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Synthesis of eight glycosides of hexasaccharide fragments representing the terminus of the O-polysaccharide of *Vibrio cholerae* O:1, serotype Inaba and Ogawa, bearing aglycons suitable for linking to proteins [1]

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Abstract

The title substances were prepared from intermediate, fully acetylated α-trimethylsilylethyl (SE) glycosides. The latter were assembled in a blockwise manner, using as the glycosyl donor the α-glycosyl chloride of a disaccharide bearing two 4-azido-4-deoxy functions. Next, the azido groups in the assembled hexasaccharides were converted to the corresponding amines, and these were acylated with 4-*O*-benzyl-3-deoxy-L-*glycero*-tetronic acid in the presence of a water-soluble carbodiimide. The SE glycosides were then transformed to glycosyl imidates, and these were coupled with methyl 6-hydroxyhexanoate or methyl 2-(2-hydroxyethylthio)propionate. The aglycons in the glycosides thus obtained were then converted to the corresponding carboxylic acids or acyl hydrazides. Such compounds are suitable for linking to proteins to obtain neoglycoproteins. Published by Elsevier Science Ltd.

Keywords: *Vibrio cholerae* O-antigen; Hexasaccharide; Neoglycoconjugate; 4-*O*-Benzyl-3-deoxy-L-*glycero*-tetronic acid

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[1] Synthesis of ligands related to the *Vibrio cholerae* O-specific antigen. Part 12. For Part 11, see ref. [8].

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1. Introduction

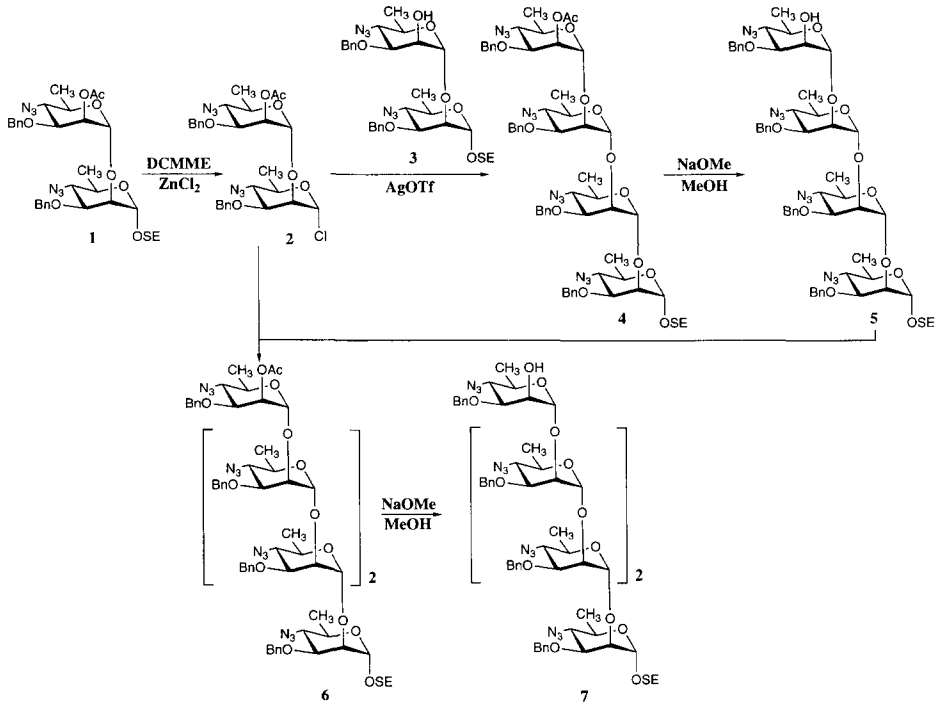
In the past, we synthesized various fragments of the O-antigen of the two main strains of *V. cholerae*, serotype Inaba and Ogawa [1–7]. As a further step in our effort to understand protective immunity to cholera, we also synthesized [8] glycosides of a disaccharide fragment of the O-specific polysaccharide (O-PS) of *Vibrio cholerae* O:1, serotype Inaba, equipped with functionalized spacers as aglycons rendering these substances amenable to conjugation to proteins. The linking of these molecules to suitable protein carriers and evaluation of the immunogenicity of the resulting neoglycoconjugates is currently in progress, and the results of these studies will be published in a separate communication. Here we report on the synthesis of similar structures derived from hexasaccharides representing termini of the two main strains of *Vibrio cholerae* O:1.

2. Results and discussion

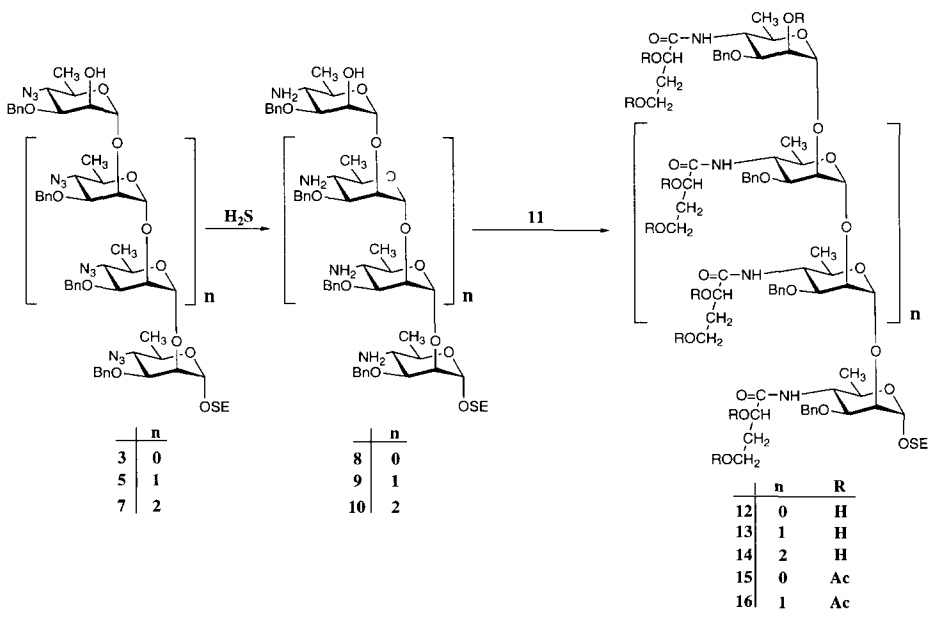
Two fundamentally different strategies for the assembly of *N*-acylated, perosamine-containing oligosaccharides have been proposed. That involving the use of glycosyl donors and glycosyl acceptors both having the required *N*-3-deoxy-L-*glycero*-tetronamido groups already in place was recently [2,6,7] developed in this laboratory. This is a variation of the approach originally introduced by Bundle et al. [9–13], which involves construction of azido oligosaccharides and their subsequent conversion, via the corresponding 4-amino derivatives, into oligosaccharides containing the requisite 4-acylamido group. We applied the latter chemistry in one of our two syntheses of the methyl α-glycoside of the disaccharide intracatenary repeating unit of the O-PS of *Vibrio cholerae* O:1 [2]. This strategy is applied here for the syntheses of some related hexasaccharides.

Compound **1** [8] was either treated with dichloromethyl methyl ether [14,15] to give the glycosyl chloride **2**, or deacetylated to give the disaccharide glycosyl acceptor **3**. The latter compound was coupled with **2** to give, after deacetylation of the intermediate **4**, the tetrasaccharide glycosyl acceptor **5** (Scheme 1). This sequence of reactions was repeated to give **6**. Subsequent deacetylation of **6** gave **7**, the final glycosyl acceptor leading to the title hexasaccharides of the Inaba series. A portion of **7** was methylated ($\rightarrow$ **17**), to give eventually the upstream terminal hexasaccharide of the O-PS of *Vibrio cholerae* O:1, serotype Ogawa [16,17]. The azido groups in the building blocks **3**, **5**, **7**, and **17** were then transformed to amino functions by treatment with H_2S, to give the corresponding amines **8**–**10** and **18** (Schemes 2).

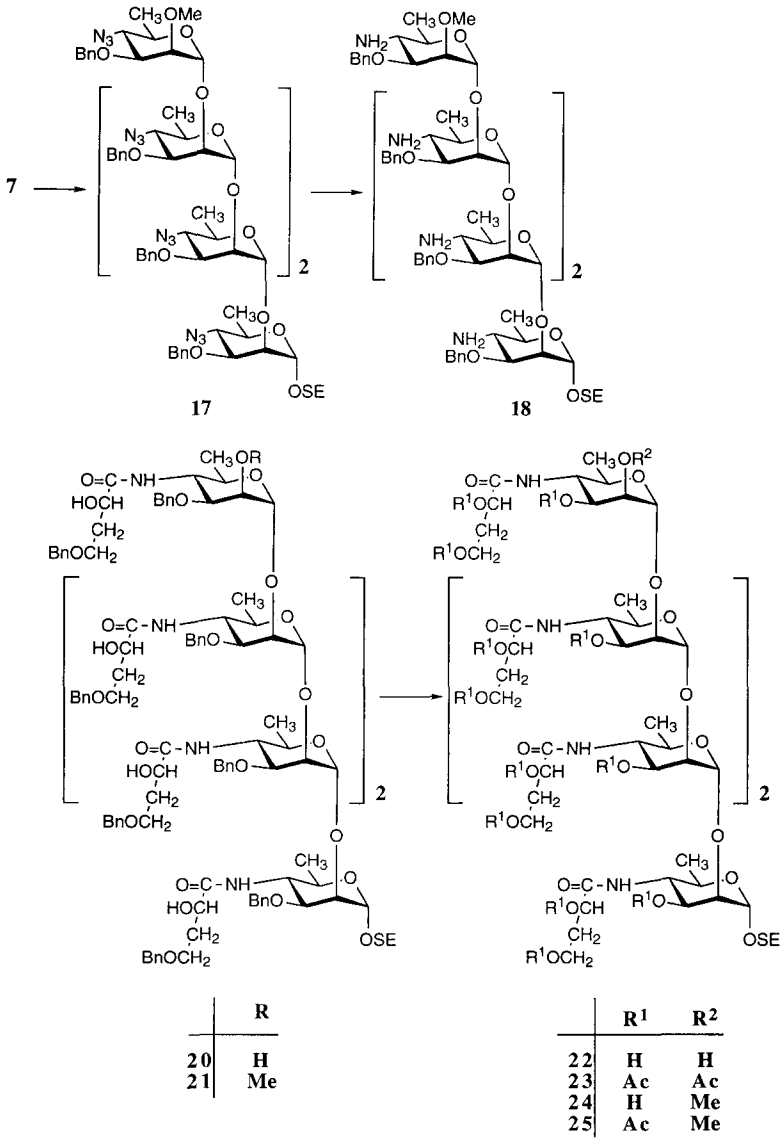
The next task was to introduce the *N*-3-deoxy-L-*glycero*-tetronoyl groups into the foregoing hexasaccharides. For *N*-acylation, we first tried 3-deoxy-L-*glycero*-tetronolactone **11** [2,4,18], which we had used successfully in previous syntheses of related substances [1–6]. However, treatment of amine **10** with **11** (not described in the Experimental), under conditions we commonly apply, resulted, inter alia, in the formation of a relatively large amount of dark material insoluble in common organic solvents. Attempts to isolate any identifiable substance from the complex reaction mixture failed.



Scheme 1.

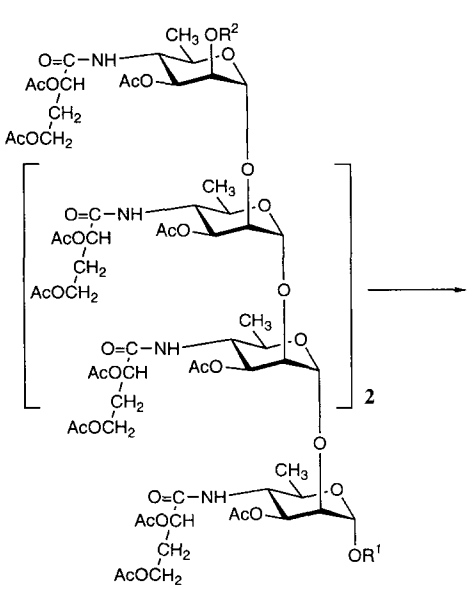


Scheme 2.

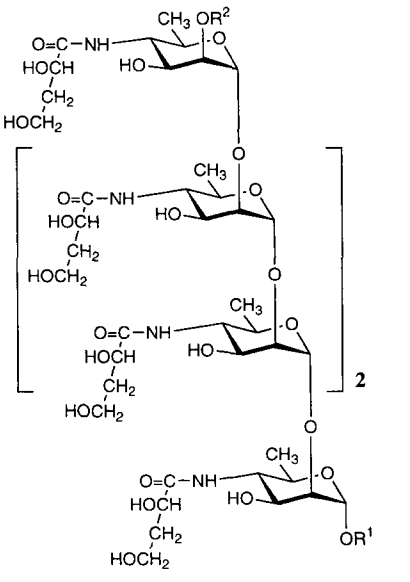


Scheme 3.

Treatment of the lower oligosaccharide amines **8** and **9** with **11** met with mixed success. As the size of the starting amine increased, the yield of the desired 4-(3-deoxytetronamido) derivatives decreased dramatically (cf., Experimental). These difficulties prompted us to synthesize [19] more efficient reagents for *N*-3-deoxy-L-*glycero*-tetronoylation of higher (1 → 2)-linked oligosaccharides composed of 4-amino-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranose. One of these, 4-*O*-benzyl-3-deoxy-L-*glycero*-



	R^1	R^2
26	**H**	**Ac**
27	**H**	**Me**
28	**$C(NH)CCl_3$**	**Ac**
29	**$C(NH)CCl_3$**	**Me**
30	**$(CH_2)_5COOMe$**	**Ac**
31	**$(CH_2)_2S(CH_2)_2COOMe$**	**Ac**
32	**$(CH_2)_5COOMe$**	**Me**
33	**$(CH_2)_2S(CH_2)_2COOMe$**	**Me**



	R^1	R^2
34	**$(CH_2)_5COOMe$**	**H**
35	**$(CH_2)_2S(CH_2)_2COOMe$**	**H**
36	**$(CH_2)_5COOMe$**	**Me**
37	**$(CH_2)_2S(CH_2)_2COOMe$**	**Me**
38	**$(CH_2)_5COOH$**	**H**
39	**$(CH_2)_2S(CH_2)_2COOH$**	**H**
40	**$(CH_2)_5CONHNH_2$**	**H**
41	**$(CH_2)_2S(CH_2)_2CONHNH_2$**	**H**
42	**$(CH_2)_5COOH$**	**Me**
43	**$(CH_2)_2S(CH_2)_2COOH$**	**Me**
44	**$(CH_2)_5CONHNH_2$**	**Me**
45	**$(CH_2)_2S(CH_2)_2CONHNH_2$**	**Me**

Scheme 4.

tetronic acid (**19**), when treated with amines **10** or **18** in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (water-soluble carbodiimide, WSC) and *N*-hydroxybenzotriazol, readily yielded the desired hexasaccharides **20** and **21** in consistently high yields [3].

