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Carbohydrate Research 288 (1996) 85–98

CARBOHYDRATE RESEARCH

Synthesis of four glycosides of a disaccharide fragment representing the terminus of the O-polysaccharide of *Vibrio cholerae* O:1, serotype Inaba, bearing aglycons suitable for linking to proteins [1]

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Received 12 February 1996; accepted 20 March 1996

Abstract

Methyl 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside was converted into the crystalline 2-(trimethylsilyl)ethyl 4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside. Debenzoylation of the latter, followed by glycosylation of the resulting 2-hydroxy derivative with 2-*O*-acetyl-4-azido-4,6-dideoxy-α-D-mannopyranosyl chloride, gave the 2-(trimethylsilyl)ethyl glycoside of the corresponding disaccharide (**8**). Deacetylation of **8**, followed by reduction of the resulting 4-azido-2-hydroxy derivative with H_2S, gave the corresponding amine **10**. The latter was treated with 4-*O*-benzyl-3-deoxy-L-*glycero*-tetronic acid to give, after debenzylation and acetylation, the fully protected 2-(trimethylsilyl)ethyl α-glycoside of the disaccharide fragment of the O–PS of *Vibrio cholerae* O:1, serotype Inaba (**13**). Compound **13** was transformed into the corresponding 1-trichloroacetimidate which was treated, separately, with methyl 6-hydroxyhexanoate and 2-(2-methoxycarbonylethylthio)ethanol, to give two analogs of **13** possessing a differing linkage arm, namely the methyl esters **16** and **17**. Each of **16** and **17** was treated with aqueous sodium hydroxide, followed by a cation-exchange resin, to give the two corresponding carboxylic acids (**19** and **22**). Alternately, treatment of **16** and **17** with hydrazine hydrate gave the acid hydrazides **20** and **23**. Published by Elsevier Science Ltd.

Keywords: *Vibrio cholerae* O:1; Disaccharide epitope; O-antigen; Neoglycoconjugate

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[1] Synthesis of ligands related to the *Vibrio cholerae* O-specific antigen. Part 11. For Part. 10, see ref. [1].

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0008-6215/96/$15.00 Published by Elsevier Science Ltd.
PII S0008-6215(96)00089-4

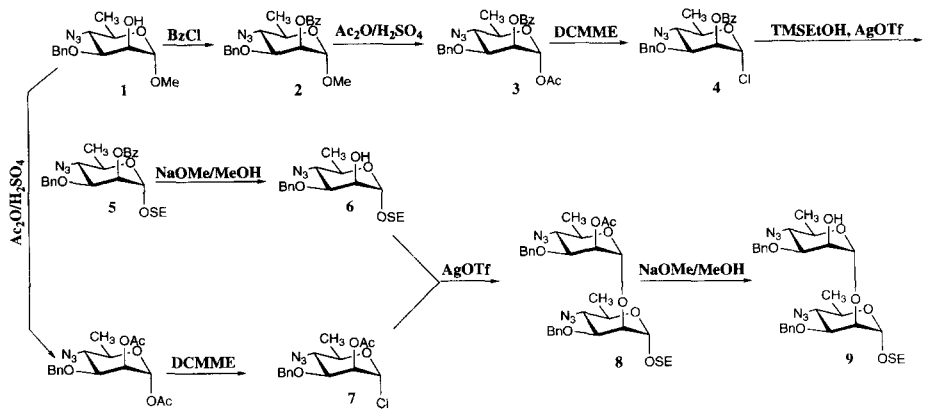
1. Introduction

Owing to lack of an efficacious vaccine, cholera causes major epidemics worldwide, particularly in developing countries. An approach towards alleviating the cholera problem could include vaccination with semisynthetic vaccines made from modified bacterial lipopolysaccharides (LPSs) that have been covalently linked to carrier proteins [2,3]. The purpose of modification of the LPS in these preparations is to reduce its toxicity which results from the presence of the lipid A. The protective nature of the antigen in *V. cholerae* resides in the LPS (for detailed discussion of this and related topics see ref. [3] and references cited therein), but not all the structural elements of the LPS may be required for eliciting immunity. Thus, a synthetic vaccine could contain, as the immunogenic component, only the part of the LPS responsible for conferring protective immunity. Experimental vaccines for *Vibrio cholerae* O:1 based on an entirely synthetic carbohydrate antigen are not available. This is so because the synthesis of oligosaccharides making up the unique structure of the O-polysaccharide (O–PS) is difficult. The O–PS of *Vibrio cholerae* serotype Inaba, consists of a chain of (1 → 2)-linked moieties of 4-amino-4,6-dideoxy-α-D-mannopyranose (perosamine), the amino groups of which are acylated with 3-deoxy-L-*glycero*-tetronic acid. We have prepared a number of oligosaccharides of this type [4–6]. We also wish to link such structures to proteins. By varying elements in the detailed architecture of the carbohydrate antigen–protein combinations and studying their immunochemical properties, we expect to unravel factors that affect the immune response to the *V. cholerae* O:1 pathogen. In this context, we have recently reported [7] on the synthesis of the 2-(trimethylsilyl)ethyl α-glycoside of a hexasaccharide fragment of the O–PS of *Vibrio cholerae* O:1, serotype Inaba. Here, we report on the synthesis of an analogous disaccharide **13** and its conversion into four glycosides, each bearing a different, reactive aglycon that are potentially suitable for conjugation with a protein carrier.

2. Results and discussion

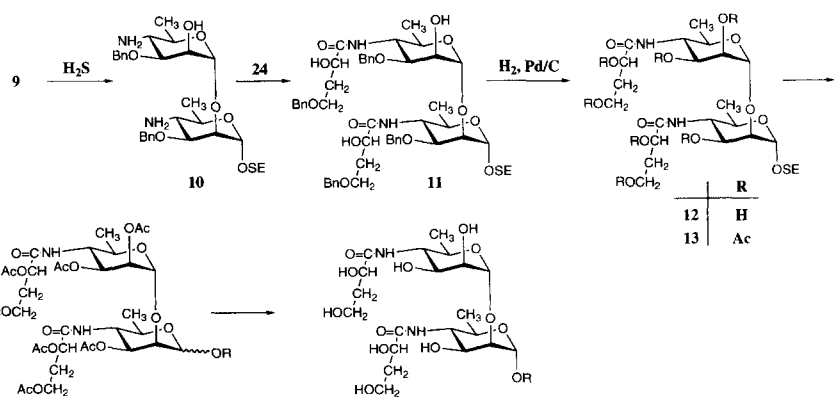
It appears [8] that when a neoglycoconjugate is to be used to raise antibodies that are cross-reactive with an O–PS, that is a homopolysaccharide, such as is the case of *V. cholerae* O:1, serotype Inaba, the oligosaccharide has to be at least two repeating units long. Such a structure mimics both the chain end and the internal residues. In order to properly link an oligosaccharide to a protein carrier, the appropriate protective group for the reducing end of the monosaccharidic, nucleophile building block has to be selected. Such a group should allow, after the product oligosaccharide of the required size had been built, the eventual conversion of the oligosaccharide into a practical glycosyl donor. Coupling with a protein carrier, either by way of a spacer or without one, is the final step in the protocol for the preparation of a neoglycoconjugate. For the aforementioned purpose, we have selected the trimethylsilylethyl (SE) group [9,10] as it offers the chemical flexibility required.

