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Synthesis of pentasaccharide core structures corresponding to the genus-specific lipopolysaccharide epitope of *Chlamydia*

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ABSTRACT

The trisaccharides allyl *O*-(sodium 3-deoxy-α-D-*manno*-2-octulopyranosylonate)-(2 → 6)-*O*-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 6)-2-acetamido-2-deoxy-α- and -β-D-glucopyranoside (**16a** and **16b**), the tetrasaccharides allyl *O*-(sodium 3-deoxy-α-D-*manno*-2-octulopyranosylonate)-(2 → 4)-*O*-(sodium 3-deoxy-α-D-*manno*-2-octulopyranosylonate)-(2 → 6)-*O*-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 6)-2-acetamido-2-deoxy-α- and -β-D-glucopyranoside (**19a** and **19b**), and the pentasaccharides allyl *O*-(sodium 3-deoxy-α-D-*manno*-2-octulopyranosylonate)-(2 → 8)-*O*-(sodium 3-deoxy-α-D-*manno*-2-octulopyranosylonate)-(2 → 4)-*O*-(sodium 3-deoxy-α-D-*manno*-2-octulopyranosylonate)-(2 → 6)-*O*-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 6)-2-acetamido-2-deoxy-α- and -β-D-glucopyranoside (**23a** and **23b**) were prepared. The glycosidic linkages were formed using 1,3,4,6-tetra-*O*-acetyl-2-chloroacetamido-2-deoxy-β-D-glucopyranose (**6**) and $FeCl_3$ as promoter as well as per-*O*-acetylated Kdo mono- and di-saccharide bromide derivatives (**12** and **20**) under Helferich conditions. The oligosaccharides, which correspond to dephosphorylated part-structures of enterobacterial and chlamydial lipopolysaccharides, were characterized by NMR spectroscopy as well as plasma desorption and matrix-assisted laser desorption mass spectrometry.

INTRODUCTION

Chlamydiae comprising the species *C. psittaci*, *C. trachomatis*, and *C. pneumoniae* are pathogenic intracellular parasites responsible for a variety of acute and chronic diseases in animals and humans[1]. The lipopolysaccharide (LPS) located at the cell surface of these unique bacteria represents a genus-specific antigen[2], which is composed of the pentasaccharide backbone α-Kdo*p*-(2 → 8)-α-Kdo*p*-(2 → 4)-α-Kdo*p*-(2 → 6)-β-D-GlcN-(1 → 6)-D-GlcN[3–5], the Kdo-trisaccharide terminus constituting the immunodominant part[6]. Glycoconjugates containing the synthetic[7] tetrasaccharide α-Kdo*p*-(2 → 8)-α-Kdo*p*-(2 → 4)-α-Kdo*p*-(2 → 6)-β-D-GlcNAc have been shown to exhibit similar serological specificities as chlamydial

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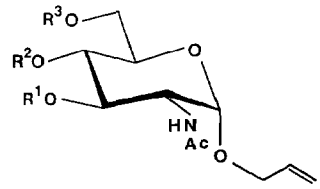


1 $R^1 = R^2 = R^3 = H$

2 $R^1 = H$, $R^2 = R^3 =$ TIPS

3 $R^1 = R^2 = H$, $R^3 =$ Tr

4 $R^1 = R^2 =$ TIPS, $R^3 =$ Tr

5a $R^1 = R^2 =$ TIPS, $R^3 = H$

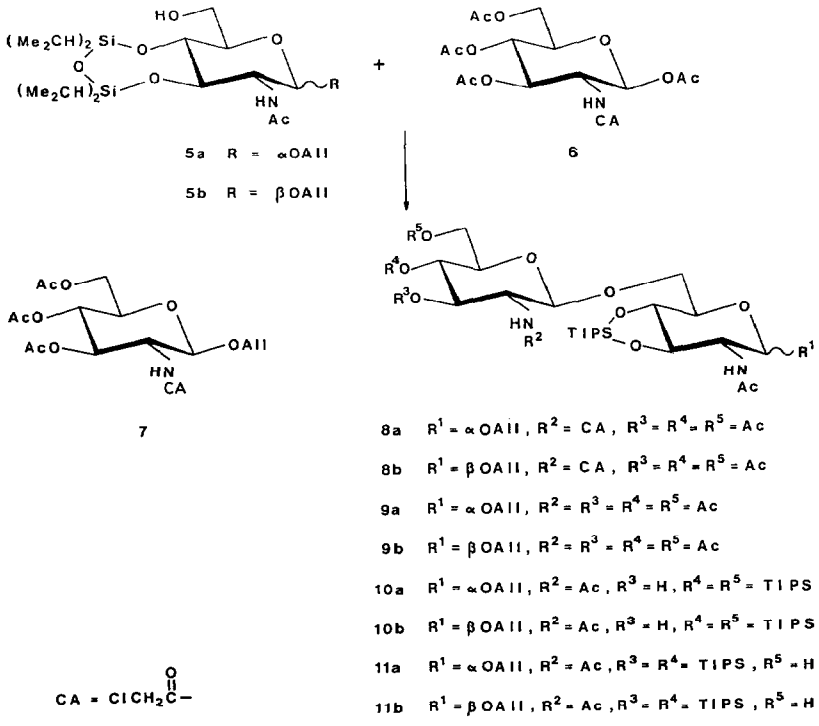
TIPS $= -Si(CHMe_2)_2OSi(CHMe_2)_2-$

LPS[8]. For a further characterization of poly- and mono-clonal antibodies, which may in addition recognize parts of the dephosphorylated lipid A backbone of chlamydial LPS, we report on the synthesis of related tri-, tetra-, and penta-saccharide derivatives as allyl glycosides (in both anomeric configurations) suitable for the subsequent preparation of glycopolymers[9,10] and neoglycoproteins[11], respectively.

RESULTS AND DISCUSSION

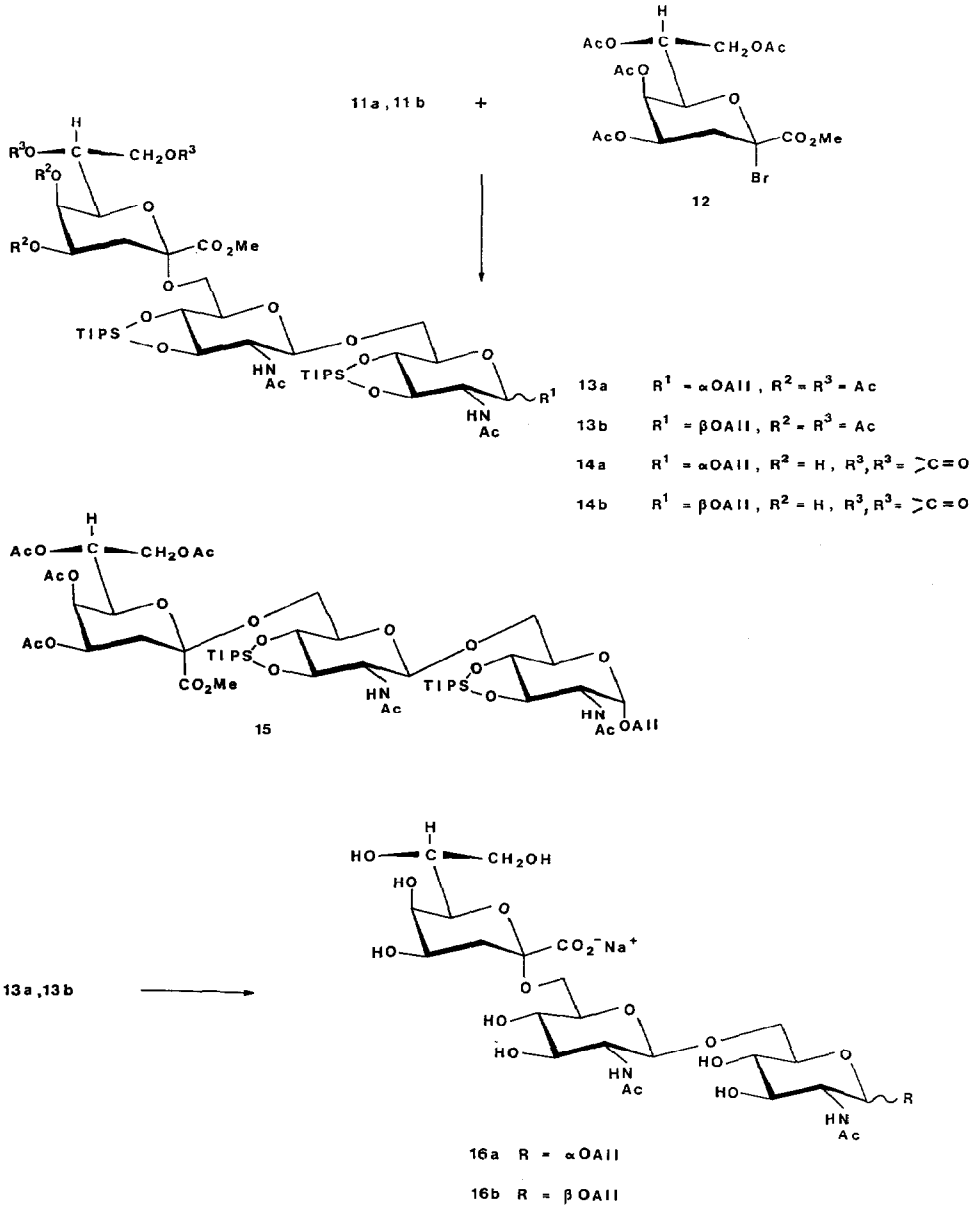
Reaction of allyl 2-acetamido-2-deoxy-α-D-glucopyranoside[11] (**1**) with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane in pyridine[12,13] afforded the 4,6-*O*-silyl derivative **2** in 83% yield, which in turn was isomerized[14,15] into the 3,4-*O*-TIPS-protected compound **5a** in moderate yield (35%). Alternatively, **5a** was prepared after silylation of the 6-*O*-trityl derivative[16] **3** (90% yield) and subsequent cleavage of the trityl group, using $SnCl_4$ in CH_2Cl_2[17], in 94% yield.

Ferric chloride-promoted coupling of the previously described[18] glycosyl donor **6** with either **5a** or **5b**[7] afforded the β-(1 → 6)-linked disaccharide derivatives **8a** and **8b** in 50 and 43% yields, respectively. The glycosylation of **5b** gave, in addition, the transglycosylation[18] product **7** in 37% yield. The α-allyl glycoside **8a** was subsequently reduced with zinc powder in glacial acetic acid[18] to give the *N*-acetyl disaccharide derivative **9a** in 84% yield. For the reduction of the chloroacetamido group of the β-allyl disaccharide derivative **8b**, tributyltin hydride[19] in the presence of 2,2′-azobisisobutyronitrile had to be used, which gave **9b** (53%) with recovery of starting material (~ 17%). Zemplén *O*-deacetylation and subsequent introduction



of the second TIPS-group afforded the 4′,6′-*O*-silyl derivatives **10a** and **10b** in 88 and 93% yield, respectively. Acid-catalyzed rearrangement of the 4′,6′-*O*-silyl group furnished the 3′,4′-*O*-silyl derivatives **11a** (65%) and **11b** (81%).

Coupling of the glycosyl acceptor derivatives **11a** and **11b** with the Kdo-bromide derivative **12** under Helferich conditions [3:1 $Hg(CN)_2$–$HgBr_2$ in 2:1 CH_3NO_2–CH_2Cl_2] afforded the α-(2″ → 6′)-linked trisaccharide derivatives **13a** and **13b** in fair yields, but with different stereoselectivity. Whereas the β-(2″ → 6′)-linked trisaccharide derivative **15** was formed in 38% yield upon glycosylation of **11a**, the corresponding β-allyl derivative **11b** afforded only trace amounts of the β-(2‴ → 6′)-linked product. The β-anomeric configuration of the Kdo residue in **15** was assigned on the basis of the downfield shift experienced by the equatorial H-3 (2.38 ppm) as well as the upfield shift of H-4 (4.89 ppm). Removal of the TIPS-protecting groups by the action of Bu_4NF in THF[20], Zemplén *O*-deacylation, and hydrolysis of the methyl ester group in aqueous NaOH afforded, in overall yields of 65 and 62%, allyl *O*-(sodium 3-deoxy-α-D-*manno*-2-octulopyranosylonate)-(2 → 6)-O-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 6)-2-acetamido-2-deoxy-α- and -β-D-glucopyranoside (**16a** and **16b**) which correspond to part structures of enterobacterial lipopolysaccharides[13,21].



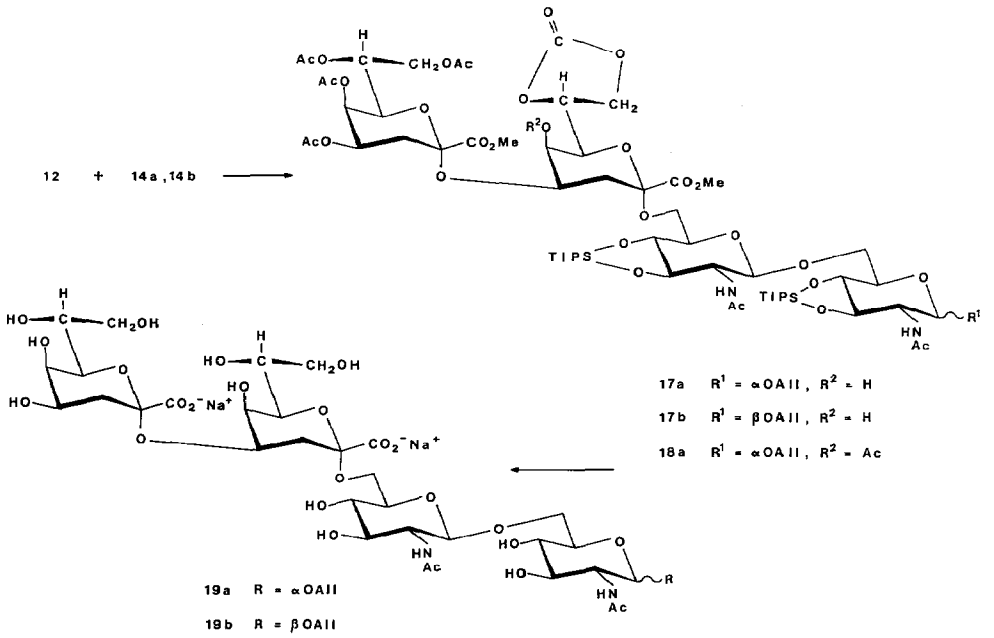
Proceeding towards the synthesis of the tetra- and penta-saccharide derivatives, the trisaccharide derivatives **13a** and **13b** were *O*-deacetylated and treated with trichloromethyl chloroformate–collidine in THF, which afforded the 7,8-*O*-carbonyl derivatives **14a** and **14b** in good regioselectivity (80 and 83% yields). Coupling of

TABLE I

^{1}H NMR chemical shifts (δ) and $J_{H,H}$ values (Hz, first-order values) for compounds **13a**, **14a**, **17a**, **18a**, **21a**, and **22a**