To convert the assembled hexasaccharides **20** and **21** into glycosides (**38–45**, Scheme 4) suitable for coupling to proteins, the silyl glycosides were first converted to reducing

[3] Since our preliminary report on a portion of this work [20], we have been able to minimize manipulative losses of the product of the conversion **20** + **19** → **14** by exhaustive extraction of the desired material from the reaction mixture.

sugars by treatment with trifluoroacetic acid (TFAA). The use of neat TFAA as both solvent and reagent for this conversion resulted in a fast, one-product reaction, unlike that carried out according to the commonly applied protocol that requires the use of dichloromethane as a solvent [21]. Compounds **26** and **27** thus obtained were converted [22] into glycosyl trichloroacetimidates **28** and **29**, respectively. Each of these were then coupled with methyl 6-hydroxyhexanoate [23] and methyl 2-(2-hydroxylethylthio)propionate [8] to give glycosides **30–33**. We previously [8] rationalized our choice of these aglycons for their future coupling to proteins. Deacetylation of **30–33**, followed by hydrolysis of the methyl ester functions on one hand, and hydrazinolysis of the esters on the other hand, yielded the title glycosides **38–45**. These were obtained, after freeze drying, as pure (TLC, NMR), white hygroscopic solids that gave NMR spectra consistent with the anticipated structures.

3. Experimental

General methods.—Instruments and laboratory techniques used were described in the previous part in this series [6]. Unless stated otherwise, optical rotations were measured at ambient temperature for solutions in chloroform ($c \sim 1$). All reactions were monitored by thin-layer chromatography (TLC) on Silica Gel 60 coated glass slides (Whatman or Analtech). The following solvent mixtures were used: *A*, 4:1 hexane–EtOAc; *B*, 15:1 CH_2Cl_2–MeOH; *C*, 5:1 CH_2Cl_2–MeOH; *D*, 30:1 CH_2Cl_2–MeOH; *E*, 1:1 CH_2Cl_2–MeOH; *F*, 1:2 CH_2Cl_2–MeOH; *G*, 1:3:0.1 CH_2Cl_2–MeOH–NH_4OH. For column chromatography, solvent mixtures slightly less polar than those used for TLC were used at the onset of development. When reporting assignments of NMR signals, sugar residues in oligosaccharides are serially numbered, beginning with the reducing end or with the residue bearing the aglycone, and are identified by a Roman numeral superscript in listings of signal assignments. Nucleus assignments without a superscript notation indicate that those signals have not been individually assigned. Thus, for example, in a spectrum of a disaccharide, a resonance denoted H-3 can be that of H-3 of either sugar residue. Palladium (5%)-on-charcoal catalyst (ESCAT 103) was a product of Engelhard Industries.

*2-(Trimethylsilyl)ethyl (2-*O*-acetyl-4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranosyl)-(1 → 2)-(4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranosyl)-(1 → 2)-(4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranosyl)-(1 → 2)-4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranoside* (**4**).—A mixture of **1** ([8], 300 mg, 0.44 mmol), DCMME (0.5 g, 4.4 mmol) and freshly fused $ZnCl_2$ (40 mg) in CH_2Cl_2 was stirred at room temperature for 3 h (TLC, solvent *A*). The mixture was filtered through Celite, the filter pad was washed with toluene, and the combined filtrate was concentrated. Chromatography of the residue gave 2-*O*-(2-*O*-acetyl-4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl)-4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl chloride (**2**, 215 mg, 81%), CIMS: *m/z* 618 ($[M + 18]^+$).

AgOTf (1.3 g, 5.1 mmol) was added to a stirred solution of **3** ([8], 2.7 g, 4.2 mmol), **2** (2.9 g, 4.6 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (1.2 g, 5.5 mmol) in CH_2Cl_2

(50 mL). After 1 h, when TLC (solvent *A*) showed that the glycosyl donor was consumed, saturated $NaHCO_3$ was added, and the mixture was filtered. The solids were washed with CH_2Cl_2, the combined filtrate was washed with NaCl solution, dried, and concentrated. Chromatography of the residue gave **4** (4.19 g, 83%), $[\alpha]_D$ +95°; ^1H NMR ($CDCl_3$): δ 5.43 (dd, 1 H, $J_{1,2}$ 1.7, $J_{2,3}$ 3.1 Hz, H-2^{IV}), 4.97, 4.91 (2 d, 1 H each, $J_{1,2}$ ~ 1.5 Hz, H-$1^{II,III}$), 4.87 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1^{IV}), 4.76–4.54 (m, partially overlapped, 8 H, 4 CH_2Ph), 4.66 (d, partially overlapped, $J_{1,2}$ 1.7 Hz, H-1^{I}), 3.90, 3.86 (2 bdd, 1 H each, H-$2^{II,III}$), 3.84–3.80 (m, partially overlapped, H-2^{I}), 3.80 (dd, partially overlapped, H-3^{IV}), 3.77–3.68 (m, 4 H, H-3^{I-III}, CH_aCH$_2$Si), 3.58–3.33 (m, 7 H, CH_bCH$_2$Si, H-5^{I-IV}, 2 H-4), 3.26, 3.22 (2 t, 2 H, partially overlapped, 2 H-4), 2.13 (s, 3 H, $COCH_3$), 1.29, 1.22, 1.18 (d, 6 H, d, 3 H, d, 3 H, $J_{5,6}$ 6.1 Hz, 4 H-6), 0.98–0.82 (m, 2 H, CH_2Si), and 0.03 (s, 9 H, 3 CH_3); ^{13}C NMR ($CDCl_3$): δ 169.73 (CO), 100.35, 100.04 (C-$1^{II,III}$), 99.08 (C-1^{IV}), 98.22 (C-1^{I}), 77.53, 76.79, 76.58 (C-3^{I-III}), 75.39 (C-3^{IV}), 73.98 (C-2^{I}), 73.48 (2 C, C-$2^{II,III}$), 72.21, 72.06, 72.01, 71.50 (4 CH_2Ph), 67.76 (2 C), 67.13, 67.04 (C-5^{I-IV}), 67.63 (C-2^{IV}), 65.17 (CH_2CH$_2$Si), 64.45, 64.25, 64.03, 63.82 (C-4^{I-IV}), 20.91 ($COCH_3$), 18.54 (2 C) 18.44, 18.34 (C-6^{I-IV}), 17.73 (CH_2Si), and −1.34 (3 CH_3); CIMS: *m/z* 1222 ($[M+18]^+$). Anal. Calcd for $C_{59}H_{76}N_{12}O_{14}Si$: C, 58.79; H, 6.35; N, 13.94. Found: C, 58.92; H, 6.41; N, 13.76.

*2-(Trimethylsilyl)ethyl (4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranosyl)-(1 → 2)-[(4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranosyl)-(1 → 2)]$_2$-4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranoside* (**5**).—Zemplén deacetylation of **4** afforded **5** in virtually theoretical yield, $[\alpha]_D$ +147°; ^1H NMR ($CDCl_3$): δ 4.98 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{IV}), 4.96, 4.89 (2 d, 1 H each, $J_{1,2}$ 1.9 and 1.8, respectively, H-$1^{II,III}$), 4.76–4.55 (m, 9 H incl d at 4.64, $J_{1,2}$ 1.9 Hz, H-1^{I}, 4 CH_2Ph), 3.99 (m, 1 H, H-2^{IV}), 3.94, 3.83 (2 bt, 1 H each, H-$2^{II,III}$) 3.79 (bt, 1 H, H-2^{I}), 3.75–3.66 (m, 5 H, CHCH$_2$Si, H-3^{I-IV}), 3.56–3.39 (m, 6 H, CHCH$_2$Si, H-4, 5^{I-IV}), 3.30, 3.25, 3.19 (3 t, 1 H, *J* ~ 10 Hz each, 3 H-4), 2.31 (d, 1 H, $J_{2,OH}$ 1.9 Hz, OH), 1.27, 1.26, 1.20, 1.17 (4 d, 3 H each, $J_{5,6}$ 6.3, 6.2, 6.0, and 6.1, respectively, 4 H-6), 0.95–0.79 (m, 2 H, CH_2Si), and 0.01 (s, 9 H, 3 CH_3); ^{13}C NMR ($CDCl_3$): δ 100.43 (C-1^{IV}), 100.34, 100.19 (C-$1^{II,III}$), 98.21 (C-1^{I}), 77.63, 77.51, 76.94, 76.58 (C-3^{I-IV}), 73.94 (C-2^{I}), 73.52, 73.22 (C-$2^{II,III}$), 72.20, 72.19, 72.04 (2 C, 4 CH_2Ph), 67.76 (2 C), 67.32, 67.01, (C-5^{I-IV}), 67.12 (C-2^{IV}), 65.17 (CH_2CH$_2$Si), 64.44, 64.17 (2 C), 63.81 (C-4^{I-IV}), 18.58, 18.54, 18.47, 18.27 (C-6^{I-IV}), 17.29 (CH_2Si), and −1.34 (3 CH_3); CIMS: *m/z* 1180 ($[M+18]^+$). Anal. Calcd for $C_{57}H_{74}N_{12}O_{13}Si$: C, 58.85; H, 6.41; N, 14.45. Found: C, 58.82; H, 6.45; N, 14.39.

*2-(Trimethylsilyl)ethyl (2-*O*-acetyl-4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranosyl)-(1 → 2)-[(4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranosyl)-(1 → 2)]$_4$-4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranoside* (**6**).—Compound **5**, when treated with **2** in the manner described for the preparation of **4**, gave **6** in 95% yield, after purification by chromatography (solvent *A*), $[\alpha]_D$ +95°. Structurally significant signals in the ^1H NMR ($CDCl_3$) were at: δ 5.41 (dd, 1 H, $J_{1,2}$ 1.7, $J_{2,3}$ 3.1 Hz, H-2^{VI}), 4.98–4.52 (m, 18 H, incl d at 4.85, *J*1,2 1.8 Hz, H-1^{VI}, H-1^{I-V}, 6 CH_2Ph), 2.10 (s, 3 H, $COCH_3$), 1.26, 1.25, 1.21, 1.18, 1.16, 1.12 (6 d, 3 H each, $J_{5,6}$ 5.9, 6.1, 6.2, 5.8, 5.5, 6.1, respectively, H-6^{I-VI}), 0.75–0.90 (m, 2 H, CH_2Si), and ~ 0.0 (s, 9 H, 3 CH_3); ^{13}C NMR ($CDCl_3$): δ 100.30, 100.09 (2 C), 100.03 (C-1^{II-V}), 99.08 (C-1^{VI}), 98.21 (C-1^{I}), 77.51, 76.79, 76.64, 76.58 (2 C, C-3^{I-V}), 75.39 (C-3^{VI}), 73.98 (C-2^{I}), 73.58, 73.44 (2

C), 73.37 (C-2^{II-V}), 72.15 (3 C), 72.06, 72.02, 71.52 (6 CH_2Ph), 67.80 (3 C), 67.73, 67.63, 67.00 (C-5^{I-VI}), 67.13 (C-2^{VI}), 65.17 (CH_2CH_2Si), 64.45, 64.20 (3 C), 64.04, 63.81 (C-4^{I-VI}), 20.94 ($COCH_3$), 18.58, 18.54, 18.47 (3 C), 18.36 (C-6^{I-VI}), and −1.33 (3 CH_3); CIMS: *m/z* 1744 ($[M + 18]^+$). Anal. Calcd for $C_{85}H_{106}N_{18}O_{20}Si$: C, 59.08; H, 6.18; N, 14.59. Found: C, 59.30; H, 6.28; N, 14.35.

*2-(Trimethylsilyl)ethyl (4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranosyl)-(1 → 2)-[(4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranosyl)-(1 → 2)]$_4$-4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranoside* (**7**).—Deacetylation of **6**, as described for the preparation of **5**, gave **7** in 91% yield, following purification by chromatography (solvent *A*), $[\alpha]_D$ +112°; ^{1}H NMR ($CDCl_3$): δ 5.01 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1^{VI}), 4.99, 4.92, 4.89–4.87 (d, 1 H, $J_{1,2}$ 1.9 Hz, d, 1 H, $J_{1,2}$ 2.0 Hz, m, 2 H, H-1^{II-V}), 4.78–4.54 (m, 13 H, 6 CH_2Ph, H-1^I), 4.03 (dd, 1 H, $J_{2,3}$ 3.1 Hz, H-2^{VI}), 3.97, 3.84–3.79 (bt, 1 H, J ~ 2.6 Hz, m, 4 H, H-2^{I-V}), 3.77–3.65 (m, 7 H, H-3^{I-VI}, $CHCH_2Si$), 3.59–3.17 (m, 13 H, H-4^{I-VI},5^{I-VI}, $CHCH_2Si$), 1.29, 1.27, 1.24, 1.22, 1.19, 1.16 (6 d, 18 H, $J_{5,6}$ ~ 6.2 Hz, H-6^{I-VI}), 0.98–0.81 (m, 2 H, CH_2Si), and 0.03 (s, 9 H, 3 CH_3); ^{13}C NMR ($CDCl_3$): δ 100.43, 100.30, 100.18, 100.09 (2 C, C-1^{II-VI}), 98.19 (C-1^I), 77.62, 77.49, 76.92, 76.56, 76.52 (2 C, C-3^{I-VI}), 73.98 (C-2^I), 73.57, 73.42 (2 C), 73.24 (C-2^{II-V}), 72.14, 72.11 (3 C), 72.03 (2 C, 6 CH_2Ph), 67.78 (3 C), 67.71, 67.32, 66.99 (C-5^{I-VI}), 67.11 (C-2^{VI}), 65.16 (CH_2CH_2Si), 64.43, 64.17 (4 C), 63.80 (C-4^{I-VI}), 18.58, 18.53, 18.48 (3 C), 18.28 (C-6^{I-VI}), 17.71 (CH_2Si), and −1.34 (3 CH_3); CIMS: *m/z* 1703 ($[M + 18]^+$); IR (film) cm^{-1} 2110 (N_3). Anal. Calcd for $C_{83}H_{104}N_{18}O_{19}Si$: C, 59.13; H, 6.22; N, 14.95. Found: C, 59.24; H, 6.26; N, 14.96.