Accordingly (Scheme 1), the known [11,12] methyl 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (**1**) was converted, via its 2-*O*-benzoyl [13] derivative **2** into the



Scheme 1.

crystalline 2-(trimethylsilyl)ethyl 4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (**5**). The latter was debenzoylated, and the 2-hydroxy derivative **6** thus formed was coupled with 2-*O*-acetyl-4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl chloride (**7**) [11,14] to give the disaccharide **8**. Deacetylation of **8**, followed by treatment of the resulting alcohol **9** with H_2S (Scheme 2), gave the amine **10** which, when treated with 4-*O*-benzyl-3-deoxy-L-*glycero*-tetronic acid (**24**) [1] (→ **11**) gave, after debenzylation (→ **12**) and acetylation, the fully protected disaccharide **13**.



	R
12	H
13	Ac

	R
14	H
15	C(NH)CCl3
16	(CH2)5COOCH3
17	(CH2)2S(CH2)2COOCH3

	R
18	(CH2)5COOCH3
19	(CH2)5COOH
20	(CH2)5CONHNH2
21	(CH2)2S(CH2)2COOCH3
22	(CH2)2S(CH2)2COOH
23	(CH2)2S(CH2)2CONHNH2

24	BnO(CH2)2CH(OH)COOH
25	HO(CH2)5COOCH3
26	HO(CH2)2S(CH2)2COOCH3

Scheme 2.

In view of the relatively low molecular weight of the natural O-PS (dp ~ 15 [15]), the single-ended mode of attachment to the carrier protein via a spacer seems to be the appropriate choice of the architecture of a potential immunogen for *V. cholerae* O:1 antibodies. Preparation of a neoglycoconjugate according to any other possible conjugation model [8] could disturb the integrity of the relatively short-chain carbohydrate antigen, especially in case of a short oligosaccharide. Thus, the nature of the spacer-arm (linker) took on importance. The role of a linker is to separate the two major components of the neoglycoconjugate, thereby facilitating the spatial access of the elements of the immune system to the carbohydrate antigen. In addition, the use of linkers often improves the antigenicity of a conjugate. The length, flexibility and hydrophobic properties of linkers can be tailored within a wide range. In practice, the spacer molecules should be inexpensive and readily available commodities. Considering the above, we decided to use methyl 6-hydroxyhexanoate (**25**) and 2-(2-methoxycarbonylethylthio)ethanol (**26**) as linkers. Compound **25**, albeit shorter, is a more easily available than the widely used nonanoic acid derivative [16]. 2-(2-Methoxycarbonylethylthio)ethyl glycosides have been previously prepared from bromoethyl glycosides of sugars and methyl 3-mercaptopropionate and appear useful for the preparation of neoglycoconjugates [17]. Due to the presence of the thioether linkage, compound **26** is a more polar variation of **25**. The replacement of a methylene bridge in the spacer with sulfur or oxygen [18,19] increases the overall polarity of the conjugate, thereby reducing its tendency for nonspecific hydrophobic interactions with the receptors of the immune system. Also, the presence of a heteroatom in the spacer would decrease the tendency of polymethylene chains to coil in aqueous milieu, thereby shortening their effective length [20]. Compound **26** (previously described but not characterized [21]) was used in this work to prepare the 2-(2-methoxycarbonylethylthio)ethyl glycoside **17** and was synthesized by a sodium methoxide-mediated condensation of 2-bromoethanol and methyl 3-mercaptopropionate (see Experimental section). We obtained compound **26** in the analytically pure state and characterized it by NMR spectroscopy.

Reactions of the trichloroacetimidate **15**, prepared conventionally from **13**, with each of methyl 6-hydroxyhexanoate (**25**) and 2-(2-methoxycarbonylethylthio)ethanol (**26**) gave the corresponding glycosides **16** and **17**, respectively. These products were isolated by chromatography, together with small amounts of the corresponding β-isomers. The fully acetylated methyl esters **16** and **17** were then deacetylated (Zemplén), and a portion of each of the deprotected methyl esters thus obtained was converted to the corresponding acid (**19** and **22**) and acid hydrazide (**20** and **23**). The latter four substances were freeze-dried and obtained as pure (NMR) hygroscopic solids, which were characterized by their $[\alpha]_D$ values and NMR data. The further use of these derivatives in immunochemical studies will be published in a separate communication.

3. Experimental

General methods.—Instruments and general laboratory techniques used were described previously [5]. 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 eluants were used: *A*, 4:1 hexane–EtOAc; *B*, 15:1 CH_2Cl_2–MeOH; *C*, 1:1 CH_2Cl_2–MeOH; *D*, 1:2:0.1 CH_2CL_2–MeOH–25% NH_4OH, and *E*, 1:1 hexane–EtOAc. 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 one bearing the aglycone, and are identified by a Roman numeral superscript in listings of signal assignments. Nuclei assignments without a superscript notation 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. DCMME was purchased from Fluka or Aldrich, and used as supplied.

*Methyl 4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranoside* (**2**).—Benzoyl chloride (1.42 g, 10 mmol) was added at 0 °C to a solution of **1** [11,12,14] (2.48 g, 8.46 mmol) in pyridine (10 mL). The mixture was stirred overnight at room temperature, when TLC (solvent *A*) showed that the reaction was complete. After concentration, a solution of the residue in CH_2Cl_2 was washed successively with 2 N HCl and aq $NaHCO_3$, dried, and concentrated. The residue was chromatographed, to give **2** (3.32 g, 98%): $[\alpha]_D$ −31°; ^{1}H NMR ($CDCl_3$): δ 5.55 (dd, 1 H, $J_{1,2}$ 1.9, $J_{2,3}$ 3.4 Hz, H-2), 4.77 (d, partially overlapped, H-1), 4.75, 4.56 (2 d, ^2J 11.3 Hz, CH_2Ph), 3.91 (dd, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 3.65–3.53 (m, partially overlapped, H-5), 3.57 (t, partially overlapped, H-4), 3.37 (s, 3 H, OCH_3), and 1.38 (d, 3 H, $J_{5,6}$ 6.0 Hz, H-6); ^{13}C NMR ($CDCl_3$): δ 98.79 (C-1), 76.11 (C-3), 71.44 (*C*H_2Ph), 67.83 (C-2), 66.82 (C-5), 64.34 (C-4), 55.10 (OCH_3), and 18.64 (C-6); CIMS: *m/z* 398 $[M + 1]^+$, 415 $[M + 18]^+$. Anal. Calcd for $C_{21}H_{23}N_3O_5$: C, 63.47; H, 5.83; N, 10.57. Found: C, 63.34; H, 5.86; N, 10.50.

