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Synthesis of chemically modified sialic acid-containing sialyl-Le^X ganglioside analogues recognized by the selectin family

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Sialyl Lewis X ganglioside analogues containing 5-acetamido-3,5-dideoxy-L-*arabino*-2-heptulopyranosylonic acid (C7-Neu5Ac), 5-acetamido-3,5-dideoxy-D-*galacto*-2-octulopyranosylonic acid (C8-Neu5Ac), and 5-acetamido-3,5-dideoxy-L-*glycero*-D-*galacto*-1-2-nonulopyranosylonic acid (8-epi-Neu5Ac) in place of *N*-acetylneuraminic acid (Neu5Ac) have been synthesized. Glycosylation of 2-(trimethylsilyl)ethyl 6-*O*-benzoyl-β-D-galactopyranoside with the phenyl or methyl 2-thioglycoside derivatives of the respective sialic acids, using *N*-iodosuccinimide (NIS)-trifluoromethanesulfonic acid as a promoter in acetonitrile, gave the three required 2-(trimethylsilyl)ethyl (2*S*)-sialyl-(2 → 3)-β-galactopyranosides. These were converted via *O*-benzoylation, selective transformation of the 2-(trimethylsilyl)ethyl group to acetyl, and introduction of the methylthio group with methylthiotrimethylsilane into the corresponding glycosyl donors. Glycosylation of 2-(trimethylsilyl)ethyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 3)-*O*-(2-acetamido-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside with these donors in the presence of dimethyl(methylthio)sulfonium triflate (DMTST) afforded the expected β-glycosides, which were converted into the corresponding α-trichloroacetimidates, and these, on coupling with (2*S*, 3*R*, 4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol, gave the required β-glycosides. Finally, these were transformed via selective reduction of the azide group, condensation with octadecanoic acid, *O*-deacylation, and de-esterification into the target compounds in good yields.

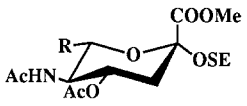
Keywords: sialic acid, (2*S*)-sialyl-(2 → 3)-glycoside, sialyl Le^X, sialoglycoconjugate, selectin family

Introduction

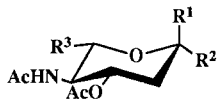
Very recently, it has been demonstrated [1–5] that the selectin family, such as E-selectin (endotherial leukocyte adhesion molecule-1, ELAM-1), P-selectin (GMP-140), and L-selectin (LECAM-1), recognizes the sialyl Le^X determinant, α-Neu5Ac-(2-3)-β-D-Gal-(1-4)-[α-L-Fuc-(1-3)]-β-GlcNAc, which is found as the terminal carbohydrate structure in both glycolipids and glycoproteins. Previously, we have reported the synthesis of sialyl Le^X ganglioside (a hexasaccharide [6] and pentasaccharide [7]), sialyl α(2-6)-Le^X ganglioside [8], and the analogues [9], and have examined recognition activity by the selectin family. The data [10–12] showed that both the fucose and sialic acid residues were required for full recognition and sialyl α(2-6)-Le^X ganglioside was not recognized at all, indicating the more detailed structural requirements necessary for selectin recognition. In view of these facts, we describe herein the stereocontrolled synthesis of sialyl Le^X ganglioside analogues containing the C7-Neu5Ac, C8-Neu5Ac and 8-epi-Neu5Ac, clarifying the structural requirements of the sialic acid moiety for the selectin recognition.

Results and discussion

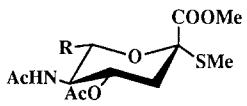
2-(Trimethylsilyl)ethyl *O*-(2,3,4-tri-*O*-benzyl-α-L-fucopyranosyl)-(1 → 3)-*O*-(2-acetamido)-6-*O*-benzyl-2-deoxy-β-D-glucopyranosyl)-(1 → 3)-2,4,6-tri-*O*-benzyl-β-D-galactopyranoside [7] (**21**) was selected as the glycosyl acceptor, and methyl *O*-(methyl 5-acetamido-4,7-di-*O*-acetyl-3,5-dideoxy-β-L-*arabino*-2-heptulopyranosylonate)-(2 → 3)-, methyl *O*-(methyl 5-acetamido-4,7,8-tri-*O*-acetyl-3,5-dideoxy-α-D-*galacto*-2-octulopyranosylonate)-(2 → 3)-, and methyl *O*-(methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-L-*glycero*-β-D-*galacto*-2-nonulopyranosylonate)-(2 → 3)-2,4,6-tri-*O*-benzoyl-1-thio-β-D-galactopyranosides (**12**, **16**, **20**) as the glycosyl donors in the synthesis of sialyl Le^X ganglioside analogues containing the modified sialic acids. Glycosylation of **21** with **12**, **16**, or **20**, yielded intermediates



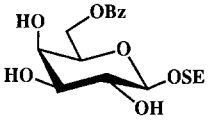
1 R = X^1
2 R = Y^1



	R^1, R^2	R^3
3	OAc, COOMe	X^1
4	SPh, COOMe	X^1
5	OAc, COOMe	Y^1
6	SPh, COOMe	Y^1



7 R = Z^1



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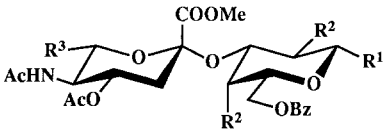
X^1 = CH_2OAc

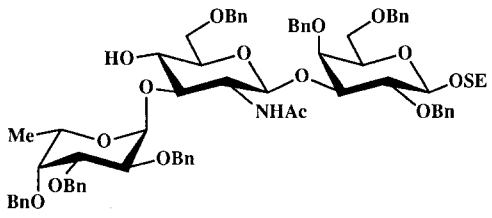
Y^1 = $HCOAc$ / CH_2OAc

Z^1 = $HCOAc$ / $AcOCH$ / CH_2OAc

SE = 2-(trimethylsilyl)ethyl
Bz = benzoyl



	R^1	R^2	R^3
9	OSE	OH	X^1
10	OSE	OBz	X^1
11	OAc	OBz	X^1
12	SMe	OBz	X^1
13	OSE	OH	Y^1
14	OSE	OBz	Y^1
15	OAc	OBz	Y^1
16	SMe	OBz	Y^1
17	OSE	OH	Z^1
18	OSE	OBz	Z^1
19	OAc	OBz	Z^1
20	SMe	OBz	Z^1



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Bn = benzyl

that could then, by introduction of the ceramide moiety, be transformed to the ganglioside analogue end products (**37**, **40**, **43**).

Treatment of methyl [2-(trimethylsilyl)ethyl 5-acetamido-4,7-di-*O*-acetyl-3,5-dideoxy-β-L-*arabino*-2-heptulopyranosid]onate [13] (**1**) or methyl[2-(trimethylsilyl)ethyl 5-acetamido-4,7,8-tri-*O*-acetyl-3,5-dideoxy-α-D-*galacto*-2-octuropyranosid]onate [14] (**2**) with trifluoroacetic acid in dichloromethane, and subsequent *O*-acetylation afforded the corresponding 2-*O*-acetyl derivatives **3** and **5**, respectively, in good yields. The replacement [15] of the anomeric acetoxy group in **3** and **5** with phenylthio by stirring for 12 h at room temperature with thiophenol in dichloromethane in the presence of boron trifluoride etherate gave the phenyl 2-thioglycosides **4** and **6** in almost quantitative yields as the anomeric mixture.

The glycosylation [16–18] of 2-(trimethylsilyl)ethyl 6-*O*-benzoyl-β-D-galactopyranoside [19] (**8**) with **4** (1.7 equiv with respect to the acceptor), in acetonitrile for 2 h at −35 °C in the presence of NIS-trifluoromethanesulfonic acid (TfOH) and 3 Å molecular sieves, gave exclusively the β-L-glycoside **9** in 45% yield. Benzoylation of **9** with benzoic anhydride in pyridine gave the benzoate **10**. In essentially the same way, glycosylation of **8** with **6** or **7** [20] furnished the corresponding sialyl-(2 → 3) galactosides **13** and **17** in 45% and 41% yields, respectively. Benzoylation of **13** and **17** gave the benzoates **14** and **18**.

The structures of the sialyl-(2 → 3) galactosides obtained were established unambiguously by 270 MHz ^{1}H-NMR spectroscopy. The observed chemical shifts and coupling constants for H-3*eq* (δ 2.72–2.75, J_{gem} 13 ≈ 14, $J_{3eq,4}$ 4.7 ≈ 4.8 Hz) and H-4 (δ 4.95–5.09) of sialic acid unit in **9**, **13**, and **17**, and for H-2 (δ 5.57–5.59, $J_{1,2}$ 8.1, $J_{2,3}$ 10.1 ≈ 10.3 Hz) and H-4 (δ 5.67–5.69, $J_{3,4}$ 3.1 ≈ 3.4 Hz) of galactose unit

in **10**, **14** and **18**, indicate the anomeric configuration [21, 22] of the newly formed glycosidic linkage to be β in **9** and **17**, and α in **13**, and the position of glycosylation to be C-3. Other ^{1}H-NMR data are given in the Materials and methods section, and are consistent with the structures assigned.

Treatment of **10**, **14**, or **18** with boron trifluoride etherate in toluene:acetic anhydride, gave the corresponding β-1-acetates **11**, **15**, and **19**, respectively, in high yield. The ^{1}H-NMR data for the galactose residue at δ 6.05–6.21 ($J_{1,2}$ 8.3 $\approx$ 8.4 Hz, H-1), 5.62–5.64 ($J_{2,3}$ 10.0 $\approx$ 10.3 Hz, H-2), and 5.64–5.66 ($J_{3,4}$ 3.1 $\approx$ 3.3 Hz, H-4) are characteristic of the structures assigned. Conversion of the β-acetates **11**, **15**, or **19** into the methyl β-thioglycosides **12**, **16**, and **20** was achieved by treatment with methylthiotrimethylsilane and boron trifluoride etherate in dichloromethane at room temperature, in high yields. Significant signals in the ^{1}H-NMR spectra of **12**, **16**, and **20** were at δ 4.72 ($J_{1,2}$ 9.7 $\approx$ 9.9 Hz, H-1), 5.59–5.62, ($J_{2,3}$ 10.3 $\approx$ 11.2 Hz, H-2) 3.57–3.66 ($J_{3,4}$ 2.5 $\approx$ 3.1 Hz, H-3), and 5.64 $\approx$ 5.74 (d, H-4), indicating the structures assigned.

The glycosylation of **21** with **12** (1.45 equiv with respect to the acceptor), in dichloromethane for 48 h at 5 °C in the presence of DMTST and 4 Å molecular sieves, gave the expected β-glycoside in 53% yield. In the same way, reaction of **21** with **16** or **20** afforded the expected β-glycosides **26** and **30** in 53% and 49% yields, respectively. H-2c proton in the ^{1}H-NMR spectrum of **22**, **26**, or **30** appeared at δ 5.45–5.47 (near t, $J_{1,2} = J_{2,3} = 9 \approx 9.3$ Hz), indicating the newly formed glycosidic linkage to be β.

Catalytic hydrogenolysis (10% Pd-C) in ethanol:acetic acid for 3 days at 45 °C of the benzyl groups in **22**, **26**, or **30**, and subsequently O-acetylation gave the per-*O*-acetyl derivatives **23**, **27**, and **31** in 85%, 87%, and 83% yields after column chromatography.