*2-(Trimethylsilyl)ethyl 3-*O*-benzyl-2-*O*-[3-*O*-benzyl-4,6-dideoxy-4-(3-deoxy-*L*-glycero-tetronamido)-α-*D*-mannopyranosyl]-4,6-dideoxy-4-(3-deoxy-*L*-glycero-tetronamido)-α-*D*-mannopyranoside* (**12**).—A mixture of the **8** (prepared from **3** by treatment with H_2S as described previously [8], 250 mg, 0.43 mmol), 3-deoxy-L-*glycero*-tetronolactone (**18**) [4] (173 mg, 1.7 mmol) and pyridine (0.1 mL) was stirred overnight at 110 °C, when TLC (solvent *C*) showed that all starting material was consumed. Chromatography gave **12** (190 mg, 56%), mp 156–158 °C (from EtOAc–hexane), $[\alpha]_D$ +10°; ^{1}H NMR (~4:1 $CDCl_3$–CD_3OD): δ 5.00 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{II}), 4.80 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1^I), 4.70–4.47 (4 d, 1 H each, ^2J ~ 11.7 Hz, 4 CH_2Ph), 4.24, 4.22 (2 dd, partially overlapped, 2 H, $J_{2,3a}$ ~ 3.8, $J_{2,3b}$ ~ 8.5 Hz, H-$2'^{I,II}$), 4.18 (dd, 1 H, $J_{2,3}$ 3.0, H-2^{II}), 4.13–3.99 (m, 2 H, H-$4^{I,II}$), 3.97 (bt, 1 H, H-2^I), 3.84–3.66 (m, 9 H, H-$3^{I,II}$,$5^{I,II}$,$4'^{I,II}_{a,b}$, CH_aCH_2Si), 3.51–3.42 (m, 1 H, CH_bCH_2Si), 2.08–1.96, 1.80–1.70 (2 d, 2 H each, $3'^{I,II}_{a,b}$), 1.20 (d, 6 H, $J_{5,6}$ 6.2 Hz, H-$6^{I,II}$), and 0.02 (s, 9 H, 3 CH_3); ^{13}C NMR (~4:1 $CDCl_3$–CD_3OD): δ 175.31, 175.10 (2 CO), 101.24 (C-1^{II}), 98.35 (C-1^I), 75.97, 75.90 (C-$3^{I,II}$), 73.78 (C-2^I), 71.45, 70.87 (2 CH_2Ph), 70.51 (2 C, C-$2'^{I,II}$), 67.98, 67.77 (C-$5^{I,II}$), 66.33 (C-2^{II}), 65.14 (CH_2CH_2Si), 59.49 (2 C, C-$4'^{I,II}$), 51.90, 51.07 (C-$4^{I,II}$), 36.03, 35.96 (C-$3'^{I,II}$), 17.71, 17.64, 7.96 (C-$6^{I,II}$, CH_2Si), and −1.30 (3 CH_3). CIMS: *m/z* 810 ($[M + 18]^+$). Anal. Calcd for $C_{39}H_{60}N_2O_{13}Si$: C, 59.07; H, 7.63; N, 3.53. Found: C, 58.81; H, 7.65; N, 3.51.

*2-(Trimethylsilyl)ethyl [2-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-L-glycero-tetronamido)-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranosyl]-(1 → 2)-4-(2,4-di-*O*-acetyl-3-deoxy-L-glycero-tetronamido)-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranoside* (**15**).—Compound **12** (90 mg) was treated overnight with 2:1 pyridine–Ac_2O (10 mL). Chromatog-

raphy (solvent *D*) of the residue obtained on concentration gave **15** (84 mg, 74%), $[\alpha]_D$ −11°; ^{1}H NMR ($CDCl_3$): δ 5.82, 5.68 (2 d, 1 H each, *J* 8.7 and 9.0, respectively, 2 NH), 5.49 (dd, 1 H, $J_{1,2}$ 2.0, $J_{2,3}$ 2.8 Hz, H-2^{II}), 5.18 (m, 2 H, H-2′^{I,II}), 4.83 (d, 1 H, H-1^{II}), 4.74 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1^{I}), 4.66, 4.60, 4.45, 4.40 (4 d, 1 H each, *J* ~ 12 Hz, 2 CH_2Ph), 4.31–3.98 (m, 4 H, H-4′^{I,II}), 3.96–3.88 (m, 3 H, H-4^{I,II},2^{I}), 3.82–3.68 (m, 5 H, CH_aCH$_2$Si, H-3^{I,II},5^{I,II}), 3.50–3.40 (m, 1 H, CH_bH$_2$Si), 2.28–2.10 (m, overlapped, H-3′^{I,II}), 2.09, 2.08, 2.04, 2.03, 2.02, (5 s, overlapped, 5 COCH_3), 1.18, 1.16 (2 d, partially overlapped, H-6^{I,II}), 1.00–0.82 (m, 2 H, CH$_2$Si), and ~ 0.0 (s, 9 H, 3 CH$_3$); ^{13}C NMR ($CDCl_3$): δ 99.76 (C-1^{II}), 98.31 (C-1^{I}), 75.20, 72.94 (C-3^{I,II}), 74.48 (C-2^{I}), 71.17 (2 C, C-2′^{I,II}), 71.02, 70.45 (2 *C*H$_2$Ph), 68.76, 67.71 (C-5^{I,II}), 66.87 (C-2^{II}), 65.29 (*C*H$_2$CH$_2$Si), 59.91, 59.88 (C-4′^{I,II}), 52.69, 51.74 (C-4^{I,II}), 30.96, 30.78 (C-3′^{I,II}), 18.03, 17.89 (C-6^{I,II}), 17.72 (CH$_2$Si), and −1.36 (3 CH$_3$); CIMS: *m/z* 1020 ([M + 18]$^+$). Anal. Calcd for $C_{49}H_{70}N_2O_{18}Si$: C, 58.67; H, 7.03; N, 2.79. Found: C, 58.46; H, 7.08; N, 2.74.

*2-(Trimethylsilyl)ethyl 2-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)-[4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]$_2$-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranoside* (**16**).—Amine **9** was prepared (89%) from **5** as described for the preparation of **8**. ^{1}H NMR ($CDCl_3$): δ 5.07 (bd, 2 H, 2 H-1), 4.99 (bd, 1 H, H-1), 4.77 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1^{I}), 4.69–4.36 (8 d, 1 H each, *J* ~ 11.5 Hz, 4 CH_2Ph), 4.03 (m, 3 H, H-2^{II-IV}), 3.91 (bdd, 1 H, $J_{2,3}$ 2.4 Hz, H-2^{I}), 3.72 (m, 1 H, CH_aCH$_2$Si), 3.64–3.38 (m, 9 H, H-3^{I-IV},5^{I-IV}, CH_bCH$_2$Si), 2.85–2.76 (m, 4 H, H-4^{I-IV}), 1.25–1.12 (m, 21 H, H-6^{I-IV}, 4 NH$_2$,OH), 0.92–0.84 (m, 2 H, CH$_2$Si), and ~ 0 (s, 9 H, 3 CH$_3$); ^{13}C NMR ($CDCl_3$): δ 101.08, 100.96 (2 C, C-1^{II-IV}), 98.76 (C-1^{I}), 79.70, 79.24 (2 C), 78.79 (C-3^{I-IV}), 73.11, 72.90 (2 C, C-2^{I-III}), 71.38, 71.15 (2 C), 71.06 (4 *C*H$_2$Ph), 70.27 (2 C), 69.58 (2 C, C-5^{I-IV}), 66.45 (C-2^{IV}), 64.67 (*C*H$_2$CH$_2$Si), 53.64 (3 C), 53.26 (C-4^{I-IV}), 18.21 (2 C), 18.12, 17.93, 17.74 (C-6^{I-IV}, CH$_2$Si), and −1.33 (3 CH$_3$); CIMS: *m/z* 1059 ([M + 1]$^+$).

A solution of compound **9** (360 mg, 0.34 mmol), and lactone **11** (277 mg, 2.7 mmol) in pyridine (5 mL) was stirred at 110 °C for 40 h (TLC, solvent *C*). After cooling, 1:1 pyridine–acetic anhydride (10 mL) was added, and stirring at room temperature was continued for 3 h. After concentration, the mixture was chromatographed (solvent *D*) to pre-purify the main product which was collected and deacetylated (Zemplén). Chromatography (solvent *E*) gave 2-(trimethylsilyl)ethyl 3-*O*-benzyl-(3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-[3-*O*-benzyl-(3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]$_2$-3-*O*-benzyl-(3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranoside (**13**, 72 mg, 10%). Structurally significant signals in the ^{1}H NMR (CD_3OD) spectrum were at: δ 5.10, 5.06, 4.90, 4.79 (4 d, 1 H each, $J_{1,2}$ ~ 1.6 Hz, H-1^{I-IV}), 2.06–1.89, 1.79–1.63 (2 m, 4 H each, H-3′$^{I-IV}_{a,b}$), 1.18, 1.16, 1.05, 1.03 (4 d, partially overlapped, 12 H, $J_{5,6}$ 6.2 Hz, H-6^{I-IV}), 0.99–0.81 (m, 2 H, CH$_2$Si), and ~ 0 (s, 9 H, 3 CH$_3$); ^{13}C NMR ($CDCl_3$): δ 103.04 (C-1^{IV}), 102.21, 102.12 (C-1^{II,III}), 99.85 (C-1^{I}), 77.25 (2 C), 77.18, 76.75, 76.00, 75.91, 75.24 (C-2^{I-III},3^{I-IV}), 73.10, 72.87, 72.83, 71.84 (4 *C*H$_2$Ph), 70.79 (4 C, C-2′$^{I-IV}$), 69.87 (2 C), 69.65, 69.15 (C-5^{I-IV}), 67.64 (C-2^{IV}), 66.11 (*C*H$_2$CH$_2$Si), 59.80 (4 C, C-4′$^{I-IV}$),

38.47 (4 C, C-3′$^{I-IV}$), 18.57, 18.52 (2 C), 18.45, 18.36 (C-6^{I-IV}, CH_2Si), and −1.19 (3 CH_3).

Conventional acetylation of **13** (40 mg) with pyridine–Ac_2O gave, after chromatography, **16** (40 mg, 83%), $[\alpha]_D$ −14°, ^{1}H NMR ($CDCl_3$, only definitely assigned signals are listed): δ 6.20, 6.05 (2 bs, 1 H each, 2 NH), 5.87, 5.70 (2 bd, 1 H each, *J* 9.0 Hz, 2 NH), 5.42 (dd, 1 H, $J_{1,2}$ 2.0, $J_{2,3}$ 2.9 Hz, H-2^{IV}), 5.20–5.14 (m, 4 H, H-2′$^{I-IV}$), 5.05, 4.98 (2 d, 1 H each, $J_{1,2}$ 2.6 and 2.4 Hz, respectively, H-1^{II,III}), 4.76 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1^{IV}), 4.73 (d, 1 H, $J_{1,2}$ 2 Hz, H-1^{I}), 3.90 (bd, 1 H, H-2^{I}), 2.25–1.95 (m, 35 H, 9 $COCH_3$, H-3′$_{a,b}^{I-IV}$), 1.16, 1.15, 1.13, 1.10 (4 d, 3 H each, $J_{5,6}$ ~6.2 Hz, H-6^{I-IV}), 0.95–0.85 (m, 2 H, CH_2Si), and ~0 (s, 9 H, 3 CH_3); ^{13}C NMR ($CDCl_3$): δ 100.89, 99.94, 98.70, 98.36 (C-1^{I-IV}), 74.96, 74.42 (2 C), 74.11, 73.75, 73.51, 73.37 (C-2^{I-III},3^{I-IV}), 71.11 (3 C), 70.98, 70.93, 70.86, 70.79, 70.59 (C-2′$^{I-IV}$, 4 CH_2Ph), 68.90 (3 C), 68.03 (C-5^{I-IV}), 67.09 (C-2^{IV}), 65.45 (CH_2CH_2Si), 60.05, 59.96 (2 C), 59.90 (C-4′$^{I-IV}$), 52.13, 51.89, 51.74, 51.67 (C-4^{I-IV}), 30.98 (3 C) 30.86 (C-3′$^{I-IV}$), 18.15, 18.09, 18.03, 17.91, 17.77 (C-6^{I-IV}, CH_2Si), and −1.31 (3 CH_3); FABMS *m/z* 1846 ($[M + 1]^+$); Anal. Calcd for $C_{91}H_{124}N_4O_{34}Si$: C, 59.21; H, 6.77; N, 3.03. Found: C, 59.28; H, 6.81; N, 3.00.