*1-*O*-Acetyl-4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranose* (**3**).—A solution of **2** (3.1 g) in 10:4:0.1 Ac_2O–AcOH–H_2SO_4 (v/v, 15 mL) was kept at room temperature for 3 h, when TLC (solvent *A*) showed that the reaction was complete. The mixture was poured into cold (0°), aq $NaHCO_3$, and when Ac_2O had hydrolyzed, the solution was extracted with CH_2Cl_2. The organic phase was dried and concentrated, and the residue was chromatographed to give **3**. The amorphous material contained ~ 7% of the β-isomer. NMR data for the α-isomer ($CDCl_3$): δ 6.15 (d, 1 H, $J_{1,2}$ 2.0 Hz, H-1), 5.56 (dd, 1 H, $J_{2,3}$ 3.3 Hz, H-3), 4.80, 4.59 (2 d, 1 H each, ^2J 11.2 Hz, CH_2Ph), 3.91 (dd, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 3.70–3.55 (m, partially overlapped, H-5), 3.57 (t, partially overlapped, H-4), 2.12 (s, 3 H, $COCH_3$), and 1.39 (d, 3 H, H-6); ^{13}C NMR ($CDCl_3$): δ 91.09 (C-1), 75.79 (C-3), 71.65 (*C*H_2Ph), 69.31 (C-5), 66.76 (C-2), 63.84 (C-4), 20.85 (*CO*CH_3), and 18.67 (C-6); CIMS: *m/z* 443 $[M + 18]^+$. Anal. Calcd for $C_{22}H_{23}N_3O_6$: C, 62.11; H, 5.45; N, 9.88. Found: C, 62.12; H, 5.45; N, 9.78.

*2-(Trimethylsilyl)ethyl 4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranoside* (**5**).—Freshly fused $ZnCl_2$ (100 mg) was added to solution of **3** (12.8 g, 30 mmol) and dichloromethyl methyl ether (10.38 g, 90 mmol) in CH_2Cl_2, and the mixture was stirred at room temperature for 3.5 h. TLC (solvent *A*) showed then that all starting material was consumed. After filtration through a Celite pad, the filtrate was concen-

trated, and the residue was chromatographed, to give 4-azido-2-*O*-benzoyl-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl chloride (**4**, 11.33 g, 93%), which was used immediately for the next step.

To a stirred solution of the foregoing compound **4** (11.3 g, 28.1 mmol), 2-trimethylsilyl)ethanol (4.99 g, 42.2 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (4.62 g, 22.5 mmol) in CH_2Cl_2 (100 mL) was added at room temperature AgOTf (14.4 g, 56.2 mmol). After 10 min, when TLC (solvent *A*) showed that the reaction was complete, aqueous $NaHCO_3$ was added, and, after a brief stirring, the mixture was filtered. The filtrate was washed with aq NaCl, dried, and concentrated. The residue was chromatographed to give **5** (11.1 g, 82%): mp 73–75 °C; $[\alpha]_D$ −1°; ^{1}H NMR ($CDCl_3$): δ 5.52 (dd, 1 H, $J_{1,2}$ 1.8, $J_{2,3}$ 3.2 Hz, H-2), 4.89 (d, 1 H, H-1), 4.75, 4.56 (2 d, 1 H each, ^2J 11.3 Hz, CH_2Ph), 3.92 (dd, 1 H, $J_{3,4}$ 9.7 Hz, H-3), 3.77, 3.52 (2 ddd, partially overlapped, *J* 6.5, 9.9, and 9.9 Hz, CH_2CH$_2$Si), 3.51 (t, overlapped, *J* 9.8 Hz, H-4), 1.37 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6), 0.94 (m, 2 H, CH_2Si), and 0.03 [s, 9 H, $(CH_3)_3$]; ^{13}C NMR ($CDCl_3$): δ 97.26 (C-1), 76.57 (C-3), 71.40 (*C*H$_2$Ph), 68.17 (C-2), 66.91 (C-5), 65.52 (*C*H$_2$CH$_2$Si), 64.47 (C-4), 18.65 (C-6), 17.85 (*C*H$_2$Si), and −1.33 [$(CH_3)_3$Si]; CIMS: *m/z* 501 $[M + 18]^+$. Anal. Calcd for $C_{25}H_{33}N_3O_5Si$: C, 62.09; H, 6.88; N, 8.69. Found: C, 62.02; H, 6.84; N, 8.75.

*2-(Trimethylsilyl)ethyl 4-azido-3-*O*-benzyl-4,6-dideoxy-α-*D*-mannopyranoside* (**6**).—Deacetylation (Zemplén) of **5**, followed by chromatography (solvent *A*), gave **6** in virtually theoretical yield: $[\alpha]_D$ +121°; ^{1}H NMR ($CDCl_3$): δ 4.83 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1), 4.72, 4.67 (2 d, 1 H each, ^2J 11.4 Hz, CH_2Ph), 3.96 (bd, 1 H, H-2), 3.81–3.72 (m, 2 H, H-3,CH_aCH$_2$Si), 3.61–3.44 (m, 3 H, H-4,5,CH_bCH$_2$Si), 2.44 (bs, 1 H, OH), 1.33 (d, 3 H, $J_{5,6}$ 6.2 Hz, H-6), 0.98–0.81 (m, 2 H, CH$_2$CH_2Si), and 0.03 [s, 9 H, $(CH_3)_3$]; ^{13}C NMR ($CDCl_3$): δ 98.48 (C-1), 78.40 (C-3), 71.98 (*C*H$_2$Ph), 67.41 (C-2), 66.48 (C-5), 65.12 (*C*H$_2$CH$_2$Si), 64.05 (C-4), 18.40 (C-6), 17.83 (CH_2Si), and −1.33 [$(CH_3)_3$]; CIMS: *m/z* 397 $[M + 18]^+$. Anal. Calcd for $C_{18}H_{29}N_3O_4Si$: C, 56.96; H, 7.70; N, 11.07. Found: C, 56.93; H, 7.75; N, 10.96.

