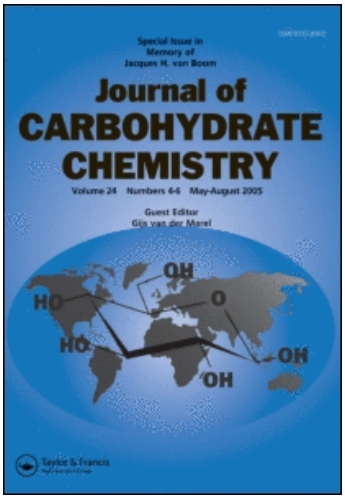

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Syntheses of Novel Nonreducing-Sugar Subunit Analogs of Lipid a Carrying 2-Acyloxytetradecanoyl and 2-Hydroxyacyl Groups of Different Carbon Chain Length

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SYNTHESES OF NOVEL NONREDUCING-SUGAR SUBUNIT ANALOGS OF LIPID A CARRYING 2-ACYLOXYTETRADECANOYL AND 2-HYDROXYACYL GROUPS OF DIFFERENT CARBON CHAIN LENGTH

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ABSTRACT

To investigate the biological influence of the 2-(acyloxy)tetradecanoyl and 2-hydroxyacyl groups in the nonreducing-sugar subunit analogs of lipid A, a novel series of 3-*O*-[(2*RS*)-2-acyloxytetradecanoyl]-2-deoxy-2-[(2*RS*)-2-hydroxytetradecanamido]-4-*O*-phosphono-D-glucoses (**10a-d**), 3-*O*-[(2*RS*)-2-acyloxytetradecanoyl]-2-deoxy-2-[(3*R*)-3-hydroxytetradecanamido]-4-*O*-phosphono-D-glucoses (**19a-d**), and 2-deoxy-2-[(2*RS*)-2-hydroxyacyl]amino-4-*O*-phosphono-3-*O*-[(3*R*)-3-tetradecanoyloxytetradecanoyl]-D-glucoses (**23e-h**) were systematically synthesized.

INTRODUCTION

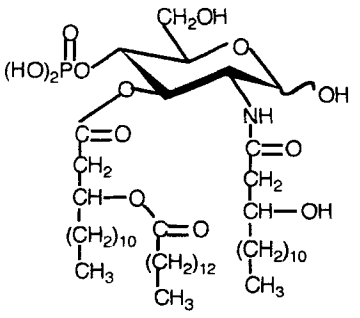
2-Deoxy-2-[(3*R*)-3-hydroxytetradecanamido]-4-*O*-phosphono-3-*O*-[(3*R*)-3-tetradecanoyloxytetradecanoyl]-D-glucose (GLA-60)[1] is an analog of the nonreducing-sugar subunit of bacterial lipid A[2] and expresses strong immunopharmacological activities.[3] In the course of our investigation[4] on the relationship between the chemical structure and biological activities of GLA-60 series, it has been demonstrated[2] that the carbon chain length not only of the 3-acyloxyacyl group but also of the 3-hydroxyacyl group at C-2 and C-3 of the D-glucosamine backbone are very important for expressing the biological activities. In addition, we have recently found[5] that the 3-acyloxyacyl group can be replaced by the 3-alkyl-branched acyl group without decreasing the parent biological activities.

In natural lipid A, the 2-hydroxytetradecanoyl group has also been found[6] as a minor fatty acyl component, but the relationship with biological activities has not been in-

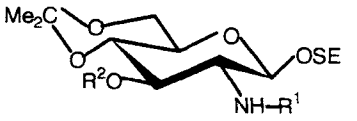
vestigated. We here report the syntheses of a novel series of 3-*O*-(2-acyloxy)acylated and / or 2-*N*-(2-hydroxy)acylated GLA-60 homologues, *i. e.*, 3-*O*-[(2*RS*)-2-acyloxytetradecanoyl]-2-deoxy-2-[(2*RS*)-2-hydroxytetradecanamido]-4-*O*-phosphono-D-glucoses (**10a-d**), 3-*O*-[(2*RS*)-2-acyloxytetradecanoyl]-2-deoxy-2-[(3*R*)-3-hydroxytetradecanamido]-4-*O*-phosphono-D-glucoses (**19a-d**), and 2-[(2*RS*)-2-hydroxyacyl]amino-2-deoxy-3-*O*-[(3*R*)-3-tetradecanoyloxytetradecanoyl]-4-*O*-phosphono-D-glucoses (**23e-h**).

RESULTS AND DISCUSSION

As a typical example, a general synthetic procedure used in this study is described for the preparations of **10a** and **23e** as follows. The syntheses of other compounds all follow essentially the same pathway. 2-(Trimethylsilyl)ethyl 2-amino-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranoside (**1**)[7] was treated with (2*RS*)-2-[2-(trimethylsilyl)-ethoxymethoxy]tetradecanoic acid in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (WSC) in dichloromethane to give **2**, which was successively esterified at *O*-3 with (2*RS*)-2-(benzyloxymethoxy)tetradecanoic acid in the presence of WSC and a catalytic amount of 4-dimethylaminopyridine (DMAP) in dichloromethane at room temperature, to afford **3** in 98% yield. These 2-*O*-protected 2-hydroxytetradecanoic acids were prepared *via* the phenacyl esters according to the procedures described previously.[1] Hydrolytic removal of the isopropylidene group in **3** with aqueous acetic acid and the following selective protection of the primary hydroxyl group in **4** with *tert*-butyldimethylsilyl (TBDMS) chloride gave the desired compound **5** in good yield. Introduction of the diphenoxyphosphinyl group at *O*-4 was carried out by using diphenyl phosphorochloridate and DMAP in pyridine in 87% yield. Hydrogenolytic removal of the benzyloxymethyl group of **6** in the presence of 10% palladium on carbon in ethanol gave 2-(trimethylsilyl)ethyl 6-*O*-*tert*-butyldimethylsilyl-2-deoxy-4-*O*-diphenoxyphosphinyl-3-*O*-[(2*RS*)-2-hydroxytetradecanoyl]-2-[(2*RS*)-2-[2-(trimethylsilyl)-ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (**7**), which is a useful intermediate for syntheses of 3-*O*-[(2*RS*)-2-acyloxytetradecanoyl]-2-deoxy-2-[(2*RS*)-2-hydroxytetradecanamido]-4-*O*-phosphono-D-glucoses (**10a-d**). The deprotected hydroxyl group of **7** was esterified with decanoic acid, WSC, and DMAP to afford **8a**. The 2-(trimethylsilyl)ethyl, 2-(trimethylsilyl)ethoxymethyl, and *tert*-butyldimethylsilyl groups of **8a** were simultaneously removed with boron trifluoride etherate in dichloromethane at 0 °C to give **9a** in 75% yield. In the ^{1}H NMR spectrum of **9a**, the anomeric proton appeared as a singlet at δ 5.23, showing that the α-D-pyranose configuration preponderates in chloroform-*d*. The phenoxy groups were finally cleaved by hydrogenolysis in the presence of Adams' platinum catalyst in ethanol, to afford the desired 3-*O*-[(2*RS*)-2-decanoyloxytetradecanoyl]-2-deoxy-2-[(2*RS*)-2-hydroxytetradecanamido]-4-



