m, $COCH_2C\underline{H}_2C_{11}H_{23}$), 2.09—2.32 (4H, m, $OCH_2C\underline{H}_2CHNH$), $COC\underline{H}_2C_{12}H_{25}$), 3.42—3.64 (3H, m, H-2, 4, $OC\underline{H}_2CH_2CHN$), 3.69—3.77 (3H, m, H-5, 6), 3.89—3.94 (1H, m, $OC\underline{H}_2CH_2CHN$), 4.41 (1H, d, J=8.2 Hz, H-1), 4.44—4.78 (10H, m, H-3, $CH_2CCl_3\times2$, $OC\underline{H}_2Ph\times2$, $OCH_2CH_2C\underline{H}N$), 5.07, 5.15 (each 1H, d, J=12.2 Hz, $COOC\underline{H}_2Ph$), 5.23 (1H, d, J=8.6 Hz, NH), 6.52 (1H, d, J=6.9 Hz, NH), 7.14—7.35 (15H, m, Ph). ^{13}C-NMR ($CDCl_3$) δ: 14.1 (q, –CH_3) 22.6, 25.6, 29.1, 29.3, 29.4, 29.5, 29.6 (t, CH_2), 31.2 (t, $OCH_2\underline{C}H_2$), 31.9, 36.3 (t, CH_2), 50.2 (d, $OCH_2CH_2\underline{C}HNH$), 56.4 (d, C-2), 66.1 (t, $O\underline{C}H_2CH_2CHNH$), 67.1 (t, $COO\underline{C}H_2Ph$), 68.2 (t, C-6), 73.5 (t, $O\underline{C}H_2Ph$), 74.4 (d, C-4), 74.6 (t, $\underline{C}H_2CCl_3$), 74.8 (t, $O\underline{C}H_2Ph$), 75.7 (d, C-5), 76.9 (t, $\underline{C}H_2CCl_3$), 79.6 (d, C-3), 95.2, 95.4 (s, $CH_2\underline{C}Cl_3$), 100.7 (d, C-1), 127.7, 127.8, 127.9, 128.3, 128.4, 128.4, 128.6 (d, Ph), 135.5, 137.4, 137.7 (s, Ph), 154.0, 154.1, 171.8, 173.3 (s, C=O). Positive FAB-MS m/z: 1111 $(M+3)^+$.

***N*-Tetradecanoyl-*O*-(2-amino-4,6-di-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-L-homoserine Benzyl Ester (25)** Activated zinc powder (77 mg, 1.2 mmol) was added to a solution of **24** (130 mg, 0.12 mmol) in AcOH (5 ml), and the mixture was vigorously stirred at 40—50 °C for 20 h. After removal of the insoluble materials by filtration, the solvent was evaporated *in vacuo*. The residue was dissolved in CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by silica gel column chromatography using CH_2Cl_2–MeOH (30 : 1) to give **25** (59 mg, 65%) as an amorphous powder. $[\alpha]_D$ +5.8° (c=0.76, $CHCl_3$). IR (Nujol): 3326, 1732, 1644, 1536 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.9 Hz, –CH_3), 1.25 (20H, br s, –CH_2–), 1.57—1.63 (2H, m, $COCH_2C\underline{H}_2C_{11}H_{23}$), 2.11—2.17 (4H, m, $OCH_2C\underline{H}_2CHNH$, $COC\underline{H}_2C_{12}H_{25}$), 2.40—2.46 (1H, m, H-2), 3.29—3.33 (3H, m, H-3, 4, 5), 3.36—3.56 (1H, m, $OC\underline{H}_2CH_2CHNH$), 3.62 (2H, m, H-6), 3.81—3.88 (1H, m, $OC\underline{H}_2CH_2CHNH$), 3.96 (1H, d, J=7.9 Hz, H-1), 4.40—4.68 (5H, m, $OCH_2CH_2C\underline{H}NH$, $OC\underline{H}_2Ph\times2$), 5.02, 5.04 (each 1H, d, J=12.2 Hz, $COOC\underline{H}_2Ph$), 6.55 (1H, d, J=7.3 Hz, NH), 7.11—7.25 (15H, m, Ph). Positive FAB-MS m/z: 762 $(M+H)^+$.