	13a	**14a**	**17a**	**18a**	**21a**	**22a**
Unit a						
α-Kdo-(2 →						
H-3*a*					2.10	2.00
H-3*e*					2.20	2.13
H-4					5.20	5.13
H-5					5.22(1.5)	5.33(1.3)
H-6					4.06(10.0)	4.07(10.0)
H-7					5.33(3.8)	5.18(4.0)
H-8a					4.45(2.4)	4.51(2.3)
H-8b					4.19(12.0)	4.25(12.5)
Unit b						
→ 8)-α-Kdo-						
H-3*a*			2.09	1.98	2.10	1.99
H-3*e*			2.15	2.22(13.3)	2.20	2.13
H-4			5.24(5.5)	5.16(5.0)	5.22	5.10
H-5			5.39(3.0)	5.34(3.0)	5.37(3.0)	5.33
H-6			4.17(1.5)	4.12(1.5)	4.51	3.99
H-7			5.15(9.5)	5.10(9.5)	5.05(9.5)	5.32
H-8a			4.74(2.5)	4.70(3.0)	n.d. [a]	n.d.
H-8b			3.97(3.5, −12.5)	4.00(2.9, −12.5)	3.62(3.3)	3.61
Unit c						
→ 4)-α-Kdo-						
H-3*a*	2.07(12.0)	1.93(12.5)	2.10(11.5)	2.21	2.11	2.12
H-3*e*	2.21(12.0)	2.15(12.7)	2.21(12.5)	2.05	2.11	2.12
H-4	5.31(5.1)	4.23(4.8)	4.29(5.0)	4.75	4.05	4.44
H-5	5.32(1.1)	3.84	3.74(3.1)	5.28(1.4)	3.74	5.37
H-6	4.18(9.5)	4.22	4.13(3.8)	4.29(4.5)	4.20(2.4)	4.46
H-7	5.22(4.0)	4.90(8.5)	4.86(8.5)	4.70(8.0)	4.93(8.5)	4.70(8.0)
H-8a	4.63(2.3)	4.76(7.4)	4.71(7.3)	4.55(8.5)	4.81(8.5)	4.62(7.3)
H-8b	4.12(12.2)	4.54(8.6)	4.53(8.5)	4.41(8.5)	4.55(8.5)	4.39(8.0)
Unit d						
→ 6)-β-D-GlcNAc-						
H-1	4.85(8.1)	5.23(8.2)	4.85(7.9)	4.88(8.0)	4.94(8.4)	5.05(8.5)
H-2	3.40(10.1)	3.00(10.1)	3.41(9.1)	3.40(9.6)	3.27(9.5)	3.25(9.5)
H-3	4.04(7.3)	4.26(7.9)	4.01(7.8)	4.11(8.0)	4.21	4.30(8.5)
H-4	3.47	3.35(8.9)	3.52	3.47	3.45(9.1)	3.40
H-5	3.58(10.8)	3.59(4.3)	3.58	3.55	3.55	3.67
H-6a	3.88(10.3)	n.d.	3.82	3.85	3.84	3.90
H-6b	3.58	n.d.	3.58	3.56	3.56	3.55
Unit e						
→ 6)-α-D-GlcNAc-(1 → OAll)						
H-1	4.80(3.6)	4.81(3.6)	4.80(3.6)	4.82(3.6)	4.81(3.4)	4.85(3.5)
H-2	4.20	4.03(9.5)	4.18(9.2)	4.20(9.9)	4.20	4.20(9.6)
H-3	3.75	3.80	3.80	3.80	3.80	3.82
H-4	3.67	3.52(8.3)	3.67	3.74	n.d.	n.d.
H-5	3.50	3.72	n.d.	n.d.	n.d.	n.d.
H-6a	4.15	3.98	4.08	4.07	4.15	4.03
H-6b	3.67(12.7)	3.90	3.51	3.72	n.d.	3.74

[a] n.d., Not determined.



the Kdo-bromide derivative **12** with the glycosyl acceptor derivatives **14a** or **14b** was promoted by 1:1 $HgBr_2$–$Hg(CN)_2$ in CH_3NO_2, which afforded the α-(2″ → 4″)-linked tetrasaccharide derivatives **17a** and **17b** in 60 and 50% yields, respectively. The α-D-anomeric configuration of the terminal Kdo residue was based on the downfield chemical shift[22] value of the H-4″ signals (5.24 ppm). *O*-Acetylation (pyridine–acetic anhydride–4-dimethylaminopyridine) of **17a** furnished the 5″-*O*-acetyl derivative **18a** in 75% yield. The ^1H NMR chemical shift data of H-5″ (5.28 ppm) and H-4″ (5.17 ppm) confirmed the linkage of the terminal Kdo residue to O-4 of the second Kdo unit as well as the α-anomeric configuration (Table I).

Removal of the protecting groups from **18a** and **17b** was accomplished in a similar way as for **13a** and **13b**, i.e., successive treatment with Bu_4NF in THF, Zemplén *O*-deacylation, and saponification of the methyl ester groups in aqueous NaOH, which gave allyl *O*-(sodium 3-deoxy-α-D-*manno*-2-octulopyranosylonate)-(2 → 4)-*O*-(sodium 3-deoxy-α-D-*manno*-2-octulopyranosylonate)-(2 → 6)-*O*-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 6)-2-acetamido-2-deoxy-α- and -β-D-glucopyranoside (**19a** and **19b**) in 91 and 79% yields, respectively.

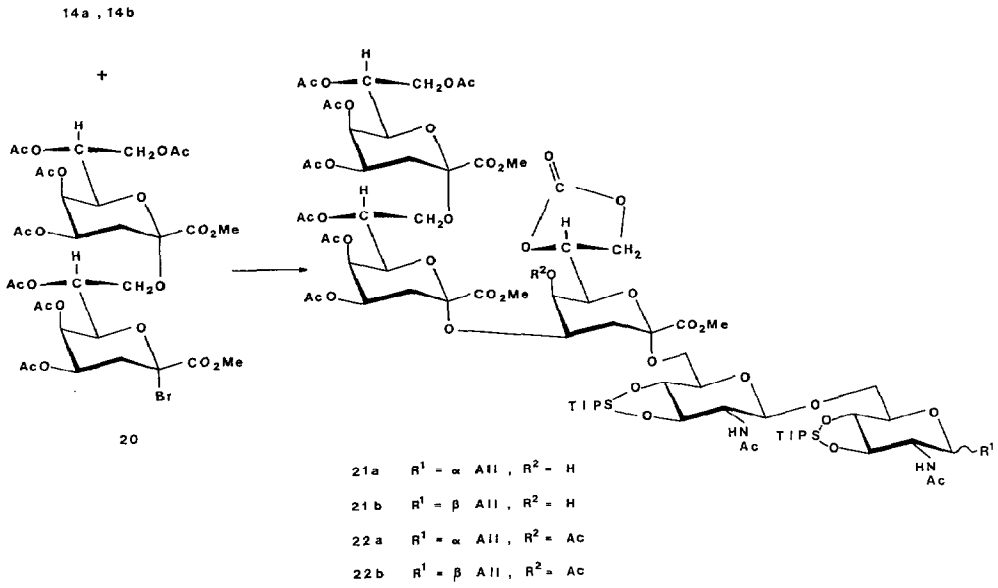
Finally, glycosylation of the trisaccharide acceptor derivatives **14a** and **14b** with the previously described[7] α-(2′ → 8)-linked Kdo-disaccharide bromide derivative **20** was performed under various conditions. Using $HgBr_2$ or 1:1 $HgBr_2$–$Hg(CN)_2$ in CH_3NO_2 as well as $HgBr_2$ in 2:1 CH_3NO_2–toluene, only low amounts (10–12%) of the pentasaccharide derivatives were formed. Best results were obtained in CH_3CN with 2:1 $HgBr_2$–$Hg(CN)_2$ as promoter, affording **21a** and **21b**

TABLE II

^{1}H NMR chemical shifts (δ) and $J_{H,H}$ values (Hz, first-order values) for compounds **13b, 14b, 17b, 21b,** and **22b**

	13b	**14b**	**17b**	**21b**	**22b**
Unit a					
α-Kdo-(2 →					
H-3*a*				n.d.	n.d.
H-3*e*				n.d.	n.d.
H-4				5.28	5.10
H-5				5.22	5.31
H-6				4.04(10.3)	4.07
H-7				5.30	5.20
H-8a				4.47	4.51(2.5)
H-8b				4.18(11.6)	4.25(4.2)
Unit b					
→ 8)-α-Kdo-(2 →					
H-3*a*			2.08	n.d. [a]	n.d.
H-3*e*			2.19	n.d.	n.d.
H-4			5.25(5.1)	5.25	5.10
H-5			5.39(2.9)	5.37	5.31
H-6			4.17	4.47	4.00
H-7			5.16(3.7)	5.08(4.0)	5.30
H-8a			4.76(2.8)	4.47	3.89
H-8b			3.99(12.5)	3.63	3.63
Unit c					
→ 4)-α-Kdo-(2 →					
H-3*a*	2.07(13.0)	1.93(13.1)	2.08	2.13	2.12
H-3*e*	2.22(13.0)	2.11(13.1)	2.19	2.13	2.12
H-4	5.31(5.3)	4.33(4.5)	4.29	4.02	4.37
H-5	5.32(1.0)	3.86	3.75	3.75	5.32
H-6	4.18(9.8)	4.18(3.7)	4.19(3.7)	4.26(2.6)	4.53
H-7	5.21(4.0)	4.93(8.5)	4.86(8.5)	4.92(8.3)	4.71(2.9)
H-8a	4.62(2.4)	4.74(8.0)	4.73(7.8)	4.79(7.7)	4.65(7.2)
H-8b	4.12(12.2)	4.55(8.6)	4.52(8.6)	4.54(8.3)	4.38
Unit d					
→ 6)-β-D-GlcNAc-					
H-1	4.95(8.6)	5.25(8.3)	5.04(8.4)	5.25	5.28
H-2	3.40	3.04(9.5)	3.32	3.10	3.09(9.4)
H-3	3.97	4.24(8.0)	4.18	4.33	4.42(8.5)
H-4	3.48	3.38	3.45	3.37	3.32(9.1)
H-5	n.d.	3.59	n.d.	3.54	3.68
H-6a	3.87(10.3)	3.86	3.84	3.85	3.89
H-6b	3.59	3.49	3.58	n.d.	3.55
Unit e					
→ 6)-β-D-GlcNAc-(1 → OAll)					
H-1	4.86(8.4)	4.76(8.5)	4.88(8.4)	4.85(9.2)	4.86(8.3)
H-2	3.51	3.38(9.6)	3.45	3.45	3.49
H-3	n.d.	4.01(7.5)	4.01	n.d.	n.d.
H-4	n.d.	n.d.	3.61	n.d.	n.d.
H-5	3.55	3.59	n.d.	n.d.	n.d.
H-6a	4.12(1.0)	3.97	4.10	4.07	n.d.
H-6b	3.76(12.5)	3.59	3.72	3.22(7.2)	n.d.

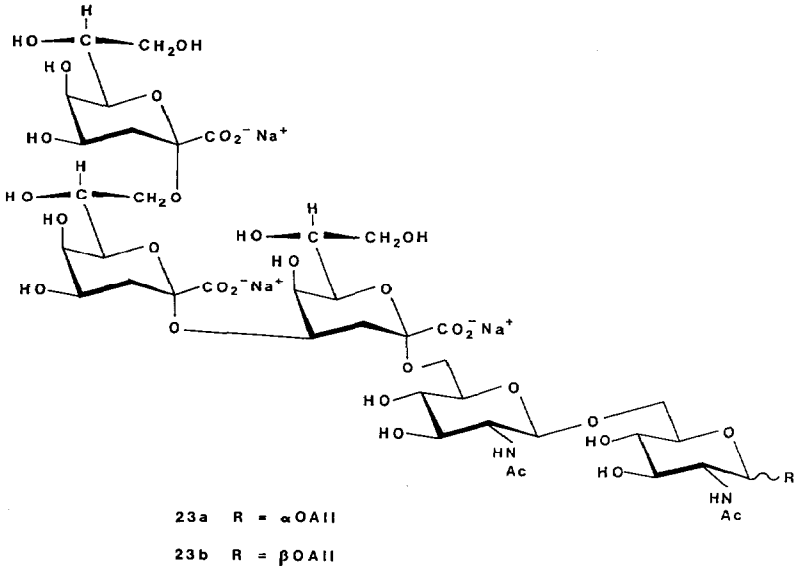
[a] n.d., Not determined.



in 20 and 19% yields, respectively. The pentasaccharide derivatives were separated by liquid chromatography from small amounts of the β-(2‴ → 4″)-linked isomers and minor impurities arising from imidate formation of the acetamido groups. *O*-Acetylation (pyridine–acetic anhydride–4-dimethylaminopyridine) furnished the 5″-*O*-acetyl derivatives **22a** and **22b** (84 and 60% yields). The α-anomeric configuration of the internal Kdo residue was deduced from the downfield shift of the respective H-4″ signals (5.25 and 5.22 ppm for **21a** and **21b**; 5.10 ppm for **22a** and **22b**; Tables I and II). Deprotection of **22a** and **22b** was performed as for the tri- and tetra-saccharide derivatives, which afforded allyl *O*-(sodium 3-deoxy-α-D-*manno*-2-octulopyranosylonate)-(2 → 8)-*O*-(sodium 3-deoxy-α-D-*manno*-2-octulopyranosylonate)-(2 → 4)-*O*-(sodium 3-deoxy-α-D-*manno*-2-octulopyranosylonate)-(2 → 6)-*O*-2-acetamido-2-deoxy-β-D-glucopyranosyl-(1 → 6)-2-acetamido-2-deoxy-α- and -β-D-glucopyranoside (**23a** and **23b**) in 94 and 65% yields, respectively.

The structures of the oligosaccharide derivatives **16a, 16b, 19a, 19b, 23a,** and **23b** were confirmed by positive- and negative-ion PD mass spectrometry (Fig. 1) as well as positive-ion MALD mass spectrometry (Fig. 2), and NMR spectroscopy (Figs. 3 and 4).