GLA-60

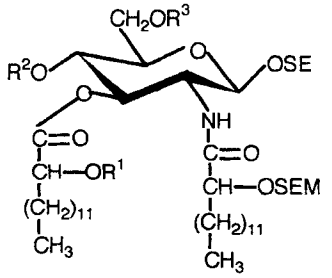


	R^1	R^2
1	H	H
2	$CH_3(CH_2)_{11}CH(OSEM)CO$	H
3	$CH_3(CH_2)_{11}CH(OSEM)CO$	$CH_3(CH_2)_{11}CH(OBOM)CO$

SE = $Me_3SiCH_2CH_2$

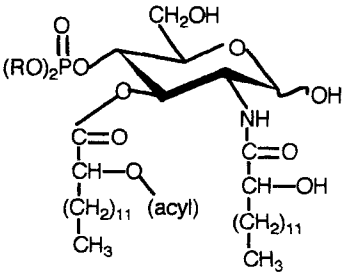
SEM = $Me_3SiCH_2CH_2OCH_2$

BOM = $C_6H_5CH_2OCH_2$



	R^1	R^2	R^3
4	BOM	H	H
5	BOM	H	TBDMS
6	BOM	$(PhO)_2P(O)$	TBDMS
7	H	$(PhO)_2P(O)$	TBDMS
8a-d	acyl (a-d)	$(PhO)_2P(O)$	TBDMS

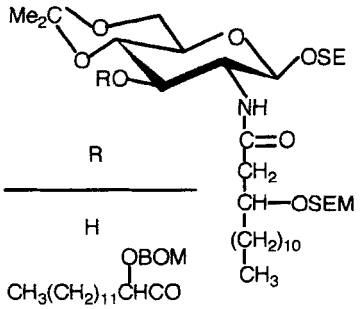
TBDMS = *tert*-$BuMe_2Si$



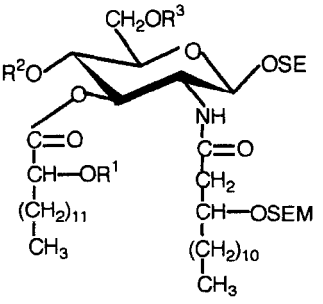
	R
9a-d	Ph
10a-d	H

$CH_3(CH_2)_nCO$

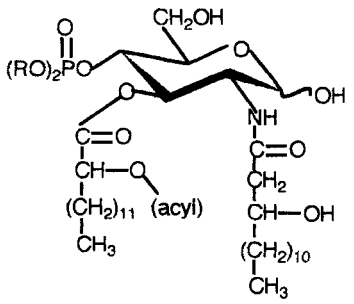
Acyl groups Series	n
a	8
b	10
c	12
d	14



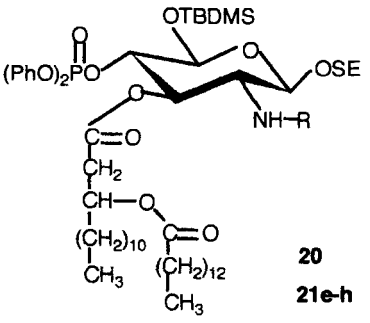
	R
11	H
12	$CH_3(CH_2)_{11}CHCO$ (OBOM)



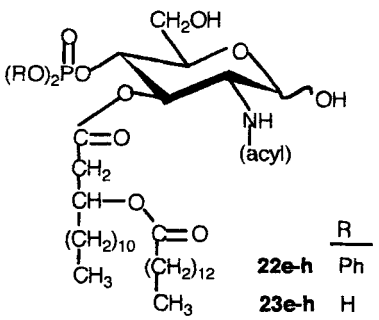
	R^1	R^2	R^3
13	BOM	H	H
14	BOM	H	TBDMS
15	BOM	$(PhO)_2P(O)$	TBDMS
16	H	$(PhO)_2P(O)$	TBDMS
17a-d	acyl (a-d)	$(PhO)_2P(O)$	TBDMS



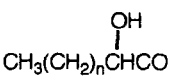
	R
18a-d	Ph
19a-d	H



	R
20	H
21e-h	acyl (e-h)



	R
22e-h	Ph
23e-h	H



Acyl groups	
Series	n
e	7
f	9
g	11
h	13

O-phosphono-D-glucopyranose (**10a**) in high yield. 3-*O*-[(2*RS*)-2-Acyloxytetradecanoyl]-2-deoxy-2-[(3*R*)-3-hydroxytetradecanamido]-4-*O*-phosphono-D-glucoses (**19a-d**) were prepared from 2-(trimethylsilyl)ethyl 2-deoxy-4,6-*O*-isopropylidene-2-[(3*R*)-3-[2-(trimethylsilyl)ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (**11**)[4] *via* the intermediate 2-(trimethylsilyl)ethyl 6-*O*-*tert*-butyldimethylsilyl-2-deoxy-4-*O*-diphenoxyphosphinyl-3-*O*-[(2*RS*)-2-hydroxytetradecanoyl]-2-[(3*R*)-3-[2-(trimethylsilyl)ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (**16**) by the same sequence as **10a**. 2-Deoxy-2-[(2*RS*)-2-hydroxyacyl]amino-4-*O*-phosphono-3-*O*-[(3*R*)-3-tetradecanoyloxytetradecanoyl]-D-glucopyranose (**23e-h**) was obtained by using 2-(trimethylsilyl)ethyl 2-amino-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-4-*O*-diphenoxyphosphinyl-3-*O*-[(3*R*)-3-tetradecanoyloxytetradecanoyl]-β-D-glucopyranoside (**20**)[8] as a starting material. The amino group of **20** was acylated with (2*RS*)-2-hydroxydecanoic acid and WSC to give **21e** in 79% yield. Compound **21e** was treated with boron trifluoride etherate in dichloromethane at 0 °C to give desilylated compound **22e**, which was hydrogenolyzed to afford the desired 2-deoxy-2-[(2*RS*)-2-hydroxydecanamido]-4-*O*-phosphono-3-*O*-[(3*R*)-3-tetradecanoyloxytetradecanoyl]-D-glucopyranose (**23e**), according to the procedures for **10a**.