***N*-Tetradecanoyl-*O*-[4,6-di-*O*-benzyl-2-deoxy-3-*O*-[(*R*)-3-tetradecanoyloxytetradecanoyl]-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-β-D-glucopyranosyl]-L-homoserine Benzyl Ester (26a)** DCC (350 mg, 0.77 mmol) was added to a solution of **25** (196 mg, 0.26 mmol), (*R*)-3-tetradecanoyloxytetradecanoic acid (350 mg, 0.77 mmol) and DMAP (31 mg, 0.26 mmol) in CH_2Cl_2 (10 ml) at 0 °C under argon. The mixture was stirred for 16 h at room temperature. The precipitated dicyclohexylurea was filtered off, and the filtrate was concentrated by evaporation. The residue was diluted with AcOEt, and then washed successively with saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by silica gel column chromatography using hexane–AcOEt (3 : 1) to give **26a** (147 mg, 35%) as an amorphous powder. $[\alpha]_D$ −11.1° (c=1.80, $CHCl_3$). IR (Nujol): 3280, 1731, 1654, 1542 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (15H, t, J=6.9 Hz, –CH_3), 1.25 (96H, br s, –CH_2–), 1.36—1.57 (10H, m, –CH_2–), 2.15—2.46 (12H, m, –CH_2–), 3.47—3.92 (7H, m, H-2, 4, 5, 6, $OC\underline{H}_2CH_2CHNH$), 4.37 (1H, d, J=8.3 Hz, H-1), 4.46—4.67 (4H, m, $OC\underline{H}_2Ph\times2$), 4.69—4.67 (1H, m, $OCH_2CH_2C\underline{H}NH$), 5.06—5.19 (5H, m, H-3, $COCH_2C\underline{H}(OCO)\times2$, $COOC\underline{H}_2Ph$), 5.99 (1H, d, J=8.6 Hz, NH), 6.85 (1H, d, J=7.6 Hz, NH), 7.13—7.38 (15H, m, Ph). ^{13}C-NMR ($CDCl_3$) δ: 14.1 (q, –CH_3), 22.7, 25.0, 25.1, 25.1, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7 (t, CH_2), 30.9 (t, $OCH_2\underline{C}H_2$), 31.9, 34.2, 34.4, 34.6, 36.1, 36.2, 39.1, 42.0 (t, CH_2), 50.2 (d, $OCH_2CH_2\underline{C}HNH$), 54.6 (d, C-2), 65.7 (t, $O\underline{C}H_2CH_2CHNH$), 66.9 (t, $COO\underline{C}H_2Ph$), 68.5 (t, C-6), 69.8, 71.0 (d, $COCH_2C\underline{H}(OCO)$), 73.6, 74.5 (t, $O\underline{C}H_2Ph$), 74.8 (d, C-4), 74.9 (d, C-5), 76.0 (d, C-3), 101.3 (d, C-1), 127.7, 127.8, 128.1, 128.4, 128.5, 128.6, 128.7 (d, Ph), 135.8, 137.7, 137.9 (s, Ph), 170.2, 170.5, 171.7, 173.3, 173.6, 173.9 (s, C=O). Positive FAB-MS m/z: 1634 $(M+H)^+$.

***N*-Tetradecanoyl-*O*-[4,6-di-*O*-benzyl-2-deoxy-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-β-D-glucopyranosyl]-L-homoserine Benzyl Ester (27)** As described for **26a**, the above compound **25** (130 mg, 0.17 mmol) was treated with (*R*)-3-tetradecanoyloxytetradecanoic acid (77 mg, 0.17 mmol) and DCC (35 mg, 0.17 mmol) to give **27** (145 mg, 71%) as an amorphous powder. $[\alpha]_D$ +7.2° (c=0.92, $CHCl_3$). IR (Nujol): 3300, 1730, 1644, 1537 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (9H, t, J=6.9 Hz, –CH_3), 1.25 (58H, br s, –CH_2–), 1.58—1.70 (6H, m, –CH_2–), 2.13—2.34 (6H, m, $OCH_2C\underline{H}_2CHNH$, –$CH_2$–), 2.53 (1H, dd, J=9.2, 14.9 Hz, $COC\underline{H}_2CH(OCO)$), 2.70 (1H, dd, J=4.0, 15.2 Hz, $COC\underline{H}_2CH(OCO)$), 3.12—3.15 (1H, m, H-2), 3.43—4.02 (7H, m, H-3, 4, 5, 6, $OC\underline{H}_2$-CH_2CHNH), 4.21 (1H, d, J=8.3 Hz, H-1), 4.48—4.60 (2H, m, $OC\underline{H}_2Ph$), 4.81—4.89 (1H, m, $OCH_2CH_2C\underline{H}NH$), 4.56, 4.98 (each 1H, d, J=10.9 Hz, $OC\underline{H}_2Ph$), 5.06, 5.15 (each 1H, d, J=12.2 Hz, $COOC\underline{H}_2Ph$), 5.40—5.52 (1H, m, $COCH_2C\underline{H}(OCO)$), 6.28 (1H, d, J=3.6 Hz, NH), 6.81 (1H, d, J=7.9 Hz, NH), 7.19—7.40 (15H, m, Ph). Positive FAB-MS m/z: 1198 $(M+H)^+$.