*2-(Trimethylsilyl)ethyl 4-azido-3-*O*-benzyl-4,6-dideoxy-3-*O*-methyl-α-*D*-mannopyranosyl-(1 → 2)-[(4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranosyl)-(1 → 2)]$_4$-4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranoside* (**17**).—Iodomethane (24 mg, 0.18 mmol) was added to a mixture of **7** (200 mg, 0.12 mmol) and KOH (17 mg, 0.36 mmol) in DMSO (3 mL), and the mixture was stirred until TLC (solvent *A*) showed that all starting material was consumed (~30–60 min). The mixture was partitioned between water and CH_2Cl_2, and the organic phase was dried and concentrated. Chromatography of the residue gave amorphous **17** (197 mg, 98%), $[\alpha]_D$ +102° (*c* 1.2); ^{1}H NMR ($CDCl_3$): δ 4.98–4.52 (m, 18 H, H-1^{I-VI}, 6 CH_2Ph), 3.99, 3.87, 3.85, 3.82, 3.79 (5 bt, partially overlapped, 5 H, H-2^{I-V}), 3.23 (s, overlapped with signals of ring protons, OCH_3), 1.36–1.08 (m, 18 H, H-6^{I-VI}), 0.96–0.81 (m, 2 H, CH_2Si), and ~0 (m, 9 H, 3 CH_3); ^{13}C NMR ($CDCl_3$): δ 100.30, 100.21, 100.11, 100.07 (C-1^{II-V}), 98.76 (C-1^{VI}), 98.19 (C-1^{I}), 77.49, 77.39 (2 C), 77.12, 76.53 (2 C), 76.34 (C-2^{VI},3^{I-VI}), 74.01, 73.57, 73.45, 73.27, 73.17 (C-2^{I-V}), 72.34, 72.14 (3 C), 72.05, 72.01 (6 CH_2Ph), 67.82 (2 C), 67.79, 67.72 (2 C), 66.99 (C-5^{I-VI}), 65.15 (CH_2CH_2Si), 64.44, 64.29, 64.19 (3 C), 64.08 (C-4^{I-VI}), 58.87 (OCH_3), 18.56, 18.52, 18.45 (3 C), 18.37 (C-6^{I-VI}), and 17.71 (CH_2Si), −1.37 (3 CH_3); FABMS: *m/z* 1673 ($[M + 1 - 26]^+$, reflecting the conversion R–N_3 → R–NH_2 [24]). Anal. Calcd for $C_{84}H_{106}N_{18}O_{19}Si$: C 59.35; H, 6.28; N, 14.83. Found: C, 59.44; H, 6.31; N, 14.74.

*2-(Trimethylsilyl)ethyl 3-*O*-benzyl-4-(4-*O*-benzyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl]-(1 → 2)-[3-*O*-benzyl-4-(4-*O*-benzyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]$_4$-3-*O*-benzyl-4-(4-*O*-benzyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**20**).—Compound **7** was treated with H_2S as described for the preparation of **8** to give 2-(trimethylsilyl)ethyl 4-amino-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-[(4-amino-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl)-(1 → 2)]$_4$-4-amino-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (**10**) in 82% yield. ^{1}H NMR ($CDCl_3$): δ 5.10, 5.78, 5.01 (4 bd, partially overlapped, 5 H, H-1^{II-VI}), 4.77 (bd, 1 H, H-1^{I}), 4.73–4.36 (m, 12 H, 6

CH_2Ph), 4.08–4.01 (m, 5 H, H-2^{II-VI}), 3.92 (m, 1 H, H-2^{I}), 3.74 (m, overlapped, CH_aCH_2Si), 3.74–3.40 (m, overlapped, CH_bCH_2Si, H-3^{I-VI}, H-5^{I-VI}), 2.90–2.78 (m, 6 H, H-4^{I-VI}), 2.40–1.02 (4 m, partially overlapped, 6 NH_2, OH, H-6^{I-VI}), 1.00–0.8 (m, 2 H, CH_2Si), and ~0 (m, 9 H, 3 CH_3); ^{13}C NMR ($CDCl_3$): δ 101.07, 100.91 (4 C, C-1^{II-VI}), 98.78 (C-1^{I}), 79.67, 79.19 (2 C), 78.75, 78.65 (2 C, C-3^{I-VI}), 73.16, 73.05, 73.01, 72.95 (2 C, C-2^{I-V}), 71.42, 71.17 (2 C), 71.12 (3 C) (6 CH_2Ph), 70.30, (4 C), 69.57 (2 C) (C-5^{I-VI}), 66.51 (C-2^{VI}), 64.75 (CH_2CH_2Si), 53.69 (5 C), 53.30 (C-4^{I-VI}), 18.25 (3 C), 18.16 (2 C), 17.97 (C-6^{I-VI}), 17.78 (CH_2Si), and −1.31 (3 CH_3); IR: absence of absorption at 2110 cm^{-1} (N_3); CIMS: *m/z* 1530 ($[M + 1]^+$).

A solution of **10** (740 mg, 0.48 mmol), **19** (812 mg, 3.8 mmol), WSC (923 mg, 4.8 mmol) and HOBT (652 mg, 4.8 mmol) in DMF (10 mL) was stirred overnight at room temperature. The mixture was extracted with CH_2Cl_2, and the extract was washed successively with 2 N HCl, sat aq $NaHCO_3$, and NaCl, dried, concentrated, and chromatography (solvent *D*) gave **20** (1.02 g, 79%), $[\alpha]_D$ −5°. Definite, structurally significant signals in the ^1H NMR spectrum ($CDCl_3$) were at: δ 6.96 (bd, 1 H, $J_{4,NH}$ ~9.2 Hz, NH), 6.83, 6.80 (2 bd, partially overlapped, 2 H, 2 NH), 6.70 (bd, 1 H, $J_{4,NH}$ 8.9 Hz, NH), 6.61, 6.58 (2 d, partially overlapped, $J_{4,NH}$ ~9.5 Hz, 2 NH), 5.06, 5.05, 5.04, 5.02 (4 bd, partially overlapped, 4 H, H-1^{II-VI}), 4.90 (bd, 1 H, $J_{1,2}$ ~1.5 Hz, H-1^{VI}), 4.74 (bd, 1 H, $J_{1,2}$ ~1.8 Hz, H-1^{I}), 3.94 (bdd, 1 H, H-2), 2.15, 1.90 (2 m, 6 H each, H-$3'^{I-VI}$), 1.21, 1.19, 1.12 (3 m, 18 H, H-6^{I-VI}), and 0.20 (s, 9 H, 3 CH_3); ^{13}C NMR ($CDCl_3$): δ 173.85, 173.66 (2 C), 173.53. 173.42, 173.28 (6 CO), 100.55 (C-1^{VI}), 99.81 (2 C), 99.52 (2 C, C-1^{II-V}), 98.35 (C-1^{I}), 76.42, 75.71, 75.37 (2 C), 75.14, 74.93 (C-3^{I-VI}), 73.45, 73.39, 73.34, 73.25 (2 C), 73.18, (C-$4'^{I-VI}$–OCH_2Ph), 73.64, 72.96 (2 C), 72.80 (3 C), 72.65, 72.49, 72.20 (2 C), 71.76 (C-2^{I-V},$2'^{I-VI}$), 71.14, 71.02 (5 C) (C-3^{I-VI}-OCH_2Ph), 69.74, 69.51, 69.32, 69.11, 69.02, 68.91, 68.80 (4 C), 68.13, 67.96 (C-$4'^{I-VI}$, C-5^{I-VI}), 66.79 (C-2^{VI}), 65.04 (CH_2CH_2Si), 51.92, 51.82 (3 C), 51.64, 51.10 (C-4^{I-VI}), 33.79, 33.66, 33.58 (2 C), 33.44, 33.34 (C-$3'^{I-VI}$), 18.13 (3 C), 18.05, 18.00, 17.76 (C-6^{I-VI}), 17.71 (CH_2Si), and −1.39 (3 CH_3); FABMS: *m/z* 2682 ($[M + 1]^+$), 2705 ($[M + Na]^+$). Anal. Calcd for $C_{149}H_{188}N_6O_{37}Si$: C, 66.70; H, 7.06; N, 3.13. Found: C, 66.41; H, 7.09; N, 3.02.

*2-(Trimethylsilyl)ethyl 3-*O*-benzyl-4-(4-*O*-benzyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-2-*O*-methyl-α-*D*-mannopyranosyl-(1 → 2)-[3-*O*-benzyl-4-(4-*O*-benzyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]$_4$-3-*O*-benzyl-4-(4-*O*-benzyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**21**).—Hydrogen sulfide was passed through a solution of **17** (900 mg) in 7:3 pyridine–triethylamine (20 mL) for 1 h, and the mixture was kept at room temperature overnight. After concentration, the residue was chromatographed on neutral alumina (solvent *D*) to give amorphous **18** (640 mg, 78%). ^1H NMR ($CDCl_3$): δ 5.07 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 5.06 (bs, 2 H, 2 H-1), 5.04 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 4.97 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1^{VI}), 4.76 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1^{I}), 4.74–4.35 (m, 12 H, 6 CH_2Ph), 4.08, 4.03, 3.91 (3 m, 5 H, H-2^{I-V}), 3.79–3.67 (m, 1 H, CH_aCH_2Si), 3.63–3.38 (m, 14 H, H-2^{VI},3^{I-VI},5^{I-VI}, CH_bCH_2Si), 3.26 (s, 3 H, OCH_3), 2.92–2.75 (m, 6 H, H-4^{I-VI}), 1.36–1.06 (m, 30 H, H-6^{I-VI}, 6 NH_2), 0.98–0.80 (m, 2 H, CH_2Si), and ~0 (m, 9 H, 3 CH_3); ^{13}C NMR ($CDCl_3$): δ 101.02, 100.93 (3 C, C-1^{II-V}), 99.15 (C-1^{VI}), 98.79 (C-1^{I}), 79.63, 79.25, 79.18, 78.79, 78.73 (2 C, C-3^{I-VI}), 75.86 (C-2^{VI}), 73.06 (2 C), 73.02, 72.64 (C-2^{II-V}),

72.94 (C-2^{I}), 71.64, 71.28, 71.11 (4 C, 6 CH_2Ph), 70.31 (3 C), 70.25 (2 C), 69.61 (C-5^{I-VI}), 64.70 (CH_2CH_2Si), 58.85 (OCH_3), 53.84, 53.68 (3 C), 53.59 (2 C, C-$4'^{I-VI}$), 18.23 (4 C), 18.15, 18.06 (C-6^{I-VI}), 17.71 (CH_2Si), ~ −1.2 (3 CH_3); FABMS: *m/z* 1544 ($[M + 1]^+$).

A solution of **18** (590 mg, 0.38 mmol), **19** (800 mg, 3.8 mmol), WSC (730 mg, 3.8 mmol) and HOBT (520 mg, 3.8 mmol) in DMF (17 mL) was stirred at room temperature overnight. The mixture was partitioned between CH_2Cl_2 and 2 M HCl, and the organic phase was washed successively with aqueous $NaHCO_3$ and NaCl solutions, dried, and concentrated. Chromatography of the residue gave amorphous **21** (872 mg, 87%), $[\alpha]_D$ −6°; ^{1}H NMR ($CDCl_3$): δ 7.4–7.2 (m, 60 H, 12 Ph), 6.94–6.49 (m, 6 H, 6 NH), 5.04, 5.02, 5.01, 4.98 (4 d, 1 H each, $J_{1,2}$ ~ 2.5–2.9 Hz, H-1^{II-V}), 4.90 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1^{VI}), 4.72 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.68–4.40 (m, 24 H, 12 CH_2Ph), 4.38–4.00 (m, 17 H, H-4^{I-VI},2^{II-VI},$2'^{I-VI}$), 3.95 (bs, 1 H, H-2^{I}), 3.82–3.54 (m, 26 H, H-2^{VI},3^{I-VI},5^{I-VI},$4'^{I-VI}$, CH_aCH_2Si), 3.50–3.39 (m, 1 H, CH_bCH_2Si), 3.21 (s, 3 H, OCH_3), 2.15, 1.89 (2 m, 6 H each, H-$3'^{I-VI}$), 1.27–1.01 (m, H-6^{I-VI}), 1.00–0.80 (m, 2 H, CH_2Si), and ~ 0 (m, 9 H, 3 CH_3); ^{13}C NMR ($CDCl_3$): δ 100.74, 100.02, 99.67 (2 C, C-1^{II-V}), 98.67 (C-1^{VI}), 98.44 (C-1^{I}), 76.17, 75.99, 75.65 (2 C), 75.38, 75.01 (C-2^{VI},3^{I-VI}), 73.55, 73.48, 73.41, 73.37, 73.30, 73.26 (6 CH_2Ph), 73.25, 73.13, 72.71 (4 C), 72.54 (2 C), 72.35 (2 C, C-2^{II-V},$2'^{I-VI}$), 71.47, 71.21, 71.07 (3 C), 70.63, 69.98, 69.76, 69.49, 69.39, 69.23, 69.13 (C-$4'^{I-VI}$, 6 CH_2Ph), 68.96 (4 C), 68.89, 68.01 (C-5^{I-VI}), 65.06 (CH_2CH_2Si), 59.06 (OCH_3), 52.00, 51.85, 51.80, 51.70, 51.63, 51.54 (C-4^{I-VI}), 33.77, 33.57 (3 C), 33.35 (2 C) (C-$3'^{I-VI}$), 18.22, 18.18, 18.14 (2 C), 18.08, 17.98 (C-6^{I-VI}), 17.75 (CH_2Si), ~ −1.2 (3 CH_3); FABMS: *m/z* 2696 ($[M + 1]^+$), 2718 ($[M + Na]^+$). Anal. Calcd for $C_{150}H_{190}N_6O_{37}Si$: C, 66.80; H, 7.10; N, 3.12. Found: C, 66.67; H, 7.05; N, 3.06.