These synthetic analogs (**10a-d**, **19a-d**, and **23e-h**) of GLA-60, having the 2-acyloxytetradecanoyl and the 2-hydroxyacyl groups, showed moderate mitogenicity and macrophage activation activities. However, no significant tumor necrosis factor (TNF)-inducing activity was expressed (personal communication from Dr. M. Matsuura *et al.*, Jichi Medical School).

EXPERIMENTAL

General methods. Melting points were determined with a Yanagimoto micro-melting point apparatus and are uncorrected. Concentrations were conducted *in vacuo*. Preparative chromatography was performed on silica gel (Wako Co., 200 mesh) with the solvent systems specified. Specific rotations were determined with a Union PM-201 polarimeter at 25 °C, and IR spectra were recorded with a JASCO A-100 spectrophotometer. NMR spectra were recorded with a JEOL JNM-GX 270 spectrometer.

2-(Trimethylsilyl)ethyl 2-Deoxy-4,6-*O*-isopropylidene-2-[(2*RS*)-2-[2-(trimethylsilyl)ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (2). To a solution of 2-(trimethysilyl)ethyl 2-amino-2-deoxy-4,6-*O*-isopropylidene-β-D-glucopyranoside[7] (**1**, 2.7 g) in CH_2Cl_2 (50 mL) were added (2*RS*)-2-[2-(trimethylsilyl)-ethoxymethoxy]tetradecanoic acid [3.8 g, IR (film); 3600-2400 (CH, COOH), 1720 (C=O), and 860 and 830 cm^{-1}(Si-C)], and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (WSC, 3.2 g). The mixture was stirred overnight at room temperature and concentrated. The residue was chromatographed on a column of silica gel with

300:1 CH_2Cl_2-MeOH to give **2** (4.0 g, 70 %) as a syrup: $[\alpha]_D$ -29.0° (*c* 1.2, CH_2Cl_2); IR (film); 3300 (OH, NH), 2940, 2850 (CH), 1650, 1540 (amide), and 860 and 830 (Si-C, Me_2C); ^1H NMR ($CDCl_3$) δ 0.0 (m, 18H, Me_3Si-), 0.83-1.0 (m, 7H, Me_3Si-C*H*$_2$- and Me), 1.2-1.8 (m, 22H, -CH_2-), 1.43, 1.51 (2s, 6H, Me_2C), 3.30 (m, 1H, H-5), 3.35-4.0 (m, 9H, Me_3SiCH_2-C*H*$_2$-, H-2 of C_{14}-OSEM, and ring protons H-3, 4, and 6), 4.04-4.1 (q, 1H, $J_{1,2} = J_{2,3} = J_{2,NH}$ = 5.5 Hz, H-2), 4.25 (broad s, 1H, OH), 4.75, 4.63 (2d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 4.7 (m, 2H, -OCH_2O-), and 6.77, 6.80 (2d, 1H, $J_{2,NH}$ = 4.9 Hz, NH).

Anal. Calcd for $C_{34}H_{69}NO_8Si_2$: C, 60.40; H, 10.39; N, 2.09. Found: C, 60.17; H, 10.63; N, 1.98.

2-(Trimethylsilyl)ethyl 3-*O*-[(2*RS*)-2-(Benzyloxymethoxy)tetradecanoyl]-2-deoxy-4,6-*O*-isopropylidene-2-[(2*RS*)-2-[2-(trimethylsilyl)ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (3). To a solution of **2** (1.8 g) in CH_2Cl_2 (50 mL) were added (2*RS*)-2-(benzyloxymethoxy)tetradecanoic acid [1.4 g; IR (film) 3600-2400 (CH, COOH), 1720 (C=O), and 730-690 cm^{-1} (Ph)], WSC (1.0 g) and a catalytic amount of 4-dimethylaminopyridine (DMAP). The mixture was stirred overnight at room temperature and concentrated. The residue was chromatographed on a column of silica gel with 300:1 CH_2Cl_2-MeOH to give **3** (2.7 g, 98 %) as a syrup: $[\alpha]_D$ -19.3° (*c* 1.0, CH_2Cl_2); IR (film) 3360 (NH), 2930, 2850 (CH), 1740 (ester) 1660, 1530 (amide), 860, 830 (Si-C, Me_2C), and 730-700 cm^{-1} (Ph); ^1H NMR ($CDCl_3$) δ 0.0 (m, 18H, Me_3Si-), 0.88-1.0 (m, 10H, Me_3Si-C*H*$_2$- and Me), 1.2-1.8 (m, 44H, -CH_2-), 1.33, 1.45 (2s, 6H, Me_2C), 3.34 (m, 1H, H-5), 3.45-4.05 (m, 9H, Me_3SiCH_2-C*H*$_2$-, H-2 of C_{14}-OSEM, H-2 of C_{14}-OBOM, H-4, and 6), 4.25 (m, 1H, H-2), 4.5-4.8 (m, 7H, -OCH_2O-, $PhCH_2$-, and H-1), 5.3 (m, 1H, H-3), 6.6 (m, 1H, NH), and 7.27-7.34 (m, 5H, Ph).

Anal. Calcd for $C_{56}H_{103}NO_{11}Si_2$: C, 65.78; H, 10.15; N, 1.37.Found: C, 65.50; H, 10.40; N, 1.19.

2-(Trimethylsilyl)ethyl 3-*O*-[(2*RS*)-2-(Benzyloxymethoxy)tetradecanoyl]-2-deoxy-2-[(2*RS*)-2-[2-(trimethylsilyl)ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (4). A solution of **3** (2.6 g) in aqueous 80% acetic acid (150 mL) was stirred for 2 h at 50 °C and then concentraed to a syrup, which was chromatographed on a column of silica gel with 150:1 CH_2Cl_2-MeOH to give **4** (2.5 g, 96%) as a syrup: $[\alpha]_D$ -5.7° (*c* 1.0, CH_2Cl_2); IR (film) 3350 (OH, NH), 2930, 2850 (CH), 1740 (ester) 1650, 1530 (amide), 860, 830 (Si-C), and 760-690 cm^{-1}(Ph); ^1H NMR ($CDCl_3$) δ 0.0 (m, 18H, Me_3Si-), 0.88-1.0 (m, 10H, Me_3Si-C*H*$_2$- and Me), 1.2-1.8 (m, 44H, -CH_2-), 3.40 (m, 1H, H-5), 3.50-4.14 (m, 10H, Me_3SiCH_2-C*H*$_2$-, H-2 of C_{14}-OSEM, H-2 of C_{14}-OBOM, H-2, 4, and 6), 4.5-4.9 (m, 7H, -OCH_2O-, $PhCH_2$-, and H-1), 5.1 (m, 1H, H-3), 6.57 (m, 1H, NH), and 7.27-7.34 (m, 5H, Ph).