***N*-Tetradecanoyl-*O*-[4,6-di-*O*-benzyl-2-deoxy-3-*O*-tetradecanoyl-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-β-D-glucopyranosyl]-L-homoserine Benzyl Ester (26b)** Tetradecanoyl chloride (11 mg, 0.046 mmol) was added to a solution of **27** (46 mg, 0.038 mmol), pyridine (79 mg, 1 mmol) and DMAP (5 mg, 0.038 mmol) in CH_2Cl_2 (2 ml) at 0 °C under argon. The mixture was stirred at room temperature for 24 h, diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and brine, and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by silica gel column chromatography using hexane–AcOEt (2 : 1) to give **26b** (40 mg, 74%) as an amorphous powder. $[\alpha]_D$ −11.5° (c=0.60, $CHCl_3$). IR (KBr): 3270, 1731, 1712, 1655, 1536 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (12H, t, J=6.9 Hz, –CH_3), 1.25 (78H, br s, –CH_2–), 1.37—1.72 (8H, m, –CH_2–), 2.10—2.44 (10H, m, $OCH_2C\underline{H}_2$-$CHNH$, –CH_2–), 3.44—3.92 (7H, m, H-2, 4, 5, 6, $OC\underline{H}_2CH_2CHNH$), 4.29 (1H, d, J=8.3 Hz, H-1), 4.45—4.71 (5H, m, $OCH_2CH_2C\underline{H}NH$, $OC\underline{H}_2Ph\times2$), 5.03—5.11 (2H, m, H-3, $COCH_2C\underline{H}(OCO)$), 5.13 (2H, br s, $COOC\underline{H}_2Ph$), 5.87 (1H, d, J=8.9 Hz, NH), 6.82 (1H, d, J=7.6 Hz, NH), 7.12—7.38 (15H, m, Ph). ^{13}C-NMR ($CDCl_3$) δ: 14.1 (q, –CH_3) 22.7, 24.8, 25.1, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7 (t, CH_2), 30.9 (t, $OCH_2\underline{C}H_2$), 31.9, 33.8, 34.4, 34.6, 35.6, 36.1, 42.1 (t, CH_2), 50.3 (d, $OCH_2CH_2\underline{C}HNH$), 54.3 (d, C-2), 65.7 (t, $O\underline{C}H_2CH_2CHNH$), 66.9 (t, $COO\underline{C}H_2Ph$), 68.6 (t, C-6), 71.2 (d, $COCH_2C\underline{H}(OCO)$), 73.6, 74.5 (t, $O\underline{C}H_2Ph$), 74.6 (d, C-4), 75.0 (d, C-5), 75.9 (d, C-3), 101.5 (d, C-1), 127.0, 127.7, 127.8, 128.2, 128.4, 128.5 (d, Ph), 135.8, 137.7, 137.9 (s, Ph), 170.0, 171.7, 173.7, 173.8, 173.9 (s, C=O). Positive FAB-MS m/z: 1408 $(M+H)^+$.