The positive-ion PD mass spectrum of **16a** (Fig. 1a) exhibits an intense $[M + Na]^+$ ion at m/z 730.27 (calculated 729.62) and a minor $[M + 2Na - H]^+$ ion. In addition to these ions, there are abundant ions at m/z 645.55 and 488.11. Both ions could be correlated with carbohydrate sequence ions and, according to the nomenclature proposed by Domon and Costello[23], they were identified as $^{1,5}A_3$-



(seldom observed) and Y_2-type ions, respectively. The negative-ion mass spectrum (Fig. 1b) contains a deprotonated molecular ion at m/z 705.74 (calculated 705.62) and a desodiated molecular ion at m/z 683.62 (calculated 683.64). The PD mass spectra of **16b** are similar to those of **16a**. For **19a, 19b, 23a**, and **23b**, no useful PD mass spectra were obtained in the positive- or in the negative-ion mode. This unsuccessful attempt can be attributed to the multiple anionic functional groups

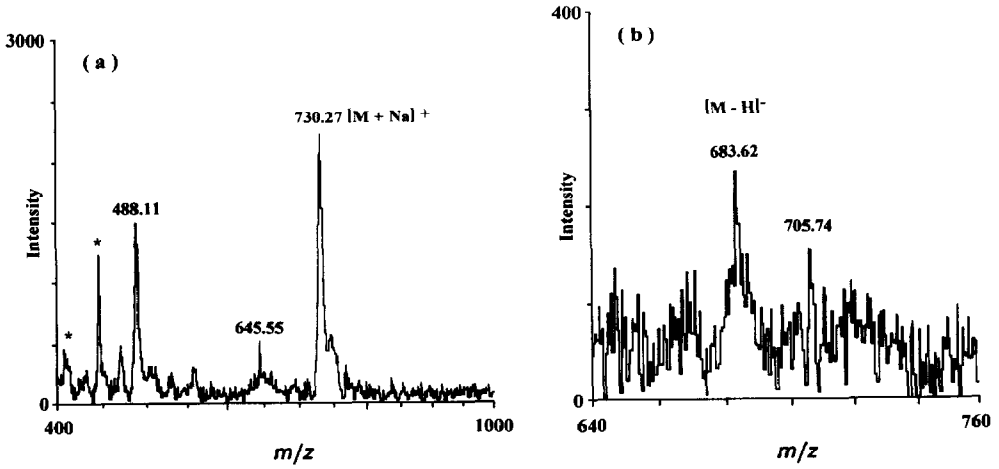


Fig. 1. PD mass spectra of the underivatized compound **16a**, using nitrocellulose as support material. Positive- (a) and negative- (b) ion extraction; * represents pump-oil-related ions.

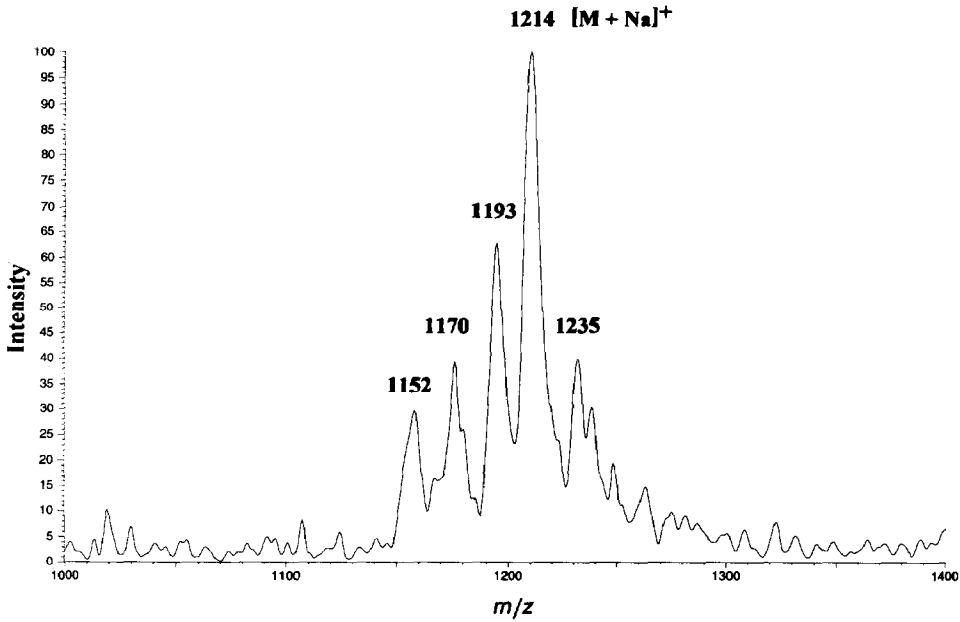


Fig. 2. Positive MALD mass spectrum of the underivatized compound **23a**, using 2,5-dihydroxybenzoic acid as matrix material.

present in these compounds in contrast to **16a** and **16b**. The application of MALD mass spectrometry solved the problem as illustrated in Fig. 2. The positive-ion MALD mass spectrum of the pentasaccharide **23a** (carrying three carboxyl groups) shows a sodiated molecular ion as the most abundant ion at m/z 1214 (calculated 1213.9). Additionally, the spectrum exhibits a $[M + 2Na - H]^+$ ion at m/z 1235 and an abundant $[M + H]^+$ ion at m/z 1193. The ions at m/z 1170 and 1152 can be associated with double- ($[M + 2Na - H]^+$) and single-sodiated ($[M + Na]^+$) molecular ions of **23a** as the free acid. For **23b**, a similar observation was found. All detected quasi-molecular ion species are listed in Table III.

The ^1H NMR data (Table IV) and ^{13}C NMR data (Table V), which were assigned on the basis of ^{13}C–^1H correlation experiments, are in good agreement with published[4] values for Kdo-oligosaccharides and the reduced pentasaccharide derivative isolated from a recombinant strain of *Salmonella minnesota* R595 harbouring the genus-specific epitope of *Chlamydia*[4]. Immunochemical results obtained with glycoconjugates derived from the allyl glycosides will be published elsewhere.

EXPERIMENTAL

General methods.—Melting points were determined with a Kofler hot stage and are uncorrected. Optical rotations were measured with a Perkin–Elmer 243 B

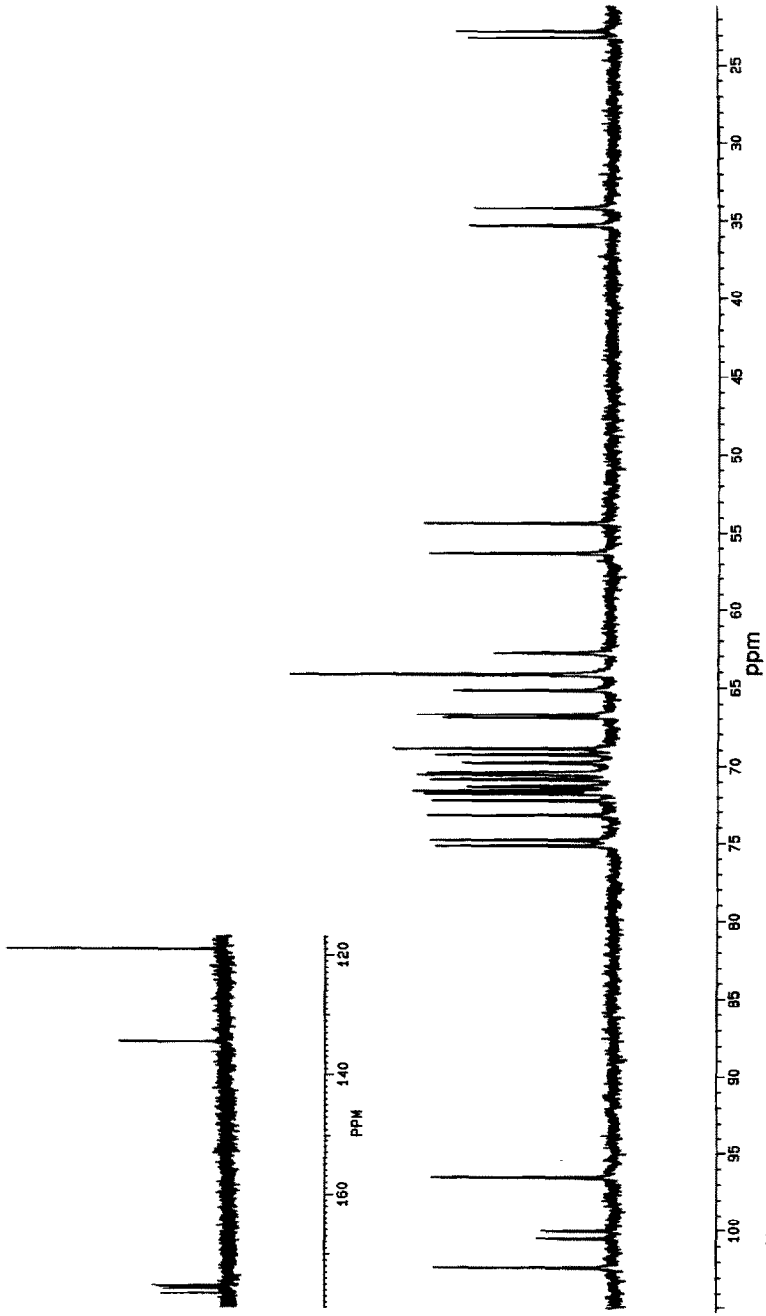


Fig. 3. ^{13}C NMR spectrum of the tetrasaccharide **19a**.

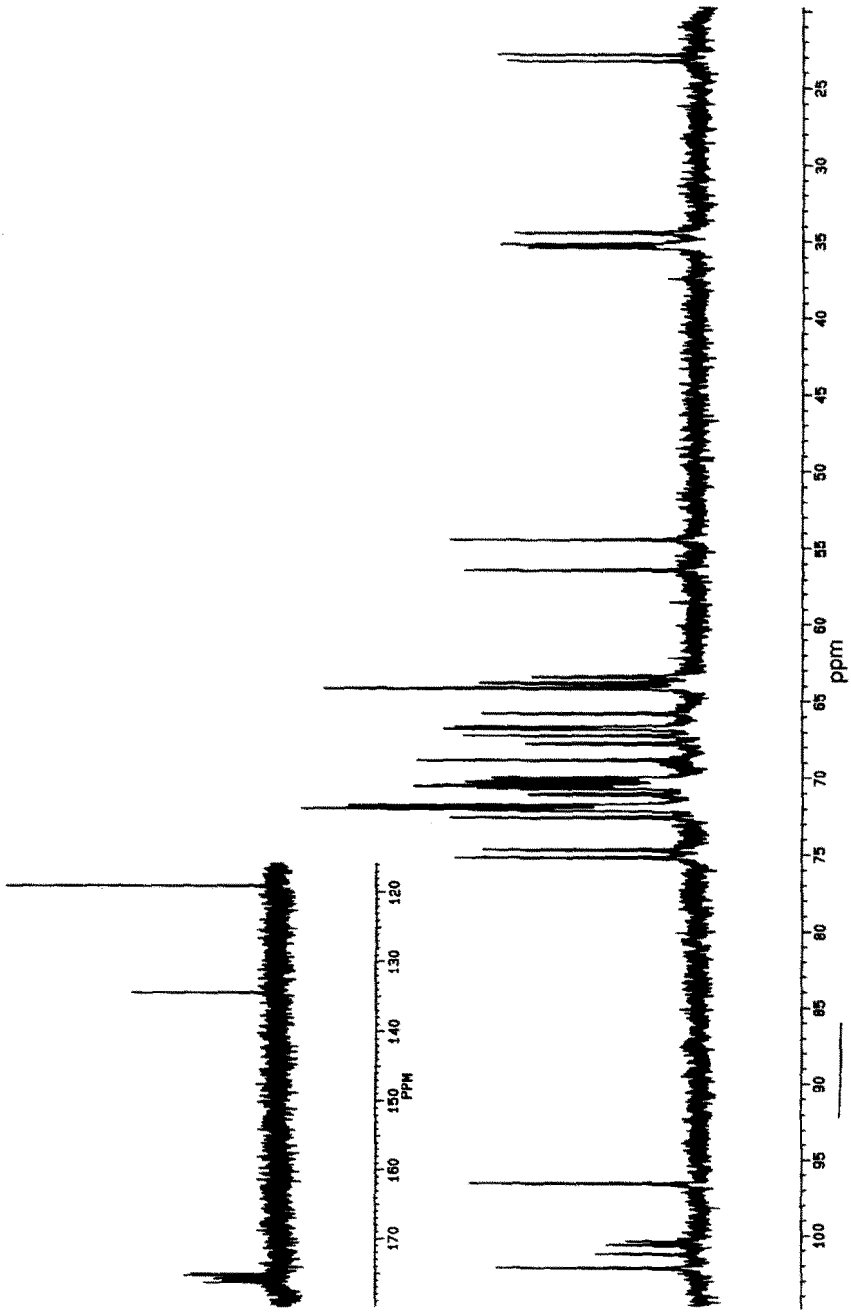


Fig. 4. ^{13}C NMR spectrum of the pentasaccharide **23a**.

TABLE III

Positive ions occurring in PD mass spectra of compounds **16a** and **16b**, and in MALD mass spectra of compounds **19a**, **19b**, **23a**, and **23b**

Compound	Quasi-molecular ion species [a]					
	As free acid			As salt with appropriate number of sodium counter-cations		
	$[M+H]^+$	$[M+Na]^+$	$[M+2Na-H]^+$	$[M+H]^+$	$[M+Na]^+$	$[M+2Na-H]^+$
16a					*(b.p.)	*
16b					*(b.p.)	*
19a		*		*(b.p.)	*	
19b	*	*(b.p.)		*	*	
23a		*	*	*	*(b.p.)	*
23b		*(b.p.)	*	*	*	

[a] * Denotes the presence of ions corresponding to this type of molecular ion species; (b.p.) indicates the base peak in the expected quasi-molecular region.

polarimeter. ^1H NMR spectra were recorded with a Bruker AC 300F instrument and tetramethylsilane or sodium 3-(trimethylsilyl)propionate-*2,2,3,3-d*$_4$ (for solutions in D_2O) as the internal standard; coupling constants are first order. ^{13}C NMR spectra were recorded at 75.47 MHz for solutions in D_2O at 24°C; the instrument was operated in the FT mode with complete proton-decoupling; chemical shifts (δ) were measured relative to that of 1,4-dioxane, set at δ 67.40 relative to tetramethylsilane. Homo- and hetero-nuclear 2D NMR spectroscopy was performed with Bruker standard NMR software. Mass spectrometric experiments were conducted by using time-of-flight instruments with two different desorption/ionization techniques. The trisaccharides were examined with a Californium-252 plasma desorption mass spectrometer (Applied Biosystems, Foster City, CA, USA), and the tetra- and penta-saccharide compounds were analyzed on a matrix-assisted laser desorption instrument (Shimadzu Kratos Analytical, Manchester, UK).