Anal. Calcd for $C_{53}H_{99}NO_{11}Si_2$: C, 64.79; H, 10.16; N, 1.43. Found: C, 65.00; H, 10.25; N, 1.40.

2-(Trimethylsilyl)ethyl 3-*O*-[(2*RS*)-2-(Benzyloxymethoxy)tetradecanoyl]-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-[(2*RS*)-2-[2-(trimethylsilyl)-ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (5). To a solution of **4** (2.5 g) in pyridine (70 mL) was added *tert*-butyldimethylsilyl chloride (784 mg), and the mixture was stirred overnight at room temperature. Methanol was added to the mixture, which was then concentrated. The residual syrup was chromatographed on a column of silica gel with 300:1 CH_2Cl_2-MeOH to obtain **5** (2.4 g, 83%) as a syrup: $[\alpha]_D$ -9.6° (*c* 1.0, CH_2Cl_2); IR (film) 3450 (OH), 3300 (NH), 2930, 2850 (CH), 1750 (ester), 1660, 1540 (amide), 860, 840 (Si-C), and 780-700 cm^{-1} (Ph); NMR ($CDCl_3$) δ 0.0 (m, 24H, Me-Si-), 0.86-1.0 (m, 19H, *tert*-Bu, Me_3Si-C*H*$_2$- and Me), 1.2-1.75 (m, 44H, -CH_2-), 3.28 (d, 1H, OH), 3.35-4.2 (m, 11H, Me_3SiCH_2-C*H*$_2$-, H-2 of C_{14}-OSEM, H-2 of C_{14}-OBOM, H-2, 4, 5, and 6), 4.47-4.9 (m, 7H, -OCH_2O-, PhC*H*$_2$-, and H-1), 5.1 (m, 1H, H-3), 6.51 (m, 1H, NH), and 7.27-7.39 (m, 5H, Ph).

Anal. Calcd for $C_{59}H_{113}NO_{11}Si_3$: C, 64.61; H, 10.38; N, 1.28. Found: C, 64.44; H, 10.59; N, 1.01.

2-(Trimethylsilyl)ethyl 3-*O*-[(2*RS*)-2-(Benzyloxymethoxy)tetradecanoyl]-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-4-*O*-diphenoxyphosphinyl-2-[(2*RS*)-2-[2-(trimethylsilyl)ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (6). To a cold solution of **5** (2.4 g) and DMAP (560 mg) in pyridine (20 mL) was added diphenyl phosphorochloridate (1.17 g) and the mixture was stirred overnight at room temperature. Methanol was added to the mixture, and it was concentrated, then the residue was extracted with $CHCl_3$. The extract was washed with 2M HCl and water, dried (Na_2SO_4) and concentrated. The residual syrup was chromatographed on a column of silica gel with 400:1 CH_2Cl_2-MeOH to give syrupy **6** (2.52 g, 87%): $[\alpha]_D$ -6.5° (*c* 1.0, CH_2Cl_2); IR (film) 3300 (NH), 2950, 2850 (CH), 1760 (ester), 1680, 1600 (amide), 960 (P-O-Ph), 860, 840 (Si-C), and 780-690 cm^{-1}(Ph); ^1H NMR ($CDCl_3$) δ 0.0 (m, 24H, Me-Si-), 0.8-1.0 (m, 19H, *tert*-Bu, Me_3Si-C*H*$_2$- and Me), 1.1-1.75 (m, 44H, -CH_2-), 3.48-4.02 (m, 9H, Me_3SiCH_2-C*H*$_2$-, H-2 of C_{14}-OSEM, H-2 of C_{14}-OBOM, H-5, and 6), 4.1 (m, 1H, H-2), 4.41-4.46 (q, 1H, $J_{3,4} = J_{4,5} = J_{4,p}$ = 9.5 Hz, H-4), 4.48-4.88 (m, 7H, -OCH_2O-, PhC*H*$_2$- and H-1), 5.5 (m, 1H, H-3), 6.61 (m, 1H, NH), and 7.07-7.39 (m, 15H, Ph).

Anal. Calcd for $C_{71}H_{122}NO_{14}PSi_3$: C, 64.17; H, 9.25; N, 1.05. Found: C, 64.22; H, 9.51; N, 1.20.

2-(Trimethylsilyl)ethyl 6-*O*-*tert*-Butyldimethylsilyl-2-deoxy-4-*O*-diphenoxyphosphinyl-3-*O*-[(2*RS*)-2-hydroxytetradecanoyl]-2-[(2*RS*)-2-[2-(trimethylsilyl)ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (7).

A mixture of **6** (2.91 g), 10% Pd-C (1.0 g) and EtOH (150 mL) was stirred overnight at room temperature under a hydrogen atmosphere. The catalyst was then filtered off and washed with EtOH. The filtrate and washings were combined and concentrated. The residue was chromatographed on a column of silica gel with 200:1 CH_2Cl_2-MeOH to give **7** (1.47 g, 60%), which was lyophilized from 1,4-dioxane solution: mp 87-89 °C, $[\alpha]_D$ -4.1° (*c* 0.9, CH_2Cl_2); IR (film) 3500 (OH), 3300 (NH), 2930, 2850 (CH), 1740 (ester), 1680, 1590 (amide), 960 (P-O-Ph), 860, 840 (Si-C), and 780-690 cm^{-1}(Ph); ^1H NMR ($CDCl_3$) δ 0.0 (m, 24H, Me-Si-), 0.85-0.98 (m, 19H, *tert*-Bu, Me_3Si-CH_2- and Me), 1.14-1.75 (m, 44H, -CH_2-), 2.96, 3.09 (2d, 1H, OH), 3.50-4.06 (m, 10H, Me_3SiCH_2-CH_2-, H-2 of C_{14}-OSEM, H-2 of C_{14}-OH, H-2, 5, and 6), 4.51-4.73 (m, 3H, -OCH_2O- and H-4), 4.85, 4.95 (2d, 1H, $J_{1,2}$ = 9.0 Hz, H-1), 5.5 (m, 1H, H-3), 6.61, 6.65 (2d, 1H, NH), and 7.07-7.39 (m, 10H, Ph).

Anal. Calcd for $C_{63}H_{114}NO_{13}PSi_3$: C, 62.60; H, 9.51; N, 1.16. Found: C, 62.43; H, 9.79; N, 1.02.