***N*-Tetradecanoyl-*O*-[2-deoxy-3-*O*-[(*R*)-3-tetradecanoyloxytetradecanoyl]-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-β-D-glucopyranosyl]-L-homoserine (6)** Palladium-black (70 mg) was added to a solution of **26a** (45 mg, 0.028 mmol) in MeOH–THF (1 : 1) (6 ml), and the mixture was stirred under a hydrogen atmosphere for 28 h at 40—45 °C. The catalyst was filtered off and the filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography using CH_2Cl_2–MeOH (10 : 1) to give **6** (32 mg, 84%), after lyophilization from dioxane. $[\alpha]_D$ −12.9° (c=0.34, $CHCl_3$: MeOH = 1 : 1). IR (Nujol): 3280, 1731, 1655, 1553 cm^{-1}. ^{1}H-NMR ($CDCl_3$–CD_3OD) δ: 0.88 (15H, t, J=6.9 Hz, –CH_3), 1.25 (96H, br s, –CH_2–), 1.57—1.87 (10H, m, –CH_2–), 2.17—2.69 (12H, m, –CH_2–), 3.25—4.04 (7H, m, H-2, 4, 5, 6, $OC\underline{H}_2CH_2CHNH$), 4.86—4.97 (1H, m, H-3), 5.07—5.13 (2H, m, $COCH_2C\underline{H}(OCO)\times2$). ^{13}C-NMR ($CDCl_3$–$CD_3OD$) δ: 13.4 (q, –CH_3), 22.2, 24.6, 24.7, 25.3, 28.6, 28.7, 28.9, 29.0, 29.2 (t, CH_2), 31.5 (t, $OCH_2\underline{C}H_2$), 31.9, 33.8, 34.0, 34.1, 35.9, 36.3, 38.6, 40.8 (t, CH_2), 52.9 (d, $OCH_2CH_2\underline{C}HNH$), 60.1 (d, C-2), 66.3 (t, $O\underline{C}H_2CH_2CHNH$), 67.5 (t, C-6), 69.9, 70.7 (d, $COCH_2C\underline{H}(OCO)$), 75.8 (d, C-4), 76.3 (d, C-5), 76.8 (d, C-3), 100.8 (d, C-1), 170.5, 171.1, 173.6, 173.7, 173.9, 179.6 (s, C=O). Positive FAB-MS m/z: 1364 $(M+H)^+$, 1386 $(M+Na)^+$.

***N*-Tetradecanoyl-*O*-[2-deoxy-3-*O*-tetradecanoyl-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-β-D-glucopyranosyl]-L-homoserine (7)** As described for **6**, compound **26b** (44 mg, 0.031 mmol) was treated with palladium-black (44 mg) to give **7** (18 mg, 50%), after lyophilization from dioxane. $[\alpha]_D$ −4.8° (c=0.21, $CHCl_3$: MeOH = 1 : 1). IR (Nujol): 3334, 1735, 1653, 1542 cm^{-1}. ^{1}H-NMR ($CDCl_3$–CD_3OD) δ: 0.89 (12H, t, J=6.9 Hz, –CH_3), 1.25 (78H, br s, –CH_2–), 1.43—1.60 (8H, m, –CH_2–), 1.90—2.01 (2H, m, –CH_2–), 2.22—2.39 (7H, m, –CH_2–), 2.52 (1H, dd, J=6.6, 14.2 Hz, $COC\underline{H}_2CH(OCO)$), 3.29—4.38 (7H, m, H-2, 4, 5, 6,

$OC\underline{H}_2CH_2CHNH$), 4.40 (1H, d, J=8.6 Hz, H-1), 4.93 (1H, dd, J=9.2, 10.6 Hz, H-3), 5.08—5.17 (1H, m, $COCH_2C\underline{H}(OCO)$). ^{13}C-NMR ($CDCl_3$–$CD_3OD$) δ: 14.3 (q, $-CH_3$) 23.0, 25.3, 25.5, 26.2, 29.7, 29.8, 29.9, 29.9, 30.1 (t, CH_2), 30.5 (t, $OCH_2\underline{C}H_2$), 32.3, 33.1, 34.4, 34.6, 35.0, 36.8, 41.7 (t, CH_2), 49.9 (d, $OCH_2CH_2\underline{C}HNH$), 53.6 (d, C-2), 60.5 (t, $O\underline{C}H_2CH_2CHNH$), 66.9 (t, C-6), 67.8 (d, $COCH_2\underline{C}H(OCO)$), 71.6 (d, C-5), 74.8 (d, C-4), 76.6 (d, C-3), 101.6 (d, C-1), 172.1, 174.5, 174.6, 174.7, 179.7 (s, C=O). Positive FAB-MS m/z: 1138 $(M+H)^+$, 1160 $(M+Na)^+$.