*2-(Trimethylsilyl)ethyl 2,3-di-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)-[3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]$_4$-3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**23**).—A solution of the foregoing compound **20** (1.02 g) in 90% acetic acid (55 mL) was stirred overnight at room temperature in a hydrogen atmosphere in the presence of 5% palladium-on-charcoal catalyst (1 g). One product was formed as shown by TLC (solvent *E*). The peak at *m/z* 1623 ($[M + Na]^+$) present in the FABMS spectrum showed that 2-(trimethylsilyl)ethyl 4-(3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-[4-(3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]$_4$-4-(3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranoside (**22**) was formed. After filtration through a Celite pad, the solids were washed with 90% acetic acid, the combined filtrate was concentrated, and a solution of the residue was treated with 2:1 pyridine–Ac_2O (60 mL) overnight at room temperature. Afer concentration, the residue was eluted from a small silica gel column (solvent *D*) to give pure **23** (790 mg, 87%), mp 112–113 °C (from ether–hexane), $[\alpha]_D$ +30°. Characteristic signals in the ^{1}H NMR ($CDCl_3$) spectrum were at: δ 6.58–6.48 (m, 4 H, 4 NH), 6.37 (d, 1 H, $J_{4,NH}$ 9.3 Hz, NH), 6.04 (d, 1 H, $J_{4,NH}$ 9.4, NH), 5.27 (dd, 1 H, $J_{2,3}$ 3.2, $J_{3,4}$ 10.9 Hz, H-3), 5.24–5.14 (m, 7 H, H-2^{VI},3^{I-VI}) 4.97 (2 bd, partially overlapped, 2 H, 2 H-1), 4.93 (bd, 1 H, H-1), 4.88, 4.86 (2 bd, partially overlapped, 2 H-1), 4.73 (bd,

1 H, H-1^{I}), 3.84 (bdd, 1 H, H-2), 3.60 (m, 1 H, H-5), 3.46 (m, 1 H, C*H*CH$_2$Si), 2.18–1.96 (m, COCH$_3$ signals overlapping H-3$'^{I-VI}$ resonances), 1.15 (m, 18 H, H-6^{I-VI}), 0.90 (m, 2 H, CH$_2$Si), and ~0.0 (s, 9 H, 3 CH$_3$); ^{13}C NMR (CDCl$_3$): δ 100.21, 99.97, 99.77 (2 C), 99.17 (C-1^{II-VI}), 97.94 (C-1^{I}), 76.35, 75.67, 75.21, 75.01, 74.73 (C-2^{I-V}), 70.80 (6 C, C-2$'^{I-VI}$), 70.03 (C-2^{VI}), 69.74, 69.61, 69.40, 69.34, 69.29, 69.15, 69.08, 68.97 (2 C), 68.73, 68.20, 68.00 (C-3^{I-VI},5^{I-VI}), 65.44 (*C*H$_2$CH$_2$Si), 60.24, 59.79 (5 C, C-4$'^{I-VI}$), 52.13, 51.70 (2 C), 51.61, 51.59, 51.31 (C-4^{I-VI}), 30.54 (4 C), 30.46 (2 C, C-3$'^{I-VI}$), 17.74 (7 C, C-6^{I-VI}, CH$_2$Si), and −1.48 (3 CH$_3$); FABMS: *m/z* 2399.9 ([M + 1]$^+$). Anal. Calcd for $C_{103}H_{154}N_6O_{56}Si$: C, 51.54; H, 6.47; N, 3.50. Found: C, 51.83; H, 6.49; N, 3.46.

*2-(Trimethylsilyl)ethyl 3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-2-*O*-methyl-α-*D*-mannopyranosyl-(1 → 2)-[3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]$_4$-3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**25**).—A mixture of compound **21** (790 mg) and 5% palladium-on-charcoal catalyst (700 mg) in 90% acetic acid (55 mL) was stirred overnight at room temperature. The catalyst was filtered off, washed with 90% acetic acid, and the filtrate was concentrated. The residue, containing **24**, was treated with 2:1 pyridine–Ac$_2$O (60 mL), at room temperature overnight, and the mixture was processed as described for the preparation of **23**, to give **25** (525 mg, 76%), $[\alpha]_D$ +28°; ^{1}H NMR (CDCl$_3$): δ 6.60–6.10 (6 d, partially overlapped, 6 NH), 5.26–5.13 (m, 6 H, H-3^{I-VI}), 5.09–4.88 (m, 11 H, incl 3 bs at 4.97, 4.99, and 4.88 for 3 H-1, 2 H-1, H-1, 2$'^{I-VI}$), 4.74 (bs, 1 H, H-1^{I}), 4.31–4.00 (m, 22 H, H-2^{II-V},4^{I-VI},4$'^{I-VI}$), 3.89 (bs, 1 H, H-2^{I}), 3.80–3.60 (m, 8 H, incl bs at 3.63 for H-2^{VI},H-5^{I-VI}, C*H*$_a$CH$_2$Si), 3.53–3.44 (m, 4 H, incl s at 3.51 for OCH$_3$, C*H*$_b$CH$_2$Si), and 2.30–1.90 (m, H-3$'^{I-VI}_{a,b}$, 18 COCH$_3$), 1.24–1.14 (m, 18 H, H-6^{I-VI}), 1.01–0.82 (m, 2 H, CH$_2$Si), ~0.0 (s, 9 H, 3 CH$_3$); ^{13}C NMR (CDCl$_3$): δ 100.15, 99.97, 99.63, 99.50, 99.12 (C-1^{II-VI}), 97.85 (C-1^{I}), 77.54 (C-2^{VI}), 75.14 (C-2^{I}), 74.72 (2 C), 74.45, 74.15 (C-2^{II-V}), 70.72 (3 C), 70.60 (3 C, C-2$'^{I-VI}$), 70.46, 69.90, 69.84, 69.54, 69.50, 69.22 (2 C), 68.93, 68.72 (2 C), 68.42, 67.90 (C-3^{I-VI},5^{I-VI}), 65.16 (*C*H$_2$CH$_2$Si), 59.66 (6 C, C-4$'^{I-VI}$), 59.38 (OCH$_3$), 52.20, 51.55 (2 C), 51.45 (2 C), 51.22 (C-4^{I-VI}), 30.31 (6 C, C-3$'^{I-VI}_{a,b}$), 17.67 (4 C), 17.59 (2 C, C-6^{I-VI}), 17.52 (CH$_2$Si), and −1.64 (3 C, 3 CH$_3$); FABMS: *m/z* 2371.9 ([M + 1]$^+$), 2394.9 ([M + Na]$^+$). Anal. Calcd for $C_{102}H_{154}N_6O_{55}Si$: C, 51.64; H, 6.54; N, 3.54. Found: C, 51.50; H, 6.52; N, 3.50.

*2,3-Di-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)-[3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]$_4$-3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranose* (**26**).—A solution of **23** (790 mg) in TFAA (20 mL) was stirred for 4 h (TLC, solvent *B*), and concentrated at room temp. The residue was chromatographed to give amorphous **26** (700 mg, 92%), $[\alpha]_D$ +19°; ^{13}C NMR (CDCl$_3$): δ 100.15 (2 C), 99.91, 99.70, 99.30 (C-1^{II-VI}), 93.01 (C-1^{I}), 59.82 (3 C), 59.79 (3 C, C-4$'^{I-VI}$), 51.89 (3 C), 51.59 (3 C, C-4^{I-VI}), 30.82 (2 C), 30.66, 30.52 (3 C, C-3$'^{I-VI}$), 18.09 (3 C), and 17.84 (3 C, C-6^{I-VI}); FABMS: *m/z* 2299.8 ([M + 1]$^+$). Anal. Calcd for $C_{98}H_{142}N_6O_{56}$: C, 51.17; H, 6.22; N, 3.65. Found: C, 50.90; H, 6.28; N, 3.43.

3-O-Acetyl-4-(2,4-di-O-acetyl-3-deoxy-L-glycero-*tetronamido)-4,6-dideoxy-2-O-methyl-α-*D-*mannopyranosyl-(1 → 2)-[3-O-acetyl-4-(2,4-di-O-acetyl-3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl-(1 → 2)]$_4$-(1 → 2)-3-O-acetyl-4-(2,4-di-O-acetyl-3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranose* (**27**).—A solution of **25** (505 mg) was treated with TFAA (16 mL) for 3 h as described for the preparation of **26**. Chromatography yielded **27** (439 mg, 90%), $[\alpha]_D$ +19°; FABMS: *m/z* 2271.8 ($[M + 1]^+$), 2293.8 ($[M + Na]^+$). Anal. Calcd for $C_{97}H_{142}N_6O_{55}$: C, 51.27; H, 6.30; N, 3.70. Found: C, 51.05; H, 6.47; N, 3.47.

2,3-Di-O-acetyl-4-(2,4-di-O-acetyl-3-deoxy-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl-(1 → 2)-[3-O-acetyl-4-(2,4-di-O-acetyl-3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl-(1 → 2)]$_4$-3-O-acetyl-4-(2,4-di-O-acetyl-3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl trichloroacetoimidate* (**28**).—1,8-Diazabicyclo[5,4,0]-undec-7-ene (DBU, 5.6 mg) was added at 0 °C to a solution of compound **26** (170 mg) and CCl_3CN (3.2 g) in CH_2Cl_2 (3 mL). The mixture was stirred for 5 min at 0 °C, and directly chromatographed (solvent *B*), to give **28** (140 mg, 78%), $[\alpha]_D$ +21°; ^{1}H NMR ($CDCl_3$): δ 6.50–6.10 (m, 7 H, include bs at 6.26, H-1^{VI}, 6 NH), 5.33–5.20 (m, 6 H, H-3^{I-VI}), 5.12–4.97 (m, 12 H, H-1^{I-VI},2′$^{I-VI}$), 4.32–4.13 (m, 24 H, H-2^{I-VI},4^{I-VI},4′$^{I-VI}_{a,b}$), 3.98–3.52 (m, 6 H, H-5^{I-VI}), 2.22–2.03 (m, overlapping signals, H-3′$^{I-VI}_{a,b}$, 19 CH_3CO), and 1.30–1.16 (m, 18 H, H-6^{I-VI}); ^{13}C NMR ($CDCl_3$): δ 160.19 (CCl_3C=NH), 100.45, 100.25, 100.07 (2 C), (C-1^{II-V}), 99.36 (C-1^{VI}), 96.17 (C-1^{I}), 77.20, 76.39, 75.26, 74.82, 73.00 (C-2^{I-V}), 71.17, 70.83 (5 C, C-2′$^{I-VI}$), 69.74, 69.55, 69.36 (3 C), 69.30 (2 C), 69.17 (3 C), 69.04 (2 C), 67.96 (C-2^{VI},3^{I-VI},5^{I-VI}), 59.76 (6 C, C-4′$^{I-VI}$), 52.00, 51.69 (3 C), 51.43, 51.18 (C-4^{I-VI}), 30.53 (6 C, C-3′$^{I-VI}$), 17.78 (3 C), and 17.63 (3 C), (C-6^{I-VI}); FABMS: *m/z* 2464.7 ($[M + Na]^+$).

3-O-Acetyl-4-(2,4-di-O-acetyl-3-deoxy-L-glycero-*tetronamido)-4,6-dideoxy-2-O-methyl-α-*D-*mannopyranosyl-(1 → 2)-[3-O-acetyl-4-(2,4-di-O-acetyl-3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl-(1 → 2)]$_4$-3-O-acetyl-4-(2,4-di-O-acetyl-3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl trichloroacetoimidate* (**29**).—The title compound **29** was obtained (333 mg, 73%) from **27** (430 mg) as described for the preparation of **28**, $[\alpha]_D$ +33°; ^{1}H NMR ($CDCl_3$): δ 6.48–6.04 (7 d, partially overlapped, incl bd at ~6.27 for H-1^{I}, 6 NH), 5.31–5.18 (m, 6 H, H-3^{I-VI}), 5.10–4.98 (m, 12 H, H-1^{I-VI},2′$^{I-VI}$), 4.15–4.05 (m, 24 H, H-2^{I-V},4^{I-VI},4′$^{I-VI}_{a,b}$), 3.95–3.70 (m, 6 H, H-5^{I-VI}), 3.65 (dd, $J_{1,2}$ 1.8, $J_{2,3}$ 3.0 Hz, H-2^{VI}), 3.54 (s, 3 H, OCH_3), 2.22–2.04 (m, overlapping signals of H-3′$^{I-VI}_{a,b}$ and 18 $COCH_3$), and 1.28–1.17 (m, 18 H, H-6^{I-VI}); ^{13}C NMR ($CDCl_3$): δ 160.01 (CCl_3C=NH), 100.32, 100.17, 99.86 (2 C), 99.28 (C-1^{I-V}), 96.07 (C-1^{I}), 77.60 (C-2^{VI}), 77.20, 74.99 (2 C), 74.50, 72.73 (C-2^{I-V}), 70.98, 70.73 (3 C), 70.64 (6 C, 2′$^{I-VI}$), 70.50, 69.87, 69.57, 69.42, 69.32 (4 C), 69.03, 68.84 (3 C, C-3^{I-VI},5^{I-VI}), 59.71 (5 C), 59.49 (C-4′$^{I-VI}$), 52.04, 51.61(2 C), 51.51, 51.31, 51.01 (C-4^{I-VI}), 30.35 (C-3′$^{I-VI}$), 17.75 (3 C), 17.68 (2 C), and 17.52 (C-6^{I-VI}); FABMS: *m/z* 2414.4 ($[M + 1]^+$), 2436.6 ($[M + Na]^+$).