Treatment of **23**, **27**, or **31** with trifluoroacetic acid in dichloromethane for 1 h at room temperature afforded the corresponding 1-hydroxy compounds **24**, **28**, and **32** in quantitative yields, which, on treatment [19, 23, 24] with trichloroacetonitrile in the presence of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) in dichloromethane at 0 °C, afforded the corresponding α-trichloroacetimidates **25**, **29**, and **33** in high yields. Significant signals in the ^{1}H-NMR spectra of **25**, **29**, and **33** were a one proton doublet at δ 6.49 ($J_{1,2}$ 3.7 Hz, H-1a) and a one proton singlet at δ 8.62–8.63 (C=NH), indicating the α-imidate formation.

The final glycosylation [19, 25] of (2*S*, 3*R*, 4*E*)-2-azido-3-*O*-benzoyl-4-octadecene-1,3-diol [26, 27] (**34**) with **25**, **29**, or **33** thus obtained, in dichloromethane in the presence of boron trifluoride etherate for 2 h at 0 °C, gave the desired β-glycosides **35**, **38**, and **41** in 52%, 43%, and 46% yields, respectively. Selective reduction [28, 29] of the azide group in **35**, **38**, or **41** with hydrogen sulfide in aqueous pyridine gave the amine which, on condensation with octadecanoic acid, using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (WSC) in dichloromethane, gave the corresponding acylated sialyl-Le^X gangliosides **36**, **39**, and **42** in 69%, 66%, and 81% yields after column chromatography. Finally, *O*-deacylation with sodium methoxide in methanol and subsequent saponification of the methyl ester group in **36**, **39**, or **42**, yielded the end products **37**, **40**, and **43** in quantitative yields after chromatography on a column of Sephadex LH-20.

The sialyl Le^X gangliosides (**37**, **40**, and **43**) containing C7-Neu5Ac, C8-Neu5Ac, and 8-epi-Neu5Ac in place of Neu5Ac were recognized (Brandley BK, Kiso M, Hasegawa A, *et al.*, unpublished results) by L-selectin in almost the same order as sialyl Le^X ganglioside, indicating that the side chain structure in the Neu5Ac part of sialyl Le^X ganglioside is not critical for L-selectin recognition. We are now testing the reactivity of these gangliosides with P- and E-selectins.

Materials and methods

General methods

Specific rotations were determined with a Union PM-201 polarimeter at 25 °C, and IR spectra were recorded with a JASCO A-100 spectrophotometer. ^{1}H-NMR spectra were recorded with a JEOL JNM-GX 270 spectrometer. Preparative chromatography was performed on silica gel (Wako Co., 200 mesh) with the solvent systems specified. Concentrations were performed *in vacuo*.

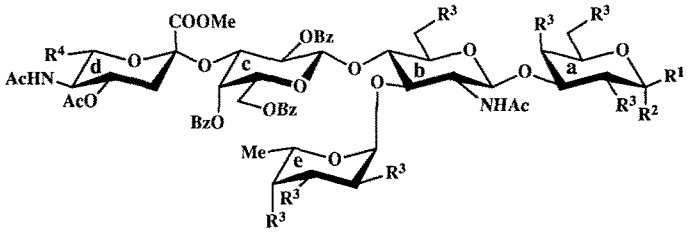
*Methyl 5-acetamido-2,4,7-tri-*O*-acetyl-3,5-dideoxy-*L*-arabino-2-heptulopyranosonate* (**3**)

To a solution of methyl [2-(trimethylsylyl)ethyl 5-acetamido-4,7-di-*O*-acetyl-3,5-dideoxy-β-L-*arabino*-2-heptolopyranosid]onate [13] (**1**; 4.5 g, 10.1 mmol) in dichloromethane (75 ml), cooled to 0 °C, was added trifluoroacetic acid (30 ml). The mixture was stirred for 2 h at room temperature and then concentrated. The residue was acetylated with acetic anhydride (20 ml):pyridine (50 ml) overnight at room temperature. Column chromatography (5:4 ethyl acetate:hexane) of the product on silica gel (200 g) gave **3** (3.9 g, 99%) as an amorphous mass: IR (film) 3300 (NH), 1750 and 1250 (ester), and 1660 and 1550 cm^{-1} (amide).

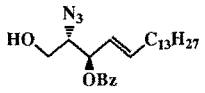
Analytical data. Calculated for $C_{16}H_{23}O_{10}N$: C, 49.36; H, 5.95; N, 3.60. Found: C, 49.24, H, 6.08; N, 3.37.

*Methyl(phenyl 5-acetamido-4,7-di-*O*-acetyl-3,5-dideoxy-2-thio-*L*-arabino-2-heptulopyranosid)onate* (**4**)

To a stirred solution of **3** (3.9 g, 9.97 mmol) in dichloromethane (40 ml), cooled to 0 °C, were added thiophenol (1.1 ml) and boron trifluoride etherate (2.5 ml), and the mixture was stirred for 12 h at room temperature. The solution was washed with 1 M sodium carbonate, dried (Na_2SO_4) and



	R^1	R^2	R^3	R^4
22	OSE	H	OBn	X^1
23	OSE	H	OAc	X^1
24	H, OH		OAc	X^1
25	H	$OC(=NH)CCl_3$	OAc	X^1
26	OSE	H	OBn	Y^1
27	OSE	H	OAc	Y^1
28	H, OH		OAc	Y^1
29	H	$OC(=NH)CCl_3$	OAc	Y^1
30	OSE	H	OBn	Z^1
31	OSE	H	OAc	Z^1
32	H, OH		OAc	Z^1
33	H	$OC(=NH)CCl_3$	OAc	Z^1



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concentrated. Column chromatography (1:1 ethyl acetate: hexane) of the residue on silica gel (250 g) gave **4** (3.8 g, 86%) as an amorphous mass; IR (film) 3300 (NH), 1760 and 1250 (ester), 1680 and 1560 (amide), and 710 cm^{-1} (Ph).

Analytical data. Calculated for $C_{20}H_{25}O_8NS$: C, 54.66; H, 5.73; N, 3.19. Found: C, 54.76; H, 5.67, N, 3.46.

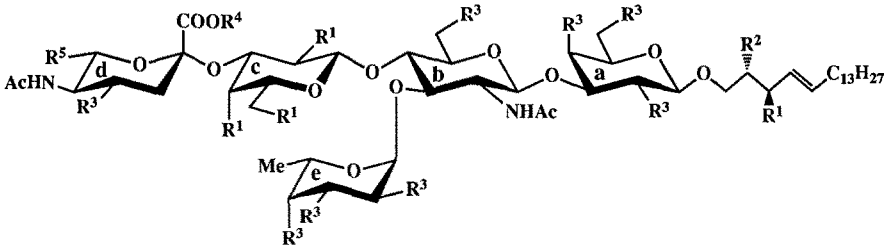
Methyl 5-acetamido-2,4,7,8-tetra-O-*acetyl-3,5-dideoxy-*D-galacto-*2-octulopyranosonate* (**5**)

To a solution of methyl [2-(trimethylsilyl)ethyl 5-acetamido-4,7,8-tri-*O*-acetyl-3,5-dideoxy-α-D-*galacto*-2-octulopyranosid)onate [14] (**2**; 4.5 g, 8.66 mmol) in dichloromethane (75 ml), cooled to 0 °C, was added trifluoroacetic acid (40 ml). The mixture was stirred for 1.5 h at room temperature and then concentrated. The residue was acetylated with acetic anhydride (10 ml):pyridine (45 ml) overnight at room temperature. Column chromatography (1:1 ethyl acetate:hexane) of the product on silica gel (250 g) gave **5** (3.9 g, quantitative) as an amorphous mass; IR (film) 3300 (NH), 1750 and 1230 (ester), and 1660 and 1550 cm^{-1} (amide).

Analytical data. Calculated for $C_{19}H_{27}O_{12}N$: C, 49.46; H, 5.90; N, 3.04. Found: C, 49.21; H, 5.86; N, 3.33.

Methyl (phenyl 5-acetamido-4,7,8-tri-O-*acetyl-3,5-dideoxy-2-thio-*D-galacto-*2-octulopyranosid)onate* (**6**)

To a stirred solution of **5** (3.9 g, 8.45 mmol) in dichloromethane (50 ml), cooled to 0 °C, were added thiophenol



	R^1	R^2	R^3	R^4	R^5
35	OBz	N_3	OAc	Me	X^1
36	OBz	$NHCOC_{17}H_{35}$	OAc	Me	X^1
37	OH	$NHCOC_{17}H_{35}$	OH	H	X^2
38	OBz	N_3	OAc	Me	Y^1
39	OBz	$NHCOC_{17}H_{35}$	OAc	Me	Y^1
40	OH	$NHCOC_{17}H_{35}$	OH	H	Y^2
41	OBz	N_3	OAc	Me	Z^1
42	OBz	$NHCOC_{17}H_{35}$	OAc	Me	Z^1
43	OH	$NHCOC_{17}H_{35}$	OH	H	Z^2

X^2 = CH_2OH $\quad$ Y^2 = $HCOH$ | CH_2OH $\quad$ Z^2 = $HCOH$ | $HOCH$ | CH_2OH

(1.1 ml) and boron trifluoride etherate (5.9 ml), and the mixture was stirred for 12 h at room temperature. The solution was washed with 1 M sodium carbonate, dried (Na_2SO_4) and concentrated. Column chromatography (4:5 ethyl acetate:hexane) of the residue on silica gel (250 g) gave **6** (4.2 g, 98%) as an amorphous mass; IR (film) 3300 (NH), 1740 and 1230 (ester), 1660 and 1550 (amide), and 690 cm^{-1} (Ph). The anomeric ratio (α:β) was estimated as $\approx$1:3 from the ratio of the intensities of the ester methyl signals.

Analytical data. Calculated for $C_{23}H_{29}O_{10}NS$: C, 54.00; H, 5.71; N, 2.74. Found: C, 53.80; H, 5.43; N, 2.76.

2-(Trimethylsilyl)ethyl O-(*methyl 5-acetamido-4,7-di*-O-*acetyl-3,5-dideoxy-β-L*-arabino-*2-heptulopyranosylonate*)-(*2 → 3*)-*6*-O-*benzoyl-β-D-galactopyranoside* (**9**)

To a solution of 2-(trimethylsilyl)ethyl 6-*O*-benzoyl-β-D-galactopyranoside (**8**) [19] (400 mg, 1.04 mmol) and **4** (777 mg, 1.77 mmol) in acetonitrile (10 ml) were added molecular sieves 3 Å (1.5 g). The mixture was stirred overnight at room temperature and then cooled to −35 °C. To the cooled mixture were added *N*-iodosuccinimide (795 mg) and trifluoromethanesulfonic acid (37 µl) and the mixture was stirred for 9 h at −35 °C. The precipitate was filtered off and washed with dichloromethane. The filtrate and washings were combined and successively washed with 1 M sodium carbonate and sodium thiosulfate, dried (Na_2SO_4) and concentrated. Column chromatography (80:1 dichloromethane:methanol) of the residue on silica gel (80 g) gave **9** (335 mg, 45%) as an amorphous mass; $[\alpha]_D$ −33.0° (*c* 1.7, chloroform); IR (film) 3400 (OH, NH), 1740 and 1250 (ester), 1670 and 1550 (amide), 860 and 840 (TMS), and 710 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) Gal unit δ 1.05 (m, 2H, $Me_3SiCH_2CH_2$), 3.70 (t, 1H, $J_{1,2} = J_{2,3}$ = 7.7 Hz, H-2), 4.33 (d, 1H, H-1) and 7.36–8.05 (m, 5H, ph); Neu5Ac unit δ 1.94 (s, 3H, AcN), 2.07 and 2.08 (2s, 6H, 2AcO), 2.68 (dd, 1H, $J_{3eq,4}$ 4.8, J_{gem} 13.2 Hz, H-3*eq*), 3.81 (s, 3H, MeO), 4.09 (q, 1H, $J_{4,5} = J_{5,6} = J_{5,NH}$ = 9.0 Hz, H-5), 5.03 (m, 1H, H-4) and 5.82 (d, 1H, NH).