*2-(Trimethylsilyl)ethyl 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*-mannopyranoside* (**8**).—Silver triflate (7.4 g, 28.8 mmol) was added to a stirred solution of **6** (8.4 g, 22.2 mmol), **7** [14] (9.0 g, 26.6 mmol), and 2,4,6-trimethylpyridine (3.2 g, 26.6 mmol) in CH_2Cl_2 (100 mL). After 1 h at room temperature, the mixture was processed as described for the preparation of **5**, to give **8** (12.4 g, 82%): $[\alpha]_D$ +95°; ^{1}H NMR ($CDCl_3$): δ 5.41 (dd, 1 H, $J_{1,2}$ 2.0, $J_{2,3}$ 3.3 Hz, H-2^{II}), 4.84 (d, 1 H, H-1^{II}), 4.71, 4.68, 4.60, 4.53 (4 d, partially overlapping, ^2J 11.0 and 11.7 Hz, 2 CH_2Ph), 3.83–3.81 (m, partially overlapped, H-2^I), 3.79 (dd, partially overlapped, $J_{2,3}$ 3.2, $J_{3,4}$ 9.8 Hz, H-3^{II}), 3.76–3.67 (m, 2 H, H-3^I,CH_aCH$_2$Si), 3.64–3.54 (m, 2 H, H-5), 3.52–3.41 (m, 2 H, H-5,CH_bCH$_2$Si), 3.38, 3.32 (2 t, partially overlapped, H-4^{I,II}), 2.08 (s, 3 H, $COCH_3$), 1.29, 1.28 (2 d, overlapping, 6 H, $J_{5,6}$ 6.2 and 6.1 Hz, H-6^{I,II}), 0.92–0.80 (m, 2 H, CH_2Si), and 0.03 [s, 9 H, $(CH_3)_3$]; ^{13}C NMR ($CDCl_3$): δ 99.36 (C-1^{II}), 98.15 (C-1^I), 77.80 (C-3^I), 75.35 (C-3^{II}), 74.07 (C-2^I), 71.99, 71.54 (2 *C*H$_2$Ph), 67.52, 67.00 (C-5^{I,II}), 67.20 (C-2^{II}), 65.16 (*C*H$_2$CH$_2$Si), 64.21, 63.83 (C-4^{I,II}), 20.91 (CO*C*H$_3$), 18.52, 18.48 (C-6^{I,II}), 17.73 (CH_2Si), and −1.33 [$(CH_3)_3$]; CIMS: *m/z* 700 $[M + 18]^+$. Anal. Calcd for $C_{33}H_{46}N_6O_8Si$: C, 58.05; H, 6.79; N, 12.31. Found: C, 57.99; H, 6.79; N, 12.28.

2-(Trimethylsilyl)ethyl 2-O-(4-azido-3-O-benzyl-4,6-dideoxy-α-D-mannopyranosyl)-4-azido-3-O-benzyl-4,6-dideoxy-α-D-mannopyranoside (**9**).—Deacetylation (Zemplén) of **8** (300 mg) gave **9** (266 mg, 95%): $[\alpha]_D$ +102°; ^{1}H NMR ($CDCl_3$): δ 4.93 (d, $J_{1,2}$ 1.6 Hz, H-1^{II}), 4.70, 4.65, 4.63, 4.59 (4 d, partially overlapped, ^2J ~ 11.5 Hz, 2 CH_2Ph), 4.68 (bd, partially overlapped, H-1^I), 3.98 (bddd, 1 H, H-2^{II}), 3.88 (dd, 1 H, $J_{1,2}$ 2.1, $J_{2,3}$ 3.0 Hz, H-2^I), 3.75–3.66 (m, 3 H, H-3^{I,II},CH_aCH$_2$Si), 3.64–3.56 (m, 1 H, H-5^I), 3.52–3.35 (m, 3 H, H-4^I,5^{II},CH_bCH$_2$Si), 3.27 (t, 1 H, J 10.0 Hz, H-4^{II}) 2.30 (bs, 1 H, OH), 1.28 (2 d, overlapped, 6 H, $J_{5,6}$ 6.1 Hz, H-6^{I,II}), 0.9–0.78 (m, 2 H, CH$_2$Si), and 0.03 [s, 9 H, (CH$_3$)$_3$]; ^{13}C NMR ($CDCl_3$): δ 100.79 (C-1^{II}), 98.36 (C-1^I), 77.93, 77.62 (C-3^{I,II}), 73.97 (C-2^I), 72.08 (2 C, 2 CH_2Ph), 67.20 (2 C, C-2^{II},5^I), 67.02 (C-5^{II}), 65.19 (CH_2CH$_2$Si), 64.42 (C-4^{II}), 63.84 (C-4^I), 18.56, 18.40 (C-6^{I,II}), and −1.33 [(CH$_3$)$_3$]; CIMS: *m/z* 658 $[M + 18]^+$. Anal. Calcd for $C_{31}H_{44}N_6O_7Si$: C, 58.10; H, 6.92; N, 13.11. Found: C, 57.97; H, 6.88; N, 13.01.

*2-(Trimethylsilyl)ethyl 3-O-benzyl-2-O-[3-O-benzyl-4-(4-O-benzyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl]-4-(4-O-benzyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-D-mannopyranoside* (**11**).—Hydrogen sulfide was passed through a solution of **9** (270 mg) in 7:3 pyridine–Et_3N (10 mL) for 1 h. The mixture was kept, in a loosely closed flask, at room temperature overnight, when TLC (solvent *B*) showed that **9** was no longer present. After concentration, the residue was chromatographed on alumina (solvent *B*) to give the amine **10** (219 mg, 88%), which was sufficiently pure for the next step: ^{1}H NMR ($CDCl_3$): δ 5.01 (d, 1 H, $J_{1,2}$ 1.0 Hz, H-1^{II}), 4.77 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1^I), 4.67, 4.66, 4.49, 4.44 (4 d, partially overlapped, 4 H, ^2J ~ 11.4 Hz, 2 CH_2Ph), 4.05 (bdd, 1 H, H-2^{II}), 3.94 (dd, 1 H, $J_{2,3}$ 2.4 Hz, H-2^I), 3.73 (m, 1 H, CH_aCH$_2$Si), 3.63 (m, 1 H, H-5^{II}), 3.54–3.38 (m, 4 H, CH_bCH$_2$Si,H-5^I,3$'^{I,II}$), 2.84, 2.82 (2 t, 1 H each, J ~ 9.8 Hz, H-4^{I,II}), 1.32 (bs, 5 H, OH, 2 NH$_2$), 1.24, 1.23 (2 d, 6 H, $J_{5,6}$ ~ 6.2 Hz, H-6^{I,II}), 0.92–0.84 (m, 2 H, CH$_2$Si), ~ 0 [s, 9 H, (CH$_3$)$_3$]; ^{13}C NMR ($CDCl_3$): δ 101.08 (C-1^{II}), 98.77 (C-1^I), 79.78, 79.63 (C-3^{I,II}), 72.56 (C-2^I), 71.41, 71.13 (2 CH_2Ph), 69.52 (2 C, C-5^{I,II}), 66.37 (C-2^{II}), 64.63 (CH_2CH$_2$Si), 53.62, 53.19 (C-4^{I,II}), 18.09, 17.95, 17.70 (C-6^{I,II},CH_2Si), and −1.37 [(CH$_3$)$_3$]; CIMS: *m/z* 589 $[M + 1]^+$.