A Bioion 20 PD linear time-of-flight instrument was used for molecular weight determinations under the following conditions: length of the field-free drift region, 141 mm; accelerating voltage, 19 kV for positive- and 15 kV for negative-ion mode; time resolution, 1 ns per channel; spectrum accumulation time, 1×10^7 fission events. Mass calibration was based on H^+ and Na^+ for the positive- and on H^- and CN^- for the negative-ion mass spectra. The underivatized oligosaccharide samples (~2 mg) were dissolved in 50 μL of ultra-high-quality water (18 $M\Omega^{-1}cm^{-1}$) produced by an Elgast apparatus (Elga, Bucks, UK), and aliquots (2–3 μL) of these solutions were deposited under slow rotation onto nitrocellulose-covered aluminized polyester backings[24]. MALDI mass spectra were generated using a MALDI III linear/reflecting time-of-flight instrument under the following conditions: length of the field-free drift region, 0.70 m; pulsed nitrogen laser (337 nm) with a pulse width of 3 ns; the power density was kept near threshold level (~ 10^6 Wcm^{-2}); ion acceleration to a final potential of 20 kV in

TABLE IV

^{1}H NMR chemical shifts (δ) and $J_{H,H}$ values (Hz, first-order values) for compounds **16a, 16b, 19a, 19b, 23a**, and **23b**

	16a	**16b**	**19a**	**19b**	**23a**	**23b**
Unit a						
α-Kdo-(2 →						
H-3*a*					1.81(12.4)	1.86(12.9)
H-3*e*					2.04	2.05
H-4					4.09	4.14
H-5					4.09	4.12
H-6					3.72	3.74
H-7					3.97	4.00
H-8a					n.d. [a]	n.d.
H-8b					n.d.	n.d.
Unit b						
→ 8)-α-Kdo						
H-3*a*			1.76(11.5)	1.81(11.8)	1.80(12.0)	1.85(12.7)
H-3*e*			2.14(13.0)	2.20(13.4)	2.15(13.0)	2.19(13.2)
H-4			4.07(4.5)	4.13(4.5)	4.10(5.0)	4.13(4.8)
H-5			4.04(2.7)	4.09(2.8)	4.09	4.12
H-6			3.62	3.66	3.77	3.82
H-7			3.98	4.05	4.20	4.22
H-8a			4.01	n.d.	n.d.	n.d.
H-8b			3.75	3.82(10.1)	n.d.	n.d.
Unit c						
→ 4)-α-Kdo						
H-3*a*	1.85(12.3)	1.84(12.0)	1.92(11.8)	1.98(11.8)	1.90(11.7)	1.94(11.9)
H-3*e*	2.12(12.1)	2.12(13.0)	2.02(13.1)	2.07(12.7)	2.01	2.08
H-4	4.12(5.1)	4.11(5.0)	4.15(5.0)	4.19(5.6)	4.09	4.13
H-5	4.07(3.3)	4.06(3.1)	4.09(3.1)	4.13	4.10	4.14
H-6	3.72(9.5)	3.69	3.64	3.68	3.72	3.74
H-7	4.00	3.98	3.92	3.98	3.95	3.94
H-8a	3.99	3.97	3.90	3.95(2.9)	3.90	3.98
H-8b	3.74	3.70	3.57	3.78	3.69	n.d.
Unit d						
→ 6)-β-D-GlcNAc-						
H-1	4.56(8.5)	4.56(8.4)	4.53(8.4)	4.59(8.4)	4.60(8.5)	4.66(8.4)
H-2	3.79(10.2)	3.77(10.1)	3.77(10.1)	3.79(10.0)	3.75(10.5)	3.78(10.3)
H-3	3.58(8.8)	3.56(8.8)	3.52(8.8)	3.58(9.1)	3.57(9.0)	3.62(8.9)
H-4	3.46(9.9)	3.47	3.45(10.1)	3.44(9.1)	3.33(9.3)	3.37(8.9)
H-5	3.64	3.60	3.59	3.62	3.62(5.0)	3.69
H-6a	3.70	3.68	3.64	3.68	3.75	n.d.
H-6b	3.65	3.62	3.52	n.d.	n.d.	n.d.
Unit e						
→ 6)-α- or β-D-GlcNAc						
H-1	4.93(3.6)	4.57(8.5)	4.89(3.6)	4.59(8.5)	4.91(3.7)	4.58(8.5)
H-2	3.94(10.8)	3.72(10.3)	3.91(10.7)	3.76(10.2)	3.95(10.6)	3.77(10.0)
H-3	3.78	3.55(9.0)	3.75(8.8)	3.58(8.8)	3.70	3.58(8.7)
H-4	3.48	3.38(9.7)	3.42	3.49(8.9)	3.52(8.9)	3.50(8.9)
H-5	3.88(8.5)	3.61	3.84(8.5)	3.62	3.84	n.d.
H-6a	4.19(1.5)	4.23(1.7)	4.18(1.7)	4.25(1.0)	n.d.	4.21
H-6b	3.72	3.70(10.9)	3.68(11.4)	3.70(10.5)	n.d.	3.70

[a] n.d., Not determined.

TABLE V

Assignments of ^{13}C NMR chemical shifts (δ) for compounds **16a, 16b, 19a, 19b, 23a**, and **23b**

Carbon atom	**16a**	**16b**	**19a**	**19b**	**23a**	**23b**
Unit a						
α-Kdo-(2 →						
C-1					175.8	175.7
C-2					100.7	100.6
C-3					35.3	35.3
C-4					67.0	67.0
C-5					67.5	67.5
C-6					72.3	72.2
C-7					70.4	70.3
C-8					64.1	64.1
Unit b						
→ 8)-α-Kdo-(2 →						
C-1			176.6	176.7	176.4	176.5
C-2			100.5	100.4	100.9	100.9
C-3			35.5	35.5	35.5	35.5
C-4			66.9	67.0	66.9	66.9
C-5			67.2	67.3	68.1	68.0
C-6			73.5	73.6	72.8	72.8
C-7			70.9	70.9	71.4	71.3
C-8			64.3	64.5	64.4	64.3
Unit c						
→ 4)-α-Kdo-(2 →						
C-1	176.0	175.6	175.7	175.7	176.0	176.0
C-2	101.0	101.0	100.9	100.9	101.6	101.4
C-3	35.2	35.2	34.3	34.3	34.6	34.5
C-4	67.2	67.2	69.6	69.5	70.7	70.6
C-5	67.5	67.4	65.5	65.5	66.1	66.0
C-6	72.7	72.6	72.5	72.6	72.3	72.2
C-7	70.7	70.6	70.8	70.8	70.8	70.8
C-8	64.5	64.4	64.3	64.4	64.4	64.3
Unit d						
→ 6)-β-D-GlcNAc-(1 →						
C-1	102.7	102.5	102.6	102.5	102.4	102.2
C-2	56.6	56.5	56.5	56.6	56.6	56.6
C-3	75.0	74.9	75.0	75.0	75.0	74.9
C-4	71.9	71.7	71.6	71.6	72.3	72.1
C-5	75.3	75.3	75.4	75.5	75.4	75.5
C-6	63.4	63.2	63.1	63.2	63.7	63.6
Unit e						
→ 6)-α- or -β-D-GlcNAc-(1 → OAll)						
C-1	97.1	101.0	96.8	101.0	96.8	100.9
C-2	54.7	56.6	54.6	56.5	54.7	56.4
C-3	72.3	75.0	72.0	75.1	72.1	75.0
C-4	71.4	71.3	71.1	71.1	71.0	70.8
C-5	71.9	75.7	71.9	75.8	72.0	75.8
C-6	69.8	69.9	70.0	70.1	70.5	70.3

TABLE V (continued)

Carbon atom	16a	16b	19a	19b	23a	23b
Allyl group						
C-1	69.4	71.3	69.1	71.2	69.1	71.1
C-2	134.7	134.4	134.5	134.3	134.6	134.3
C-3	119.2	119.3	119.1	119.3	119.1	119.3
NHAc						
CO	175.5	175.5	175.3	175.3	175.2	175.3
	175.5	175.5	175.2	175.6	175.4	175.6
CH_3	23.4	23.3	23.3	23.4	23.3	23.3
	23.0	23.2	22.9	23.2	22.9	23.2

the positive-ion mode. Spectra from multiple laser shots were accumulated until an acceptable signal-to-noise ratio was obtained (typically 50 to 180 single shots). Mass calibration was performed using signals from singly charged gramicidin and insulin ions. The tetra- and penta-saccharide samples (0.5–2.7 mg) were dissolved in 320 μL of ultra-high-quality water (18 $M\Omega^{-1}cm^{-1}$). The selected and preferred matrix for native oligosaccharides is 2,5-dihydroxybenzoic acid and a saturated matrix solution in water was prepared[25]. An aliquot (0.2 μL) of sample solution was mixed with matrix solution (0.5 μL) in the centre of the disposable sample probe and the solvent was removed slowly in the system drying unit before insertion into the instrument. Thin layer chromatography was performed on Merck precoated plates (5 × 10 cm; layer thickness, 0.25 mm; Silica Gel $60F_{254}$); spots were detected by spraying with anisaldehyde–H_2SO_4 reagent[26]. Column chromatography was performed on Merck Lichroprep columns (size *A*, 24 × 1; *B*, 31 × 2.5; and *C*, 44 × 3.7 cm; silica gel 40–63 μm) under pressure (0.2 MPa). Elemental analyses were performed by Mag. J. Theiner, Mikroanalytisches Laboratorium am Institut für Physikalische Chemie, Universität Wien.

*Allyl 2-acetamido-2-deoxy-4,6-O-(tetraisopropyldisiloxane-1,3-diyl)-α-*D*-glucopyranoside*(**2**).—To a solution of **1** (252 mg, 1 mmol) in dry pyridine (5 mL) was added 1,3-dichloro-1,1,3,3,-tetraisopropyldisiloxane (0.35 mL, 1.1 mmol) at −10°C under N_2. The solution was stirred for 3 h, MeOH (1 mL) was added, and stirring was continued for 15 min. The solution was evaporated and the residue was dissolved in CH_2Cl_2 (50 mL). The organic layer was washed with satd aq $NaHCO_3$, dried (Na_2SO_4), and evaporated. Silica gel chromatography of the residue (*C*, 1:2 toluene–EtOAc) afforded 342 mg (83%) of **2** as colorless needles; mp 121°C (from EtOAc–hexane); $[\alpha]_D^{20}$ +35° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.90 (m, 1 H, =CH–), 5.87 (d, 1 H, NH), 5.30 (dq, 1 H, $=CH_{2trans}$), 5.23 (dq, 1 H, $=CH_{2cis}$), 4.89 (d, 1 H, $J_{1,2}$ ~ 4.0 Hz, H-1), 4.16 (m, 1 H, OCH_2), 4.14 (ddd, 1 H, $J_{2,3}$ ~ 10.0 Hz, H-2), 4.14 (dd, 1 H, $J_{6a,6b}$ ~ −12.5, $J_{6a,5}$ ~ 2.0 Hz, H-6a), 3.98 (m, 1 H, OCH_2), 3.88 (dd, 1 H, $J_{6b,5}$ ~ 1.5 Hz, H-6b), 3.82 (t, 1 H, $J_{3,4} \simeq J_{4,5} \simeq$ 9.0 Hz, H-4), 3.72 (dt,

1 H, $J_{3,OH}$ ~ 4.5 Hz, H-3), 3.53 (ddd, 1 H, H-5), 2.90 (d, 1 H, OH), 2.05 (s, 3 H, NHAc), 1.08 [m, 28 H, 4$(CH_3)_2CH$]. Anal. Calcd for $C_{23}H_{45}NO_7Si_2$: C, 54.84; H, 9.00; N, 2.78. Found: C, 54.89; H, 8.99; N, 2.73.

Allyl 2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-α-D-glucopyranoside (**5a**).—A solution of **2** (100 mg, 0.2 mmol) and dry toluene-*p*-sulfonic acid (5 mg) in dry *N*,*N*-dimethylformamide (DMF) (5 mL) was stirred for 24 h at 50°C. The solution was concentrated, diluted with CH_2Cl_2 (50 mL), washed with satd aq $NaHCO_3$, dried (Na_2SO_4), and evaporated. Purification of the residue on silica gel (*B*, 1:2 toluene–EtOAc) gave **5a** as colorless needles. Yield: 35 mg (35%); mp 127–128°C (from EtOAc–hexane); $[\alpha]_D^{20}$ +78° (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 5.91 (m, 1 H, =CH–), 5.45 (d, 1 H, $J_{NH,2}$ ~ 10.0 Hz, NH), 5.31 (dq, 1 H, $=CH_{2trans}$), 5.23 (dq, 1 H, $=CH_{2cis}$), 4.84 (d, 1 H, $J_{1,2}$ ~ 3.7 Hz, H-1), 4.20 (dt, 1 H, $J_{2,3}$ ~ 9.9 Hz, H-2), 4.18 (m, 1 H, OCH_2), 3.99 (m, 1 H, OCH_2), 3.86 (ddd, 1 H, $J_{6a,6b}$ ~ −11.5, $J_{6a,5}$ ~ 2.9, $J_{6a,OH}$ ~ 5.8 Hz, H-6a), 3.78 (dd, 1 H, $J_{3,4}$ ~ 7.9 Hz, H-3), 3.79–3.70 (m, 1 H, H-5), 3.71 (dd, 1 H, H-4), 3.65 (ddd, 1 H, H-6b), 1.99 (s, 3 H, NHAc), 1.91 (dd, 1 H, $J_{OH,6b}$ ~ 7.2 Hz, OH), 1.09–0.98 [m, 28 H, 4 $(CH_3)_2CH$]. Anal. Calcd for $C_{23}H_{45}NO_7Si_2$: C, 54.84; H, 9.00; N, 2.78. Found: C, 54.80; H, 9.15; N, 2.83.

Allyl 2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-6-O-triphenylmethyl-α-D-glucopyranoside (**4**).—A solution of **3** (2.4 g, 4.8 mmol) and 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (3.1 mL, 9.8 mmol) in dry pyridine (10 mL) was stirred for 3 days at 40°C. MeOH (5 mL) was added, and the solution was stirred for 30 min at room temperature. The solution was concentrated, then diluted with CH_2Cl_2 (50 mL), washed with satd aq $NaHCO_3$, and dried (Na_2SO_4). The solvents were evaporated and the residue was purified by silica gel chromatography (*C*, 1:1 toluene–EtOAc) which furnished **4** as colorless crystals. Yield: 3.3 g (90%); mp 230°C (EtOAc); $[\alpha]_D^{20}$ +39° (*c* 1.2, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ 7.51–7.42 (m, 6 H) and 7.32–7.17 (m, 9 H, arom. H), 6.04 (m, 1 H, =CH–), 5.55 (d, 1 H, $J_{NH,2}$ ~ 9.5 Hz, NH), 5.38 (dq, 1 H, $=CH_{2trans}$), 5.29 (dq, 1 H, $=CH_{2cis}$), 4.95 (d, 1 H, $J_{1,2}$ ~ 4.0 Hz, H-1), 4.41 (m, 1 H, OCH_2), 4.26 (dt, 1 H, $J_{2,3}$ ~ 9.5 Hz, H-2), 4.17 (m, 1 H, OCH_2), 3.89 (ddd, 1 H, H-5), 3.74 (dd, 1 H, $J_{3,4}$ ~ 9.0 Hz, H-3), 3.47 (dd, 1 H, $J_{4,5}$ ~ 8.0 Hz, H-4), 3.36 (dd, 1 H, $J_{6a,6b}$ ~ 9.5, $J_{6a,5}$ ~ 2.0 Hz, H-6a), 3.17 (dd, 1 H, $J_{6b,5}$ ~ 7.5 Hz, H-6b), 1.99 (s, 3 H, NHAc), and 1.08–0.66 [m, 28 H, 4 $(CH_3)_2CH$]. Anal. Calcd for $C_{42}H_{59}NO_7Si_2$: C, 67.61; H, 7.97; N, 1.88. Found: C, 67.88; H, 8.05; N, 1.75.