Analytical data. Calculated for $C_{32}H_{47}O_{15}NSi$: C, 53.85; H, 6.64; N, 1.96. Found: C, 53.94; H, 6.44; N, 2.06.

2-(Trimethylsilyl)ethyl O-(*methyl 5-acetamide-4,7-di*-O-*acetyl-3,5-dideoxy-β-L*-arabino-*2-heptulopyranosylonate*)-(*2 → 3*)-*2,4,6-tri*-O-*benzoyl-β-D-galactopyranoside* (**10**)

To a solution of **9** (330 mg, 0.46 mmol) in pyridine (12 ml) were added benzoic anhydride (420 mg) and 4-dimethylaminopyridine (60 mg), and the mixture was stirred for 12 h at room temperature; the course of the reaction was monitored by TLC. After completion of the reaction, methanol (1 ml) was added, the mixture was stirred for 30 min, concentrated and extracted with dichloromethane. The extract was successively washed with 2 M hydrochloric acid and water, dried (Na_2SO_4) and concentrated. Column chromatography (100:1 dichloromethane:methanol) of the residue on silica gel (60 g) gave **10** (328 mg, 77%) as an amorphous mass; $[\alpha]_D$ +3.6° (*c* 2.1, chloroform); IR (film) 3350 (NH), 1740 and 1230 (ester), 1650 and 1540 (amide), 860 and 840 (TMS), and 740 and 700 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) Gal unit δ 1.02 (m, 2H, $Me_3SiCH_2CH_2$), 4.46 (dd, 1H, $J_{5,6}$ 6.0, J_{gem} 11.4 Hz, H-6), 4.62 (dd, 1H, $J_{5,6'}$ 7.0 Hz, H-6′), 4.82 (d, 1H, $J_{1,2}$ 8.1 Hz, H-1), 5.54 (dd, 1H, $J_{2,3}$ 10.1 Hz, H-2), 5.67 (d, 1H, $J_{3,4}$ 3.3 Hz, H-4), 7.46–8.20 (m, 15H, 3Ph); Neu5Ac unit δ 1.70 (t, 1H, $J_{3ax,4} = J_{gem}$ = 12.6 Hz, H-3*ax*), 1.92 (s, 3H, AcN), 1.96 and 2.13 (2s, 6H, 2AcO), 2.36 (dd, 1H, $J_{3eq,4}$ 4.8 Hz, H-3*eq*), 3.72 (s, 3H, MeO), 4.12 (dd, 1H, $J_{6,7}$ 5.7, J_{gem} 10.1 Hz, H-7), 4.77 (dd, 1H, $J_{6,7'}$ 3.7 Hz, H-7′), and 4.94 (m, 1H, $J_{4,5}$ 12.1 Hz, H-4).

Analytical data. Calculated for $C_{46}H_{55}O_{17}NSi$: C, 59.92; H, 6.01; N, 1.52. Found: C, 60.10; H, 6.22; N, 1.55.

O-(*Methyl 5-acetamido-4,7-di*-O-*acetyl-3,5-dideoxy-β-L*-arabino-*2-heptulopyranosylonate*)-(*2 → 3*)-*1*-O-*acetyl-2,4,6-tri*-O-*benzoyl-β-D-galactopyranose* (**11**)

To a solution of **10** (259 mg, 0.28 mmol) in toluene (3 ml) and acetic anhydride (0.4 ml) was added boron trifluoride etherate (31 µl), and the mixture was stirred for 3 h at room temperature. Dichloromethane (50 ml) was added and the mixture was washed with 1 M sodium carbonate, dried (Na_2SO_4) and concentrated. Column chromatography (80:1 dichloromethane:methanol) of the residue on silica gel (60 g) gave **11** (230 mg, 95%) as an amorphous mass; $[\alpha]_D$ +2.6° (*c* 1.1, chloroform); IR (film) 3400 (NH), 1740 and 1230 (ester), 1680 and 1550 (amide), and 720 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) Gal unit δ 4.35 (broad t, 1H, $J_{5,6}$ 5.8, $J_{5,6'}$ 6.8 Hz, H-5), 4.44 (dd, 1H, J_{gem} 11.4 Hz, H-6), 4.59 (dd, 1H, H-6′), 5.67 (t, 1H, $J_{1,2} = J_{2,3}$ = 8.2 Hz, H-2), 5.70 (d, 1H, $J_{3,4}$ 2.2 Hz, H-4), 6.08 (d, 1H, H-1), 7.45–8.18 (m, 15H, 3Ph); Neu5Ac unit δ 1.67 (t, 1H, $J_{3ax,4} = J_{gem}$ = 12.5 Hz, H-3*ax*), 1.91 (s, 3H, AcN), 2.41 (dd, 1H, $J_{3eq,4}$ 4.9 Hz, H-3*eq*), 3.61 (q, 1H, $J_{4,5} = J_{5,6} = J_{5,NH}$ = 10.4 Hz, H-5), 4.92 (m, 1H, H-4); *O*-acetyl groups δ 1.97, 2.14, 2.16 (3s, 9H, 3AcO).

Analytical data. Calculated for $C_{43}H_{45}O_{18}N$: C, 59.79; H, 5.25; N, 1.62. Found: C, 59.86; H, 5.51; N, 1.66.

Methyl O-(*methyl 5-acetamido-4,7-di*-O-*acetyl-3,5-dideoxy-β-L*-arabino-*2-heptulopyranosylonate*)-(*2 → 3*)-*2,4,6-tri*-O-*benzoyl-1-thio-β-D-galactopyranoside* (**12**)

To a solution of **11** (229 mg, 0.27 mmol) in dichloromethane (3 ml) were added, with stirring, methylthiotrimethylsilane (94 µl) and boron trifluoride etherate (33 µl), and the mixture was stirred for 4 h at room temperature. Dichloromethane (50 ml) was added and the mixture was washed with 1 M sodium carbonate, dried (Na_2SO_4) and concentrated. Column chromatography (80:1 dichloromethane:methanol) of the residue on silica gel (50 g) gave **12** (226 mg, 91%) as an amorphous mass; $[\alpha]_D$ +12.5° (*c* 0.8, chloroform); IR (film) 3400 (NH), 1750 and 1230 (ester), 1680 and 1550 (amide), and 720 cm^{-1} (Ph); ^{1}H-NMR Gal unit δ 2.37 (s, 3H, SMe), 4.26 (dd, 1H, $J_{5,6}$ 5.9, $J_{5,6'}$ 6.7 Hz, H-5), 4.41 (dd,

1H, J_{gem} 11.3 Hz, H-6), 4.62 (dd, 1H, H-6'), 4.76 (d, 1H, $J_{1,2}$ 9.8 Hz, H-1), 5.65 (t, 1H, $J_{2,3}$ 9.8 Hz, H-2), 5.74 (d, 1H, $J_{3,4}$ 3.1 Hz, H-4), 7.45–8.21 (m, 15H, 3Ph); Neu5Ac unit δ 1.69 (t, 1H, $J_{3ax,4} = J_{gem} = 12.5$ Hz, H-3*ax*), 1.91 (s, 3H, AcN) 1.96, 2.13 (2s, 6H, 2AcO), 2.38 (dd, 1H, $J_{3eq,4}$ 4.8 Hz, H-3*eq*), 3.71 (s, 3H, MeO), 4.95 (m, 1H, $J_{4,5}$ 11.5 Hz, H-4).

Analytical data. Calculated for $C_{42}H_{45}O_{16}NS$: C, 59.22; H, 5.32; N, 1.64. Found: C, 59.25; H, 5.55; N, 1.75.

2-(Trimethylsilyl)ethyl O-(*methyl 5-acetamido-4,7,8-tri*-O-*acetyl-3,5-dideoxy-α-D*-galacto-*2-octulopyranosylonate*)-(*2 → 3*)-*6*-O-*benzoyl-β-D-galactopyranoside* (**13**)

Glycosylation of **8** (900 mg, 2.34 mmol) with **6** (2 g, 3.91 mmol), as described for the synthesis of **9**, gave **13** (828 mg, 45%) as an amorphous mass; $[\alpha]_D$ − 9.1°; (*c* 0.9, chloroform); IR (film) 3400 (OH, NH), 1740 and 1230 (ester), 1660 and 1550 (amide), 860 and 840 (TMS), and 720 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) Gal unit δ 1.05 (m, 2H, $Me_3SiCH_2CH_2$), 3.66 (m, 1H, $Me_3SiCH_2CH_2$), 3.97 (m, 1H, $Me_3SiCH_2CH_2$), 4.45 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1), and 7.41–8.05 (m, 5H, Ph); Neu5Ac unit δ 1.90, 2.05 and 2.09 (3s, 12H, 3AcO and AcN), 2.14 (t, 1H, $J_{3ax,4} = J_{gem} = 13.4$ Hz, H-3*ax*), 2.72 (dd, 1H, $J_{3eq,4}$ 4.7 Hz, H-3*eq*), 3.80 (s, 3H, MeO), 4.15 (q, 1H, $J_{4,5} = J_{5,6} = J_{5,NH} = 10.4$ Hz, H-5), 4.55 (dd, 1H, $J_{7,8}$ 5.7, J_{gem} 13.2 Hz, H-8), 4.98 (ddd, 1H, H-4), 5.22 (m, 1H, H-7) and 5.60 (d, 1H, NH).

Analytical data. Calculated for $C_{35}H_{51}O_{17}NSi$: C, 53.49; H, 6.54; N, 1.78. Found: C, 53.62; H, 6.49; N, 1.68.