A mixture of **10** (1.15 g, 1.95 mmol), **24** (985 mg, 4.89 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (1.12 g, 5.85 mmol), and 1-hydroxybenzotriazole (792 mg, 5.85 mmol) in CH_2Cl_2 was stirred at room temperature overnight, when TLC (solvent *B*) showed that all **10** was consumed. The mixture was washed successively with aq 2 M HCl, satd Na_2CO_3 and NaCl, dried, and concentrated. Chromatography gave **11** (1.37 g, 72%): mp 87–88° (from EtOAc–hexane); $[\alpha]_D$ +6°. ^{1}H NMR ($CDCl_3$): δ 6.60, 6.57 (2 d, 1 H each, $J_{4,NH}$ 9.7 Hz, 2 NH), 5.03 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1^{II}), 4.74 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1^I), 4.67, 4.62, 4.49, 4.43 (4 d, 1 H each, ^2J ~ 12 Hz, 2 CH_2Ph), 4.51, 4.44 (2 s, 2 H each, 2 CH_2Ph), 4.30–4.00 (m, 5 H, H-2^{II},4^{I,II},2$'^{I,II}$), 3.97 (dd, 1 H, $J_{2,3}$ 2.5 Hz, H-2^I), 3.84–3.58 (m, 9 H, H-3^{I,II},5^{I,II},4$'^{I,II}$a,b,CH_aCH$_2$Si), 3.44 (CH_bCH$_2$Si), 2.20, 1.93 (2 m, 2 H each, H-3$'^{I,II}$a,b), 1.20 (d, 6 H, $J_{5,6}$ 6.3 Hz, H-6^{I,II}), 0.88 (m, 2 H, CH$_2$Si), ~ 0 [m, 9 H, (CH$_3$)$_3$]; ^{13}C NMR ($CDCl_3$): δ 100.85 (C-1^{II}), 98.43 (C-1^I), 76.01 (2 C, C-3^{I,II}), 73.38, 73.26 (2 CH_2Ph), 72.93, 72.81, 71.29 (C-2^I,2$'^{I,II}$), 71.19, 70.84 (2 CH_2Ph), 69.67, 69.45 (C-4$'^{I,II}$), 68.04, 68.15 (C-5^{I,II}), 66.49 (C-2^{II}), 64.98 (CH_2CH$_2$Si), 51.80, 50.95 (C-4^{I,II}),

33.30 (2 C, C-3′^{I,II}), 17.99, 17.84, 17.68 (C-6^{I,II},CH_2Si), −1.40 [$(CH_3)_3$]; CIMS: *m/z* 973 $[M + 18]^+$. Anal. Calcd for $C_{53}H_{72}N_2O_{13}$: C, 65.40; H, 7.46; N, 2.88. Found: C, 65.67; H, 7.43; N, 2.78.

*2-(Trimethylsilyl)ethyl 3-*O*-acetyl-2-*O*-[3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl]-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**13**).—A mixture of **11** (900 mg) and 5% palladium-on-charcoal catalyst (500 mg) in 90% AcOH (11 mL) was stirred overnight at room temperature in a hydrogen atmosphere. TLC (solvent *B*) showed that the reaction was complete. The catalyst was filtered off and washed with 90% AcOH. The combined filtrates were concentrated, and the residue containing **12** was treated overnight with 2:1 pyridine–Ac_2O (30 mL). After concentration with coevaporation of toluene, the residue was chromatographed to give **13** (570 mg, 68%): $[\alpha]_D$ +28°; ^{1}H NMR ($CDCl_3$): δ 6.47 (d, 1 H, $J_{4,NH}$ 9.3 Hz, NH^{II}), 6.12 (d, 1 H, $J_{4,NH}$ 9.3 Hz, NH^{I}), 5.29 (dd, 1 H, $J_{2,3}$ 3.4, $J_{4,5}$ 11.1 Hz, H-3^{II}), 5.19–5.14 (m, 2 H, H-3^{I},2^{II}), 5.06 (m, 2 H, H-2′^{I,II}), 4.86 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{II}), 4.76 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{I}), 4.26–3.98 (m, 4 H, H-4^{I,II},4′^{I,II}a,b), 3.81 (dd, partially overlapped, $J_{2,3}$ 3.1 Hz, H-2^{I}), 3.83–3.77 (m, partially overlapped, H-5^{II}), 3.76–3.67 (m, partially overlapped, C$H_a$$CH_2Si$), 3.64–3.58 (m, partially overlapped, H-5^{I}), 3.48–3.40 (m, 1 H, C$H_b$$CH_2Si$), 2.17, 2.13, 2.10, 2.08, 2.04, 2.01, 2.00 (7 s, 7 $COCH_3$, overlapping signals, C-3′^{I,II}a,b), 1.17 (d, partially overlapped, H-6^{I}), 1.15 (d, partially overlapped, C-6^{II}), 0.97–0.80 (m, 2 H, CH_2Si), −0.2 [s, 9 H, $(CH_3)_3$]; ^{13}C NMR ($CDCl_3$): δ 99.15 (C-1^{II}), 97.83 (C-1^{I}), 76.63 (C-2^{I}), 70.81 (2 C, C-2′^{I,II}), 69.75 (C-3^{I}), 69.48 (C-2^{I}), 69.02 (C-5^{II}), 68.33 (C-5^{I}), 67.97 (C-3^{II}), 65.36 (C$H_2$$CH_2Si$), 59.80, 59.72 (C-4′^{I,II}), 51.78 (C-4^{I}), 51.50 (C-4^{II}), 30.61, 30.42 (C-3′^{I,II}), 17.75 (2 C, C-6, CH_2Si), 17.58 (C-6), −1.46 [$(CH_3)_3$]; CIMS: *m/z* 907 $[M + 1]^+$. Anal. Calcd for $C_{39}H_{62}N_2O_{20}Si$: C, 51.65; H, 6.89; N, 3.09. Found: C, 51.71; H, 6.93; N, 2.89.