5-Methoxycarbonylpentyl 2,3-di-O-acetyl-4-(2,4-di-O-acetyl-3-deoxy-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl-(1 → 2)-[3-O-acetyl-4-(2,4-di-O-acetyl-3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl-(1 → 2)]$_4$-3-O-acetyl-4-(2,4-di-O-acetyl-3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranoside* (**30**).—To a mixture of **28** (140 mg, 57 μmol), methyl 6-hydroxyhexanoate [23] (83 mg,

0.57 mmol) and 4 Å molecular sieves (500 mg) in CH_2Cl_2 (8 mL) was added, at −20 °C, triethylsilyltrifluoromethanesulfonate (TESOTf, 1 drop). The mixture was stirred at −20 °C for 1 h and directly chromatographed to give **30** (100 mg, 72%), $[\alpha]_D$ +28°; ^{1}H NMR ($CDCl_3$): δ 6.58 (bs, NH), 6.51, 6.50, 6,48, 6.45, 6.34 (5 d, partially overlapped, $J_{4,NH}$ ~ 9 Hz, 5 NH), 5.31 (dd, 1 H, $J_{2,3}$ 3.2, $J_{3,4}$ 10.9 Hz, H-3^{VI}), 5.27–5.18 (m, 6 H, H-3^{I-V},2^{VI}), 5.12–4.90 (m, 11 H, H-1^{II-V},2$'^{I-VI}$, incl d at 4.95, $J_{1,2}$ 1.7 Hz, H-1^{VI}), 4.73 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{I}), 4.31–4.00 (m, 22 H, H-2^{II-V},4^{I-VI},4$'^{I-VI}_{a,b}$), 3.92 (dd, 1 H, $J_{2,3}$ 2.9 Hz, H-2^{I}), 3.89–3.62 (m, 10 H, H-5^{I-VI}, OCH_a, $COOCH_3$), 3.46–3.38 (m, 1 H, OCH_b), 2.37 (bt, 2 H, CH_2CO), 2.26–2.02 (m, H-3$'^{I-VI}$, 19 $COCH_3$), 1.75–1.57 (m, 4 H, $OCH_2CH_2CH_2CH_2$), 1.48–1.35 (m, 2 H, $OCH_2CH_2CH_2$), and 1.24–1.17 (m, 18 H, H-6^{I-VI}); ^{13}C NMR ($CDCl_3$): δ 100.32, 100.17, 99.92, 99.82 (C-1^{II-V}), 99.29 (C-1^{VI}), 98.52 (C-1^{I}), 76.38, 75.46, 75.30, 75.03, 74.65 (C-2^{I-V}), 70.98, 70.86 (2 C), 70.81 (3 C, C-2$'^{I-VI}$), 70.05 (C-2^{VI}), 69.75, 79.70, 69.31 (2 C), 69.14 (2 C), 68.98 (2 C), 68.67 (2 C), 67.84 (C-3^{I-V},5^{I-VI}), 67.98 (C-3^{VI}), 67.08 (OCH_2), 59.87 (3 C), 59.80 (3 C, C-4$'^{I-VI}$), 52.27, 51.67 (2 C), 51.60 (2 C), 51.41 (2 C, C-4^{I-VI},OCH_3), 33.78 (CH_2CO), 30.54 (6 C, C-3$'^{I-VI}$), 28.55, 24.16 ($OCH_2CH_2CH_2CH_2$), 25.34 ($OCH_2CH_2CH_2$), 17.84 (3 C), and 17.76 (3 C, C-6^{I-VI}); FABMS: *m/z* 2427.8 ([M + 1]$^+$), 2450.8 ([M + Na]$^+$).

*2-[2-(Methoxycarbonyl)ethylthio]ethyl 2,3-di-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)-[3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]$_4$-3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**31**).—Compound **31** (95 mg, 71%) was prepared from **28** (135 mg) and methyl 2-(2-hydroxyethylthio)propionate [8] (90 mg) as described for the preparation of **30**, $[\alpha]_D$ +28°; ^{1}H NMR ($CDCl_3$): δ 6.60–6.23 (m, 6 H, 6 NH), 5.30 (dd, 1 H, $J_{2,3}$ 3.2, $J_{3,4}$ 11.1 Hz, H-3^{VI}), 5.27–5.18 (m, 6 H, H-2^{VI},3^{I-V}), 5.12–4.89 (m, H-1^{II-V},2$'^{I-VI}$, incl d at 4.95, $J_{1,2}$ 1.7 Hz, H-1^{VI}), 4.79 (d, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.32–4.02 (m, 22 H, H-2^{II-V},4^{I-VI},4$'^{I-VI}$), 3.97 (dd, 1 H, $J_{2,3}$ 2.9 Hz, H-2^{I}), 3.90–3.64 (m, 11 H, H-5^{I-VI}, OCH_2, incl s at 3,72, OCH_3), 3.00–2.82 (m, 2 H, CH_2CH_2CO), 2.80–2.72 (m, 2 H, OCH_2CH_2), 2.70–2.56 (m, 2 H, CH_2CO), 2.24–2.03 (m, H-3^{I-VI}, 19 $COCH_3$), and 1.25–1.18 (m, 18 H, H-6^{I-VI}); ^{13}C NMR ($CDCl_3$): δ 100.29, 100.20, 99.94, 99.85 (C-1^{II-V}), 99.33 (C-1^{VI}), 98.70 (C-1^{I}), 76.37, 75.24, 74.98, 74.60, 74.65 (C-2^{I-V}), 75.09 (C-2^{VI}), 70.91, 70.87 (2 C), 70.82 (2 C), 70.76 (C-2$'^{I-VI}$), 69.88, 69.77, 69.69 (2 C), 69.39, 69.33, 69.18 (2 C), 69.00 (2 C), 68.75, 68.33, 68.00 (C-2^{VI},3^{I-VI},5^{I-VI}), 68.05 (OCH_2), 59.85 (3 C), 59.80 (3 C, C-4$'^{I-VI}$), 52.27, 51.87, 51.72 (3 C), 51.44, 51.32 (C-4^{I-VI}, $COOCH_3$), 34.53 (CH_2CO), 31.80 (OCH_2CH_2), 30.53 (6 C, C-3$'^{I-VI}$), 27.85 (CH_2CH_2CO), 17.85 (3 C), and 17.79 (3 C, C-$^{I-VI}$); FABMS: *m/z* 2445.9 ([M + 1]$^+$), 2467.9 ([M + Na]$^+$).

*5-Methoxycarbonylpentyl 3-*O*-Acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-2-*O*-methyl-α-*D*-mannopyranosyl-(1 → 2)-[3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]$_4$-3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**32**).—Compound **32** (105 mg, 70%) was obtained from **29** (150 mg) and methyl 6-hydroxyhexanoate (90 mg) as described for the preparation of **30**, $[\alpha]_D$ +32°; ^{1}H NMR ($CHCl_3$): δ 6.54–6.38 (m, 4 H, 4 NH), 6.34, 6.26 (2 d, $J_{4,NH}$ 8.7 and

9.1 Hz, respectively, 2 NH), 5.38–5.18 (m, 6 H, H-3^{I-VI}), 5.12–5.00 (m, 9 H, H-$2'^{I-VI}$, 3 H-1), 4.97 (bd, partially overlapped, H-1), 4.91 (bd, 1 H, $J_{1,2}$ ~ 2.6 Hz, H-1), 4.74 (bd, 1 H, $J_{1,2}$ ~ 2.0 Hz, H-1^{I}), 4.36–4.06 (m, 22 H, H-2^{II-V},4^{I-VI},$4'^{I-VI}$), 3.93 (bdd, 1 H, H-2^{I}), 3.86–3.15 (m, 11 H, H-5^{I-VI}, OCH_a, incl s for $COCH_3$ at 3.72 and bdd for H-2^{VI} at 3.66), 3.55 (s, 3 H, OCH_3), 3.46–3.36 (m, 1 H, OCH_b), 2.40–2.32 (m, 2 H, CH_2CO), 2.24–2.04 (m, H-$3'^{I-VI}$, 18 $COCH_3$), 1.84–1.56 (m, 4 H, $OCH_2CH_2CH_2CH_2$), 1.50–1.35 (m, 2 H, $OCH_2CH_2CH_2$), and 1.27–1.17 (18 H, H-6^{I-VI}); ^{13}C NMR ($CDCl_3$): δ 100.37, 100.25, 99.88, 99.72, 99.37 (C-1^{II-VI}), 98.75 (C-1^{I}), 77.05 (C-2^{VI}), 75.27 (C-2^{I}), 74.95 (2 C), 74.78, 74.36 (C-2^{II-V}), 70.96, 70.85 (2 C), 70.73 (3 C, C-$2'^{I-VI}$), 70.61, 70.03 (2 C), 69.67 (2 C), 69.42, 69.31, 69.12, 68.90 (2 C), 68.58, 67.76 (C-3^{I-VI},5^{I-VI}), 67.01 (OCH_2), 59.87, 59.78 (5 C, C-$4'^{I-VI}$), 59.55 (OCH_3), 52.35, 51.70, 51.61, 51.52, 51.40 (3 C, C-4^{I-VI}, $COOCH_3$), 33.72 (CH_2CO), 30.46 (6 C, C-$3'^{I-VI}$), 28.49, 24.12 ($OCH_2CH_2CH_2CH_2$), 25.28 ($OCH_2CH_2CH_2$), 17.84 (3 C), 17.80 (2 C), and 17.72 (C-6^{I-VI}); FABMS: *m/z* 2399.9 ($[M + 1]^+$), 2421.9 ($[M + Na]^+$).

*2-[2-(Methoxycarbonyl)ethylthio]ethyl 3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-2-*O*-methyl-α-*D*-mannopyranosyl-(1 → 2)-[3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl]$_4$-3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**33**).—This compound was obtained (100 mg, 64%) from compound **29** (157 mg) and methyl 2-(2-hydroxyethylthio)propionate (106 mg), as described for the preparation of **30**; $[\alpha]_D$ +31°; ^1H NMR ($CDCl_3$): δ 6.56–6.22 (m, 6 H, 6 NH), 5.26–5.18 (m, 6 H, H-3^{I-VI}), 5.10–4.90 (m, 11 H, H-$2'^{I-VI}$, incl 3 d, 4.99, 4.96, 4.90, $J_{1,2}$ ~ 2 Hz, H-1^{II-V}), 4.78 (d, $J_{1,2}$ 1.7 Hz, H-1^{I}), 4.35–4.07 (m, 22 H, H-2^{II-V},4^{I-VI},$4'^{I-VI}$), 3.97 (bdd, 1 H, H-2^{I}), 3.91–3.63 (m, 12 H, H-5^{I-VI}, OCH_2, incl s, 3.72, $COOCH_3$, bdd, 3.65, H-2^{VI}), 3.54 (s, 3 H, OCH_3), 3.01–2.78 (m, partially overlapped, CH_2CH_2CO), 2.77 (t, partially overlapped, OCH_2CH_2), 2.75–2.55 (m, partially overlapped, CH_2CO), 2.20–2.0 (m, 19 $COCH_3$ overlapping C-$3'^{I-VI}$ signals), 1.26–1.15 (m, 18 H, H-6^{I-VI}); ^{13}C NMR ($CDCl_3$): δ 100.36 (2 C), 100.04, 99.97, 99.48 (C-1^{II-VI}), 98.71 (C-1^{I}), 77.77 (C-2^{VI}), 75.24 (2 C), 75.15 (2 C), 74.73 (C-2^{I-V}), 70.90 (3 C), 70.81 (3 C, C-$2'^{I-V}$), 70.71 (C-3^{VI}), 70.04, 69.89, 69.73, 69.67, 69.48, 69.40, 69.21, 69.01 (2 C), 68.81, 68.37 (C-3^{I-V},5^{I-VI}), 68.10 (OCH_2), 59.87 (6 C, C-$4'^{I-VI}$), 59.69 (OCH_3), 52.24 ($COOCH_3$), 51.92, 51.75 (2 C), 51.66, 51.47, 51.35 (C-4^{I-VI}), 34.55 ($COCH_2$), 31.84 (OCH_2CH_2), 30.55 (6 C, C-$3'^{I-VI}$), 27.89 (CH_2CH_2CO), 17.93 (3 C), 17.89 (2 C), 17,78 (C-6^{I-VI}); FABMS: *m/z* 2417.8 ($[M + 1]^+$), 2439.8 ($[M + Na]^+$).

*5-Methoxycarbonylpentyl 4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)-[4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]$_4$-4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**34**).—A solution of **30** (83 mg) in MeOH (8 mL) was treated with a catalytic amount of NaOMe for 1 h at room temperature. After neutralization with Amberlite IR 120 (H^+) resin and concentration, the product was freeze-dried to give amorphous, hygroscopic **34**, $[\alpha]_D$ +2° (*c* 1, MeOH); ^1H NMR (CD_3OD): δ 5.13–5.10 (m, 3 H, 3 H-1), 5.09 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 4.97 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{VI}), 4.79 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1^{I}), 4.20–4.15 (m, 6 H, H-$2'^{I-VI}$), 4.08–4.05 (m, 4 H, H-2^{II-V}), 4.03–3.35 (m,

37 H, 2 H-2, H-3^{I-VI},4^{I-VI},5^{I-VI}, OCH_2, incl m at ~3.72 for H-$4'^{I-VI}_{a,b}$, and s for $COOCH_3$ at 3.64), 2.31 (t, 2 H, J ~7.5 Hz, CH_2CO), 2.06–1.93, 1.86–1.74 (2 m, 6 H each, H-$3'^{I-VI}_{a,b}$), 1.68–1.53 (m, 4 H, $OCH_2CH_2CH_2CH_2$), 1.44–1.33 (m, 2 H, $OCH_2CH_2CH_2$), and 1.18–1.10 (m, 18 H, C-6^{I-VI}); ^{13}C NMR (CD_3OD): δ 103.78 (C-1^{VI}), 102.72, 102.47 (3 C, C-1^{II-V}), 100.23 (C-1^{I}), 79.81 (C-2^{I}), 79.18 (2 C), 78.99, 78.92, (C-2^{II-V}), 70.98 (C-2^{VI}), 70.68 (6 C, C-$2'^{I-VI}$), 70.04, 69.66, 69.46 (8 C), 69.31, 68.77 (C-3^{I-VI},5^{I-VI}), 68.45 (OCH_2), 59.45 (6 C, C-$4'^{I-VI}$), 54.74, 54.61 (4 C), 54.16 (C-4^{I-VI}), 52.08 ($COOCH_3$), 38.25 (6 C, C-$3'^{I-VI}$), 34.64 (CH_2O), 30.04 (OCH_2CH_2), 26.73 ($OCH_2CH_2CH_2$), 25.62 (CH_2CH_2CO), 18.31 (5 C), and 18.20 (C-6^{I-VI}); FABMS: m/z 1651.7 ($[M + Na]^+$).