2-(Trimethylsilyl)ethyl O-(*methyl 5-acetamido-4,7,8-tri*-O-*acetyl-3,5-dideoxy-α-D*-galacto-*2-octulopyranosylonate*)-(*2 → 3*)-*2,4,6-tri*-O-*benzoyl-β-D-galactopyranoside* (**14**)

To a solution of **13** (1.2 g, 1.53 mmol) in pyridine (35 ml) was added benzoic anhydride (10 g), and the mixture was stirred for 7 days at 45 °C; the course of the reaction was monitored by TLC. After completion of the reaction, methanol (10 ml) was added, the mixture was stirred for 30 min, concentrated, and extracted with dichloromethane. The extract was successively washed with 2 M hydrochloric acid and water, dried (Na_2SO_4) and concentrated. Column chromatography (3:2 ethyl acetate:hexane) of the residue on silica gel (200 g) gave **14** (1.2 g, 82%) as an amorphous mass: $[\alpha]_D$ + 22.5° (*c* 0.8, chloroform); IR (film) 3400 (NH), 1740 and 1230 (ester), 1680 and 1540 (amide), 860 and 840 (TMS), and 710 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) Gal unit δ 1.00 (m, 2H, $Me_3SiCH_2CH_2$), 3.64 (dd, 1H, H-3), 3.74 (m, 1H, $Me_3SiCH_2CH_2$), 4.11 (m, 1H, $Me_3SiCH_2CH_2$), 4.43 (dd, 1H, $J_{5,6}$ 6.4, J_{gem} 11.2 Hz, H-6), 4.66 (dd, 1H, $J_{5,6'}$ 6.8 Hz, H-6'), 4.87 (d, 1H, $J_{1,2}$ 8.1 Hz, H-1), 5.57 (dd, 1H, $J_{2,3}$ 10.1 Hz, H-2), 5.67 (d, 1H, $J_{3,4}$ 3.3 Hz, H-4) and 7.49–8.22 (m, 15H, 3Ph); Neu5Ac unit δ 1.77, 1.89, 2.01 and 2.16 (4s, 12H, 3AcO and AcN), 1.93 (t, 1H, $J_{3ax,4} = J_{gem} = 13.0$ Hz, H-3*ax*), 2.40 (dd, 1H, $J_{3eq,4}$ 4.9 Hz, H-3*eq*), 3.75 (s, 3H, MeO), 4.76 (dd, 1H, $J_{7,8}$ 3.3, J_{gem} 10.3 Hz, H-8), 4.96 (ddd, 1H, $J_{4,5}$ 9.9 Hz, H-4), 5.25 (m, 1H, H-7) and 5.43 (d, 1H, $J_{5,NH}$ 9.9 Hz, NH).

Analytical data. Calculated for $C_{49}H_{59}O_{19}NSi$: C, 59.20; H, 5.98; N, 1.41. Found: C, 59.44; H, 6.04; N, 1.37.

O-(*Methyl 5-acetamido-4,7,8-tri*-O-*acetyl-3,5-dideoxy-α-D*-galacto-*2-octulopyranosylonate*)-(*2 → 3*)-*1*-O-*acetyl-2,4,6-tri*-O-*benzoyl-β-D-galactopyranose* (**15**)

To a solution of **14** (971 mg, 0.98 mmol) in toluene (10 ml) and acetic anhydride (1.4 ml) was added boron trifluoride etherate (0.22 ml), and the mixture was stirred for 3 h at room temperature. Dichloromethane (30 ml) was added and the solution was washed with 1 M sodium carbonate, dried (Na_2SO_4) and concentrated. Column chromatography (2:1 ethyl acetate:hexane) of the residue on silica gel (100 g) gave **15** (912 mg, quantitative) as an amorphous mass; $[\alpha]_D$ + 35.5° (*c* 0.9, chloroform); IR (film) 3300 (NH), 1740 and 1230 (ester), 1680 and 1540 (amide), and 710 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) Gal unit δ 3.55 (dd, 1H, $J_{2,3}$ 10.3, $J_{3,4}$ 2.4 Hz, H-3), 4.73 (dd, 1H, $J_{5,6}$ 6.5, J_{gem} 11.8 Hz, H-6), 5.62 (dd, 1H, $J_{1,2}$ 8.3 Hz, H-2), 5.64 (d, 1H, H-4), 6.05 (d, 1H, H-1) and 7.40–8.12 (m, 15H, 3Ph); Neu5Ac unit δ 2.35 (dd, 1H, $J_{3eq,4}$ 4.9, J_{gem} 12.7 Hz, H-3*eq*), 3.69 (s, 3H, MeO), 4.02 (q, 1H, $J_{4,5} = J_{5,6} = J_{5,NH} = 10.1$ Hz, H-5), 4.87 (ddd, 1H, H-4), 5.18 (m, 1H, H-7) and 5.35 (d, 1H, NH); *O*-acetyl and *N*-acetyl groups δ 1.70, 1.80, 1.91, 2.04 and 2.09 (5s, 15H, 4AcO and AcN).

Analytical data. Calculated for $C_{46}H_{49}O_{20}N$: C, 59.04; H, 5.28; N, 1.45. Found: C, 59,25; H, 5.16; N, 1.68.

Methyl O-(*methyl 5-acetamido-4,7,8-tri*-O-*acetyl-3,5-dideoxy-α-D*-galacto-*2-octulopyranosylonate*)-(*2 → 3*)-*2,4,6-tri*-O-*benzoyl-1-thio-β-D-galactopyranoside* (**16**)

To a solution of **15** (912 mg, 0.97 mmol) in dichloromethane (7 ml) were added, with stirring, methylthiotrimethylsilane (0.34 ml) and boron trifluoride etherate (0.24 ml), and the mixture was stirred for 3 h at room temperature. The solution was washed with 1 M sodium carbonate, dried (Na_2SO_4) and concentrated. Column chromatography (3:2 ethyl acetate:hexane) of the residue on silica gel (100 g) gave **16** (828 mg, 92%) as an amorphous mass; $[\alpha]_D$ + 25.0° (*c* 1.1, chloroform); IR (film) 3300 (NH), 1740 and 1230 (ester), 1670 and 1550 (amide), and 710 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) Gal unit δ 3.57 (dd, 1H, $J_{2,3}$ 10.3, $J_{3,4}$ 3.1 Hz, H-3), 4.31 (dd, 1H, $J_{5,6}$ 6.5 Hz, J_{gem} 11.2 Hz, H-6), 4.56 (dd, 1H, $J_{5,6'}$ 6.3 Hz, H-6'), 4.72 (d, 1H, $J_{1,2}$ 9.7 Hz, H-1), 5.59 (dd, 1H, $J_{2,3}$ 10.3 Hz, H-2), 5.64 (d, 1H, H-4), and 7.40–8.14 (m, 15H, 3Ph); Neu5Ac unit δ 1.70, 1.80, 1.92 and 2.07 (4s, 12H, 3AcO and AcN), 2.28 (s, 3H, MeS), 3.43 (dd, 1H, $J_{3eq,4}$ 4.9, J_{gem} 12.3 Hz, H-3*eq*), 3.68 (s, 3H, MeO), 4.86 (ddd, 1H, $J_{4,5}$ 10.1 Hz, H-4), 5.18 (m, 1H, H-7) and 5.42 (d, 1H $J_{5,NH}$ 10.1 Hz, NH).

Analytical data. Calculated for $C_{45}H_{49}O_{18}NS$: C, 58.50; H, 5.35; N, 1.52. Found: C, 58.23; H, 5.05; N, 1.47.

2-(Trimethylsilyl)ethyl O-(*methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-*L*-*glycero*-β-*D*-galacto-2-nonulopyranosylonate*)-(*2 → 3*)-*6*-O-*benzoyl*-β-*D*-*galactopyranoside* (**17**)

Glycosylation of **8** (1.6 g, 4.08 mmol) with methyl (methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-2-thio-L-*glycero*-β-D-*galacto*-2-nonulopyranosid)onate (**7**; 3.6 g, 6.81 mmol) as described for the synthesis of **9**, gave **17** (1.4 g, 41%) as an amorphous mass; $[\alpha]_D$ −14.0° (*c* 1.3, chloroform); IR (film) 3400 (OH, NH), 1740 and 1230 (ester), 1680 and 1540 (amide), 860 and 840 (TMS) and 710 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) Gal unit δ 1.04 (m, 2H, $Me_3SiCH_2CH_2$), 3.65 (m, 1H, $Me_3SiCH_2CH_2$), 3.88 (m, 1H, $Me_3SiCH_2CH_2$), 4.43 (d, 1H, $J_{1,2}$ 7.5 Hz, H-1), and 7.41–8.05 (m, 5H, Ph); Neu5Ac unit δ 1.90, 2.04, 2.05, 2.06 and 2.11 (5s, 15H, 4AcO and AcN), 2.09 (t, 1H, $J_{3ax,4} = J_{gem}$ = 13.4 Hz, H-3*ax*), 2.75 (dd, 1H, $J_{3eq,4}$ 4.4 Hz, H-3*eq*), 3.83 (s, 3H, MeO), 3.98 (q, 1H, $J_{4,5} = J_{5,6} = J_{5,NH}$ = 9.9 Hz, H-5), 5.09 (ddd, 1H, H-4), 5.25 (m, 1H, H-7), 5.43 (m, 1H, H-8) and 5.72 (d, 1H, NH).

Analytical data. Calculated for $C_{38}H_{55}O_{19}N$: C, 53.20; H, 6.46; N, 1.63. Found: C, 53.18; H, 6.55; N, 1.47.

2-(Trimethylsilyl)ethyl O-(*methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-*L*-glycero-β-*D*-galacto-2-nonulopyranosylonate*)-(*2 → 3*)-*2,4,6-tri*-O-*benzoyl*-β-*D*-*galactopyranoside* (**18**)

To a solution of **17** (690 mg, 0.80 mmol) in pyridine (20 ml) was added benzoic anhydride (6 g), and the mixture was stirred for 7 days at 45 °C; the course of the reaction was monitored by TLC. After completion of the reaction, methanol (5 ml) was added, the mixture was stirred for 30 min, concentrated, and extracted with dichloromethane. The extract was successively washed with 2 M hydrochloric acid and water, dried (Na_2SO_4) and concentrated. Column chromatography (2:1 ethyl acetate:hexane) of the residue on silica gel (80 g) gave **18** (620 mg, 72%) as an amorphous mass; $[\alpha]_D$ − 9.0° (c 0.8, chloroform); IR (film) 3350 (NH), 1740 and 1230 (ester), 1680 and 1540 (amide), 860 and 840 (TMS) and 710 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) Gal unit δ 0.99 (m, 2H, $Me_3SiCH_2CH_2$), 3.76 (m, 1H, $Me_3SiCH_2CH_2$), 4.09 (m, 1H, $Me_3SiCH_2CH_2$), 4.50 (dd, 1H, $J_{5,6}$ 5.6, J_{gem} 11.3 Hz, H-6), 4.99 (d, 1H, $J_{1,2}$ 8.1 Hz, H-1), 5.59 (dd, 1H, $J_{2,3}$ 10.3 Hz, H-2), 5.69 (d, 1H, $J_{3,4}$ 3.1 Hz, H-4) and 7.46–8.28 (m, 15H, 3Ph); Neu5Ac unit δ 1.63, 1.89, 2.01, 2.15 and 2.19 (5s, 15H, 4AcO and AcN), 2.13 (t, 1H, $J_{3ax,4} = J_{gem}$ = 13.0 Hz, H-3*ax*), 2.49 (dd, 1H, $J_{3eq,4}$ 4.6 Hz, H-3*eq*), 3.87 (s, 3H, MeO), 4.76 (m, 1H, H-8), 4.99 (m, 1H, $J_{4,5}$ 10.3 Hz, H-4), 5.28 (dd, 1H, H-7) and 5.27 (d, 1H, $J_{5,NH}$ 10.3 Hz, NH).

Analytical data. Calculated for $C_{52}H_{63}O_{21}NSi$: C, 58.58; H, 5.96; N, 1.31. Found: C, 58.32; H, 6.12; N, 1.46.