Detritylation of **4**.—A solution of **4** (3.5 g, 4.5 mmol) in dry CH_2Cl_2 (10 mL) was treated with $SnCl_4$ (1.5 mL, 12.8 mmol) for 15 min at 0°C. The yellow solution was diluted with CH_2Cl_2 (50 mL), poured into ice-cold satd aq $NaHCO_3$, and stirred for 10 min. The organic layer was separated, dried (Na_2SO_4), and evaporated. Purification of the residue by silica gel chromatography (*C*, 1:1 → 1:1.5 toluene–EtOAc) afforded **5a**. Yield: 2.14 g (94%).

Allyl O-(3,4,6-tri-O-acetyl-2-chloroacetamido-2-deoxy-β-D-glucopyranosyl)-(1 → 6)-2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-α-D-glucopyranoside

(8a).—A suspension of **5a** (1.5 g, 3 mmol), **6** (1.3 g, 3.1 mmol), and 4A molecular sieves (2 g) in dry CH_2Cl_2 (20 mL) was stirred for 30 min at room temperature. $FeCl_3$ (0.5 g, 3.2 mmol) was added, and stirring was continued for 48 h. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and filtered over Celite. The filtrate was stirred with water (50 mL), and the organic layer was separated, washed with satd aq $NaHCO_3$, dried (Na_2SO_4), and evaporated. Purification of the residue by silica gel chromatography (*C*, 2:1 EtOAc–toluene) afforded unreacted **6** (165 mg, 15%) and **5a** (270 mg, 18%). Further elution of the column with 1:1 EtOAc–toluene gave **8a** as colorless crystals. Yield: 1.3 g (50%); mp 214–216°C (from EtOAc–hexane); $[\alpha]_D^{20}$ +39° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 6.58 (d, 1 H, $J_{NH',2'} \sim 8.9$ Hz, NH′), 5.91 (m, 1 H, =CH–), 5.48 (d, 1 H, $J_{NH,2} \sim 9.7$ Hz, NH), 5.33 (dd, 1 H, $J_{3',4'} \sim 9.3$, $J_{3',2'} \sim 9.8$ Hz, H-3′), 5.31 (dq, 1 H, $=CH_{2trans}$), 5.23 (dq, 1 H, $=CH_{2cis}$), 5.08 (t, 1 H, $J_{4',5'} \sim 9.3$ Hz, H-4′), 4.79 (d, 1 H, $J_{1',2'} \sim 8.2$ Hz, H-1′), 4.78 (d, 1 H, $J_{1,2} \sim 3.5$ Hz, H-1), 4.26 (dd, 1 H, $J_{6'a,5'} \sim 5.1$, $J_{6'a,6'b} \sim -12.3$ Hz, H-6′a), 4.25–4.15 (m, 3 H, H-2,6a, OCH_2), 4.13 (dd, 1 H, $J_{6'b,5'} \sim 2.6$ Hz, H-6′b), 3.97–3.89 (m, 4 H, H-2′, OCH_2Cl, OCH_2), 3.82 (ddd, 1 H, H-5), 3.75 (dd, 1 H, H-4), 3.74 (m, 1 H, H-5′), 3.60 (dd, 1 H, $J_{3,4} \sim 8.0$, $J_{2,3} \sim 10.6$ Hz, H-3), 3.49 (dd, 1 H, $J_{6b,5} \sim 8.2$, $J_{6a,6b} \sim -9.7$ Hz, H-6b), 2.08 (s, 3 H), 2.04 (s, 6 H), and 1.98 (s, 3 H, 4 CH_3CO), 1.08–0.99 [m, 28 H, 4 $(CH_3)_2CH$]. Anal. Calcd for $C_{37}H_{63}ClN_2O_{15}Si_2$: C, 51.23; H, 7.32; N, 3.23. Found: C, 51.25; H, 7.19; N, 3.06.

Allyl O-*(3,4,6-tri-*O*-acetyl-2-chloroacetamido-2-deoxy-β-*D*-glucopyranosyl)-(1 → 6)-2-acetamido-2-deoxy-3,4-*O*-(tetraisopropyldisiloxane-1,3-diyl)-β-*D*-glucopyranoside* **(8b)** *and allyl 3,4,6-tri-*O*-acetyl-2-chloroacetamido-2-deoxy-β-*D*-glucopyranoside* **(7)**. —A suspension of **5b** (1 g, 2 mmol), **6** (0.92 g, 1 mmol), and 4A molecular sieves (2 g) in dry CH_2Cl_2 (10 mL) was stirred for 30 min at room temperature. $FeCl_3$ (0.3 g, 2 mmol) was added, and stirring was continued for 45 h. Work-up of the mixture, as in the preparation of **8a**, furnished a syrup which was purified by silica gel chromatography (*C*, 1:1 → 1:3 toluene–EtOAc). Product-containing fractions having R_f-values between 0.30–0.45 (1:1 toluene–EtOAc) and consisting of unreacted **5b**, **6**, and **7** as the major components were pooled and evaporated. Crystallization from EtOAc–hexane afforded **7** as colorless needles. Yield: 350 mg (37%); mp 165–166°C; $[\alpha]_D^{20}$ −8° (*c* 1.0, $CHCl_3$); lit.[18] mp 166–167°C; $[\alpha]_D^{20}$ −9° ($CHCl_3$); ^1H NMR ($CDCl_3$): δ 6.60 (d, 1 H, $J_{NH,2} \sim 8.7$ Hz, NH), 5.86 (m, 1 H, =CH–), 5.27 (dq, 1 H, $=CH_{2trans}$), 5.21 (dq, 1 H, $=CH_{2cis}$), 5.09 (t, 1 H, $J_{4,5} \sim 9.3$ Hz, H-4), 4.78 (d, 1 H, $J_{1,2} \sim 8.2$ Hz, H-1), 4.35 (m, 1 H, OCH_2), 4.28 (dd, 1 H, $J_{6a,6b} \sim -12.3$, $J_{6a,5} \sim 4.8$ Hz, H-6a), 4.15 (dd, 1 H, $J_{6b,5} \sim 2.5$ Hz, H-6b), 4.09 (m, 1 H, OCH_2), 4.01 (m, 2 H, CH_2Cl), 3.89 (ddd, 1 H, H-2), 3.72 (ddd, 1 H, H-5), 2.10 (s, 3 H) and 2.03 (s, 6 H, CH_3CO).

Further elution of the column gave **8b** as colorless crystals. Yield: 750 mg (43%); mp 218–220°C (EtOAc); $[\alpha]_D^{20}$ +6° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 6.59 (d, 1 H, $J_{NH',2'} \sim 8.7$ Hz, NH′), 5.91 (m, 1 H, =CH–), 5.51 (d, 1 H, $J_{NH,2} \sim 8.1$ Hz, NH), 5.32 (dd, 1 H, $J_{3',2'} \sim 10.2$ Hz, H-3′), 5.32 (dq, 1 H, $=CH_{2trans}$), 5.21 (dq, 1 H, $=CH_{2cis}$), 5.09 (t, 1 H, $J_{4',5'} \simeq J_{4',3'} \simeq 9.4$ Hz, H-4′), 4.94 (d, 1 H, $J_{1,2} \sim 8.5$ Hz,

H-1), 4.88 (d, 1 H, $J_{1',2'}$ ~ 8.2 Hz, H-1'), 4.32 (m, 1 H, OCH_2), 4.26 (dd, 1 H, $J_{6'a,6'b}$ ~ −12.2, $J_{6'a,5'}$ ~ 4.7 Hz, H-6'a), 4.16 (m, 1 H, H-6a), 4.15 (m, 1 H, H-6'b), 4.14 (m, 1 H, OCH_2), 4.08 (dd, 1 H, $J_{2,3}$ ~ 9.6, $J_{3,4}$ ~ 7.7 Hz, H-3), 4.00 (m, 2 H, CH_2Cl), 3.91 (ddd, 1 H, H-2'), 3.71 (ddd, 1 H, $J_{5',6'b}$ ~ 2.4 Hz, H-5'), 3.69 (dd, 1 H, $J_{6a,6b}$ ~ −11.3 Hz, H-6b), 3.57 (m, 1 H, H-5), 3.43 (dd, 1 H, $J_{4,5}$ ~ 9.4 Hz, H-4), 3.32 (ddd, 1 H, H-2), 2.08 (s, 3 H), 2.04 (s, 3 H), 2.03 (s, 3 H) and 1.96 (s, 3 H, CH_3CO), 1.06–0.99 [m, 28 H, 4 $(CH_3)_2CH$]. Anal. Calcd for $C_{37}H_{63}ClN_2O_{15}Si_2$: C, 51.23; H, 7.32; N, 3.23. Found: C, 51.44; H, 7.21; N, 3.10.

Allyl O-*(2-acetamido-3,4,6-tri*-O-*acetyl-2-deoxy-β-*D-*glucopyranosyl)-(1 → 6)-2-acetamido-2-deoxy-3,4*-O-*(tetraisopropyldisiloxane-1,3-diyl)-α-*D-*glucopyranoside* (**9a**).—A suspension of **8a** (1.9 g, 2.2 mmol) and Zn dust (1.5 g) in AcOH (12 mL) was heated at 110°C for 2.5 h, additional Zn dust (0.5 g) being added after 1 h. After cooling to room temperature, the suspension was diluted with CH_2Cl_2 (50 mL) and filtered over Celite. The filtrate was concentrated and purified by column chromatography on silica gel (*C*, EtOAc → 5:1 EtOAc–MeOH), giving 1.54 g (~ 84%) of **9a** as colorless needles; mp 220–222°C (from EtOAc–hexane); $[\alpha]_D^{20}$ +33° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.90 (m, 1 H, =CH–), 5.49 (d, 1 H, $J_{NH,2}$ ~ 9.3 Hz, NH), 5.47 (d, 1 H, $J_{NH',2'}$ ~ 9.0 Hz, NH'), 5.31 (dq, 1 H, $=CH_{2trans}$), 5.24 (dq, 1 H, $=CH_{2cis}$), 5.22 (dd, 1 H, $J_{2',3'}$ ~ 9.2, $J_{3',4'}$ ~ 9.4 Hz, H-3'), 5.07 (t, 1 H, $J_{4',5'}$ ~ 9.4 Hz, H-4'), 4.78 (d, 1 H, $J_{1,2}$ ~ 3.7 Hz, H-1), 4.66 (d, 1 H, $J_{1',2'}$ ~ 8.2 Hz, H-1') 4.23 (dd, 1 H, $J_{6'a,6'b}$ ~ −12.4, $J_{6'a,5'}$ ~ 5.0 Hz, H-6'a), 4.22–4.14 (m, 3 H, H-2,6a, OCH_2), 4.11 (dd, 1 H, $J_{6'b,5'}$ ~ 2.6 Hz, H-6'b), 3.98 (ddd, 1 H, H-2'), 3.93 (m, 1 H, OCH_2), 3.83 (ddd, 1 H, H-5), 3.75 (dd, 1 H, $J_{2,3}$ ~ 9.8, $J_{3,4}$ ~ 8.2 Hz, H-3), 3.69 (ddd, 1 H, H-5'), 3.57 (dd, 1 H, $J_{6b,5}$ ~ 8.0, $J_{6a,6b}$ ~ −10.6 Hz, H-6b), 3.49 (dd, 1 H, $J_{4,5}$ ~ 9.6 Hz, H-4), 2.07 (s, 3 H), 2.02 (s, 6 H), 1.98 (s, 3 H) and 1.91 (s, 3 H, CH_3CO), 1.07–0.99 [m, 28 H, 4$(CH_3)_2CH$]. Anal. Calcd. for $C_{37}H_{64}N_2O_{15}Si_2$: C, 53.34; H, 7.74; N, 3.36. Found: C, 53.50; H, 7.70; N, 3.28.

Allyl O-*(2-acetamido-3,4,6-tri*-O-*acetyl-2-deoxy-β-*D-*glucopyranosyl)-(1 → 6)-2-acetamido-2-deoxy-3,4*-O-*(tetraisopropyldisiloxane-1,3-diyl)-β-*D-*glucopyranoside* (**9b**).—A solution of **8b** (866 mg, 1 mmol), tributyltin hydride (2 mL), and 2,2'-azobisisobutyronitrile (20 mg) in dry toluene was heated for 90 min at 85°C. The solution was concentrated and purified by silica gel chromatography (*C*, EtOAc) affording, first, unreacted **8b** (150 mg, 17%), then **9b** as an amorphous solid. Yield: 440 mg (53%); $[\alpha]_D^{20}$ −2° (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.90 (m, 1 H, =CH–), 5.50 (d, 1 H, $J_{NH,2}$ ~ 8.3 Hz, NH), 5.47 (d, 1 H, $J_{NH,2}$ ~ 7.7 Hz, NH), 5.32 (dq, 1 H, $=CH_{2trans}$), 5.22 (dq, 1 H, $=CH_{2cis}$), 5.22 (dd, 1 H, $J_{2',3'}$ ~ 10.4, $J_{3',4'}$ ~ 9.6 Hz, H-3'), 4.91 (d, 1 H, $J_{1,2}$ ~ 8.7 Hz, H-1), 4.74 (d, 1 H, $J_{1',2'}$ ~ 8.3 Hz, H-1'), 4.32 (m, 1 H, OCH_2), 4.24 (dd, 1 H, $J_{6'a,6'b}$ ~ −12.2, $J_{6'b,5'}$ ~ 4.5 Hz, H-6'a), 4.17 (dd, 1 H, H-6a), 4.14 (m, 1 H, OCH_2), 4.12 (dd, 1 H, H-6'b), 4.04 (dd, 1 H, $J_{2,3}$ ~ 9.9, $J_{3,4}$ ~ 7.8 Hz, H-3), 3.95 (ddd, 1 H, H-2'), 3.69 (ddd, 1 H, $J_{5',6'}$ ~ 2.5 Hz, H-5'), 3.65–3.44 (m, 3 H, H-4,5,6b), 3.37 (ddd, 1 H, H-2), 2.07 (s, 3 H), 2.02 (s, 6 H), 1.96 (s, 3 H) and 1.92 (s, 3 H, CH_3CO), 1.06–0.98 [m, 28 H, 4

$(CH_3)_2CH$]. Anal. Calcd for $C_{37}H_{64}N_2O_{15}Si_2$: C, 53.34; H, 7.74; N, 3.36. Found: C, 53.61; H, 7.59; N, 3.28.