2-(Trimethylsilyl)ethyl 6-*O*-*tert*-Butyldimethylsilyl-3-*O*-[(2*RS*)-2-decanoyloxytetradecanoyl]-2-deoxy-4-*O*-diphenoxyphosphinyl-2-[(2*RS*)-2-[2-(trimethylsilyl)ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (8a). To a solution of **7** (200 mg) in CH_2Cl_2 (10 mL) were added decanoic acid (57 mg), WSC (95 mg) and a catalytic amount of DMAP. The mixture was stirred overnight at room temperature and concentrated. The residue was chromatographed on a column of silica gel with 200:1 CH_2Cl_2-MeOH to give **8a** (225 mg, 96%) as a syrup: $[\alpha]_D$ -10.5° (*c* 0.6, CH_2Cl_2); IR (film) 3350 (NH), 2930, 2850 (CH), 1740 (ester), 1680, 1590 (amide), 950 (P-O-Ph), 860, 840 (Si-C), and 780-690 cm^{-1} (Ph); ^1H NMR ($CDCl_3$) δ 0.0 (m, 24H, Me-Si-), 0.85-0.98 (m, 22H, *tert*-Bu, Me_3Si-CH_2- and Me), 1.12-1.75 (m, 58H, -CH_2-), 2.28-2.35 (m, 2H, -$COCH_2$-) 3.50-4.04 (m, 8H, Me_3SiCH_2-CH_2-, H-2 of C_{14}-OSEM, H-5, and 6), 4.04-4.17 (m, 1H, H-2), 4.6-4.73 (m, 3H, -OCH_2O- and H-4), 4.81-5.0 [m, 1H, H-2 of C_{14}-(O-C_{10})], 5.07, 5.17 (2d, 1H, $J_{1,2}$ = 8.0 Hz, H-1), 5.5, 5.8 (2m, 1H, H-3), 6.61, 6.82 (2m, 1H, NH), and 7.1-7.4 (m, 10H, Ph).

Anal. Calcd for $C_{73}H_{132}NO_{14}PSi_3$: C, 64.33; H, 9.76; N, 1.03. Found: C, 64.12; H, 9.90; N, 1.31.

3-*O*-[(2*RS*)-2-Decanoyloxytetradecanoyl]-2-deoxy-4-*O*-diphenoxyphosphinyl-2-[(2*RS*)-2-hydroxytetradecanamido]-D-glucopyranose (9a). To a solution of **8a** (200 mg) in CH_2Cl_2 (10 mL) was added boron trifluoride etherate (0.5 mL) at 0 °C. The mixture was stirred for 2 h at the same temperature. The mixture was washed with sat $NaHCO_3$ and water, dried (Na_2SO_4) and concentrated. The residue was chromatographed on a column of silica gel with 40:1 CH_2Cl_2-MeOH to give **9a** (110 mg, 75%), which was lyophilized from 1,4-dioxane solution: mp 47-49 °C,

$[\alpha]_D$ -2.3° (*c* 0.3, CH_2Cl_2); IR (KBr) 3350 (OH, NH), 2930, 2850 (CH), 1740 (ester), 1640, 1540 (amide), 950 (P-O-Ph), and 780-690 cm^{-1}(Ph); ^1H NMR ($CDCl_3$) δ 0.88 (m, 9H, Me), 1.12-1.75 (m, 58H, -CH_2-), 2.28-2.45 (m, 2H, -$COCH_2$-) 3.50-4.04 (m, 7H, H-2 of C_{14}-OH, OH, H-2, 5, and 6), 4.55 (broad s, 1H, OH), 4.6 (m, 1H, H-4), 5.23 (s, 1H, H-1), 5.34 [m, 1H, H-2 of C_{14}-(O-C_{10})], 5.8 (m, 1H, H-3), 6.82 (m, 1H, NH), and 7.1-7.4 (m, 10H, Ph).

Anal. Calcd for $C_{56}H_{92}NO_{13}P$: C, 66.05; H, 9.11; N, 1.38. Found: C, 65.78; H, 9.37; N, 1.30.

3-*O*-[(2*RS*)-2-Decanoyloxytetradecanoyl]-2-deoxy-2-[(2*RS*)-2-hydroxytetradecanamido]-4-*O*-phosphono-D-glucopyranose (10a). To a solution of **9a** (50 mg) in EtOH (100 mL) was added Adams' platinum catalyst (60 mg), and the mixture was stirred overnight in a hydrogen atmosphere. The catalyst was filtered off and washed with EtOH. The filtrate and washings were combined and concentrated to afford **10a** (45 mg, 95%), which was lyophilized from 1,4-dioxane suspension: IR (KBr) 3300 (OH, NH), 2930, 2850 (CH), 1740 (ester), and 1680, 1590 cm^{-1}(amide). Other physical and analytical data are given in the Table.

Other 3-*O*-[(2*RS*)-2-Acyloxytetradecanoyl]-2-deoxy-2-[(2*RS*)-2-hydroxytetradecanamido]-4-*O*-phosphono-D-glucopyranoses (10b-d). Compounds **10b-d** were prepared *via* **8b-d** and **9b-d** from **7** by the same sequence as described for **10a**, and the physical and analytical data are recorded in the Table.

2-(Trimethylsilyl)ethyl 3-*O*-[(2*RS*)-2-(Benzyloxymethoxy)tetradecanoyl]-2-deoxy-4,6-*O*-isopropylidene-2-[(3*R*)-3-[2-(trimethylsilyl)ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (12). Compound **12** was obtained by treatment of 2-(trimethylsilyl)ethyl 2-deoxy-4,6-*O*-isopropylidene-2-[(3*R*)-3-[2-(trimethylsilyl)ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (**11**, 2.83 g) with (2*RS*)-2-(benzyloxymethoxy)tetradecanoic acid (2 g) in nearly quantitative yield, according to the method described for **3**: $[\alpha]_D$ -10.9° (*c* 1.0, CH_2Cl_2); IR (film) 3300 (NH), 2930, 2850 (CH), 1740 (ester) 1660, 1530 (amide), 860, 830 (Si-C, Me_2C), and 730-700 cm^{-1}(Ph); ^1H NMR ($CDCl_3$) δ 0.0 (m, 18H, Me_3Si-), 0.75-1.0 (m, 10H, Me_3Si-CH_2- and Me), 1.1-1.7 (m, 42H, -CH_2-), 1.32, 1.33, 1.43, 1.44 (4s, 6H, Me_2C), 2.2-2.35 (m, 2H, -$COCH_2$-), 3.34 (m, 1H, H-5), 3.45-4.0 (m, 9H, Me_3Si-CH_2-CH_2-, H-3 of C_{14}-OSEM, H-2 of C_{14}-OBOM, H-4, and 6), 4.23 (m, 1H, H-2), 4.5-4.9 (m, 7H, -OCH_2O-, PhCH_2-, and H-1), 5.24, 5.25 (2t, 1H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H-3), 6.18 (m, 1H, NH), and 7.2-7.4 (m, 5H, Ph).