O-(*Methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-*L*-glycero-β-*D*-galacto-2-nonulopyranosylonate*)-(*2 → 3*)-1-O-*acetyl-2,4,6-tri*-O-*benzoyl*-β-*D*-*galactropyranose* (**19**)

To a solution of **18** (621 mg, 0.58 mmol) in toluene (6.5 ml) and acetic anhydride (0.8 ml) was added boron trifluoride etherate (0.13 ml), and the mixture was stirred for 3 h at room temperature. Dichloromethane (50 ml) was added and the solution was washed with 1 M sodium carbonate, dried (Na_2SO_4) and concentrated. Column chromatography (3:2 ethyl acetate:hexane) of the residue on silica gel (60 g) gave **19** (502 mg, 86%) as an amorphous mass; $[\alpha]_D$ +4.6° (*c* 1.1, chloroform); IR (film) 3350 (NH), 1740 and 1230 (ester), 1680 and 1540 (amide) and 710 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) Gal unit δ 3.69 (dd, 1H, $J_{2,3}$ 10.0, $J_{3,4}$ 2.9 Hz, H-3), 5.64 (dd, 1H, $J_{1,2}$ 8.4 Hz, H-2), 5.66 (d, 1H, H-4), 6.21 (d, 1H, $J_{1,2}$ 8.4 Hz, H-1) and 7.27–8.13 (m, 15H, 3Ph); Neu5Ac unit δ 2.42 (dd, 1H, $J_{3eq,4}$ 4.6, J_{gem} 12.8 Hz, H-3*eq*), 3.79 (s, 3H, MeO), 3.88 (q, 1H, $J_{4,5} = J_{5,6} = J_{5,NH}$ = 10.5 Hz, H-5), 4.90 (ddd, 1H, H-4) and 4.99 (m, 1H, H-7); *O*-acetyl and *N*-acetyl groups δ 1.54, 1.79, 1.91, 2.00, 2.04 and 2.11 (6s, 18H, 5AcO and AcN).

Analytical data. Calculated for $C_{49}H_{53}O_{22}N$: C, 58.39; H, 5.30; N, 1.39. Found: C, 58.31; H, 5.48; N, 1.35.

Methyl O-(*methyl 5-acetamido-4,7,8,9-tetra-*O*-acetyl-3,5-dideoxy-*L*-glycero-β-*D*-galacto-2-nonulopyranosylonate*)-(*2 → 3*)-*2,4,6-tri*-O-*benzoyl-1-thio*-β-*D*-*galactopyranoside* (**20**)

To a solution of **19** (502 mg, 0.5 mmol) in dichloromethane (4 ml) were added, with stirring, methylthiotrimethylsilane (0.18 ml) and boron trifluoride etherate (0.12 ml), and the mixture was stirred for 3 h at room temperature. Dichloromethane (50 ml) was added and the solution was washed with 1 M sodium carbonate, dried (Na_2SO_4) and concentrated. Column chromatography (2:1 ethyl acetate:hexane) of the residue on silica gel (60 g) gave **20** (433 mg, 87%) as an amorphous mass; $[\alpha]_D$ − 3.1° (*c* 1.1, chloroform); IR (film) 3350 (NH), 1740 and 1230 (ester), 1680 and 1540 (amide) and 710 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) Gal unit δ 3.66 (dd, 1H, $J_{2,3}$ 11.2, $J_{3,4}$ 2.5 Hz, H-3), 4.72 (d, 1H, $J_{1,2}$ 9.9 Hz, H-1), 5.62 (dd, 1H, H-2), 5.64 (d, 1H, H-4) and 7.37–8.15 (m, 15H, 3Ph); Neu5Ac unit δ 1.53, 1.79, 1.91, 2.06 and 2.09 (5s, 15H, 4AcO and AcN), 2.27 (s, 3H, MeS), 2.43 (dd, 1H, $J_{3eq,4}$ 4.6, J_{gem} 12.7 Hz, H-3*eq*), 3.80 (s, 3H, MeO), 4.91 (ddd, 1H, H-4) and 4.96 (m, 1H, H-7).

Analytical data. Calculated for $C_{48}H_{53}O_{20}NS$: C, 57.84; H, 5.36; N, 1.41. Found: C, 58.07; H, 5.20; N, 1.27.

2-(Trimethylsilyl)ethyl O-(*methyl 5-acetamido-4,7-di-*O*-acetyl-3,5-dideoxy*-β-*L*-arabino-2-heptulopyranosylonate*)-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl*-β-*D*-*galactopyranosyl*)-(*1 → 4*)-O-[(*2,3,4-tri*-O-*benzyl*-α-*L*-*fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*benzyl-2-deoxy*-β-*D*-*glucopyranosyl*)-(*1 → 3*)-*2,4,6-tri*-O-*benzyl*-β-*D*-*galactopyranoside* (**22**)

To a solution of **21** (66 mg, 0.05 mmol) and **12** (67 mg, 0.08 mmol), in dichloromethane (1.5 ml) were added molecular sieves 4 Å (400 mg), and the mixture was stirred for 7 h at room temperature, then cooled to 0 °C. A mixture (160 mg; 50% DMTST by weight) was added, the mixture of DMTST and molecular sieves 4 Å was stirred for 48 h at 5 °C. The precipitate was filtered off, and washed with dichloromethane. The filtrate and washings were combined, and successively washed with 1 M sodium carbonate and water, dried (Na_2SO_4) and concentrated. Column chromatography (70:1 dichloromethane:methanol) of the residue on silica gel (30 g) gave **22** (45 mg, 42%) as an amorphous mass; $[\alpha]_D$ −41.6° (*c* 0.8, chloroform); IR film 3350 (NH), 1740 and 1260 (ester), 1660 and 1550 (amide), 860 and 840 (TMS), and 740 and 720 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) δ 0.99 (m, 2H, $Me_3SiCH_2CH_2$), 1.24 (d, 3H, $J_{5,6}$ 6.4 Hz, H-6e), 1.61, 1.90, 1.94, and 1.99 (4s, 12H, 2AcO and 2AcN), 2.32 (dd, 1H, $J_{3eq,4}$ 4.8, J_{gem} 12.8 Hz, H-3d-*eq*), 3.64 (s, 3H, MeO), 5.24 (d, 1H, $J_{3,4}$ 3.5Hz, H-4c), 5.40 (t, 1H, $J_{1,2} = J_{2,3}$ = 8.5 Hz, H-2c), 5.67 (d, 1H, NH) and 7.13–8.13 (m, 50H, 10Ph).

Analytical data. Calculated for $C_{115}H_{130}O_{31}N_2Si$: C, 66.91; H, 6.35; N 1.36. Found: C, 66.79; H, 6.48; N, 1.13.

2(Trimethylsilyl)ethyl O-(*methyl 5-acetamido-4,7-di*-O-*acetyl-3,5-dideoxy-β-L*-arabino-*2-heptulopyranosylonate*)-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*2,3,4-tri*-O-*acetyl-α-L-flucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*acetyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-*2,4,6-tri*-O-*acetyl-β-D-galactopyranoside* (**23**)

A solution of **22** (131 mg, 0.08 mmol) in ethanol (24 ml) and acetic acid (4 ml) was stirred with 10% Pd-C (130 mg) for 12 h at 45 °C under hydrogen. The catalyst was collected and washed with ethanol, the combined filtrate and washings were concentrated, and the residue was heated with acetic anhydride (2 ml) and pyridine (4 ml) for 12 h at 40 °C. The mixture was concentrated and extracted with dichloromethane, and the extract was successively washed with 2 M hydrochloric acid and water, dried (Na_2SO_4) and concentrated. Column chromatography (25:1 dichloromethane:methanol) of the residue on silica gel (30 g) gave **23** (94 mg, 86%) as an amorphous mass; $[\alpha]_D$ − 40.5° (*c* 0.5, chloroform); IR (film) 3400 (NH), 1750 and 1230 (ester), 1670 and 1550 (amide); 860 and 840 (TMS), and 720 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) δ 0.90 (m, 2H, $Me_3SiCH_2CH_2$), 1.27 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6e), 1.85 and 1.86 (2s, 6H, 2AcN), 1.91–2.11 (9s, 27H, 9AcO), 2.29 (dd, 1H, $J_{3eq,4}$ 5.1, J_{gem} 12.6 Hz, H-3d-*eq*), 3.64 (s, 3H, MeO) and 7.45–8.15 (m, 15H, 3Ph).

Analytical data. Calculated for $C_{80}H_{102}O_{38}N_2Si$: C, 55.61; H, 5.95; N, 1.62. Found: C, 55.49; H, 6.08; N, 1.39.

O-(*Methyl 5-acetamido-4,7-di*-O-*acetyl-3,5-dideoxy-β-L*-arabino-*2-heptulopyranosylonate*)-(*2 → 3*)-O-(*2,4,6*-tri-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*2,3,4-tri*-O-*acetyl-α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*acetyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-*2,4,6-tri*-O-*acetyl-D-galactopyranose* (**24**)

To a solution of **23** (80 mg, 0.05 mmol) in dichloromethane (0.3 ml) was added trifluoroacetic acid (0.6 ml); the mixture was stirred for 30 min at room temperature and concentrated. Column chromatography (20:1 dichloromethane:methanol) of the residue on silica gel (20 g) gave **24** (66 mg, 88%) as an amorphous mass; IR (film) 3500 (OH), 3400 (NH), 1750 and 1240 (ester), 1680 and 1550 (amide), and 720 cm^{-1} (Ph).

Analytical data. Calculated for $C_{75}H_{90}O_{38}N_2$: C, 55.35; H, 5.57; N, 1.72. Found: C, 55.57; H, 5.31; N, 1.98.

O-(*Methyl 5-acetamido-4,7-di*-O-*acetyl-3,5-dideoxy-β-L*-arabino-*2-heptulopyranosylonate*)-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*2,3,4*-tri-O-*acetyl-α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*acetyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-*2,4,6-tri*-O-*acetyl-α-D-galactopyranosyl trichloroacetimidate* (**25**)

To a solution of **24** (66 mg, 0.04 mmol) in dichloromethane (1 ml) and trichloroacetonitrile (162 µl) DBU (7 mg) was added at −5 °C, and the mixture was stirred for 2 h at 0 °C, then concentrated. Column chromatography (20:1 dichloromethane:methanol) of the residue on silica gel (20 g) gave **25** (69 mg, 96%) as an amorphous mass; $[\alpha]_D$ − 10.1° (*c* 0.4, chloroform); IR (film) 3300 (NH), 1750 and 1240 (ester), 1680 and 1550 (amide), and 720 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) δ 1.25 (d, 3H, $J_{5,6}$ 6.4 Hz, H-6e), 1.83–2.13 (11s, 33H, 9AcO and 2AcN), 2.27 (dd, 1H, $J_{3eq,4}$ 5.7, J_{gem} 12.8 Hz, H-3d-*eq*), 3.53 (q, 1H, $J_{4,5} = J_{5,6} = J_{5,NH}$ = 10.4 Hz, H-5d), 3.62 (s, 3H, MeO), 6.48 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1a), 7.44–8.14 (m, 15H, 3Ph) and 8.61 (s, 1H, C=NH).