Allyl O-[2-acetamido-2-deoxy-4,6-O-(tetraisopropyldisiloxane-1,3-diyl)-β-D-glucopyranosyl]-(1 → 6)-2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-α-D-glucopyranoside (**10a**).—A solution of **9a** (300 mg, 0.36 mmol) and 0.1 M methanolic NaOMe (1 mL) in dry MeOH (10 mL) was stirred for 2 h at room temperature. Dowex 50 (H^+) cation-exchange resin was added to neutral pH, and the mixture was filtered. The filtrate was evaporated to dryness and the residue was dissolved in pyridine (10 mL). 1,3-Dichloro-1,1,3,3-tetraisopropyldisiloxane (0.8 mL, 2.5 mmol) was added and the solution was stirred for 12 h at room temperature. MeOH (1 mL) was added and stirring was continued for 20 min. The solution was concentrated and the product was isolated by silica gel chromatography (*C*, EtOAc). Yield: 300 mg (88%) of **10a** as colorless needles; mp 215–217°C (from hexane–EtOAc); $[\alpha]_D^{20}$ +6° (*c* 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.91 (m, 1 H, =CH–), 5.91 (d, 1 H, $J_{NH',2'}$ ~ 5.1 Hz, NH'), 5.49 (d, 1 H, $J_{NH,2}$ ~ 9.7 Hz, NH), 5.27 (dq, 1 H, $=CH_{2trans}$), 5.23 (dq, 1 H, $=CH_{2cis}$), 4.81 (d, 1 H, $J_{1,2}$ ~ 3.6 Hz, H-1), 4.61 (d, 1 H, $J_{3',OH}$ ~ 2.8 Hz, OH), 4.47 (d, 1 H, $J_{1',2'}$ ~ 8.2 Hz, H-1') 4.26 (dd, 1 H, $J_{6a,6b}$ ~ −10.3, $J_{6a,5}$ ~ 1.9 Hz, H-6a), 4.20 (m, 2 H, H-2, OCH_2), 4.11 (dd, 1 H, $J_{6'a,6'b}$ ~ −12.5, $J_{6'a,5'}$ ~ 2.2 Hz, H-6'a), 3.97 (m, 1 H, OCH_2), 3.96–3.80 (m, 4 H, H-3,5,4',6'b), 3.77 (dd, 1 H, $J_{2',3'}$ ~ 10.2, $J_{3',4'}$ ~ 8.0 Hz, H-3'), 3.57 (dd, 1 H, $J_{6b,5}$ ~ 8.3 Hz, H-6b), 3.50 (dd, 1 H, $J_{4,5}$ ~ 9.8, $J_{4,3}$ ~ 8.2 Hz, H-4), 3.46 (ddd, 1 H, H-2'), 3.21 (br d, 1 H, H-5), 2.00 (s, 3 H) and 1.98 (s, 3 H, NHAc), 1.11–0.98 [m, 56 H, 8 $(CH_3)_2CH$]. Anal. Calcd for $C_{43}H_{84}N_2O_{13}Si_4$: C, 54.39; H, 8.92; N, 2.95. Found: C, 54.17; H, 8.83; N, 2.95.

Allyl O-[2-acetamido-2-deoxy-4,6-O-(tetraisopropyldisiloxane-1,3-diyl)-β-D-glucopyranosyl]-(1 → 6)-2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-β-D-glucopyranoside (**10b**).—A solution of **9b** (799 mg, 0.84 mmol) and 0.1 M methanolic NaOMe (6 mL) in dry MeOH (10 mL) was stirred for 6 h at room temperature. Work-up of the solution as described for **10a** gave a syrup (590 mg, quantitative), which was dissolved in pyridine (10 mL) and stirred with 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (12 mL) for 2 h. Purification as in the preparation of **10a** afforded **10b** as colorless needles. Yield: 790 mg (99%); mp 250–260°C (from hexane–EtOAc); $[\alpha]_D^{20}$ −26° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 6.10 (d, 1 H, $J_{NH',2'}$ ~ 4.4 Hz, NH'), 5.87 (m, 1 H, =CH–), 5.49 (d, 1 H, $J_{NH,2}$ ~ 8.3 Hz, NH), 5.29 (dq, 1 H, $=CH_{2trans}$), 5.20 (dq, 1 H, $=CH_{2cis}$), 4.94 (d, 1 H, $J_{1,2}$ ~ 8.5 Hz, H-1), 4.54 (d, 1 H, $J_{1',2'}$ ~ 8.3 Hz, H-1'), 4.30 (m, 2 H, OCH_2, H-6a), 4.12 (m, 1 H, OCH_2), 4.11 (dd, 1 H, $J_{6'a,6'b}$ ~ −12.1 Hz, $J_{6'a,5'}$ ~ 1.5 Hz, H-6'a), 4.00 (dd, 1 H, $J_{2,3}$ ~ 9.8, $J_{3,4}$ ~ 8.1 Hz, H-3), 3.94 (dd, 1 H, $J_{6'b,5'}$ ~ 1.0 Hz, H-6'b), 3.83 (t, 1 H, $J_{3',4'} \simeq J_{4',5'} \simeq 9.0$ Hz, H-4'), 3.69 (t, 1 H, $J_{2',3'}$ ~ 9.0 Hz, H-3'), 3.64–3.42 (m, 5 H, H-2,4,5,6b,2'), 3.20 (br d, 1 H, H-5'), 2.04 (s, 3 H) and 1.98 (s, 3 H, NHAc), 1.12–0.99 [m, 56 H, 8$(CH_3)_2CH$]. Anal. Calcd. for $C_{43}H_{84}N_2O_{13}Si_4$: C, 54.39; H, 8.92; N, 2.95. Found: C, 54.12; H, 8.96; N, 2.89.

Allyl O-[2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-β-D-glu-

copyranosyl]-(1 → 6)-2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-α-D-glucopyranoside (**11a**).—A solution of **10a** (200 mg, 0.21 mmol) and a catalytic amount of toluene-*p*-sulfonic acid in dry DMF (8 mL) was stirred for 15 h at room temperature. The solution was concentrated and purified by silica gel chromatography (*B*, EtOAc), which afforded **11a** as colorless crystals. Yield: 130 mg (65%); mp (dec) 140–142°C (from hexane–EtOAc); $[\alpha]_D^{20}$ +48° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.94 (m, 1 H, =CH–), 5.51 (d, 1 H, $J_{NH',2'}$ ~ 8.0 Hz, NH′), 5.50 (d, 1 H, $J_{NH,2}$ ~ 9.6 Hz, H-2), 5.30 (dq, 1 H, $=CH_{2trans}$), 5.23 (dq, 1 H, $=CH_{2cis}$), 4.93 (d, 1 H, $J_{1',2'}$ ~ 8.4 Hz, H-1′), 4.80 (d, 1 H, $J_{1,2}$ ~ 3.6 Hz, H-1), 4.23 (ddd, 1 H, $J_{2,3}$ ~ 9.9 Hz, H-2), 4.20 (m, 1 H, OCH_2), 4.12 (dd, 1 H, $J_{6a,5}$ ~ 1.5, $J_{6a,6b}$ ~ −10.9 Hz, H-6a), 4.09 (dd, 1 H, $J_{2',3'}$ ~ 9.9 Hz, H-3′), 3.96 (m, 1 H, OCH_2), 3.87 (ddd, 1 H, $J_{6'a,6'b}$ ~ −11.7, $J_{6'a,5'}$ ~ 3.0 Hz, H-6′a), 3.79 (ddd, 1 H, $J_{5,4}$ ~ 9.6, $J_{5,6b}$ ~ 7.5 Hz, H-5), 3.75 (dd, 1 H, $J_{3,4}$ ~ 8.1 Hz, H-3), 3.72 (ddd, 1 H, $J_{6'b,5'}$ ~ 5.5 Hz, H-6′b), 3.68 (dd, 1 H, H-6b), 3.63 (dd, 1 H, $J_{4',5'}$ ~ 9.2 Hz, H-4′), 3.55 (dd, 1 H, H-4), 3.42 (ddd, 1 H, H-5′), 3.38 (ddd, 1 H, H-2′), 1.98 (s, 3 H) and 1.93 (s, 3 H, NHAc), 1.07–1.00 [m, 56 H, 8 $(CH_3)_2CH$]. Anal. Calcd for $C_{43}H_{84}N_2O_{13}Si_4$: C, 54.39; H, 8.92; N, 2.95. Found: C, 54.65; H, 8.82; N, 3.08.

*Allyl O-[2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-β-*D-*glucopyranosyl]-(1 → 6)-2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-β-*D-*glucopyranoside* (**11b**).—Compound **11b** was prepared from **10b** (336 mg, 0.35 mmol) as described for **11a**. Yield: 271 mg (81%); colorless needles; mp 235–246°C (from EtOAc–hexane); $[\alpha]_D^{20}$ +18° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.90 (m, 1 H, =CH–), 5.52 (d, 1 H, $J_{NH',2'}$ ~ 8.2 Hz, NH′), 5.50 (d, 1 H, $J_{NH,2}$ ~ 7.8 Hz, NH), 5.30 (dq, 1 H, $=CH_{2trans}$), 5.19 (dq, 1 H, $=CH_{2cis}$), 4.98 (d, 1 H, $J_{1',2'}$ ~ 8.5 Hz, H-1′), 4.94 (d, 1 H, $J_{1,2}$ ~ 8.4 Hz, H-1), 4.33 (m, 1 H, OCH_2), 4.13 (m, 1 H, OCH_2), 4.10 (m, 2 H, H-3,3′), 3.89 (ddd, 1 H, $J_{6'a,5'}$ ~ 2.9, $J_{6'a,OH}$ ~ 6.5, $J_{6'a,6'b}$ ~ −11.4 Hz, H-6′a), 3.62 (dd, 1 H, $J_{4',5'}$ ~ 9.5, $J_{4',3'}$ ~ 8.0 Hz, H-4′), 3.53 (m, 1 H, H-5), 3.52–3.30 (m, 3 H, H-4,2′,5′), 3.30 (ddd, 1 H, H-2), 2.03 (t, 1 H, OH), 1.96 (s, 3 H) and 1.95 (s, 3 H, NHAc), 1.07–1.00 [m, 56 H, 8 $(CH_3)_2CH$]. Anal. Calcd for $C_{43}H_{84}N_2O_{13}Si_4$: C, 54.39; H, 8.92; N, 2.95. Found: C, 54.33; H, 8.78; N, 2.90.

*Allyl O-(methyl 4,5,7,8-tetra-O-acetyl-3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 6)-O-[2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-β-*D-glucopyranoysyl]-(1 → 6)-2-acetamido-2-deoxy-3,4-O-*(tetraisopropyldisiloxane-1,3-diyl)-α-*D-glucopyranoside (**13a**) *and allyl O-(methyl 4,5,7,8-tetra-O-acetyl-3-deoxy-β-*D-manno-*2-octulopyranosylonate)-(2 → 6)-O-[2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-β-*D-*glucopyranosyl]-(1 → 6)-2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-α-*D-*glucopyranoside* (**15**).—A solution of **12** (1.1 g, 2.4 mmol) in CH_3NO_2 (4 mL) was added in 4 portions during 48 h to a suspension of **11a** (400 mg, 0.42 mmol), $Hg(CN)_2$ (131 mg, 0.52 mmol), $HgBr_2$ (66 mg, 0.18 mmol), and 4A molecular sieves (1 g) in 1 : 1 CH_2Cl_2–CH_3NO_2 (5 mL) at room temperature. Stirring was continued for 48 h, and the suspension was diluted with CH_2Cl_2 (50 mL) and filtered over Celite. The filtrate was washed with aq 10% KI and satd aq $NaHCO_3$, and dried (Na_2SO_4). Concentration of the solution

gave a syrup, which was purified by silica gel chromatography (*C*, 1:1 toluene–EtOAc → EtOAc). Yield: 272 mg (48%) of **13a**; colorless crystals; mp 197–198°C (from hexane–EtOAc); $[\alpha]_D^{20}$ +62° (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.93 (m, 1 H, =CH–), 5.61 (d, 1 H, $J_{NH,2}$ ~ 9.5 Hz, NH), 5.48 (d, 1 H, $J_{NH',2'}$ ~ 8.2 Hz, NH'), 5.33 (dq, 1 H, $=CH_{2trans}$), 5.24 (dq, 1 H, $=CH_{2cis}$), 4.22 (m, 1 H) and 3.96 (m, 1 H, OCH_2), 3.77 (s, 3 H, CO_2CH_3), 2.08 (s, 3 H), 2.07 (s, 3 H), 1.98 (s, 6 H), 1.95 (s, 3 H), and 1.93 (s, 3 H, CH_3CO), 1.07–1.00 [m, 56 H, 8 $(CH_3)_2CH$]. Anal. Calcd for $C_{60}H_{106}N_2O_{24}Si_4$: C, 53.31; H, 7.90; N, 2.07. Found: C, 53.16; H, 7.94; N, 1.97.

Further elution of the column afforded **15** as a syrup. Yield: 215 mg (38%); $[\alpha]_D^{20}$ +53° (*c* 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.92 (m, 1 H, =CH–), 5.52 (d, 1 H, $J_{NH,2}$ ~ 8.6 Hz, NH), 5.49 (d, 1 H, $J_{NH',2'}$ ~ 8.4 Hz, NH'), 5.31 (dq, 1 H, $=CH_{2trans}$), 5.29 (br s, 1 H, H-5″), 5.23 (dq, 1 H, $=CH_{2cis}$), 5.16 (ddd, 1 H, $J_{7'',6''}$ ~ 9.5, $J_{7'',8''a}$ ~ 2.1, $J_{7'',8''b}$ ~ 4.9 Hz, H-7″), 4.89 (ddd, 1 H, $J_{4'',3''e}$ ~ 4.7, $J_{4'',3''a}$ ~ 13.1, $J_{4'',5''}$ ~ 3.0 Hz, H-4″), 4.79 (d, 1 H, $J_{1,2}$ ~ 3.7 Hz, H-1), 4.72 (d, 1 H, $J_{1',2'}$ ~ 8.4 Hz, H-1'), 4.44 (dd, 1 H, $J_{8''a,8''b}$ ~ −12.3 Hz, H-8″a), 4.20 (m, 4 H, H-2,6a,8″b, OCH_2), 4.13 (dd, 1 H, $J_{6'a,5'}$ ~ 1.2, $J_{6'a,6'b}$ ~ −9.9 Hz, H-6'a), 4.05 (dd, 1 H, $J_{6'',5''}$ ~ 1.3 Hz, H-6″), 3.95 (m, 1 H, OCH_2), 3.94 (dd, 1 H, $J_{3',4'}$ ~ 10.1 Hz, H-3'), 3.80 (m, 1 H, H-5), 3.78 (s, 3 H, CO_2CH_3), 3.75 (dd, 1 H, $J_{3,4}$ ~ 10.0 Hz, H-3), 3.60–3.45 (m, 6 H, H-4,6b,2',4',5',6'b), 2.38 (dd, 1 H, $J_{3''e,3''a}$ ~ −12.0 Hz, H-3″*e*), 2.10 (t, 1 H, H-3″*a*), 2.11 (s, 3 H), 2.08 (s, 3 H), 1.99 (s, 3 H), and 1.98 (s, 6 H, CH_3CO), 1.07–0.98 [m, 56 H, 8 $(CH_3)_2CHSi$]. Anal. Calcd for $C_{60}H_{106}N_2O_{24}Si_4$: C, 53.31; H, 7.90; N, 2.07. Found: C, 53.61; H, 7.73; N, 2.18.