*3-*O*-Acetyl-2-*O*-[3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-d-mannopyranosyl]-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranose* (**14**).—$BF_3 \cdot Et_2O$ (0.5 mL) was added at 0° to a solution of **13** (290 mg) in CH_2Cl_2 (6 mL), and the mixture was stirred at this temperature for 3 h. TLC (solvent *B*) showed that the reaction was complete. The mixture was extracted with aqueous Na_2CO_3, dried and concentrated, and the residue was chromatographed to give an anomeric mixture of **14** (210 mg, 81%): $[\alpha]_D$ +6°, where the α-anomer strongly predominated. ^{1}H NMR data for the α-anomer ($CDCl_3$): δ 6.50, 6.45 (2 d, 1 H each, $J_{4,NH}$ 9.4 and 9.0 Hz, respectively, 2 NH), 5.31 (2 dd, overlapping, 2 H, $J_{2,3}$ 3.2, $J_{3,4}$ 10.9 Hz, H-3^{I,II}), 5.23 (dd, 1 H, $J_{1,2}$ 1.7 Hz, H-2^{II}), 5.17 (bd, 1 H, H-1^{I}), 5.09, 5.07 (2 dd, partially overlapped, $J_{2',3'a}$ 2.9, $J_{2',3'b}$ 5.1 Hz, H-2′^{I,II}), 4.91 (dd, 1 H, H-1^{II}), 4.31–4.04 (m, 6 H, H-4^{I,II},4′^{I,II}a,b), 4.04–3.94 (m, 2 H, H-5^{I},2^{I}), 3.87–3.78 (m, 1 H, H-5^{II}), 2.20, 2.17, 2.15, 2.11, 2.08, 2.07, 2.06 (7 s, 7 $COCH_3$ overlapping H-3′^{I,II}a,b signals), 1.21, 1.19 (2 d, partially overlapped, 6 H, H-6^{I,II}); ^{13}CNMR ($CDCl_3$): δ 99.12 ($J_{C,H}$ 172.2 Hz, C-1^{II}), 93.00 ($J_{C,H}$ 170.4 Hz, C-1α), 76.27 (C-2^{I}), 70.92, 70.82 (C-2′^{I,II}), 69.53 (C-3^{I}), 69.49 (C-2^{II}), 68.89 (C-5^{II}), 68.00 (C-3^{II}), 67.79 (C-5^{I}), 59.87 (2 C, C-4′^{I,II}), 51.59, 51.50 (C-4^{I,II}), 30.57, 30.52 (C-3′^{I,II}), 17.79, 17.55 (C-6^{I,II}); $\delta_{H\text{-}1^I\beta}$ 4.93, $J_{1,2}$ 2.1 Hz, $\delta_{C\text{-}1^I\beta}$ 93.25, $J_{C,H}$ 159.4 Hz; CIMS: *m/z* 824 $[M + 18]^+$. Anal. Calcd for $C_{34}H_{50}N_2O_2$: C, 50.62; H, 6.25; N, 3.47. Found: C, 50.80; H, 6.18; N, 3.39.

*5-(Methoxycarbonyl)pentyl 3-O-acetyl-2-O-[2,3-di-O-acetyl-4-(2,4-di-O-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl]-4-(2,4-di-O-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**16a**) and β-D-*mannopyranoside* (**16b**).— 1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU, 12 mg, 0.08 mol) was added at 0 °C to a solution of **14** (130 mg, 0.16 mmol) and CCl_3CN (6.9 g, 46 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at 0 °C for 5 min and, without work-up, chromatographed (solvent *B*) to give first 3-*O*-acetyl-2-*O*-[2,3-di-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl]-4-(2,4-di-*O*-acetyl-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl trichloroacetimidate (**15a**, 130 mg, 85%): $[\alpha]_D$ +22° (*c* 1.8); ^{1}H NMR ($CDCl_3$): δ 8.72 (s, 1 H, C = NH), 6.39 (d, 1 H, $J_{4,NH}$ 9.3 Hz, NH), 6.27 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1^I), 6.21 (d, 1 H, $J_{4,NH}$ 8.8 Hz, NH), 5.36–5.30 (dd, partially overlapped, $J_{2,3}$ 3.3 Hz, H-3^{II}), 5.32–5.26 (dd, partially overlapped, $J_{2,3}$ 3.2 Hz, H-3^I), 5.23 (m, 1 H, H-2^{II}), 5.15–5.05 (m, 2 H, H-2′^{I,II}), 5.00 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1^{II}), 4.34–4.18 (m, partially overlapped, H-4^{I,II}), 4.24–4.05 (m, H-2^I,4′^{I,II}a,b), 3.98–3.88 (m, 1 H, H-5^I), 3.92–3.82 (m, 1 H, H-5^{II}), 2.22–2.06 (25 H, H-3′^{I,II}a,b, 7 $COCH_3$), 1.28, 1.24 (2 d, 3 H each, $J_{5,6}$ 6.2 Hz, H-6^{I,II}); ^{13}C NMR ($CDCl_3$): δ 99.17 (C-1^{II}), 96.16 (C-1^I), 73.64 (C-2^I), 71.33 (C-5^I), 70.82 (2 C, C-2′^{I,II}), 69.46 (2 C, C-2^{II},5^{II}), 69.25 (C-3^I), 67.88 (C-3^{II}), 59.79, 59.72 (C-4′^{I,II}), 51.49, 51.31 (C-4^{I,II}), 30.61, 30.42 (C-3′^{I,II}), 17.83, 17.49 (C-6^{I,II}); FABMS: *m/z* 974 [M + Na].

Eluted next was **15b** (10 mg, 7%): $[\alpha]_D$ +6°; ^{1}H NMR ($CDCl_3$): δ 8.72 (s, 1 H, C = NH), 6.11 (d, 1 H, $J_{4,NH}$ 9.2 Hz, NH), 5.98 (d, 1 H, $J_{4,NH}$ 8.8 Hz, NH), 5.74 (s, 1 H, H-1^I), 5.35 (dd, 1 H, $J_{2,3}$ 3.2, $J_{3,4}$ 10.9 Hz, H-3^{II}), 5.23 (m, 1 H, H-2^{II}), 5.18 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{II}), 5.15 (dd, 1 H, $J_{2,3}$ 2.6, $J_{3,4}$ 10.9 Hz, H-3^I), 5.06, 5.02 (2 dd, 2 H, $J_{2',3'a}$ 4.7, $J_{2',3'b}$ 7.7 Hz, H-2′^{I,II}), 4.30–3.98 (m, 8 H, H-2^I,4^{I,II}a,b,5,4′^{I,II}a,b), 3.64–3.54 (m, 1 H, H-5), 2.16–1.98 (25 H, H-3′^{I,II}a,b, 7 $COCH_3$), 1.21, 1.11 (2 d, 3 H each, $J_{5,6}$ 6.1 Hz, H-6^{I,II}); ^{13}C NMR ($CDCl_3$): δ 97.31 ($J_{C,H}$ 171.0 Hz, C-1^{II}), 95.11 ($J_{C,H}$ 163.0 Hz, C-1^I), 72.94 (C-2^I), 72.25, 71.04 (C-3^I,5^I), 70.95 (2 C, C-2′^{I,II}), 69.68 (C-2^{II}), 68.75 (C-5^{II}), 68.17 (C-3^{II}), 59.82, 59.78 (C-4′^{I,II}), 51.90, 51.61 (C-4^{I,II}), 30.82, 30.52 (C-3′^{I,II}), 18.09, 17.85 (C-6^{I,II}); FABMS: *m/z* 974 [M + Na].