Phenyl 2-Deoxy-1-thio-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (28) NaOMe (497 mg, 9.2 mmol) was added to a solution of compound **13** (5.3 g, 9.2 mmol) in MeOH (50 ml) at 0 °C under argon, and the mixture was stirred for 20 min at the same temperature, then evaporated *in vacuo*. The residue was purified by silica gel column chromatography using hexane–AcOEt (3 : 1) to give **28** (3.65 g, 88%) as a white solid, mp 164—166 °C. $[\alpha]_D$ +76.9° (c=0.56, $CHCl_3$: MeOH = 1 : 1). IR (Nujol): 3308, 1702, 1541 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.29—3.52 (4H, m, H-2, 3, 4, 5), 3.73 (1H, dd, J=5.0, 12.2 Hz, H-6), 3.89 (1H, dd, J=2.6, 12.2 Hz, H-6), 4.65—4.88 (3H, m, H-1, CH_2CCl_3), 7.26—7.58 (5H, m, Ph).

Phenyl 2-Deoxy-4,6-*O*-*p*-methoxybenzylidene-1-thio-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (29) *p*-Methoxybenzaldehyde dimethylacetal (2.55 g, 13.8 mmol) was added to a solution of compound **28** (1.77 g, 3.95 mmol) and *p*-toluenesulfonic acid (380 mg, 2 mmol) in DMF (20 ml) at 0 °C under argon. The mixture was stirred for 2 h at room temperature, then diluted with CH_2Cl_2, and the solution was washed with saturated aqueous $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated *in vacuo*. The residue was purified by silica gel column chromatography using hexane–AcOEt (3 : 1) to give **29** (1.95 g, 87%) as a white solid, mp 196—200 °C. $[\alpha]_D$ −16.1° (c=0.99, $CHCl_3$). IR (Nujol): 3326, 1702 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.29—3.49 (3H, m, H-2, 3, 5), 3.67—3.83 (2H, m, H-4, 6), 3.75 (3H, s, OCH_3), 4.31 (1H, dd, J=5.0, 10.9 Hz, H-6), 4.67, 4.83 (each 1H, d, J=11.9 Hz, CH_2CCl_3), 4.72 (1H, d, J=10.6 Hz, H-1), 5.35 (1H, d, J=8.6 Hz, NH), 5.44 (1H, s, $C\underline{H}Ph$), 6.88 (2H, d, J=8.9 Hz, Ph), 7.26—7.48 (7H, m, Ph).

Phenyl 2-Deoxy-4,6-*O*-*p*-methoxybenzylidene-1-thio-3-*O*-(2,2,2-trichloroethoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (30) 2,2,2-Trichloroethyl chloroformate (1.37 g, 6.45 mmol) was added to a solution of **29** (2.43 g, 4.3 mmol) and DMAP (131 mg, 1.08 mmol) in pyridine–CH_2Cl_2 (2 : 1) (60 ml) at 0 °C under argon. The mixture was stirred at room temperature for 10 h, then concentrated by evaporation. The residue was dissolved in CH_2Cl_2, and this solution was washed with saturated aqueous $NaHCO_3$ and brine, and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by silica gel column chromatography using hexane–AcOEt (3 : 1) to give **30** (2.96 g, 93%) as a white solid, mp 126—128 °C. $[\alpha]_D$ −18.2° (c=0.94, $CHCl_3$). IR (Nujol): 1762, 1715, 1611, 1542 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.45—3.54 (1H, m, H-5), 3.63—3.82 (3H, m, H-2, 4, 6), 3.76 (3H, s, OCH_3), 4.32 (1H, dd, J=4.9, 10.6 Hz, H-6), 4.59—4.83 (4H, m, CH_2CCl_3 × 2), 4.92 (1H, d, J=10.6 Hz, H-1), 5.27 (1H, t, J=9.6 Hz, H-3), 5.43 (1H, s, $C\underline{H}Ph$), 5.60 (1H, d, J=8.9 Hz, NH), 6.84 (2H, d, J=8.9 Hz, Ph), 7.26—7.55 (7H, m, Ph).