Allyl O-*(methyl 4,5,7,8-tetra*-O-*acetyl-3-deoxy-α*-D-manno-*2-octulopyranosylonate)-(2 → 6)-[2-acetamido-2-deoxy-3,4*-O-*(tetraisopropyldisiloxane-1,3-diyl)-β*-D-glucopyranosyl]-(1 → 6)-2-acetamido-2-deoxy-3,4-O-*(tetraisopropyldisiloxane-1,3-diyl)-β*-D-glucopyranoside (**13b**).—Compound **13b** was prepared, similarly to **13a**, from **11a** (265 mg, 0.28 mmol), $Hg(CN)_2$ (374 mg, 1.48 mmol), $HgBr_2$ (178 mg, 0.49 mmol), 4A molecular sieves (1 g), and **12** (790 mg, 1.64 mmol) in 2:1 CH_3NO_2–CH_2Cl_2 (5 mL). The mixture was purified as described for **13a**. For the final purification, a second chromatography was performed using 1:1 hexane–EtOAc (*C*) which afforded **13b** as colorless crystals. Yield: 196 mg (52%); mp 240° (from EtOAc–hexane); $[\alpha]_D^{20}$ +40° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.90 (m, 1 H, =CH–), 5.68 (d, 1 H, $J_{NH',2'}$ ~ 8.6 Hz, NH'), 5.52 (d, 1 H, $J_{NH,2}$ ~ 8.1 Hz, NH), 5.31 (dq, 1 H, $=CH_{2trans}$), 5.18 (dq, 1 H, $=CH_{2cis}$), 4.34 (m, 1 H) and 4.18 (m, 1 H, OCH_2), 3.77 (s, 3 H, CO_2CH_3), 2.08 (s, 6 H), 1.98 (s, 3 H), 1.97 (s, 3 H), 1.96 (s, 3 H), and 1.95 (s, 3 H, CH_3CO), 1.06–0.98 [m, 56 H, 8 $(CH_3)_2CH$]. Anal. Calcd for $C_{60}H_{106}N_2O_{24}Si_4$: C, 53.31; H, 7.90; N, 2.07. Found: C, 53.42; H, 7.90; N, 1.99.

Allyl O-*(sodium 3-deoxy-α*-D-manno-*2-octulopyranosylonate)-(2 → 6)*-O-*(2-acetamido-2-deoxy-β*-D-*glucopyranosyl)-(1 → 6)-2-acetamido-2-deoxy-α*-D-*glucopyranoside* (**16a**).—A solution of **13a** (30 mg, 0.02 mmol) and tetrabutylammonium fluoride (80 μL of a 1.1 M solution in THF) in dry THF (6 mL) was stirred for 2 h at room temperature. The solution was evaporated in vacuo and the residue was dissolved in dry MeOH (8 mL) and 0.1 M methanolic NaOMe (1.5 mL). The

solution was kept at room temperature for 4 h. Dowex 50 (H^+) ion-exchange resin was added to neutral pH and then the resin was filtered off. The filtrate was taken to dryness. A solution of the residue in water (4 mL) was treated with 0.2 M aq NaOH (4 mL) for 12 h at 4°C. The pH of the solution was adjusted to 8.5 by addition of Dowex 50 (H^+) resin, the suspension was filtered, and the filtrate was lyophilized. Purification of the residue on a Biogel P-2 column (2.8 × 100 cm, 20:1 H_2O–EtOH) afforded **16a** as an amorphous powder. Yield: 9.8 mg (62%); $[\alpha]_D^{20}$ +61° (*c* 0.4, H_2O); ^1H NMR (D_2O): δ 6.01 (m, 1 H, =CH–), 5.39 (dq, 1 H, $=CH_{2trans}$), 5.31 (dq, 1 H, $=CH_{2cis}$), 4.22 and 4.04 (m, 2 H, OCH_2), 2.08 (s, 6 H, NHAc). PDMS: *m/z* 730.27 $[M + Na]^+$, 705.74 $[M - H]^-$.

Allyl O-*(sodium 3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 6)-O-(2-acetamido-2-deoxy-β-*D-*glucopyranosyl)-(1 → 6)-2-acetamido-2-deoxy-β-*D-*glucopyranoside* (**16b**).—Compound **16b** was prepared from **13b** (22 mg, 0.016 mmol), similarly to **16a**. Yield: 7.3 mg (65%) of **16b**; amorphous powder; $[\alpha]_D^{20}$ −1° (*c* 0.6, H_2O); ^1H NMR (D_2O): δ 5.93 (m, 1 H, =CH–), 5.34 (dq, 1 H, $=CH_{2trans}$), 5.29 (dq, 1 H, $=CH_{2cis}$), 4.34 (m, 1 H) and 4.15 (m, 1 H, OCH_2), 2.07 (s, 3 H) and 2.06 (s, 3 H, NHAc). PDMS: *m/z* 730.29 $[M + Na]^+$, 705.67 $[M - H]^-$.

Allyl O-*(methyl 7,8-*O-*carbonyl-3-deoxy-α-*D-*manno-2-octulopyranosylonate)-(2 → 6)-[2-acetamido-2-deoxy-3,4-*O-*(tetraisopropyldisiloxane-1,3-diyl)-β-*D-*glucopyranosyl]-(1 → 6)-2-acetamido-2-deoxy-3,4-*O-*(tetraisopropyldisiloxane-1,3-diyl)-α-*D-*glucopyranoside* (**14a**).—A solution of **13a** (121 mg, 0.09 mmol) and 0.1 M methanolic NaOMe (1.5 mL) in dry MeOH (15 mL) was stirred for 2 h at room temperature. The solution was de-ionized by addition of Dowex 50 (H^+) ion-exchange resin, and filtered. The filtrate was evaporated, and the residue was dried and dissolved in dry THF (8 mL) and 2,4,6-trimethylpyridine (110 μL, 0.8 mmol). A solution of trichloromethyl chloroformate (10 μL, 0.08 mmol) in THF (0.5 mL) was added dropwise at −20°C during 50 min under N_2. MeOH (0.5 mL) was added, and the solution was taken to dryness. The residue was purified on silica gel (*B*, EtOAc), which gave **14a** as colorless crystals. Yield: 88 mg (82%); mp 134–135°C (from EtOAc–hexane); $[\alpha]_D^{20}$ +68° (*c* 1.9, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.92 (m, 1 H, =CH–), 5.63 (d, 1 H, $J_{NH,2}$ ~ 9.6 Hz, NH), 5.59 (d, 1 H, $J_{NH',2'}$ ~ 7.6 Hz, NH'), 5.33 (dq, 1 H, $=CH_{2trans}$), 5.24 (dq, 1 H, $=CH_{2cis}$), 4.23 and 4.00 (m, 2 H, OCH_2), 3.74 (s, 3 H, CO_2CH_3), 2.62 (br s, 1 H, OH), 1.99 (s, 3 H) and 1.94 (s, 3 H, NHAc), 1.07–1.00 [m, 56 H, 8 $(CH_3)_2CHSi$]. Anal. Calcd for $C_{53}H_{96}N_2O_{21}Si_4$: C, 52.62; H, 8.00; N, 2.32. Found: C, 52.92; H, 7.78; N, 2.19.

Allyl O-*(methyl 7,8-*O-*carbonyl-3-deoxy-α-*D-*manno-2-octulopyranosylonate)-(2 → 6)-O-[2-acetamido-2-deoxy-3,4-*O-*(tetraisopropyldisiloxane-1,3-diyl)-β-*D-*glucopyranosyl]-(1 → 6)-2-acetamido-2-deoxy-3,4-*O-*(tetraisopropyldisiloxane-1,3-diyl)-α-*D-*glucopyranoside* (**14b**).—A solution of **13b** (140 mg, 0.1 mmol) in MeOH (10 mL) was stirred with 0.1 M methanolic NaOMe (2 mL) for 3.5 h at room temperature. De-ionization of the solution by addition of Dowex 50 (H^+) ion-exchange resin, filtration, and evaporation of the filtrate afforded a syrup (120 mg), which was treated in the same way as for **14a**. Work-up and column chromatography, as

described, gave **14b** as an amorphous powder. Yield: 102 mg (83%); $[\alpha]_D^{20}$ +31° (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.90 (m, 1 H, =CH–), 5.69 (dd, 1 H, $J_{NH,2}$ ~ 7.8 Hz, NH), 5.66 (d, 1 H, $J_{NH,2}$ ~ 8.8 Hz, NH), 5.32 (dq, 1 H, $=CH_{2trans}$), 5.19 (dq, 1 H, $=CH_{2cis}$), 3.74 (s, 3 H, CO_2CH_3), 1.97 (s, 3 H) and 1.95 (s, 3 H, NHAc), 1.07–0.97 [m, 56 H, 8 $(CH_3)_2CHSi$]. Anal. Calcd for $C_{53}H_{96}N_2O_{21}Si_4$: C, 52.62; H, 8.00; N, 2.32. Found: C, 52.64; H, 7.75; N, 2.34.

Allyl O-*(methyl 4,5,7,8-tetra*-O-*acetyl-3-deoxy-α*-D-manno-*2-octulopyranosylonate)-(2 → 4)*-O-*(methyl 7,8*-O-*carbonyl-3-deoxy-α*-D-manno-*2-octulopyranosylonate)-(2 → 6)*-O-*[2-acetamido-2-deoxy-3,4*-O-*(tetraisopropyldisiloxane-1,3-diyl)-β*-D-*glucopyranosyl]-(1 → 6)-2-acetamido-2-deoxy-3,4*-O-*(tetraisopropyldisiloxane-1,3-diyl)-α*-D-*glucopyranoside* (**17a**).—A solution of **12** (350 mg, 0.7 mmol) in dry CH_3NO_2 (2 mL) was added dropwise during 5 h to a suspension of **14a** (51 mg, 0.04 mmol), $Hg(CN)_2$ (120 mg, 0.48 mmol), $HgBr_2$ (110 mg, 0.31 mmol), and 4A molecular sieves (1 g) in 1:1 CH_3CN–CH_3NO_2 (2 mL) under N_2. The suspension was stirred for 24 h at room temperature, diluted with EtOAc (30 mL), and filtered over Celite. The filtrate was washed with aq 10% KI and satd aq $NaHCO_3$, dried ($MgSO_4$), and concentrated. The residue was purified by chromatography (*B*, 1:3 toluene–EtOAc), which afforded **17a** as a syrup. Yield: 41 mg (60%); $[\alpha]_D^{20}$ +63° (*c* 0.4, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.93 (m, 1 H, =CH–), 5.62 (d, 1 H, $J_{NH',2'}$ ~ 8.6 Hz, NH'), 5.49 (d, 1 H, $J_{NH,2}$ ~ 9.4 Hz, NH), 5.31 (dq, 1 H, $=CH_{2trans}$), 5.22 (m, 1 H, $=CH_{2cis}$), 4.23 and 4.00 (m, 1 H, OCH_2), 3.81 (s, 3 H) and 3.75 (s, 3 H, CO_2CH_3), 2.40 (br s, 1 H, OH), 2.14 (s, 3 H), 2.08 (s, 6 H), and 1.98 (s, 9 H, CH_3CO), 1.07–0.99 [m, 56 H, 8 $(CH_3)_2CHSi$]. Anal. Calcd for $C_{70}H_{118}N_2O_{32}Si_4$: C, 52.16; H, 7.38; N, 1.74. Found: C, 51.91; H, 7.20; N, 1.63.

Allyl O-*(methyl 4,5,7,8-tetra*-O-*acetyl-3-deoxy-α*-D-manno-*2-octulopyranosylonate)-(2 → 4)*-O-*(methyl 7,8*-O-*carbonyl-3-deoxy-α*-D-manno-*2-octulopyranosylonate)-(2 → 6)*-O-*[2-acetamido-2-deoxy-3,4*-O-*(tetraisopropyldisiloxane-1,3-diyl)-β*-D-*glucopyranosyl]-(1 → 6)-2-acetamido-2-deoxy-3,4*-O-*(tetraisopropyldisiloxane-1,3-diyl)-β*-D-*glucopyranoside* (**17b**).—A solution of **12** (300 mg, 0.61 mmol) in dry MeCN (2.5 mL) was added dropwise during 3 h to a suspension of **14b** (45 mg, 0.037 mmol), $Hg(CN)_2$ (120 mg, 0.48 mmol), $HgBr_2$ (120 mg, 0.33 mmol), and 4A molecular sieves (1 g) in CH_3CN (5 mL) under N_2. The suspension was stirred for 20 h at room temperature. Work-up as described for **17a** gave a syrup which was chromatographed on silica gel (*B*, 1:2 → 1:5 toluene–EtOAc). The crude product was purified on silica gel, using 20:1 ether–EtOAc, which gave **17b** as a syrup. Yield: 30 mg (50%); $[\alpha]_D^{20}$ +36° (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.89 (m, 1 H, =CH–), 5.84 (d, 1 H, $J_{NH',2'}$ ~ 8.2 Hz, NH'), 5.54 (d, 1 H, $J_{NH,2}$ ~ 7.6 Hz, NH), 5.30 (dq, 1 H, $=CH_{2trans}$), 5.17 (dq, 1 H, $=CH_{2cis}$), 4.32 (m, 1 H) and 4.14 (m, 1 H, OCH_2), 3.83 (s, 3 H) and 3.75 (s, 3 H, CO_2CH_3), 2.42 (br s, 1 H, OH), 2.13 (s, 3 H), 2.09 (s, 3 H), 1.99 (s, 3 H), 1.98 (s, 3 H), 1.96 (s, 3 H), and 1.94 (s, 3 H, CH_3CO), 1.05–1.00 [m, 56 H, 8 $(CH_3)_2CHSi$]. Anal. Calcd for $C_{70}H_{118}N_2O_{32}Si_4$: C, 52.16; H, 7.38; N, 1.74. Found: C, 52.25; H, 7.19; N, 1.79.

Allyl O-*(methyl 4,5,7,8-tetra*-O-*acetyl-3-deoxy-α*-D-manno-*2-octulopyrano-*

*sylonate)-(2 → 4)-O-(methyl 5-O-acetyl-7,8-O-carbonyl-3-deoxy-α-*D-manno*-2-octulopyranosylonate)-(2 → 6)-O-[2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-β-*D-*glucopyranosyl]-(1 → 6)-2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-α-*D-*glucopyranoside* (**18a**).—A solution of **17a** (16 mg, 0.01 mmol) in dry pyridine (5 mL) was stirred with Ac_2O (0.1 mL) and a catalytic amount of 4-dimethylaminopyridine for 12 h at room temperature. The solution was coevaporated three times with addition of toluene (10 mL) and purified by silica gel chromatography (*A*, 1:2 toluene–EtOAc), which afforded 13 mg (78%) of **18a** as a syrup; $[\alpha]_D^{20}$ +66° (*c* 0.7, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.94 (m, 1 H, =CH–), 5.55 (d, 1 H, $J_{NH',2'}$ ~ 8.0 Hz, NH′), 5.47 (d, 1 H, $J_{NH,2}$ ~ 9.7 Hz, NH), 5.30 (dq, 1 H, $=CH_{2trans}$), 5.20 (dq, 1 H, $=CH_{2cis}$), 3.80 (s, 3 H) and 3.77 (s, 3 H, CO_2CH_3), 2.12 (s, 6 H), 2.07 (s, 3 H), 1.98 (s, 3 H), and 1.97 (s, 6 H, CH_3CO), 1.08–1.00 [m, 56 H, 8 $(CH_3)_2CHSi$]. Anal. Calcd for $C_{72}H_{120}N_2O_{33}Si_4$: C, 52.28; H, 7.31; N, 1.69. Found: C, 52.19; H, 7.32; N, 1.44.