2-[2-(Methoxycarbonyl)ethylthio]ethyl 4-(3-deoxy-L-glycero-*tetronamido)-4,6-dideoxy-α*-D-*mannopyranosyl-(1 → 2)-[4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α*-D-*mannopyranosyl-(1 → 2)]$_4$-4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α*-D-*mannopyranoside* (**35**).—This compound was obtained (58 mg, 98%) from **31** (88 mg), as described for the preparation of **34**, $[\alpha]_D$ +2° (c 1, MeOH); ^{1}H NMR (CD_3OD): δ 5.13–5.11 (m, 4 H, H-1^{II-V}), 4.97 (bd, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{VI}), 4.83 (bd, 1 H, $J_{1,2}$ 1.6 Hz, H-1^{I}), 4.20–4.15 (m, 6 H, H-$2'^{I-VI}$), 4.09–4.05 (m, partially overlapped, H-2^{II-V}), 4.03–3.78 (m, partially overlapped, incl 2 m at 4.01 and 3.81 for H-2^{VI} and H-2^{I}, respectively, H-3^{I-VI},4^{I-VI},5^{I-VI}, OCH_a), 3.73 (m, partially overlapped, H-$4'^{I-VI}_{a,b}$), 3.68 (s, partially overlapped, $COOCH_3$), 3.67 (m, partially overlapped, OCH_b), 2.88–2.78 (m, partially overlapped, CH_2CH_2CO), 2.75 (bt, partially overlapped, J 5.8 Hz, OCH_2CH_2), 2.65–2.60 (m, 2 H, CH_2CO), 2.08–1.94, 1.89–1.75 (2 m, 6 H each, H-$3'^{I-VI}_{a,b}$), and 1.19–1.11 (m, 18 H, H-6^{I-VI}); ^{13}C NMR (CD_3OD): δ 103.71 (C-1^{VI}), 102.60, 102.38 (3 C, C-1^{II-V}), 100.33 (C-1^{I}), 79.44 (C-2^{I}), 79.07 (2 C), 78.92, 78.80 (C-2^{II-V}), 70.91 (C-2^{VI}), 70.62 (6 C, C-$2'^{I-VI}$), 69.97, 69.40 (10 C), 68.94 (C-3^{I-VI},5^{I-VI}), 68.69 (OCH_2), 59.40 (6 C, C-$4'^{I-VI}$), 54.54 (5 C), 54.09 (C-4^{I-VI}), 52.35 ($COOCH_3$), 38.18 (6 C, C-$3'^{I-VI}$), 35.58 (CH_2CO), 32.50 (OCH_2CH_2), 28.40 (CH_2CH_2CO), 18.28 (5 C), and 18.19 (C-6^{I-VI}); FABMS: m/z 1647.7 ($[M + 1]^+$), 1669.7 ($[M + Na]^+$).

5-Methoxycarbonylpentyl 4-(3-deoxy-L-glycero-*tetronamido)-4,6-dideoxy-2-O-methyl-α*-D-*mannopyranosyl-(1 → 2)-[4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α*-D-*mannopyranosyl-(1 → 2)]$_4$-4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α*-D-*mannopyranoside* (**36**).—This compound was obtained (122 mg, 98%) from compound **32** (180 mg) as described for prepatation of **34**, $[\alpha]_D$ −2° (c 1, MeOH); ^{1}H NMR (CD_3OD): δ 5.14–5.12 (m, 3 H), 5.10 (2 d, overlapped, $J_{1,2}$ 1.7 Hz, 5 H total, H-1^{II-VI}), 4.81 (d, H-1, $J_{1,2}$ 1.6 Hz, H-1^{I}), 4.21–4.15 (m, 6 H, H-$2'^{I-VI}$), 4.11–3.57 (m, 40 H, H-3^{I-VI},4^{I-VI},5^{I-VI}, OCH_a, incl m for H-2^{II-V} at ~4.11–4.05, m for H-2^{I} at ~3.75, m for H-$4'^{I-VI}$ at ~3.72, s for $COOCH_3$ at 3.68 overlapping m for H-2^{VI}), 3.40 (s, OCH_3 overlapping m for OCH_b), 2.33 (t, 2 H, J ~6 Hz, CH_2CO), 2.07–1.95, 1.87–1.76 (2 m, 6 H each, H-$3'^{I-VI}$), 1.68–1.56 (m, 4 H, $OCH_2CH_2CH_2CH_2$), 1.47–1.37 (m, 2 H, $OCH_2CH_2CH_2$), and 1.18–1.12 (m, 18 H, H-6^{I-VI}); ^{13}C NMR (CD_3OD): δ 102.66, 102.38 (3 C, C-1^{II-V}), 100.43 (C-1^{VI}), 100.17 (C-1^{I}), 80.64 (C-2^{VI}), 79.73 (C-2^{I}), 79.06 (2 C), 78.91 (2 C, C-2^{II-V}), 70.68 (6 C, C-$2'^{I-VI}$), 69.72, 69.63, 69.41 (9 C), 68.72 (C-3^{I-VI},5^{I-VI}), 68.41 (OCH_2), 59.43 (6 C, C-$4'^{I-VI}$), 59.12 (OCH_3), 54.71, 54.57 (3 C), 54.51 (2 C, C-4^{I-VI}), 52.06 ($COOCH_3$), 38.19 (6 C,

C-3′$^{I-VI}$), 34.60 (CH_2CO), 29.98, 25.56 (2 CH_2), 26.67 ($OCH_2CH_2CH_2$), 18.30 (2 C), 18.27 (2 C), 18.24, and 18.19 (C-6^{I-VI}); FABMS: *m/z* 1643.8 ($[M + 1]^+$), 1665.8 ($[M + Na]^+$).

2-[2-(Methoxycarbonyl)ethylthio]ethyl 4-(3-deoxy-L-glycero-*tetronamido)-4,6-dideoxy-2-*O*-methyl-α-*D*-mannopyranosyl-(1 → 2)-[4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]$_4$-4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**37**).—Compound **33** (80 mg), when treated as described for the preparation of **34**, gave amorphous **37** (47 mg, 85%), $[\alpha]_D$ −4° (*c* 1, MeOH); ^{1}H NMR (CD_3OD): δ 5.13–5.11, 5.10 (m, d, partially overlapped, $J_{1,2}$ 1.8 Hz, 5 H total, H-1^{II-VI}), 4.87 (d, H-1, $J_{1,2}$ 1.6 Hz, H-1^I), 4.21–4.15 (m, 6 H, H-2′$^{I-VI}$), 4.11–3.57 (m, 41 H, H-4^{I-VI},5^{I-VI}, OCH_a, incl m for H-2^{II-V} at ~4.11–4.05, m for H-3^{I-VI} at ~3.93–3.87, m for H-2^I at ~3.81, m for H-4′$^{I-VI}$ at 3.77–3.69, s for $COOCH_3$ at 3.68, m for H-2^{VI} at 3.66 and m for OCH_b at 3.62), 3.46 (s, 3 H, OCH_3), 2.89–2.76 (m, partially overlapped, CH_2CH_2CO), 2.75 (bt, partially overlapped, OCH_2CH_2), 2.65–2.60 (m, 2 H, CH_2CO), 2.07–1.94, 1.88–1.75 (2 m, 6 H each, H-3′$^{I-VI}$), and 1.18–1.10 (m, 18 H, H-6^{I-VI}); ^{13}C NMR (CD_3OD): δ 102.66, 102.43 (3 C) (C-1^{II-V}), 100.53 (C-1^{VI}), 100.40 (C-1^I), 80.71 (C-2^{VI}), 79.53 (C-2^I), 79.16 (2 C), 79.00 (2 C, C-2^{II-V}), 70.73 (6 C, C-2′$^{I-VI}$), 69.80, 69.61, 69.48 (9 C), 69.02 (C-3^{I-VI},5^{I-VI}), 68.75 (OCH_2), 59.46 (6 C, C-4′$^{I-VI}$), 59.15 (OCH_3), 54.63 (3 C), 54.56 (3 C, C-4^{I-VI}), 52.80 ($COOCH_3$), 38.24 (6 C, C-3′$^{I-VI}$), 35.65 (CH_2CO), 32.59 (OCH_2CH_2), 28.48 (CH_2CH_2CO), 18.35, 18.30 (3 C), and 18.21 (2 C, C-6^{I-VI}); FABMS: *m/z* 1661.7 ($[M + 1]^+$), 1683.6 ($[M + Na]^+$).

5-Carboxypentyl 4-(3-deoxy-L-glycero-*tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)-[4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]$_4$-4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**38**).—2 M NaOH (1 mL) was added to a solution of **34** (26 mg) in MeOH (1 mL), and the mixture was kept at room temperature for 3 h, when TLC (solvent *G*) showed that the reaction was complete. After processing, as described for the preparation of **34**, the freeze-dried, title substance showed $[\alpha]_D$ −3° (*c* 1, MeOH); ^{1}H NMR (CD_3OD): δ 5.14–5.12 (m, 3 H, 3 H-1), 5.10 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1), 4.97 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1^{VI}),4.81 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1^I), 4.20–4.15 (m, 6 H, H-2′$^{I-VI}$), 4.10–4.05 (m, 4 H, H-2^{II-V}), 4.03–3.65 (m, 33 H, incl m at 3.74 for H-4′$^{I-V}_{a,b}$, H-2^{I,VI}, H-3^{I-VI},4^{I-VI},5^{I-VI}, OCH_a), 3.47–3.30 (m, 1 H, OCH_b), 2.31 (t, 2 H, *J* 7.5 Hz, CH_2CO), 2.08–1.97, 1.88–1.78 (2 m, 6 H each, H-3′$^{I-VI}_{a,b}$), 1.67–1.57 (m, 4 H, $OCH_2CH_2CH_2CH_2$), 1.47–1.36 (m, 2 H, $OCH_2CH_2CH_2$), and 1.17–1.14 (m, 18 H, C-6^{I-VI}); ^{13}C NMR (CD_3OD): δ 103.86 (C-1^{VI}), 102.72, 102.47 (3 C, C-1^{II-V}), 100.25 (C-1^I), 79.85 (C-2^I), 79.25, 79.18, 79.04, 78.97 (C-2^{II-V}), 71.01 (C-2^{VI}), 70.74 (6 C, C-2′$^{I-VI}$), 70.11, 69.50 (9 C), 69.38, 68.83 (C-3^{I-VI},5^{I-VI}), 68.56 (OCH_2), 59.48 (6 C, C-4′$^{I-VI}$), 54.78, 54.68 (4 C), 54.20 (C-4^{I-VI}), 38.28 (6 C, C-3′$^{I-VI}$), 35.21 (CH_2O), 30.17 (OCH_2CH_2), 26.86 ($OCH_2CH_2CH_2CH_2$), 25.90 ($OCH_2CH_2CH_2$), 18.33 (5 C), and 18.21 (C-6^{I-VI}); CIMS: *m/z* 1637.8 ($[M + Na]^-$).

2-[2-(Carboxy)ethylthio]ethyl 4-(3-deoxy-L-glycero-*tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)-[4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]$_4$-4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**39**).—The title compound **39**, $[\alpha]_D$ −2° (*c* 1, MeOH), was prepared (22 mg,

89%) from **35** (25 mg) as described for the preparation of **38**. ^{1}H NMR (CD_3OD): δ 5.13–5.11 (m, 4 H, H-1^{II-V}), 4.97 (bd, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{VI}), 4.88 (bd, 1 H, $J_{1,2}$ 1.6 Hz, H-1^{I}), 4.21–4.16 (m, 6 H, H-2′$^{I-VI}$), 4.09–4.05 (m, partially overlapped, H-2^{II-V}), 4.03–3.60 (m, 38 H, H-3^{I-VI},4^{I-VI},5^{I-VI}, OCH_b, incl 2 m at 3.99, 3.81 for H-2^{VI} and H-2^{I}, respectively, m at 3.73 for H-4′$^{I-VI}_{a,b}$, and m at 3.64 for OCH_a), 2.88–2.78 (m, partially overlapped, CH_2CH_2CO), 2.76 (bt, partially overlapped, J ~5.8 Hz, OCH_2CH_2), 2.58–2.52 (m, 2 H, CH_2CO), 2.08–1.94, 1.89–1.75 (2 m, 6 H each, H-3′$^{I-VI}_{a,b}$), and 1.19–1.11 (m, 18 H, H-6^{I-VI}); ^{13}C NMR (CD_3OD): δ 103.80 (C-1^{VI}), 102.61, 102.43 (3 C, C-1^{II-V}), 100.37 (C-1^{I}), 79.46 (C-2^{I}), 79.16 (2 C), 78.96, 78.91 (C-2^{II-V}), 70.97 (C-2^{VI}), 70.71 (6 C, C-2′$^{I-VI}$), 70.08, 69.60, 69.47 (8 C), 69.34, 69.04 (C-3^{I-VI},5^{I-VI}), 68.64 (OCH_2), 59.48 (6 C, C-4′$^{I-VI}$), 54.62 (4 C), 54.53, 54.18 (C-4^{I-VI}), 38.22 (6 C, C-3′$^{I-VI}$), 36.44 (CH_2CO), 32.61 (OCH_2CH_2), 28.79 (CH_2CH_2CO), 18.32, 18.29, 18.26 (3 C), and 18.19 (C-6^{I-VI}); FABMS: *m/z* 1633.6 ([M + 1]$^+$).

*5-Hydrazinocarbonylpentyl 4-(3-deoxy-*L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl-(1 → 2)-[4-(3-deoxy-*L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl-(1 → 2)]$_4$-4-(3-deoxy-*L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranoside* (**40**).—A solution of **34** (26 mg) in MeOH (1 mL) was treated with hydrazine hydrate (0.2 mL), and the mixture was stirred at room temperature overnight. After concentration the residue was was eluted from a column of Sephadex LH-20 to give **40** (24 mg, 92%), [α]$_D$ −4° (*c* 1, MeOH); ^{1}H NMR (CD_3OD): δ 5.14–5.12 (m, 3 H, 3 H-1), 5.10 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1), 4.97 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{VI}), 4.80 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.20–4.18 (m, 6 H, 2′$^{I-VI}$), 4.09–4.05 (m, 4 H, 4 H-2), 4.03–3.80 (m, 19 H, H-2,3^{I-VI},4^{I-VI},5^{I-VI}), 3.78–3.64 (m, 14 H, H-2,4′$^{I-VI}_{a,b}$, OCH_a), 3.44–3.35 (m, 1 H, OCH_b), 2.16 (t, *J* 7.5 Hz, CH_2CO), 2.07–1.94, 1.88–1.75 (2 m, 6 H each, H-3′$^{I-VI}_{a,b}$), 1.70–1.53 (m, 4 H, $OCH_2CH_2CH_2CH_2$), 1.48–1.33 (m, 2 H, $OCH_2CH_2CH_2CH_2$), and 1.15 (bd, 18 H, *J* ~5.6 Hz, H-6^{I-VI}); ^{13}C NMR (CD_3OD): δ 103.84 (C-1^{VI}), 102.74, 102.48 (3 C, C-1^{II-V}), 100.18 (C-1^{I}), 79.91 (C-2^{I}), 79.22 (2 C), 79.01, 78.95 (C-2^{II-V}), 71.00 (C-2^{VI}), 70.74 (6 C, C-2′$^{I-VI}$), 70.11, 69.67, 69.49 (8 C), 69.37, 68.72 (C-3^{I-VI},5^{I-VI}), 68.28 (OCH_2), 59.48 (6 C, C-4′$^{I-VI}$), 54.84, 54.65 (3 C), 54.57, 54.19 (C-4^{I-VI}), 38.28 (6 C, C-3^{I-VI}), 34.75 (CH_2CO), 30.02, 26.24 ($OCH_2CH_2CH_2CH_2$), 26.75 ($OCH_2CH_2CH_2$), 18.32 (5 C), and 18.21 (C-6^{I-VI}); CIMS: *m/z* 1629.8 ([M + 1]$^+$), 1651.8 ([M + Na]$^+$).