Phenyl 2-Deoxy-1-thio-3-*O*-(2,2,2-trichloroethoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (31) A solution of **30** (1.07 g, 1.45 mmol) in 83% AcOH (36 ml) was stirred at room temperature for 2 h. After evaporation of the solvent, the residue was purified by silica gel column chromatography using hexane–AcOEt (1 : 1) to give **31** (818 mg, 91%) as a white solid, mp 95—98 °C. $[\alpha]_D$ −10.9° (c=1.18, $CHCl_3$). IR (Nujol): 3308, 1755, 1714, 1540 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.51—3.55 (1H, m, H-5), 3.86—3.94 (5H, m, H-2, 4, 6), 4.64, 4.79 (each 1H, d, J=11.9 Hz, CH_2CCl_3), 4.66, 4.81 (each 1H, d, J=11.9 Hz, CH_2CCl_3), 5.05—5.09 (2H, m, H-1, 3), 5.86 (1H, d, J=9.2 Hz, NH), 7.20—7.36 (5H, m, Ph).

Phenyl 6-*O*-Benzyloxymethyl-2-deoxy-1-thio-3-*O*-(2,2,2-trichloroethoxyoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranoside (32) Benzyl chloromethyl ether (769 mg, 4.9 mmol) was added to a solution of **31** (1.53 g, 2.5 mmol) and 1,1,3,3-tetramethylurea (856 mg, 7.4 mmol) in CH_2Cl_2 (35 ml) at 0 °C under argon. The mixture was stirred at room temperature for 24 h, washed with saturated aqueous $NaHCO_3$ and brine, and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by silica gel column chromatography using hexane–AcOEt (2 : 1) to give **32** (1.29 g, 71%). $[\alpha]_D$ −11.0° (c=1.52, $CHCl_3$). IR (Nujol): 3336, 1752 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.54—3.94 (5H, m, H-2, 4, 5, 6), 4.54—4.84 (8H, m, $C\underline{H}_2OC\underline{H}_2Ph$, CH_2CCl_3 × 2), 4.94 (1H, d, J=10.2 Hz, H-1), 5.08 (1H, t, J=9.9 Hz, H-3), 5.54 (1H, d, J=8.6 Hz, NH), 7.21—7.50 (5H, m, Ph). Positive FAB-MS m/z: 742 $(M+3)^+$.

Phenyl 6-*O*-Benzyloxymethyl-2-deoxy-4-*O*-diphenoxyphosphoryl-3-*O*-(2,2,2-trichloroethoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-1-thio-β-D-glucopyranoside (33) Diphenylphosphoryl chloride (1.68 g, 6.27 mmol) was added to a solution of **32** (930 mg, 1.25 mmol), pyridine (496 mg, 6.27 mmol) and DMAP (765 mg, 6.27 mmol) in CH_2Cl_2 (30 ml) at 0 °C under argon. The mixture was stirred at room temperature for 3 h, washed with saturated aqueous $NaHCO_3$ and brine, and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by silica gel column chromatography using hexane–AcOEt (4 : 1) to give **33** (1.13 g, 93%) as a syrup. $[\alpha]_D$ −6.9° (c=0.88, $CHCl_3$). IR (Nujol): 3280, 1764, 1536 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.48—3.87 (4H, m, H-2, 5, 6), 4.55 (2H, d, J=4.0 Hz, $CH_2OC\underline{H}_2Ph$), 4.59—4.93 (7H, m, H-4, $C\underline{H}_2OCH_2Ph$, CH_2CCl_3 × 2), 5.13 (1H, d, J=10.2 Hz, H-1), 5.41 (1H, d, J=8.2 Hz, NH), 5.50 (1H, t, J=9.9 Hz, H-3), 7.05—7.60 (20H, m, Ph). Positive FAB-MS m/z: 976 $(M+3)^+$.