Anal. Calcd for $C_{56}H_{103}NO_{11}Si_2$: C, 65.78; H, 10.15; N, 1.37. Found: C, 65.91; H, 10.04; N, 1.09.

2-(Trimethylsilyl)ethyl 3-*O*-[(2*RS*)-2-(Benzyloxymethoxy)tetradecanoyl]-2-deoxy-2-[(3*R*)-3-[2-(trimethylsilyl)ethoxymethoxy]tetradecan-

TABLE. Some physical properties of the compounds **10a-d, 19a-d,** and **23e-h.**

Compd. No.	Mp (°C)	$[\alpha]_D$ (°) (*c*)[a]	Molecular formula	Found (Calcd) % of C	H	N
10a	152-153	+5.5 (1.2)	$C_{44}H_{84}NO_{13}P$	60.82 (61.02)	10.02 (9.78)	1.58 (1.62)
b	151-153	+6.0 (1.4)	$C_{46}H_{88}NO_{13}P$	61.51 (61.79)	10.08 (9.92)	1.77 (1.57)
c	154-155	+5.4 (0.9)	$C_{48}H_{92}NO_{13}P$	62.60 (62.51)	10.13 (10.05)	1.70 (1.52)
d	155-156	+6.5 (1.0)	$C_{50}H_{96}NO_{13}P$	63.03 (63.20)	10.33 (10.18)	1.58 (1.47)
19a	160-161	+15.5 (0.1)	$C_{44}H_{84}NO_{13}P$	60.80 (61.02)	10.01 (9.78	1.45 (1.62)
b	158-159	+10.0 (0.1)	$C_{46}H_{88}NO_{13}P$	61.90 (61.79)	9.72 (9.92)	1.60 (1.57)
c	161	+13.3 (0.1)	$C_{48}H_{92}NO_{13}P$	62.29 (62.51)	10.25 (10.05)	1.30 (1.52)
d	159-160	+7.1 (0.1)	$C_{50}H_{96}NO_{13}P$	63.01 (63.20)	10.38 (10.18)	1.44 (1.47)
23e	162-163	+14.2 (0.2)	$C_{44}H_{84}NO_{13}P$	61.30 (61.02)	9.90 (9.78)	1.57 (1.62)
f	158	+18.5 (0.4)	$C_{46}H_{88}NO_{13}P$	61.71 (61.79)	9.68 (9.92)	1.56 (1.57)
g	161-162	+20.3 (0.1)	$C_{48}H_{92}NO_{13}P$	62.38 (62.51)	10.26 (10.05)	1.48 (1.52)
h	159-160	+16.5 (0.1)	$C_{50}H_{96}NO_{13}P$	63.36 (63.20)	10.33 (10.18)	1.50 (1.47)

a. 50:25:4:2 $CHCl_3$-MeOH-H_2O-NH_4OH

amido]-β-D-glucopyranoside (13). Hydrolytic removal of the isopropylidene group from **12**, as described for **4**, gave **13** in 70% yield: $[\alpha]_D$ +1.6° (*c* 1.4, CH_2Cl_2); IR (film) 3300 (OH, NH), 2930, 2850 (CH), 1760 (ester) 1650, 1560 (amide), 860, 840 (Si-C), and 730-700 cm^{-1}(Ph); ^1H NMR ($CDCl_3$) δ 0.0 (m, 18H, Me_3-Si-), 0.75-1.0

(m, 10H, Me_3Si-C*H*$_2$- and Me), 1.1-1.7 (m, 42H, -CH_2-), 2.15-2.4 (m, 3H, -$COCH_2$- and OH), 3.40 (m, 1H, H-5), 3.45-4.0 (m, 9H, Me_3SiCH_2-C*H*$_2$-, H-3 of C_{14}-OSEM, H-2 of C_{14}-OBOM, H-4, and 6), 4.1 (m, 1H, H-2), 4.5-4.85 (m, 7H, -OCH_2O-, PhC*H*$_2$-, and H-1), 5.13 (t, 1H, $J_{2,3} = J_{3,4} = 10$ Hz, H-3), 6.19, 6.28 (2d, 1H, NH), and 7.2-7.4 (m, 5H, Ph).

Anal. Calcd for $C_{53}H_{99}NO_{11}Si_2$: C, 64.79; H, 10.16; N, 1.43. Found: C, 64.99; H, 9.80; N, 1.21.

2-(Trimethylsilyl)ethyl 3-*O*-[(2*RS*)-2-(Benzyloxymethoxy)tetradecanoyl]-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-2-[(3*R*)-3-[2-(trimethylsilyl)-ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (14). Compound **14** was quantitatively obtained by treatment of **13** (2.5 g) with *tert*-butyldimethylsilyl chloride (762 mg) as described for **5**: $[\alpha]_D$ -2.9° (*c* 1.1, CH_2Cl_2); IR (film) 3300 (OH, NH), 2930, 2850 (CH), 1740 (ester), 1640, 1540 (amide), 860, 840 (Si-C), and 780-700 cm^{-1} (Ph); ^1H NMR ($CDCl_3$) δ 0.0 (m, 24H, Me-Si-), 0.8-1.0 (m, 19H, Me_3Si-C*H*$_2$-, *tert*-Bu, and Me), 1.1-1.9 (m, 42H, -CH_2-), 2.2-2.4 (m, 2H, -$COCH_2$-), 3.25-4.0 (m, 10H, Me_3SiCH_2-C*H*$_2$-, H-3 of C_{14}-OSEM, H-2 of C_{14}-OBOM, OH, H-5, and 6), 4.1 (m, 1H, H-2), 4.5-4.9 (m, 7H, -OCH_2O-, PhC*H*$_2$-, and H-1), 5.13 (t, 1H, $J_{2,3} = J_{3,4} = 9.5$ Hz, H-3), 6.01, 6.11 (2d, 1H, NH), and 7.2-7.4 (m, 5H, Ph).

Anal. Calcd for $C_{59}H_{113}NO_{11}Si_3$: C, 64.61; H, 10.38; N, 1.28. Found: C, 64.50; H, 10.60; N, 1.01.