Allyl O-*(sodium 3-deoxy-α-*D-manno*-2-octulopyranosylonate)-(2 → 4)-O-(sodium 3-deoxy-α-*D-*manno*-2-octulopyranosylonate)-(2 → 6)-O-(2-acetamido-2-deoxy-β-*D-*glucopyranosyl)-(1 → 6)-2-acetamido-2-deoxy-α-*D-*glucopyranoside* (**19a**).—The preparation of **19a** was analogous to that of **16a**, by treating **18a** (9.0 mg, 0.005 mmol) successively with 1.1 M Bu_4NF in THF (30 μL), 0.1 M methanolic NaOMe (0.25 mL), and 0.2 M aq NaOH (4 mL). Yield: 4.2 mg of **19a** (91%); amorphous powder; $[\alpha]_D^{20}$ +62° (*c* 0.4, H_2O); ^1H NMR (D_2O): δ 5.96 (m, 1 H, =CH–), 5.35 (dq, 1 H, $=CH_{2trans}$), 5.27 (dq, 1 H, $=CH_{2cis}$), 4.19 (m, 1 H) and 4.03 (m, 1 H, OCH_2), 2.03 (s, 6 H, NHAc). MALDMS: *m/z* 950 $[M + H]^+$.

Allyl O-*(sodium 3-deoxy-α-*D-manno*-2-octulopyranosylonate)-(2 → 4)-O-(sodium 3-deoxy-α-*D-*manno*-2-octulopyranosylonate)-(2 → 6)-O-(2-acetamido-2-deoxy-β-*D-*glucopyranosyl)-(1 → 6)-2-acetamido-2-deoxy-β-*D-*glucopyranoside* (**19b**).—Compound **17b** (14 mg, 0.009 mmol) was treated similarly to **16a**, using 1.1 M Bu_4NF in THF (40 μL), 0.1 M methanolic NaOMe (0.5 mL), and 0.2 M aq NaOH (5 mL). Yield: 6.5 mg (79%) of **19b**; amorphous powder; $[\alpha]_D^{20}$ +23° (*c* 0.6, H_2O); ^1H NMR (D_2O): δ 5.95 (m, 1 H, =CH–), 5.36 (dq, 1 H, $=CH_{2trans}$), 5.32 (dq, 1 H, $=CH_{2cis}$), 4.36 (m, 1 H) and 4.17 (m, 1 H, OCH_2), 2.08 (s, 6 H, NHAc). MALDMS: *m/z* 949 $[M + H]^+$.

Allyl O-*(methyl 4,5,7,8-tetra-*O*-acetyl-3-deoxy-α-*D-*manno*-2-octulopyranosylonate)-(2 → 8)-O-(methyl 4,5,7-tri-*O*-acetyl-3-deoxy-α-*D-*manno*-2-octulopyranosylonate)-(2 → 4)-O-(methyl 7,8-*O*-carbonyl-3-deoxy-α-*D-*manno*-2-octulopyranosylonate)-(2 → 6)-O-[2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-β-*D-*glucopyranosyl]-(1 → 6)-2-acetamido-2-deoxy-3,4-O-(tetraisopropyldisiloxane-1,3-diyl)-α-*D-*glucopyranoside* (**21a**).—A solution of **20** (125 mg, 0.15 mmol) in dry CH_3CN (2 mL) was added dropwise during 6 h to a suspension of **14a** (63 mg, 0.05 mmol), $Hg(CN)_2$ (25 mg, 0.1 mmol), $HgBr_2$ (72 mg, 0.2 mmol), and 4A molecular sieves (1 g) in CH_3CN (5 mL) under N_2. The suspension was stirred for 48 h at room temperature, diluted with EtOAc (50 mL), and filtered over Celite. The filtrate was washed with satd aq $NaHCO_3$, 5% aq KI, and water, and dried

($MgSO_4$). Concentration gave a syrup, which was purified by silica gel chromatography (1:2 → 0:1 toluene–EtOAc). The product which was eluted prior to unreacted **14a** (50 mg) was subjected to liquid chromatography on Lichrosorb Si 60 (10 μm), using 1:3 hexane–EtOAc as eluant. Yield 20 mg (20%) of **21a**; colorless syrup; $[\alpha]_D^{20}$ +50° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.92 (m, 1 H, =CH–), 5.49 (d, 1 H, $J_{NH',2'}$ ~ 8.5 Hz, NH'), 5.48 (d, 1 H, $J_{NH,2}$ ~ 9.6 Hz, NH), 5.35 (dq, 1 H, $=CH_{2trans}$), 5.26 (dq, 1 H, $=CH_{2cis}$), 4.22 (m, 1 H) and 3.98 (m, 1 H, OCH_2), 3.84 (s, 3 H), 3.79 (s, 3 H), and 3.76 (s, 3 H, CO_2CH_3), 2.20 (br s, 1 H, OH), 2.11 (s, 3 H), 2.10 (s, 3 H), 2.09 (s, 3 H), 2.07 (s, 3 H), 2.05 (s, 3 H), 2.00 (s, 3 H), 1.98 (s, 6 H), and 1.92 (s, 3 H, CH_3CO), 1.08–0.98 [m, 56 H, 8 $(CH_3)_2CHSi$]. Anal. Calcd for $C_{85}H_{138}N_2O_{42}Si_4$: C, 51.76; H, 7.05; N, 1.42. Found: C, 51.89; H, 7.18; N, 1.29.

Allyl O-*(methyl 4,5,7,8-tetra*-O-*acetyl-3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 8)*-O-*(methyl 4,5,7-tri*-O-*acetyl-3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 4)*-O-*(methyl 7,8*-O-*carbonyl-3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 6)*-O-*[2-acetamido-2-deoxy-3,4*-O-*(tetraisopropyldisiloxane-1,3-diyl)-β-*D-*glucopyranosyl]-(1 → 6)-2-acetamido-2-deoxy-3,4*-O-*(tetraisopropyldisiloxane-1,3-diyl)-β-*D-*glucopyranoside* (**21b**).—Glycosylation of **14b** (100 mg, 0.08 mmol) was performed similarly to **14a**, using $Hg(CN)_2$ (40 mg, 0.16 mmol), $HgBr_2$ (80 mg, 0.22 mmol), and 4A molecular sieves (1 g) in dry CH_3CN (5 mL). Work-up as described for **21a** furnished a syrup, which was chromatographed first using 1:2 toluene–EtOAc (*B*). The crude product was further purified by LC (2:5 hexane–EtOAc) to give 30 mg (19%) of **21b** as a syrup; $[\alpha]_D^{20}$ +41° (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.88 (m, 1 H, =CH–), 5.87 (d, 1 H, $J_{NH',2'}$ ~ 7.5 Hz, NH'), 5.49 (d, 1 H, $J_{NH,2}$ ~ 7.8 Hz, NH), 5.29 (dq, 1 H, $=CH_{2trans}$), 5.17 (dq, 1 H, $=CH_{2cis}$), 4.34 (m, 1 H) and 4.03 (m, 1 H, OCH_2), 3.86 (s, 3 H), 3.79 (s, 3 H), and 3.75 (s, 3 H, CO_2CH_3), 2.10 (s, 3 H), 2.09 (s, 6 H), 2.05 (s, 3 H), 2.03 (s, 3 H), 2.01 (s, 3 H), 1.97 (s, 3 H), 1.96 (s, 3 H), and 1.95 (s, 3 H, CH_3CO), 1.06–0.99 [m, 56 H, 8 $(CH_3)_2CHSi$]. Anal. Calcd for $C_{85}H_{138}N_2O_{42}Si_4$: C, 51.76; H, 7.05; N, 1.42. Found: C, 51.50; H, 6.98; N, 1.35.

Allyl O-*(methyl 4,5,7,8-tetra*-O-*acetyl-3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 8)*-O-*(methyl 4,5,7-tri*-O-*acetyl-3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 4)*-O-*(methyl 5*-O-*acetyl-7,8*-O-*carbonyl-3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 6)*-O-*[2-acetamido-2-deoxy-3,4*-O-*(tetraisopropyldisiloxane-1,3-diyl)-β-*D-*glucopyranosyl]-(1 → 6)-2-acetamido-2-deoxy-3,4*-O-*(tetraisopropyl-disiloxane-1,3-diyl)-α-*D-*glucopyranoside* (**22a**).—A solution of **21a** (10 mg, 5 μmol) and Ac_2O (0.1 mL) in dry pyridine (4 mL) was stirred for 48 h at room temperature. The solution was coevaporated twice with addition of toluene (5 mL). The residue was purified by silica gel chromatography (*A*, 2:5 toluene–EtOAc). Yield: 8.5 mg (84%) of **22a**; colorless syrup; $[\alpha]_D^{20}$ +67° (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 5.94 (m, 1 H, =CH–), 5.64 (d, 1 H, $J_{NH',2'}$ ~ 7.6 Hz, NH'), 5.48 (d, 1 H, $J_{NH,2}$ ~ 9.5 Hz, NH), 5.29 (dq, 1 H, $=CH_{2trans}$), 5.20 (dq, 1 H, $=CH_{2cis}$), 4.27 (m, 1 H) and 4.02 (m, 1 H, OCH_2), 3.82 (s, 3 H), 3.81 (s, 3 H), and 3.76 (s, 3 H, CO_2CH_3), 2.13 (s, 3 H), 2.10 (s, 6 H), 2.08 (s, 3 H), 2.01 (s, 3 H), 1.98 (s, 3 H), 1.97

(s, 3 H), 1.96 (s, 3 H), and 1.95 (s, 3 H, CH_3CO), 1.08–1.00 [m, 56 H, 8 $(CH_3)_2CHSi$]. Anal. Calcd for $C_{87}H_{140}N_2O_{43}Si_4$: C, 51.87; H, 7.01; N, 1.39. Found: C, 51.70; H, 6.97; N, 1.25.

Allyl O-*(methyl 4,5,7,8-tetra*-O-*acetyl-3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 8)*-O-*(methyl 4,5,7-tri*-O-*acetyl-3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 4)*-O-*(methyl 5*-O-*acetyl-7,8*-O-*carbonyl-3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 6)*-O-*[2-acetamido-2-deoxy-3,4*-O-*(tetraisopropyldisiloxane-1,3-diyl)-β-*D-*glucopyranosyl]-(1 → 6)-2-acetamido-2-deoxy-3,4*-O-*(tetraisopropyl-disiloxane-1,3-diyl)-β-*D-*glucopyranoside* (**22b**).—Compound **22b** was prepared in a similar manner as **22a**. Yield: 12 mg (60%) of **22b**; colorless syrup; $[\alpha]_D^{20}$ +51° (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$): δ 6.01 (d, 1 H, $J_{NH',2'}$ ~ 7.4 Hz, NH'), 5.88 (m, 1 H, =CH–), 5.46 (d, 1 H, $J_{NH,2}$ ~ 8.1 Hz, NH), 5.30 (dq, 1 H, $=CH_{2trans}$), 5.18 (dq, 1 H, $=CH_{2cis}$), 4.34 (m, 1 H) and 4.17 (m, 1 H, OCH_2), 3.85 (s, 3 H), 3.81 (s, 3 H), and 3.76 (s, 3 H, CO_2CH_3), 2.14 (s, 6 H), 2.12 (s, 3 H), 2.10 (s, 3 H), 2.09 (s, 3 H), 2.08 (s, 3 H), 2.01 (s, 3 H), 1.97 (s, 6 H), and 1.95 (s, 3 H, CH_3CO), 1.09–1.00 [m, 56 H, 8 $(CH_3)_2CHSi$]; ^{13}C NMR ($CDCl_3$): δ 170.4–169.6 (10 CO), 176.1, 166.8, and 166.7 (3 CO_2CH_3), 116.9 ($=CH_2$), 99.5, 99.1, 98.4, 98.3, and 97.9 (C-1,1',2'',2''',2''''), 33.9, 32.0, and 31.7 (C-3'',3''',3''''). Anal. Calcd for $C_{87}H_{140}N_2O_{43}Si_4$: C, 51.87; H, 7.01; N, 1.39. Found: C, 52.02; H, 7.09; N, 1.44.

Allyl O-*(sodium 3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 8)*-O-*(sodium 3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 4)*-O-*(sodium 3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 6)*-O-*(2-acetamido-2-deoxy-β-*D-*glucopyranosyl)-(1 → 6)-2-acetamido-2-deoxy-α-*D-*glucopyranoside* (**23a**).—Compound **23a** was prepared as described for **19a**, starting from **22a** (9 mg), which was treated successively with 1.1 M Bu_4NF (20 μL) in THF (5 mL), 0.1 M methanolic NaOMe (0.2 mL), and 0.2 M aq NaOH (5 mL). Yield: 5.0 mg (94%) of **23a**; amorphous powder; $[\alpha]_D^{20}$ +50° (*c* 0.5, H_2O); ^1H NMR (D_2O): δ 5.97 (m, 1 H, =CH–), 5.36 (dq, 1 H, $=CH_{2trans}$), 5.28 (dq, 1 H, $=CH_{2cis}$), 4.20 and 3.97 (m, 1 H, OCH_2), 2.104 (s, 3 H) and 2.03 (s, 3 H, NHAc). MALDMS: *m/z* 1214 $[M + Na]^+$.

Allyl O-*(sodium 3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 8)*-O-*(sodium 3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 4)*-O-*(sodium 3-deoxy-α-*D-manno-*2-octulopyranosylonate)-(2 → 6)*-O-*(2-acetamido-2-deoxy-β-*D-*glucopyranosyl)-(1 → 6)-2-acetamido-2-deoxy-β-*D-*glucopyranoside* (**23b**).—Compound **22b** (9.2 mg) was deprotected as described for **19a**. Yield: 3.5 mg (65%); amorphous powder; $[\alpha]_D^{20}$ +33° (*c* 0.3, H_2O); ^1H NMR (D_2O): δ 5.95 (m, 1 H, =CH–), 5.36 (dq, 1 H, $=CH_{2trans}$), 5.32 (dq, 1 H, $=CH_{2cis}$), 4.26 (m, 1 H) and 4.17 (m, 1 H, OCH_2), 2.08 (s, 3 H) and 2.07 (s, 3 H, NHAc). MALDMS: *m/z* 1213 $[M + Na]^+$.

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