Methyl 6-hydroxyhexanoate (**25**) [22] (200 mg, 1.3 mmol), followed by triethysilyl trifluoromethanesulfonate (TESOTf, 1 drop), was added at −20 °C to a solution of **15a** and powdered 4 Å molecular sieves (600 mg) in CH_2Cl_2 (10 mL). The mixture was stirred for 1 h at 0 °C and, without workup, chromatographed (solvent *B*) to give first **16a** (92 mg, 73%): $[\alpha]_D$ +24°; ^{1}H NMR ($CDCl_3$): δ 6.34, 6.31 (2 d, 1 H each, $J_{4,NH}$ 8.2 and 9.2 Hz, respectively, 2 NH), 5.30 (dd, 1 H, $J_{2,3}$ 3.2, $J_{3,4}$ 11 Hz, H-3^{II}), 5.22–5.20 (m, partially overlapped, H-2^{II}), 5.19 (dd, partially overlapped, $J_{2,3}$ 3.2 Hz, H-3^I), 5.10, 5.09 (2 dd, partially overlapped, 2 H, *J* 7.8 Hz, H-2′^{I,II}), 4.90 (d, 1 H, $J_{1,2}$ 1.6 Hz, H-1^{II}), 4.74 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1^I), 4.31–4.23 (m, 1 H, H-4^{II}), 4.23–4.05 (m, 5 H, H-4^I,4′^{I,II}a,b), 3.88 (dd, 1 H, $J_{1,2}$ 1.8, $J_{2,3}$ 2.9 Hz, H-2^I), 3.83–3.73 (m, 1 H, H-5^{II}), 3.71–3.64 (m, overlapped, H-5^I,OC$H_a$$CH_2$), 3.69 (s, overlapped, $COOCH_3$), 3.43–3.36 (m, 1 H, OC$H_b$$CH_2$), 2.34 (t, 2 H, *J* 7.4 Hz, C$H_2$$COCH_3$), 2.32–2.04 (m, 25 H, H-3′^{I,II}a,b, 7 $COCH_3$), 1.70–1.58 (m, 4 H, 2 CH_2), 1.43–1.38 (m, 2 H, CH_2), 1.23, 1.20 (2 d, 3 H each, $J_{5,6}$ 6.2 Hz, H-6^{I,II}); ^{13}C NMR ($CDCl_3$): δ 99.18 (C-1^{II}), 98.36 (C-1^I), 76.36 (C-2^I), 70.89, 70.80 (C-2′^{I,II}), 69.75 (C-3^I), 69.55 (C-2^{II}), 69.07 (C-5^{II}), 68.04 (C-5^I), 67.92 (C-3^{II}), 67.16 (OCH_2), 59.79 (2 C, C-4′^{I,II}), 51.63 (2 C),

51.55 (C-4^{I,II}, OCH_3), 33.86 (CH_2COOCH_3), 30.64, 30.55 (C-3$'^{I,II}$), 28.73, 25.46, 24.34 (3 CH_2), 17.84, 17.66 (C-6^{I,II}); FABMS: m/z 935 $[M + 1]^+$, 597 $[M + Na]^+$. Anal. Calcd for $C_{41}H_{62}N_2O_{22}$: C, 52.67; H, 6.68; N, 3.00. Found: C, 52.75; H, 6.72; N, 2.92.

Eluted next was **16b** (17 mg, 13%): $[\alpha]_D$ −14° (*c* 0.9); ^{1}H NMR ($CDCl_3$): δ 6.41, 6.05 (2 d, 1 H each, $J_{4,NH}$ 8.8 Hz, 2 NH), 5.36 (dd, 1 H, $J_{2,3}$ 3.3, $J_{3,4}$ 10.6 Hz, H-3^{II}), 5.22 (dd, 1 H, $J_{1,2}$ 1.9 Hz, H-2^{II}), 5.13–5.06 (m, partially overlapped, H-2$'^{I,II}$), 5.05 (dd, partially overlapped, $J_{2,3}$ 2.7 Hz, H-3^I), 4.90 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1^{II}), 4.45 (d, 1 H, $J_{1,2}$ 0.6 Hz, H-1^I), 4.31–3.96 (m, 9 H, H-2^I,4^{I,II},5^{II},4$'^{I,II}$a,b,OCH_a), 2.31 (t, 2 H, *J* 7.3 Hz, CH_2CO), 2.20–2.05 (m, 25 H, H-3$'^{I,II}$a,b, 7 $COCH_3$), 1.70–1.58 (m, 4 H, 2 CH_2), 1.40–1.37 (m, 2 H, CH_2), 1.29 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^I), 1.15 (d, 3 H, $J_{5,6}$ 6.7 Hz, H-6^{II}); ^{13}C NMR ($CDCl_3$): δ 99.74 ($J_{C,H}$ 154.1 Hz, C-1^I), 98.77 ($J_{C,H}$ 172.8 Hz, C-1^{II}), 75.38 (C-2^I), 71.99 (C-5^I), 71.82 (C-3^I), 70.93, 70.86 (C-2$'^{I,II}$), 70.00 (OCH_2CH_2), 69.86 (C-2^{II}), 68.39 (C-5^{II}), 68.22 (C-3^{II}), 59.89, 59.76 (C-4$'^{I,II}$), 52.32, 51.67 (C-4^{I,II}), 51.58 (OCH_3), 33.82 (CH_2CO), 30.69, 30.50 (C-3$'^{I,II}$), 29.16, 25.35, 24.46 (3 CH_2), 17.92 (C-6^I), 17.48 (C-6^{II}); FABMS: m/z 935 $[M + 1]^+$, 974 [M + Na]. Anal. Calcd for $C_{41}H_{62}N_2O_{22}$: C, 52.67; H, 6.68; N, 3.00. Found: C, 52.59; H, 6.68; N, 2.96.

*2-[2-(Methoxycarbonyl)ethylthio]ethyl 3-*O*-acetyl-2-*O*-[2,3-di-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl]-4-(2,4-di-*O*-acetyl-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**17b**).—TESOTf (1 drop) was added at −20 °C to a stirred mixture of **15a** (180 mg, 0.19 mmol), methyl 2-(2-hydroxyethylthio)propionate (310 mg, 1.9 mmol), and powdered 4 Å molecular sieves (800 mg). After stirring at −20 °C for 30 min, workup, as described for the preparation of **16**, and chromatography gave first **17a** (133 mg, 74%): $[\alpha]_D$ +25° (*c* 0.7); ^{1}H NMR ($CDCl_3$): δ 6.40 (d, 1 H, $J_{4,NH}$ 9.3 Hz, NH^{II}), 6.35 (d, 1 H, $J_{4,NH}$ 9.4 Hz, NH^I), 5.32 (dd, 1 H, $J_{2,3}$ 3.4, $J_{3,4}$ 11.2 Hz, H-3^{II}), 5.21 (dd, partially overlapped, 1 H, $J_{1,2}$ 2.0, $J_{2,3}$ 3.2 Hz, H-2^{II}), 5.20 (dd, partially overlapped, 1 H, $J_{2,3}$ 3.1, $J_{3,4}$ 11.2 Hz, H-3^I), 5.11, 5.08 (2 dd, partially overlapped, $J_{2',3'a}$ 3.2, $J_{2',3'b}$ 4.9 Hz, H-2$'^{I,II}$), 4.91 (d, 1 H, H-1^{II}), 4.82, (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^I), 4.31–4.05 (m, 6 H, H-4^{I,II},4$'^{I,II}$a,b), 3.92 (dd, 1 H, $J_{2,3}$ 3.3 Hz, H-2^I), 3.90–3.62 (m, 7 H, H-5^{I,II},OCH_2CH_2, incl s at 3.71, $COOCH_3$), 2.89–2.81 (m, 2 H, SC$H_2CH_2COOCH_3$), 2.80–2.71 (m, 2 H, OCH_2CH_2), 2.70–2.58 (m, 2 H, CH_2COOCH_3), 2.22–2.04 (m, 25 H, incl 7 s at 2.22, 2.16, 2.15, 2.12, 2.10, 2.07, 2.05, 7 $COCH_3$, H-3$'^{I,II}$a,b), 1.24 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6^I), 1.20 (d, 3 H, $J_{5,6}$ 6.3 Hz, H-6^{II}); ^{13}C NMR ($CDCl_3$): δ 99.23 ($J_{C,H}$ 171.9 Hz, C-1^{II}), 98.59 (169.6 Hz, C-1^I), 76.06 (C-2^I), 70.85, 70.83 (C-2$'^{I,II}$), 69.60, 69.52 (C-2^{II},3^I), 69.13 (C-5^{II}), 68.49 (C-5^I), 67.94 (C-3^{II}), 67.86 (OCH_2CH_2), 59.79 (2 C, C-4$'^{I,II}$), 51.84 ($COOCH_3$), 51.59 (C-4^{II}), 51.40 (C-4^I), 34.57 (CH_2COOCH_3), 31.73 (OCH_2CH_2S), 30.58, 30.48 (C-3$'^{I,II}$), 27.75 ($CH_2CH_2COOCH_3$), 17.78 (C-6^I), 17.60 (C-6^{II}); CIMS: m/z 953 $[M + 1]^+$, 970 $[M + 18]^+$. Anal. Calcd for $C_{40}H_{60}N_2O_{22}S$: C, 50.41; H, 6.35; N, 2.94; S, 3.36. Found: C, 50.29; H, 6.42; N, 2.88; S, 3.27.