Analytical data. Calculated for $C_{77}H_{90}O_{38}N_3Cl_3$: C, 52.19; H, 5.12; N, 2.37. Found: C, 52.29; H, 5.06; N, 2.64.

2-(Trimethylsilyl)ethyl O-(*methyl 5-acetamido-4,7,8-tri*-O-*acetyl-3,5-dideoxy-α-D*-galacto-*2-octulopyranosylonate*)-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-(*2,3,4-tri*-O-*benzyl-α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*benzyl-2-deoxy-β-D-galactopyranoside* (**26**)

To a solution of **21** (273 mg, 0.22 mmol) and **16** (300 mg, 0.32 mmol) in dichloromethane (4 ml) 4 Å molecular sieves (600 mg) were added, and the mixture was stirred for 7 h at room temperature, then cooled to 0 °C. A mixture of DMTST and molecular sieves (4 Å) (320 mg; 70% DMTST by weight) was added, and the resultant mixture was stirred for 48 h at 5 °C. The precipitate was filtered off, and washed with dichloromethane. The filtrate and washings were combined and successively, washed with 1 M sodium carbonate and water, dried (Na_2SO_4) and concentrated.

Column chromatography (4:1 ethyl acetate:hexane) of the residue on silica gel (50 g) gave **26** (245 mg, 53%) as an amorphous mass; $[\alpha]_D - 31.5°$ (*c* 1.0, chloroform); IR (film) 3400 (NH), 1740 and 1230 (ester), 1660 and 1540 (amide), 860 and 840 (TMS), and 710 cm^{-1} (Ph); ^{1}H-NMR data $CDCl_3$) δ 0.99 (m, 2H, $Me_3SiCH_2CH_2$), 1.24 (d, 3H, $J_{5,6}$ 6.2 Hz, H-6e), 1.61, 1.80, 1.84, 1.95 and 2.06 (5s, 15H, 3AcO and 2AcN), 2.26 (dd, 1H, $J_{3eq,4}$ 5.2, J_{gem} 12.8 Hz, H-3d-*eq*), 3.52 (s, 3H, MeO), 4.92 (m, 1H, H-4d), 5.23 (d, 1H, H-4c), 5.45 (t, 1H, $J_{1,2} = J_{2,3} = 9.3$ Hz, H-2c) and 7.14–8.12 (m, 50H, 10Ph).

Analytical data. Calculated for $C_{118}H_{134}O_{33}N_2Si$: C, 66.34; H, 6.32; N, 1.31. Found: C, 66.35; H, 6.33; N, 1.45.

2-(Trimethylsilyl)ethyl O-(*methyl 5-acetamido-4,7,8-tri*-O-*acetyl-3,5-dideoxy-α-D*-galacto-*2-octulopyranosylonate*)-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-(*2,3,4-tri*-O-*acetyl-α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*acetyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-*2,4,6-tri*-O-*acetyl-β-D-galactopyranoside* (**27**)

A solution of **26** (402 mg, 0.19 mmol) in ethanol (60 ml) and acetic acid (10 ml) was stirred with 10% Pd-C (480 mg) for 72 h at 45 °C under hydrogen. The catalyst was collected and washed with ethanol, the combined filtrate and washings were concentrated, and the residue was heated with acetic anhydride (5 ml) and pyridine (10 ml) for 14 h at 40 °C. The mixture was concentrated and extracted with dichloromethane, and the extract was successively washed with 2 M hydrochloric acid and water, dried (Na_2SO_4) and concentrated. Column chromatography (3:1 ethel acetate: hexane) of the residue on silica gel (50 g) gave **27** (294 mg, 87%) as an amorphous mass; $[\alpha]_D - 32.5°$ (*c* 1.6, chloroform); IR (film) 3400 (NH), 1740 and 1225 (ester), 1680 and 1540 (amide), 860 and 840 (TMS), and 710 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) δ 0.91 (m, 2H, $Me_3SiCH_2CH_2$), 1.27 (d, 3H, $J_{5,6}$ 6.1 Hz, H-6e), 1.80–2.11 (11s, 36H, 10AcO and 2AcN), 2.27 (dd, 1H, H-3d-*eq*), 3.58 (s, 3H, MeO), and 7.47–8.14 (m, 15H, 3Ph).

Analytical data. Calculated for $C_{83}H_{106}O_{40}N_2Si$: C, 55.39; H, 5.94; N, 1.56. Found: C, 55.32; H, 6.15; N, 1.82.

O-(*Methyl 5-acetamido-4,7,8-tri*-O-*acetyl-3,5-dideoxy-α-D*-galacto-*2-octulopyranosylonate*)-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-(*2,3,4-tri*-O-*acetyl-α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*acetyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-*2,4,6-tri*-O-*acetyl-D-galactopyranose* (**28**)

To a solution of **27** (213 mg, 0.12 mmol) in dichloromethane (2.5 ml) trifluoroacetic acid (1.8 ml) was added; the mixture was stirred for 1 h at room temperature and concentrated. Column chromatography (4:1 ethyl acetate:hexane) of the residue on silica gel (30 g) gave **28** (200 mg, quantitative) as an amorphous mass; IR (film) 3500 (OH), 3400 (NH), 1740 and 1230 (ester), 1660 and 1550 (amide), and 710 cm^{-1} (Ph).

Analytical data. Calculated for $C_{78}H_{94}O_{40}N_2$: C, 55.12; H, 5.78; N. 1.65. Found: C, 54.96; H, 5.52; N, 1.42.

O-(*Methyl 5-acetamido-4,7,8-tri*-O-*acetyl-3,5-dideoxy-α-D*-galacto-*2-octulpyranosylonate*)-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*2,3,4-tri*-O-*acetyl-α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*acetyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-*2,4,6-tri*-O-*acetyl-α-D-galactopyranosyl trichloroacetimidate* (**29**)

To a solution of **28** (205 mg, 0.12 mmol) in dichloromethane (3 ml) and trichloroacetonitrile (0.8 ml) was added DBU (19 mg) at −5 °C, and the mixture was stirred for 4 h at 0 °C, then concentrated. Column chromatography (30:1 dichloromethane:methanol) of the residue on silica gel (30 g) gave **29** (183 mg, 82%) as an amorphous mass; $[\alpha]_D - 3.3°$ (*c* 1.1, chloroform); IR (film) 3400 (NH), 1740 and 1230 (ester), 1680 and 1540 (amide), and 710 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) δ 1.25 (d, 3H, $J_{5,6}$ 6.1 Hz, H-6e), 1.80–2.12 (9s, 36H, 10AcO and 2AcN), 2.27 (dd, 1H, H-3d-*eq*), 3.59 (s, 3H, MeO), 5.60 (d, 1H, $J_{3,4}$ 3.5 Hz, H-4c), 6.49 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1a), 7.44–8.14 (m, 15H, 3Ph) and 8.62 (s, 1H, C=NH).

Analytical data. Calculated for $C_{80}H_{94}O_{40}N_3Cl_3$: C, 52.11; H, 5.14; N, 2.28. Found: C, 51.85; H, 4.95; N, 2.13.

2-(Trimethylsilyl)ethyl O-(*methyl 5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy-L*-glycero-*β-D*-galacto-*2-nonulopyranosylonate*)-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*2,3,4-tri*-O-*benzyl-α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*benzoyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-*2,4,6-tri*-O-*benzyl-β-D-galactopyranoside* (**30**)

To a solution of **21** (127 mg, 0.1 mmol) and **20** (200 mg, 0.2 mmol) in dichloromethane (3 ml) were added molecular sieves 4 Å (400 mg), and the mixture was stirred for 7 h at room temperature, then cooled to 0 °C. A mixture of DMTST and molecular sieves 4 Å (210 mg; 50% DMTST by weight) was added to the mixture, and the resultant mixture was stirred for 72 h at 5 °C. The precipitate was filtered off and washed with dichloromethane. The filtrate and washings were combined, and successively washed with 1 M sodium carbonate and water, dried (Na_2SO_4) and concentrated. Column chromatography (4:1 ethyl acetate: hexane) of the residue on silica gel (25 g) gave **30** (109 mg, 49%) as an amorphous mass; $[\alpha]_D - 39.0°$ (*c* 1.2, chloroform); IR (film) 3400 (NH), 1740 and 1230 (ester), 1680 and 1540 (amide), 860 and 840 (TMS), and 710 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) δ 0.95 (m, 2H, $Me_3SiCH_2CH_2$), 1.21 (d, 3H, $J_{5,6}$ 6.4 Hz, H-6e), 1.59, 1.62, 1.83, 1.93, 2.03 and 2.07 (6s, 18H, 4AcO and 2AcN), 2.34 (dd, 1H, H-3d-*eq*), 3.66 (s, 3H, MeO), 5.47 (t, 1H, $J_{1,2} = J_{2,3} = 9.3$ Hz, H-2c), 5.55 (d, 1H, H-4c), 5.72 (m, 1H, H-8d) and 7.16–8.14 (m, 50H, 10Ph).

Analytical data. Calculated for $C_{121}H_{138}O_{35}N_2Si$: C, 65.81; H, 6.30; N, 1.27. Found: C, 66.00; H, 6.38; N, 1.16.

2-(Trimethylsilyl)ethyl O-(*methyl 5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy-L*-glycero-*β-D*-galacto-*2-nonulopyranosylonate*)-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*2,3,4-tri*-O-*acetyl-α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*acetyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-*2,4,6-tri*-O-*acetyl-β-D-galactopyranoside* (**31**)

A solution of **30** (230 mg, 0.1 mmol) in ethanol (35 ml) and acetic acid (6 ml) was stirred with 10% Pd-C (280 mg) for 72 h at 45 °C under hydrogen. The catalyst was collected and washed with ethanol, the combined filtrate and washings were concentrated, and the residue was heated with acetic anhydride (3 ml) and pyridine (6 ml) for 14 h at 40 °C. The mixture was concentrated, extracted with dichloromethane, and this was successively washed with 2 M hydrochloric acid and water, dried (Na_2SO_4) and concentrated. Column chromatography (3:1 ethyl acetate:hexane) of the residue on silica gel (30 g) gave **31** (162 mg, 83%) as an amorphous mass; $[\alpha]_D$ − 42.0° (*c* 1.2, chloroform); IR (film) 3350 (NH), 1740 and 1230 (ester), 1680 and 1540 (amide), 860 and 840 (TMS), and 710 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) δ 0.93 (m, 2H, $Me_3SiCH_2CH_2$), 1.24 (d, 3H, $J_{5,6}$ 6.4 Hz, H-6e), 1.80–2.12 (11s, 39H, 11AcO and 2AcN), 2.35 (dd, 1H, H-3d-*eq*), 3.74 (s, 3H, MeO), 5.58 (d, 1H, $J_{3,4}$ 3.1 Hz, H-4c), 5.66 (m, 1H, H-8d) and 7.41–8.17 (m, 15H, 3Ph).

Analytical data. Calculated for $C_{86}H_{110}O_{42}N_2Si$: C, 55.18; H, 5.92; N 1.50, Found: C, 55.18; H, 5.78; N, 1.38.