2-(Trimethylsilyl)ethyl 3-*O*-[(2*RS*)-2-(Benzyloxymethoxy)tetradecanoyl]-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-4-*O*-diphenoxyphosphinyl-2-[(3*R*)-3-[2-(trimethylsilyl)ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (15). Compound **14** (2 g) was treated with diphenyl phosphorochloridate as described for **6**, to afford srupy **15** (1.9 g, 80%): $[\alpha]_D$ -3.7° (*c* 1.1, CH_2Cl_2); IR (film) 3300 (NH), 2930, 2850 (CH), 1750 (ester), 1640, 1540 (amide), 950 (P-O-Ph), 860, 840 (Si-C), and 780-700 cm^{-1} (Ph); ^1H NMR ($CDCl_3$) δ 0.0 (m, 24H, Me-Si-), 0.8-1.0 (m, 19H, Me_3Si-C*H*$_2$-, *tert*-Bu, and Me), 1.1-1.7 (m, 42H, -CH_2-), 2.2-2.4 (m, 2H, -$COCH_2$-), 3.5-4.0 (m, 9H, Me_3SiCH_2-C*H*$_2$-, H-3 of C_{14}-OSEM, H-2 of C_{14}-OBOM, H-5, and 6), 4.12, 4.21 (2dd, 1 H, H-2), 4.4-4.8 (m, 7H, -OCH_2O-, PhC*H*$_2$-, and H-4), 4.81 (2d, 1H, $J_{1,2} = 8$ Hz, H-1), 5.56, 5.66 (2t, 1H, $J_{2,3} = J_{3,4} = 10$Hz, H-3), 6.21 (d, 1H, NH), and 7.2-7.4 (m, 15H, Ph).

Anal. Calcd for $C_{71}H_{122}NO_{14}PSi_3$: C, 64.17; H, 9.25; N, 1.05. Found: C, 63.89; H, 9.50; N, 0.90.

2-(Trimethylsilyl)ethyl 6-*O*-*tert*-Butyldimethylsilyl-2-deoxy-4-*O*-diphenoxyphosphinyl-3-*O*-[(2*RS*)-2-hydroxytetradecanoyl]-2-[(3*R*)-3-[2-(trimethylsilyl)ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (16). Compound **15** (1.1 g) was hydrogenolyzed in the presence of palladium catalyst

as described for **7**, to give **16** (750 mg, 74%) as a syrup: $[\alpha]_D$ +8.1° (*c* 0.9, CH_2Cl_2); IR (film) 3300 (OH, NH), 2930, 2850 (CH), 1750 (ester), 1660, 1540 (amide), 960 (P-O-Ph), 860, 840 (Si-C), and 780-700 cm^{-1}(Ph); ^1H NMR ($CDCl_3$) δ 0.0 (m, 24H, Me-Si-), 0.8-1.0 (m, 19H, Me_3Si-C*H*$_2$-, *tert*-Bu, and Me), 1.1-1.7 (m, 42H, -CH_2-), 2.2-2.4 (m, 2H, -$COCH_2$-), 3.05 (broad s, 1H, OH), 3.5-4.0 (m, 10H, Me_3SiCH_2-C*H*$_2$-, H-3 of C_{14}-OSEM, H-2 of C_{14}-OH, H-2, 5, and 6), 4.6-4.8 (m, 3H, -OCH_2O- and H-4), 4.81, 4.92 (2d, 1H, $J_{1,2}$ = 8.2 Hz, H-1), 5.61, 5.64 (2t, 1H, $J_{2,3}$ = $J_{3,4}$ = 8.8 Hz, H-3), 6.32, 6.35 (2d, 1H, NH), and 7.2-7.4 (m, 10H, Ph).

Anal. Calcd for $C_{63}H_{114}NO_{13}PSi_3$: C, 62.60; H, 9.51; N, 1.16. Found: C, 62.40; H, 9.66; N, 0.98.

2-(Trimethylsilyl)ethyl 6-*O*-*tert*-Butyldimethylsilyl-3-*O*-[(2*RS*)-2-decanoyloxytetradecanoyl]-2-deoxy-4-*O*-diphenoxyphosphinyl-2-[(3*R*)-3-[2-(trimethylsilyl)ethoxymethoxy]tetradecanamido]-β-D-glucopyranoside (17a). Esterification of **16** (170 mg) was performed with decanoic acid (72 mg) in the presence of WSC (134 mg) and a catalytic amount of DMAP as described for **8a**, to give **17a** (173 mg, 90%) as a syrup: $[\alpha]_D$ +6.4° (*c* 0.8, CH_2Cl_2); IR (film) 3300 (NH), 2930, 2850 (CH), 1740 (ester), 1660, 1540 (amide), 960 (P-O-Ph), 860, 840 (Si-C), and 780-690 cm^{-1} (Ph); ^1H NMR ($CDCl_3$) δ 0.0 (m, 24H, Me-Si-), 0.8-1.0 (m, 22H, Me_3Si-C*H*$_2$-, *tert*-Bu, and Me), 1.1-1.7 (m, 56H, -CH_2-), 2.2-2.4 (m, 4H, -$COCH_2$-), 3.18-4.0 (m, 9H, Me_3SiCH_2-C*H*$_2$-, H-3 of C_{14}-OSEM, H-2, 5, and 6), 4.5-4.8 (m, 3H, -OCH_2O- and H-4), 4.87, 4.89 (2d, 1H, $J_{1,2}$ = 8.2 Hz, H-1), 5.14 [t, 1H, H-2 of C_{14}-(O-C_{10})], 5.75, 5.82 (2t, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, H-3), 6.30 (m, 1H, NH), and 7.2-7.4 (m, 10H, Ph).

Anal. Calcd for $C_{73}H_{132}NO_{14}PSi_3$: C, 64.33; H, 9.76; N, 1.03. Found: C, 64.12; H, 9.88; N, 0.90.

3-*O*-[(2*RS*)-2-Decanoyloxytetradecanoyl]-2-deoxy-4-*O*-diphenoxyphosphinyl-2-[(3*R*)-3-hydroxytetradecanamido]-D-glucopyranose (18a). Compound **17a** (150 mg) was treated with boron trifluoride etherate (0.5 mL) as described for **9a** to give **18a** (97 mg, 86%), which was lyophilized from 1,4-dioxane solution: mp 38-39 °C, $[\alpha]_D$ -2.4° (*c* 1.0, CH_2Cl_2); IR (film) 3400 (OH, NH), 2930, 2850 (CH), 1740 (ester), 1660, 1540 (amide), 960 (P-O-Ph), and 780-690 cm^{-1} (Ph); ^1H NMR ($CDCl_3$) δ 0.88 (t, 9H, Me), 1.1-1.7 (m, 56H, -CH_2-), 2.2-2.4 (m, 4H, -$COCH_2$-), 3.45-4.0 (m, 6H, OH, H-3 of C_{14}-OH, H-5, and 6), 4.24 (m, 1H, H-2), 4.74 (q, 1H, $J_{3,4}$ = $J_{4,3}$ = $J_{4,P}$ = 9.5 Hz, H-4), 4.8 (broad s, 1H, OH), 5.12 [t, 1H, H-2 of C_{14}-(O-C_{10})], 5.24 (s, 1H, H-1), 5.55, 5.59 (2t, 1H, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, H-3), 6.25-6.35 (m, 1H, NH), and 7.2-7.4 (m, 10H, Ph).