***N*-Tetradecanoyl-*O*-[6-*O*-benzyloxymethyl-2-deoxy-4-*O*-diphenoxyphosphoryl-3-*O*-(2,2,2-trichloroethoxycarbonyl)-2-(2,2,2-trichloroethoxycarbonylamino)-β-D-glucopyranosyl]-L-homoserine Benzyl Ester (34)** The same procedure as described for the preparation of **14** provided a crude product from **33** (417 mg, 0.43 mmol), **11** (231 mg, 0.55 mmol), NBS (305 mg, 1.71 mmol), TBAOTf (34 mg, 0.086 mmol), iodine (435 mg, 1.71 mmol), and 4 Å powdered molecular sieves in CH_2Cl_2. This was purified by silica gel column chromatography using hexane–AcOEt (2 : 1) to give **34** (328 mg, 60%) as an amorphous powder. $[\alpha]_D$ +6.4° (c=1.06, $CHCl_3$). IR (Nujol): 3280, 1764, 1643, 1588, 1536 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (3H, t, J=6.9 Hz, $-CH_3$), 1.25 (20H, br s, $-CH_2-$), 1.51—1.76 (2H, br s, $COCH_2C\underline{H}_2C_{11}H_{23}$), 2.04—2.31 (4H, m, $OCH_2C\underline{H}_2CHNH$, $COC\underline{H}_2C_{12}H_{25}$), 3.18—3.29 (1H, m, H-2), 3.44—3.94 (5H, m, H-5, 6, $OC\underline{H}_2CH_2CHNH$), 4.49—4.79 (11 H, H-1, 4, $OCH_2CH_2C\underline{H}NH$, $C\underline{H}_2OC\underline{H}_2Ph$, CH_2CCl_3 × 2), 5.08, 5.19 (each 1H, d, J=12.2 Hz, $COOC\underline{H}_2Ph$), 5.38—5.47 (2H, m, H-3, NH), 6.32 (1H, d, J=7.3 Hz, NH), 7.14—7.42 (20H, m, Ph). ^{13}C-NMR ($CDCl_3$) δ: 14.0 (q, $-CH_3$) 22.6, 25.5, 29.1, 29.3, 29.4, 29.5, 29.6 (t, CH_2), 31.1 (t, $OCH_2\underline{C}H_2$), 31.8, 36.2 (t, CH_2), 49.9 (d, $OCH_2CH_2\underline{C}HNH$), 56.3 (d, C-2), 65.5 (t, $O\underline{C}H_2CH_2CHNH$), 65.9 (d, C-6), 67.1 (t, $COO\underline{C}H_2Ph$), 69.2 (t, $CH_2O\underline{C}H_2Ph$), 73.4 (d, C-5), 74.4 (d, C-4), 74.5 (t, $\underline{C}H_2CCl_3$), 76.5 (d, C-3), 76.8 (t, $\underline{C}H_2CCl_3$), 94.0 (s, $CH_2\underline{C}Cl_3$), 94.8 (t, $\underline{C}H_2$-OCH_2Ph), 95.2 (s, $CH_2\underline{C}Cl_3$), 99.8 (d, C-1), 120.0, 120.1, 120.2, 125.5, 125.6, 127.6, 127.7, 128.1, 128.3, 128.5, 128.6, 129.7 (d, Ph), 135.4, 137.6, 142.6, 143.3 (s, Ph), 150.2, 153.6, 154.0, 173.2 (s, C=O). Positive FAB-MS m/z: 1283 $(M+3)^+$.