O-(*Methyl 5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy-L*-glycero-*β-D*-galacto-*2-nonulopyranosylonate*)-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*2,3,4-tri*-O-*acetyl-α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*acetyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-*2,4,6-tri*-O-*acetyl-D-galactopyranose* (**32**)

To a solution of **31** (110 mg, 0.06 mmol) in dichloromethane (1.3 ml) was added trifluoroacetic acid (1.5 ml), the mixture was stirred for 1.5 h at room temperature and concentrated. Column chromatography (4:1 ethyl acetate:hexane) of the residue on silica gel (20 g) gave **32** (104 mg, quantitative) as an amorphous mass; IR (film) 3500 (OH), 3400 (NH), 1740 and 1225 (ester), 1660 and 1540 (amide), and 710 cm^{-1} (Ph).

Analytical data. Calculated for $C_{81}H_{98}O_{42}N_2$: C, 54.91; H, 5.58; N, 1.58. Found: C, 54.66; H, 5.60; N, 1.38.

O-(*Methyl 5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy-L*-glycero-*β-D*-galacto-*2-nonulopyranosylonate*)-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranonsyl*)-(*1 → 4*)-O-[(*2,3,4-tri*-O-*acetyl-α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*acetyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-*2,4,6-tri*-O-*acetyl-α-D-galactopyranosyl trichloroacetimidate* (**33**)

To a solution of **32** (104 mg, 0.06 mmol) in dichloromethane (2 ml) and trichloroacetonitrile (0.19 ml) was added DBU (10 mg) at −5 °C, and the mixture was stirred for 1 h at 0 °C, then concentrated. Column chromatography (30:1 dichloromethane:methanol) of the residue on silica gel (30 g) gave **33** (100 mg, 89%) as an amorphous mass; $[\alpha]_D$ − 15.1° (*c* 2.0, chloroform); IR (film) 3400 (NH), 1740 and 1230 (ester), 1680 and 1540 (amide), and 710 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) δ 1.23 (d, 3H, $J_{5,6}$ 6.6 Hz, H-6c), 1.78–2.15 (12s, 39H, 11AcO and 2AcN), 2.36 (dd, 1H, $J_{3eq,4}$ 4.3, J_{gem} 12.6 Hz, H-3d-*eq*), 3.73 (s, 3H, MeO), 6.49 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1a), 7.40–8.16 (m, 15H, 3Ph) and 8.63 (s, 1H, C=NH).

Analytical data. Calculated for $C_{83}H_{98}O_{42}N_3Cl_3$: C, 52.03; H, 5.16; N, 2.19. Found: C, 52.04; H, 5.10; N, 2.43.

O-(*Methyl 5-acetamido-4,7-di*-O-*acetyl-3,5-dideoxy-β-L*-arabino-*2-heptulopyranosylonate*)-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*2,3,4-tri*-O-*acetyl-α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*acetyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-O-(*2,4,6-tri*-O-*acetyl-β-D-galactopyranosyl*)-(*1 → 1*)-(2S, 3R, 4E)-*2-azido-3*-O-*benzoyl-4-octadecene-1,3-diol* (**35**)

To a solution of **25** (69 mg, 0.04 mmol) and **34** (83 mg, 0.19 mmol) in dichloromethane (1 ml) were added molecular sieves 4 Å (type AW 300; 1 g) and the mixture was stirred for 2 h at room temperature, and then cooled to 0 °C. Boron trifluoride etherate (10 µl) was added to the mixture, and this was stirred for 3 h at 0 °C. The precipitate was filtered off and washed with dichloromethane. The filtrate and washings were combined, and successively washed with 1 M sodium carbonate and water, dried (Na_2SO_4) and concentrated. Column chromatography (20:1 dichloromethane: methanol) of the residue on silica gel (20 g) gave **35** (54 mg, 68%) as an amorphous mass; $[\alpha]_D$ − 48.2° (*c* 0.2, chloroform); IR (film) 3400 (NH), 3150-2800 (Me, methylene), 2150 (N_3), 1750 and 1240 (ester), 1680 and 1550 (amide), and 720 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) δ 0.88 (t, 3H, $MeCH_2$), 1.25 (s, 22H, $11CH_2$), 1.85–2.11 (11s, 33H, 9AcO and 2AcN), 2.28 (dd, 1H, $J_{3eq,4}$ 4.5, J_{gem} 12.4Hz, H-3d-*eq*), 3.63 (s, 3H, MeO), 5.90 (d, 1H, H-5 for sphingosine) 7.41–8.13 (m, 20H, 4Ph).

Analytical data. Calculated for $C_{100}H_{127}O_{40}N_5$: C, 58.90; H, 6.28; N, 3.43. Found: C, 58.99; H, 6.08; N, 3.53.

O-(*Methyl 5-acetamido-4,7-di*-O-*acetyl, 3,5-dideoxy-β-L*-arabino-*2-heptulopyranosylonate*)-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*2,3,4-tri*-O-*α-L-fucopyranosyl*-(*1 → 3*)]-O-(*2-acetamido-6*-O-*acetyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-O-(*2,4,6-tri*-O-*acetyl-β-D-galactopyranosyl*)-(*1 → 1*)-(2S, 3R, 4E)-*3*-O-*benzoyl-2-octadecanamido-4-octadecene-1,3-diol* (**36**)

Hydrogen sulfide was bubbled through a stirred solution of **35** (54 mg, 0.03 mmol) in pyridine (5 ml) and water (1 ml) for 48 h at 0 °C. The mixture was concentrated to give the

syrupy amine, which was used for the next reaction without further purification. To a solution of the amine in dichloromethane (1 ml) were added octadecanoic acid (22 mg) and 1-ethyl-3-(3-dimethylaminopropyl)carbodi-imide hydrochloride (WSC; 15 mg), and the mixture was stirred overnight at room temperature. After completion of the reaction, the solution was washed with water, dried (Na_2SO_4) and concentrated. Column chromatography (25:1 dichloromethane:methanol) of the residue on silica gel (20 g) gave **36** (38 mg, 62%) as an amorphous mass; $[\alpha]_D$ − 27.7° (*c* 0.2, chloroform); IR (film) 3350 (NH), 3150–2800 (Me, methylene), 1750 and 1230 (ester), 1660 and 1550 (amide), and 720 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) δ 0.88 (t, 6H, *2Me*CH_2), 1.26 (s, 52H, 26CH_2), 1.84–2.11 (10s, 33H, 9AcO and 2AcN), 2.28 (dd, 1H, $J_{3eq,4}$ 5.1, J_{gem} 13.4 Hz, H-3d-*eq*), 3.62 (s, 3H, MeO), 5.86 (m, 1H, H-5 for sphingosine), and 7.40–8.13 (m, 20H, 4Ph).

Analytical data. Calculated for $C_{118}H_{163}O_{41}N_3$: C, 62.17; H, 7.21; N, 1.84. Found: C. 62.35; H, 7.42; N, 1.87.

O-(*5-Acetamido-3,5-dideoxy-β-L*-arabino-*2-heptulopyranosylonic acid*)-(*2 → 3*)-(*β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-O-(*β-D-galactopyranosyl*)-(*1 → 1*)-(2S, 3R, 4E)-*2-octadecanamido-4-octadecene-1,3-diol* (**37**)

To a solution of **36** (38 mg, 0.02 mmol) in methanol (5 ml) was added sodium methoxide (20 mg) and the mixture was stirred for 12 h at 40 °C; the course of the reaction was monitored by TLC. Water (1 ml) was added to the mixture, and this was stirred for 12 h at 40 °C, neutralized with Amberlite IR-120 (H^+) resin and filtered. The resin was washed with methanol, and the combined filtrate and washings were concentrated. Column chromatography (5:4:0.7 chloroform:methanol:water) of the residue on Sephadex LH-20 (40 g) gave **37** (24 mg, quantitative) as an amorphous mass; $[\alpha]_D$ − 17.8° (*c* 0.6, 5:4:0.7 chloroform: methanol:water); IR (KBr) 3600–3400 (OH, NH), 2920 and 2850 (Me, methylene), 1710 (COOH), 1660 and 1550 cm^{-1} (amide); ^{1}H-NMR data (1:1 $CDCl_3$–CDO^2) δ 0.89 (t, 6H, *2Me*CH_2), 1.12 (d, 3H, $J_{5,6}$ 6.4 Hz, H-6e), 1.18 (s, 52H, 26CH_2), 1.91 and 1.93 (2s, 6H, 2AcN), 2.08 (t, 2H, CO*C*$H_2$$CH_2$), 2.65 (broad dd, 1H, H-3d-*eq*), 4.25 (d, 1H, $J_{1,2}$ 7.0 Hz, H-1a), 5.00 (broad d, 1H, H-1e), 5.35 (dd, 1H, $J_{3,4}$ 6.8, $J_{4,5}$ 15.0 Hz, H-4 for sphingosine) and 5.60 (dt, 1H, $J_{5,6} = J_{5,6'} = 7.7$ Hz, H-5 for sphingosine).

Analytical data. Calculated for $C_{71}H_{127}O_{28}N_3$: C, 57.98; H, 8.70; N, 2.86. Found: C, 57.86; H, 8.83; N, 2.63.

O-(*Methyl 5-acetamido-4,7,8-tri*-O-*acetyl-3,5-dideoxy-α-D*-galacto-*2-octulopyranosylonate*)-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*2,3,4-tri*-O-*acetyl-α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*acetyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-O-(*2,4,6-tri*-O-*acetyl-β-D-galactopyranosyl*)-(*1 → 1*)-(2S, 3R, 4E)-*2-azido-3*-O-*benzoyl-4-octadecene-1,3-diol* (**38**)

To a solution of **29** (183 mg, 0.1 mmol) and **34** (90 mg, 0.21 mmol) in dichloromethane (5.5 ml) 4 Å molecular sieves (type AW 300; 4g) were added, and the mixture was stirred for 2 h at room temperature and then cooled to 0 °C. Boron trifluoride etherate (85 µl) was added to the mixture and this was stirred for 2 h at 0 °C. The precipitate was filtered off and washed with dichloromethane. The filtrate and washing were combined and successively washed with 1 M sodium carbonate and water, dried (Na_2SO_4) and concentrated. Column chromatography (50:1 dichloromethane:methanol) of the residue on silica gel (30 g) gave **38** (90 mg, 43%) as an amorphous mass; $[\alpha]_D$ − 30.0° (*c* 1.7, chloroform); IR (film) 3350 (NH), 3150–2800 (Me, methylene), 2100 (N_3), 1740 and 1230 (ester), 1680 and 1540 (amide), and 710 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) δ 0.88 (t, 3H, *Me*CH_2), 1.12 (d, 3H, $J_{5,6}$ 6.4 Hz, H-6e), 1.25 (s, 22H. 11CH_2), 1.79–2.10 (11s, 36H, 10AcO and 2AcN), 2.27 (dd, 1H, $J_{3eq,4}$ 4.6, J_{gem} 12.6 Hz, H-3d-*eq*), 3.58 (s, 3H, MeO), 5.90 (m, 1H, H-5 for sphingosine) and 7.41–8.14 (m, 20H, 4Ph).

Analytical data. Calculated for $C_{103}H_{131}O_{42}N_5$: C, 58.60; H, 6.25; N, 3.32. Found: C, 58.62; H, 6.02; N, 3.60.