Anal. Calcd for $C_{56}H_{92}NO_{13}P$: C, 66.05; H, 9.11; N, 1.38. Found: C, 66.00; H, 9.22; N, 1.13.

3-*O*-[(2*RS*)-2-Decanoyloxytetradecanoyl]-2-deoxy-2-[(3*R*)-3-hydroxytetradecanamido]-4-*O*-phosphono-D-glucopyranose (19a). Compound **18a** (95 mg) was hydrogenolyzed in the presence of platinum catalyst as dscribed for **10a**, to afford the desired compound **19a** (79 mg, 97%): IR (KBr) 3400 (OH, NH), 2930, 2850 (CH), 1740 (ester), 1660, 1540 cm^{-1}(amide). Other physical and analytical data are given in the Table.

3-*O*-[(2*RS*)-2-Acyloxytetradecanoyl]-2-deoxy-2-[(3*R*)-3-hydroxytetradecanamido]-4-*O*-phosphono-D-glucopyranoses (19b-d). Compounds **19b-d** were prepared *via* **17b-d** and **18b-d** from **16** by the same sequence described for **10a**, and the physical and analytical data are recorded in the Table.

2-(Trimethylsilyl)ethyl 6-*O*-*tert*-Butyldimethylsilyl-2-deoxy-4-*O*-diphenoxyphosphinyl-2-[(2*RS*)-2-hydroxydecanamido]-3-*O*-[(3*R*)-3-tetradecanoyloxytetradecanoyl]-β-D-glucopyranoside (21e). A mixture of 2-(trimethylsilyl)ethyl 2-amino-6-*O*-*tert*-butyldimethylsilyl-2-deoxy-4-*O*-diphenoxyphosphinyl-3-*O*-[(3*R*)-3-tetradecanoyloxytetradecanoyl]-β-D-glucopyranoside (**20**, 200 mg), (2*RS*)-2-hydroxydecanoic acid (131 mg), and WSC (200 mg) in $CHCl_3$ (10 mL) was stirred overnight at room temperature. The reaction mixture was directly chromatographed on a column of silica gel with 250:1 CH_2Cl_2-MeOH to give **21e** (182 mg, 79%) as a syrup: $[\alpha]_D$ -2.2° (*c* 0.8, CH_2Cl_2); IR (film) 3300 (OH, NH), 2930, 2850 (CH), 1740 (ester), 1660, 1540 (amide), 960 (P-O-Ph), 840 (Si-C), and 780-690 cm^{-1} (Ph); ^1H NMR ($CDCl_3$) δ 0.0 (m, 15H, Me-Si-), 0.8-1.0 (m, 20H, Me_3Si-C*H*$_2$-, *tert*-Bu, and Me), 1.1-2.5 (m, 60H, -CH_2- and -$COCH_2$-), 3.2-4.2 (m, 6H, Me_3SiCH_2-C*H*$_2$-, H-2 of C_{10}-OH, H-5, and 6), 4.25 (m, 1H, H-2), 4.5-4.8 (m, 2H, H-1 and 4), 5.0-5.5 [m, 2H, OH and H-3 of C_{14}-(O-C_{14})], 6.30 (m, 1H, NH), and 7.2-7.4 (m, 10H, Ph).

Anal. Calcd for $C_{67}H_{118}NO_{13}PSi_2$: C, 65.28; H, 9.65; N, 1.14. Found: C, 65.02; H, 9.60; N, 1.02.

2-Deoxy-4-*O*-diphenoxyphosphinyl-2-[(2*RS*)-2-hydroxydecanamido]-3-*O*-[(3*R*)-3-tetradecanoyloxytetradecanoyl]-D-glucopyranose (22e). Cleavage of the silyl groups of **21e** (85 mg) as described for **9a**, gave **22e** (61 mg, 85%) as amorphous: $[\alpha]_D$ +11.3° (*c* 0.6, CH_2Cl_2); IR (film) 3300 (OH, NH), 2930, 2850 (CH), 1740 (ester), 1660, 1540 (amide), 960 (P-O-Ph), and 780-690 cm^{-1} (Ph); ^1H NMR ($CDCl_3$) δ 0.88 (t, 9H, Me), 1.1-2.0 (m, 56H, -CH_2-), 2.0-2.7 (m, 4H, -$COCH_2$-), 3.2-4.2 (m, 5H, OH, H-5, and 6), 4.15-4.5 (m, 2H, H-2 of C_{10}-OH, and H-2), 4.75 (m, 1H, H-4), 5.07 [m, 1H, H-3 of C_{14}-(O-C_{14})], 5.20 (m, 2H, OH and H-1), 5.46 (m, 1H, H-3), 6.55 (m, 1H, NH), and 7.1-7.4 (m, 10H, Ph).

Anal. Calcd for $C_{56}H_{92}NO_{13}P$: C, 66.05; H, 9.11; N, 1.38. Found: C, 65.78; H, 8.96; N, 1.64.

2-Deoxy-2-[(2*RS*)-2-hydroxydecanamido]-4-*O*-phosphono-3-*O*-[(3*R*)-3-tetradecanoyloxytetradecanoyl]-D-glucopyranose (23e). Cleavage of the

phenyl groups of **22e** (50 mg) with platinum catalyst as described for **10a**, gave **23e** (40 mg, 93%): IR (KBr) 3300 (OH, NH), 2930, 2850 (CH), 1740 (ester), 1660, 1540 cm^{-1} (amide). Other physical and analytical data are given in the Table.

2-Deoxy-2-[(2*RS*)-2-hydroxyacyl]amino-4-*O*-phosphono-3-*O*-[(3*R*)-3-tetradecanoyloxytetradecanoyl]-D-glucopyranoses (23f-h). Compounds **23f-h** were prepared *via* **21f-h** and **22f-h** from **20** by the same sequence described for **23e**. The physical and analytical data are shown in the Table.

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