***N*-Tetradecanoyl-*O*-[6-*O*-benzyloxymethyl-2-deoxy-4-*O*-diphenoxyphosphoryl-3-*O*-[(*R*)-3-tetradecanoyloxytetradecanoyl]-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-β-D-glucopyranosyl]-L-homoserine Benzyl Ester (36)** As described for **26a**, compound **34** (166 mg, 0.13 mmol) was reacted with activated zinc powder in AcOH and the resulting syrup **35** was treated with (*R*)-3-tetradecanoyloxytetradecanoic acid (113 mg, 0.26 mmol), DMAP (16 mg, 0.13 mmol) and DCC (62 mg, 0.30 mmol) to give **36** (108 mg, 46%) as a syrup. $[\alpha]_D$ −9.2° (c=0.36, $CHCl_3$). IR (Nujol): 3312, 1735, 1653, 1541 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.88 (15H, t, J=6.9 Hz, $-CH_3$), 1.25 (96H, br s, $-CH_2-$), 1.51—1.67 (10H, m, $-CH_2-$), 2.05—2.58 (12H, m, $-CH_2-$), 3.27—3.89 (6H, m, H-2, 5, 6, $OC\underline{H}_2CH_2CHNH$), 4.51—4.72 (6H, H-4, $OCH_2CH_2C\underline{H}NH$, $C\underline{H}_2OC\underline{H}_2Ph$), 4.85 (1H, d, J=8.25 Hz, H-1), 5.05—5.27 (4H, m, $COCH_2C\underline{H}(OCO)$ × 2, $COOC\underline{H}_2Ph$), 5.52 (1H, t, J=8.9 Hz, H-3), 6.16 (1H, d, J=7.3 Hz, NH), 6.80 (1H, d, J=7.9 Hz, NH), 7.12—7.42 (20H, m, Ph). ^{13}C-NMR ($CDCl_3$) δ: 14.1 (q, $-CH_3$). 22.7, 24.9, 25.0, 25.1, 29.2, 29.3, 29.4, 29.5, 29.7, 29.9 (t, CH_2), 31.1 (t, $OCH_2\underline{C}H_2$), 31.9, 34.3, 34.5, 34.6, 36.1, 36.2, 39.6 (t, CH_2), 49.9 (d, $OCH_2CH_2\underline{C}HNH$), 56.1 (d, C-2), 65.7 (t, $O\underline{C}H_2CH_2CHNH$), 66.8 (t, C-6), 69.2 (t, $CH_2O\underline{C}H_2Ph$), 69.3 (t, $COO\underline{C}H_2Ph$), 70.2, 70.8 (d, $COCH_2\underline{C}H(OCO)$), 76.2 (d, C-5), 77.2 (d, C-4), 78.6 (d, C-3), 94.8 (t, $\underline{C}H_2OCH_2Ph$), 100.0 (d, C-1), 120.0, 120.1, 120.2, 125.6, 127.4, 127.8, 128.1, 128.4, 128.5, 128.6, 128.9 (d, Ph), 135.7, 137.7, 143.4, 143.8 (s, Ph), 150.3, 170.0, 170.7, 171.8, 173.5, 173.8 (s, C=O). Positive FAB-MS m/z: 1806 $(M+H)^+$.

***N*-Tetradecanoyl-*O*-[2-deoxy-4-*O*-phosphono-3-*O*-[(*R*)-3-tetradecanoyloxytetradecanoyl]-2-[(*R*)-3-tetradecanoyloxytetradecanoylamino]-β-D-glucopyranosyl]-L-homoserine (8)** Palladium-black (40 mg) was added to a solution of **36** (44 mg, 0.022 mmol) in MeOH–THF (1 : 1) (5 ml), and the mixture was stirred under a hydrogen atmosphere for 5 h at 40—45 °C. The catalyst was filtered off and the filtrate was concentrated

under reduced pressure, then the resulting syrup was dissolved in MeOH–THF (1 : 1) (5 ml). Next, platinum dioxide (13 mg) was added to the solution and the mixture was stirred under a hydrogen atmosphere for 10 h at 40—45 °C. The catalyst was filtered off and the filtrate was concentrated under reduced pressure, then the resulting residue was purified by silica gel column chromatography using CH_2Cl_2–MeOH (4 : 1) to give **8** (24 mg, 77%) as a white powder, after lyophilization from dioxane. $[\alpha]_D$ −6.7° (c = 0.48, $CHCl_3$: MeOH = 2 : 3). IR (Nujol): 1730, 1674, 1553 cm^{-1}. ^{1}H-NMR ($CDCl_3$–CD_3OD) δ: 0.88 (15H, t, J = 6.9 Hz, –CH_3), 1.25 (96H, br s, –CH_2–), 1.53—1.72 (10H, m, –CH_2–), 1.98—2.53 (12H, m, –CH_2–), 5.01—5.17 (3H, m, H-3, $COCH_2CH$-(OCO) × 2). ^{13}C-NMR ($CDCl_3$–CD_3OD) δ: 13.4 (q, –CH_3), 21.9, 25.1, 25.4, 25.9, 28.6, 29.0, 29.3, 29.5, 29.7, 29.9 (t, CH_2), 31.2 (t, OCH_2CH_2), 31.9, 33.3, 35.8, 36.1, 36.2, 40.9, 43.1 (t, CH_2), 50.3 (d, OCH_2CH_2-CHNH), 57.1 (d, C-2), 66.2 (t, OCH_2CH_2CHNH), 66.9 (t, C-6), 70.0, 70.7 (d, $COCH_2CH(OCO)$), 75.2 (d, C-4), 76.3 (d, C-5), 77.6 (d, C-3), 100.2 (d, C-1), 170.0, 170.9, 171.6, 173.1, 173.7, 179.8 (s, C=O). Positive FAB-MS m/z: 1466 $(M+Na)^+$.

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