O-(*Methyl 5-acetamido-4,7,8-tri*-O-*acetyl-3,5-dideoxy-α-D*-galacto-*2-octulopyranosylonate*)-O-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*2,3,4-tri*-O-*acetyl-α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*acetyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-O-(*2,4,6-tri*-O-*acetyl-β-D-galactopyranosyl*)-(*1 → 1*)-(2S, 3R, 4E)-3-O-*benzoyl-2-octadecanamido-4-octadecene-1,3-diol* (**39**)

Hydrogen sulfide was bubbled through a stirred solution of **38** (90 mg, 0.04 mmol) in pyridine (5 ml) and water (1 ml) for 5 days at 0 °C. The mixture was concentrated to give the syrupy amine, which was used for the next reaction without further purification. To a solution of the amine in dichloromethane (2 ml) were added octadecanoic acid (60 mg) and WSC (60 mg), and the mixture was stirred overnight at room temperature. After completion of the reaction, dichloromethane (20 ml) was added to the mixture, and the solution was washed with water, dried (Na_2SO_4) and concentrated. Column chromatography (60:1 dichloromethane:methanol) of the residue on silica gel (30 g) gave **39** (66 mg, 66%) as an amorphous mass; $[\alpha]_D$ − 18.5° (*c* 1.3, chloroform); IR (film) 3350 (NH), 3150–2800 (Me, methylene), 1740 and 1230 (ester), 1660 and 1540 (amide), and 710 cm^{-1} (Ph); ^{1}H-NMR data ($CDCl_3$) δ 0.96 (t, 6H, *2Me*CH_2), 1.21 (d, 3H, $J_{5,6}$ 5.0 Hz, H-6e), 1.34 (s, 52H, 26 CH_2), 1.86–2.18 (8s, 36H, 10AcO and 2AcN), 3.67 (s, 3H, MeO), 5.90 (m, 1H, N-5 for sphingosine) and 7.38–8.27 (m, 20H, 4Ph).

Analytical data. Calculated for $C_{121}H_{167}O_{43}N_3$: C, 61,80; H, 7.16; N, 1.79. Found: C, 61.79; H, 7.30; N, 1.59.

O-(*5-Acetamido-3,5-dideoxy-α-D*-galacto-*2-octulopyranosylonic acid*)-(*2 → 3*)-O-(*β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-O-(*β-D-galactopyranosyl*)-(*1 → 1*)-(2S, 3R, 4E)-*2-octadecanamido-4-octadecene-1,3-diol* (**40**)

To a solution of **39** (66 mg, 0.03 mmol) in methanol (5 ml) sodium methoxide (40 mg) was added and the mixture was stirred for 12 h at 40 °C; the course of the reaction was monitored by TLC. Water (1 ml) was added to the mixture and this was stirred for 12 h at 40 °C, neutralized with Amberlite IR-120 (H^+) resin and filtered. The resin was washed with methanol, and the combined filtrate and washings were concentrated. Column chromatography (5:4:0.7 chloroform:methanol:water) of the residue on Sephadex LH-20 (50 g) gave **40** (41 mg, quantitative) as an amorphous mass; $[\alpha]_D$ − 28.1° (*c* 0.8, 1:1 methanol:chloroform); IR (KBr) 3600–3400 (OH, NH), 2920 and 2850 (Me, methylene), 1710 (COOH), and 1630 and 1540 cm^{-1} (amide); ^{1}H-NMR data (1:1 $CDCl_3$–CD_3OD) δ 0.89 (t, 6H, *2MeCH*$_2$), 1.20 (d, 3H, $J_{5,6}$ 7.0 Hz, H-6e), 1.27 (s, 52H, 26CH_2), 2.01 and 2.05 (2s, 6H, 2AcN), 2.18 (t, 2H, CO*CH*$_2$CH$_2$), 2.77 (broad dd, 1H, H-3d-*eq*), 4.25 (d, 1H, $J_{1,2}$ 6.6 Hz, H-1a), 5.09 (broad d, 1H, $J_{1,2}$ 3.3 Hz, H-1e), 5.45 (dd, 1H, $J_{3,4}$ 7.1, $J_{4,5}$ 15.4 Hz, H-4 for sphingosine) and 5.70 (m, 1H, H-5 for sphingosine).

Analytical data. Calculated for $C_{72}H_{129}O_{29}N_3$: C, 57.62; H, 8.66; N, 2.80. Found: C, 57.72; H, 8.55; N, 2.85.

O-(*Methyl 5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy-L*-glycero-*β-D*-galacto-*2-nonulopyranosylonate*)-(*2 → 3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*2,3,4-tri*-O-*acetyl-α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*acetyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-O-(*2,4,6-tri*-O-*acetyl-β-D-galactopyranosyl*)-(*1 → 1*)-(2S, 3R, 4E)-*2-azido-3*-O-*benzoyl-4-octadecene-1,3-diol* (**41**)

To a solution of **33** (100 mg, 0.05 mmol) and **34** (45 mg, 0.1 mmol) in dichloromethane (3 ml) 4 Å molecular sieves (type AW 300; 2 g) were added, and the mixture was stirred for 2 h at room temperature and then cooled to 0 °C. Boron trifluoride etherate (44 µl) was added to the mixture and this was stirred for 2 h at 0 °C. The precipitate was filtered off and washed with dichloromethane. The filtrate and washings were combined and successively washed with 1 M sodium carbonate and water, dried (Na_2SO_4) and concentrated. Column chromatography (30:1 dichloromethane: methanol) of the residue on silica gel (20 g) gave **41** (52 mg, 46%) as an amorphous mass; $[\alpha]_D$ − 37.5° (*c* 1.0, chloroform); IR (film) 3350 (NH), 3150–2800 (Me, methylene), 2100 (N_3), 1740 and 1230 (ester), 1680 and 1550 (amide), and 710 cm^{-1} (Ph); ^{1}H-NMR data (C^2HCl_3) δ 0.88 (t, 3H, *Me*CH_2), 1.13 (d, 3H, $J_{5,6}$ 5.1 Hz, H-6e), 1.25 (s, 22H, 11CH_2), 1.61–2.12 (12s, 39H, 11AcO and 2AcN), 2.36 (dd, 1H, $J_{3eq,4}$ 4.5, J_{gem} 12.9 Hz, H-3d-*eq*), 3.73 (s, 3H, MeO), 5.68 (m, 1H, H-8d), 5.91 (m, 1H, H-5 for sphingosine) and 7.37–8.16 (m, 20H, 4Ph).

Analytical data. Calculated for $C_{106}H_{135}O_{44}N_5$: C, 58.32; H, 6.23; N, 3.21. Found: C, 58.05; H, 6.44; N, 3.03.

O-(*Methyl 5-acetamido-4,7,8,9-tetra*-O-*acetyl-3,5-dideoxy-L*-glycero-*β-D*-galacto-*2-nonulopyranosylonate*)-(*2 →3*)-O-(*2,4,6-tri*-O-*benzoyl-β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*2,3,4-tri*-O-*acetyl-α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-6*-O-*acetyl-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-O-(*2,4,6-tri*-O-*acetyl-β-D-galactopyranosyl*)-(*1 → 1*)-(*2S, 3R, 4E*)-*3*-O-*benzoyl-2-octadecanamido-4-octadecene-1,3-diol* (**42**)

Hydrogen sulfide was bubbled through a stirred solution of **41** (52 mg, 0.02 mmol) in pyridine (5 ml) and water (1 ml) for 5 days at 0 °C. The mixture was concentrated to give the syrupy amine. To a solution of the amine dichloromethane (3 ml) were added octadecanoic acid (40 mg) and WSC (40 mg) and the mixture was stirred overnight at room temperature. After completion of the reaction, dichloromethane (20 ml) was added to the mixture and the solution was washed with water, dried (Na_2SO_4) and concentrated. Column chromatography (55:1 dichloromethane:methanol) of the residue on silica gel (20 g) gave **42** (47 mg, 81%) as an amorphous mass; $[\alpha]_D$ − 28.0° (*c* 0.9, chloroform); IR (film) 3400 (NH), 3150–2800 (Me, methylene), 1740 and 1230 (ester), 1680 and 1540 (amide), and 720 cm^{-1} (Ph); ^{1}H-NMR data (C^2HCl_3) δ 0.85 (t, 6H, *2MeCH*$_2$), 1.13 (d, 3H, $J_{5,6}$ 5.0 Hz, H-6e), 1.26 (s, 52H, 26CH_2), 1.57–2.12 (11s, 39H, 11AcO and 2AcN), 2.35 (m, 1H, H-3d-*eq*), 3.74 (s, 3H, MeO), 5.83 (m, 1H, H-5 for sphingosine) and 7.40–8.27 (m, 20H, 4Ph).

Analytical data. Calculated for $C_{124}H_{171}O_{45}N_3$: C, 61.45; H, 7.11; N, 1.73. Found: C, 61.52; H, 7.01; N, 2.02.

O-(*5-Acetamido-3,5-dideoxy-L*-glycero-*β-D*-galacto-*2-nonulopyranosylonic acid*)-(*2 → 3*)-O-(*β-D-galactopyranosyl*)-(*1 → 4*)-O-[(*α-L-fucopyranosyl*)-(*1 → 3*)]-O-(*2-acetamido-2-deoxy-β-D-glucopyranosyl*)-(*1 → 3*)-O-(*β-D-galactopyranosyl*)-(*1 → 1*)-(2S, 3R, 4E)-*2-octadecanamido-4-octadecene-1,3-diol* (**43**)

To a solution of **42** (47 mg, 0.02 mmol) in methanol (5 ml) sodium methoxide (40 mg) was added and the mixture was stirred for 12 h at 40 °C; the course of the reaction was monitored by TLC. Water (1 ml) was added to the mixture and this was stirred for 12 h at 40 °C neutralized with Amberlite IR-120 (H^+) resin and filtered. The resin was washed with methanol, and the combined filtrate and washings were concentrated. Column chromatography (5:4:0.7 chloroform:methanol:water) of the residue on

Sephadex LH-20 (40 g) gave **43** (30 mg, quantitative) as an amorphous mass; $[\alpha]_D$ − 20.0° (*c* 0.5, 1:1 methanol:chloroform); IR (KBr) 3600–3400 (OH, NH), 2920 and 2850 (Me, methylene), 1730 (COOH), and 1630 and 1540 cm^{-1} (amide); ^{1}H-NMR data (1:1 $CDCl_3$–CD_3OD) δ 0.89 (t, 6H, $2MeCH_2$), 1.17 (d, 3H, $J_{5,6}$ 5.1 Hz, H-6e), 1.27 (s, 52H, $26CH_2$), 2.01 and 2.05 (2s, 6H, 2AcN), 2.19 (near t, 2H, $COCH_2CH_2$), 2.78 (broad dd, 1H, H-3d-*eq*), 4.25 (d, 1H, $J_{1,2}$ 7.3 Hz, H-1 for Gal), 4.51 (d, 1H, $J_{1,2}$ 7.7 Hz, H-1a), 5.06 (broad d, 1H, $J_{1,2}$ 3.4 Hz, H-1e), 5.46 (dd, 1H, $J_{3,4}$ 7.3, $J_{4,5}$ 15.6 Hz, H-4 for sphingosine), 5.70 (m, 1H, H-5 for sphingosine).

Analytical data. Calculated for $C_{73}H_{131}O_{30}N_3$: C, 57.28; H, 8.63; N, 2.74. Found: C, 57.49; H, 8.76; N, 2.70.

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