*2-[2-(Hydrazinocarbonyl)ethylthio]ethyl 4-(3-deoxy-*L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl-(1 → 2)-[4-(3-deoxy-*L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl-(1 → 2)]$_4$-4-(3-deoxy-*L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranoside* (**41**).—Compound **41** [(83 mg, 92%), [α]$_D$ −1°, (*c* 1, MeOH)], was prepared from **35** (90 mg) as described for the preparation of **40**. ^{1}H NMR (CD_3OD): 5.13–5.11 (m, 4 H, H-1^{II-V}), 4.98 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{VI}), 4.87 (bd, 1 H, $J_{1,2}$ 1.6 Hz, H-1^{I}), 4.21–4.16 (m, 6 H, H-2′$^{I-VI}$), 4.10–4.06 (m, partially overlapped, H-2^{II-V}), 4.03–3.81 (m, partially overlapped, incl 2 m at 4.03 and 3.82 for H-2^{VI} and H-2^{I}, respectively, H-3^{I-VI},4^{I-VI},5^{I-VI}, OCH_a), 3.73 (m, partially overlapped, H-4′$^{I-VI}_{a,b}$), 3.73–3.65 (m, partially overlapped, OCH_b), 2.98–2.78 (2 m, partially overlapped, CH_2CH_2CO), 2.75 (bt, partially overlapped, OCH_2CH_2), 2.50–2.38 (m, 2 H, CH_2CO), 2.07-1.95, 1.89-1.76 (2 m, 6 H each, H-3′$^{I-VI}_{a,b}$), and 1.18–1.16 (m, 18 H, H-6^{I-VI}); ^{13}C

NMR (CD_3OD): δ 103.76 (C-1^{VI}), 102.63, 102.40 (3 C, C-1^{II-V}), 100.35 (C-1^{I}), 79.49 (C-2^{I}), 79.10 (2 C), 78.90, 78.85 (C-2^{II-V}), 70.96 (C-2^{VI}), 70.71 (6 C, C-$2'^{I-VI}$), 70.04, 69.46 (9 C), 69.35, 69.00 (C-3^{I-VI},5^{I-VI}), 68.91 (OCH_2), 59.45 (6 C, C-$4'^{I-VI}$), 54.71, 54.60 (3 C), 54.52, 54.16 (C-4^{I-VI}), 38.20 (6 C, C-$3'^{I-VI}$), 35.32 (CH_2CO), 32.58 (OCH_2CH_2), 29.16 (CH_2CH_2CO), 18.35, 18.31 (4 C), and 18.21 (C-6^{I-VI}); CIMS: *m/z* 1647.7 ($[M + 1]^+$).

5-Carboxypentyl 4-(3-deoxy-L-glycero-*tetronamido)-4,6-dideoxy-2-*O-*methyl-α-*D-*mannopyranosyl-(1 → 2)-[4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl-(1 → 2)]$_4$-4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranoside* (**42**).—Compound **36** (18 mg), when treated as described for the preparation of **38**, gave **42** (14 mg, 79%), $[\alpha]_D$ −2° (*c* 1, MeOH); ^1H NMR (CD_3OD): δ 5.13–5.11, 5.10 (m, d $J_{1,2}$, 1.6 Hz, 5 H, 5 H-1), 4.80 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1^{I}), 4.21–4.15 (m, 6 H, H-$2'^{I-VI}$), 4.11–3.65 (m, 37 H, incl m for 2^{II-V} at 4.11–4.04, m for H-2^{I} at ~ 3.75, m for H-$4'^{I-VI}$ at ~ 3.73, and m for H-2^{VI} at ~ 3.67, H-3^{I-VI},4^{I-VI},5^{I-VI}, OCH_a), 3.47 (s, OCH_3), 3.49–3.39 (m, overlapped, OCH_b), 2.30 (bt, 2 H, CH_2CO), 2.07–1.95, 1.89–1.75 (2 m, 6 H each, H-$3'^{I-VI}_{a,b}$), 1.67–1.57 (m, 4 H, $OCH_2CH_2CH_2CH_2$), 1.49–1.37 (m, 2 H, $OCH_2CH_2CH_2$), and 1.18–1.11 (m, 18 H, H-6^{I-VI}); ^{13}C NMR (CD_3OD): δ 102.70, 102.42 (3 C, C-1^{II-V}), 100.50 (C-1^{VI}), 100.22 (C-1^{I}), 80.70 (C-2^{VI}), 79.81 (C-2^{I}), 79.15 (2 C), 78.99 (2 C, C-2^{II-V}), 70.73 (6 C, C-$2'^{I-VI}$), 69.79, 69.68, 69.47 (9 C), 68.78 (C-3^{I-VI},5^{I-VI}), 68.51 (OCH_2), 59.46 (6 C, C-4^{I-VI}), 59.14 (OCH_3), 54.76, 54.62 (3 C), 54.56 (2 C, C-4^{I-VI}), 38.24 (6 C, C-$3'^{I-VI}$), 34.70 (CH_2CO), 30.07 (OCH_2CH_2), 25.66 ($OCH_2CH_2CH_2CH_2$), 26.75 ($OCH_2CH_2CH_2$), 18.30 (4 C), 18.26, and 18.21 (C-6^{I-VI}); FABMS: *m/z* 1629.7 ($[M + 1]^+$).

2-[2-(Carboxy)ethylthio]ethyl 4-(3-deoxy-L-glycero-*tetronamido)-4,6-dideoxy-2-*O-*methyl-α-*D-*mannopyranosyl-(1 → 2)-[4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl-(1 → 2)]$_4$-4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranoside* (**43**).—Compound **43** was obtained (20 mg, 81%) from **37** (25 mg), as described for the preparation of **38**, $[\alpha]_D$ −1° (*c* 1, MeOH); ^1H NMR (CD_3OD): δ 5.13–5.10 (m, partially overlapped, 4 H-1), 5.10 (d, partially overlapped, $J_{1,2}$ ~ 1.8 Hz, H-1), 4.88 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1^{I}), 4.21–4.15 (m, 6 H, H-$2'^{I-VI}$), 4.11–3.55 (m, 38 H, H-,3^{II-V},4^{I-VI},5^{I-VI}, OCH_a, incl m for 2^{II-V} at 4.11–4.05, m for H-2^{I} at ~ 3.81, m at 3.75–3.70 for H-$4'^{I-VI}$, m for H-2^{VI} at ~ 3.66, and m for OCH_b at ~ 3.61), 3.47 (s, 3 H, OCH_3), 2.85–2.75, 2.76 (m, bt, partially overlapped, 4 H, CH_2CH_2CO and OCH_2CH_2, respectively), 2.62–2.56 (m, 2 H, CH_2CO), 2.07–1.94, 1.88–1.75 (2 m, 6 H each, H-$3'^{I-VI}_{a,b}$), and 1.18–1.10 (m, 18 H, H-6^{I-VI}); ^{13}C NMR (CD_3OD): δ 102.69, 102.45 (3 C, C-1^{II-V}), 100.52 (C-1^{VI}), 100.41 (C-1^{I}), 80.73 (C-2^{VI}), 79.55 (C-2^{I}), 79.20 (2 C), 79.03 (2 C, C-2^{II-V}), 70.75 (6 C, C-$2'^{I-VI}$), 69.82, 69.64, 69.50 (8 C), 69.42, 69.05 (C-3^{I-VI},5^{I-VI}), 68.65 (OCH_2), 59.48 (6 C, C-4^{I-VI}), 59.15 (OCH_3), 54.64 (3 C), 54.55 (3 C, C-4^{I-VI}), 38.26 (6 C, C-$3'^{I-VI}$), 35.73 (CH_2CO), 32.66 (OCH_2CH_2CO), 18.37, 18.33, 18.33, 18.31 (2 C), 18.29, and 18.22 (C-6^{I-VI}); FABMS: *m/z* 1647.7 ($[M + 1]^+$), 1669.7 ($[M + Na]^+$).

5-Hydrazinocarbonylpentyl 4-(3-deoxy-L-glycero-*tetronamido)-4,6-dideoxy-2-*O-*methyl-α-*D-*mannopyranosyl-(1 → 2)-[4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl-(1 → 2)]$_4$-4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranoside* (**44**).—Treatment of **36** (55 mg), as described for the preparation of **40**,

gave amorphous **44** (50 mg, 91%), $[\alpha]_D$ −1° (*c* 1, MeOH); ^{1}H NMR (CD_3OD): δ 5.14–4.99 (m, 5 H, H-1^{II-VI}), 4.80 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1^I), 4.22–4.16 (m, 6 H, H-$2'^{I-VI}$), 4.12–3.65 (m, 37 H, H-3^{II-V},4^{I-VI},5^{I-VI}, OCH, incl m for 2^{II-V} at 4.12–4.04, m for H-2^I at ~3.76, m at ~3.73 for H-$4'^{I-VI}$, and m for H-2^{VI} at ~3.67_a), 3.47 (s, partially overlapped, OCH_3), 3.45–3.35 (m, overlapped, OCH_b), 2.76 (bt, 2 H, CH_2CO), 2.07–1.87, 1.84–1.74 (2 m, 6 H each, H-$3'^{I-VI}_{a,b}$), 1.69–1.53 (m, 4 H, $OCH_2CH_2CH_2CH_2$), 1.47–1.32 (m, 2 H, $OCH_2CH_2CH_2$), and 1.18–1.08 (m, 18 H, H-6^{I-VI}); ^{13}C NMR (CD_3OD): δ 102.68, 102.41 (3 C, C-1^{II-V}), 100.49 (C-1^{VI}), 100.15 (C-1^I), 80.68 (C-2^{VI}), 79.82 (C-2^I), 79.12 (2 C), 78.97 (2 C), (C-2^{II-V}), 70.72 (6 C, C-$2'^{I-VI}$), 69.75, 69.64, 69.45 (9 C), 68.72 (C-3^{I-VI},5^{I-VI}), 68.33 (OCH_2), 59.44 (6 C, C-$4'^{I-VI}$), 59.18 (OCH_3), 54.80, 54.60 (2 C), 54.54 (3 C, C-4^{I-VI}), 38.20 (6 C, C-$3'^{I-VI}$), 34.75 (CH_2CO), 29.99, (OCH_2CH_2), 26.24 ($OCH_2CH_2CH_2CH_2$), 26.72 ($OCH_2CH_2CH_2$), 18.32 (2 C), 18.29 (3 C), and 18.20 (C-6^{I-VI}); FABMS: *m/z* 1643.9 ($[M + 1]^+$), 1665.9 ($[M + Na]^+$).

2-[2-(Hydrazinocarbonyl)ethylthio]ethyl 4-(3-deoxy-L-glycero-*tetronamido)-4,6-dideoxy-2-*O*-methyl-α*-D-*mannopyranosyl-(1 → 2)-[4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α*-D-*mannopyranosyl-(1 → 2)]$_4$-4-(3-deoxy*-L-glycero-*tetronamido)-4,6-dideoxy-α*-D-*mannopyranoside* (**45**).—Treatment of **37** (20 mg), as described for the preparation of **40**, gave **45** (19 mg, 95%), $[\alpha]_D$ −1° (*c* 1, MeOH); ^{1}H NMR (CD_3OD): δ 5.14–5.12, 5.10 (m, d, partially overlapped, 5 H-1), 4.87 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1^I), 4.21–4.16 (m, 6 H, H-$2'^{I-VI}$), 4.11–3.59 (m, 38 H, H-3^{I-VI},4^{I-VI},5^{I-VI}, OCH_2, incl m for 2^{II-V} at 4.11–4.04, m for H-2^I at ~3.81, m at ~3.73 for H-$4'^{I-VI}$, and m for H-2^{VI} at ~3.66), 3.47 (s, 3 H, OCH_3), 2.99–2.77 (2 m, partially overlapped, ~2 H, CH_2CH_2CO), 2.75 (bt, 2 H, OCH_2CH_2), 2.46–2.34 (m, 2 H, CH_2CO) 2.07–1.87, 1.84–1.95, 1.87–1.75 (2 m, 6 H each, H-$3'^{I-VI}$), and 1.18–1.10 (m, 18 H, H-6^{I-VI}); ^{13}C NMR (CD_3OD): δ 102.68, 102.45 (3 C, C-1^{II-V}), 100.51 (C-1^{VI}), 100.40 (C-1^I), 80.73 (C-2^{VI}), 79.58 (C-2^I), 79.20 (2 C), 79.01, 78.98 (C-2^{II-V}), 70.76 (6 C, C-$2'^{I-VI}$), 69.81, 69.50 (9 C), 69.42, 68.98 (C-3^{I-VI},5^{I-VI}), 69.03 (OCH_2), 59.48 (6 C, C-$4'^{I-VI}$), 59.14 (OCH_3), 54.76, 54.64 (3 C), 54.57 (2 C, C-4^{I-VI}), 38.27 (6 C, C-$3'^{I-VI}$), 35.32 (CH_2CO), 32.61 (OCH_2CH_2), 29.21 (CH_2CH_2CO), 18.35, 18.31 (4 C), and 18.22 (C-6^{I-VI}); FABMS: *m/z* 1661.8 ($[M + 1]^+$).

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