Eluted next was **17b**: $[\alpha]_D$ −8° (*c* 0.9); ^{1}H NMR ($CDCl_3$): δ 6.37 (d, 1 H, $J_{4,NH}$ 8.8 Hz, NH^{II}), 6.05 (d, 1 H, $J_{4,NH}$ 8.7 Hz, NH^I), 5.35 (dd, 1 H, $J_{2,3}$ 3.5, $J_{3,4}$ 10.8 Hz, H-3^{II}), 5.23 (dd, 1 H, $J_{1,2}$ 1.7, $J_{2,3}$ 3.0 Hz, H-2^{II}), 5.12–5.08 (m, partially overlapped, H-2$'^{I,II}$), 5.05 (dd, partially overlapped, $J_{2,3}$ 2.8, $J_{3,4}$ 8.7 Hz, H-3^I), 4.92 (d, 1 H, H-1^{II}),

4.53 (s, 1 H, H-1^{I}), 4.32–3.95 (m, 9 H, H-2^{I},4^{I,II},5^{II},4′^{I,II}a,b,OCH_aCH$_2$), 3.72–3.64 (m, partially overlapped, OCH$_2$), 3.66 (s, partially overlapped, COOCH$_3$), 3.54–3.44 (m, 1 H, H-5^{I}), 2.86–2.80 (m, 2 H, SCH_2CH$_2$COOCH$_3$), 2.79–2.68 (m, 2 H, OCH$_2$CH_2S), 2.66–2.60 (m, 2 H, CH_2COOCH$_3$), 2.20, 2.17, 2.15, 2.12, 2.08, 2.06 (6 s, overlapping H-3′^{I,II}a,b resonances, the one at the highest field showing ~ double intensity, 7 COCH$_3$), 1.29 (d, 3 H, $J_{5,6}$ 6.1 Hz, H-6^{I}), 1.16 (d, 3 H, $J_{5,6}$ 5.6 Hz, H-6^{II}); ^{13}C NMR (CDCl$_3$): δ 99.73 ($J_{C,H}$ 157.1 Hz, C-1^{I}), 98.50 ($J_{C,H}$ 172.0 Hz, C-1^{II}), 74.50 (C-2^{I}), 72.07 (C-5^{I}), 71.79 (C-3^{I}), 70.93, 70.90 (C-2′^{I,II}), 69.83 (C-2^{II}), 69.01 (OCH$_2$), 68.35 (C-5^{II}), 68.25 (C-3^{II}), 59.93, 59.76 (C-4′^{I,II}), 52.24 (C-4^{I}), 51.92 (COOCH$_3$), 51.56 (C-4^{II}), 34.76 (CH$_2$COOCH$_3$), 31.74 (OCH$_2$$CH_2$), 30.69, 30.49 (C-3′^{I,II}), 27.87 (CH$_2$CH$_2$COOCH$_3$), 17.88 (C-6^{I}), 17.54 (C-6^{II}); CIMS: *m/z* 953 [M + 1]$^+$, 970 [M + 18]$^+$. Anal. Calcd for $C_{40}H_{60}N_2O_{22}S$: C, 50.41; H, 6.35; N, 2.94; S, 3.36. Found: C, 50.27; H, 6.37; N, 2.88; S, 3.24.

*5-(Methoxycarbonyl)pentyl 2-*O*-[4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl]-4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**18**).—A solution of compound **16a** (75 mg) was deacetylated (Zemplén) to give pure (NMR) **18** (45 mg, 88%): [α]$_D$ +12° (*c* 1, MeOH); ^{1}H NMR (CD$_3$OD): δ 4.96 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{II}), 4.84 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.19 (2 dd, overlapped, $J_{2',3'a}$ 7.9, $J_{2',3'b}$ 7.9 Hz, H-2′^{I,II}), 4.03 (dd, $J_{2,3}$ 3.0 Hz, H-2^{II}), 4.00–3.62 (m, 15 H, H-3^{I,II},4^{I,II},5^{I,II},4′^{I,II}a,b,OCH$_a$CH$_2$, incl dd at 3.81, $J_{2,3}$ 2.9 Hz, for H-2^{I}, and s at 3.67 for OCH$_3$), 2.34 (t, 2 H, CH$_2$CO), 2.07–1.95, 1.90–1.77 (2 m, 2 H each, H-3′^{I,II}a,b), 1.69–1.54 (m, 4 H, OCH$_2$CH_2CH$_2$CH_2), 1.47–1.36 (m, 2 H, OCH$_2$CH$_2$CH_2), 1.17, 1.15 (2 d, 3 H each, $J_{5,6}$ 6,1 Hz, C-6^{I,II}); ^{13}C NMR (CD$_3$OD): δ 177.95, 175.88 (2 CONH), 175.85 (COOCH$_3$), 104.08 (C-1^{II}), 100.23 (C-1^{I}), 79.63 (C-2′^{I,II}), 70.90 (C-2^{II}), 70.70 (C-2′^{I,II}), 69.99, 69.65, 69.25, 68.71 (C-3^{I,II},5^{I,II}), 68.44 (OCH$_2$), 59.41 (C-4′^{I,II}), 54.66, 54.11 (C-4^{I,II}), 52.04 (OCH$_3$), 38.17 (C-3′^{I,II}), 34.62 (CH$_2$CO), 30.04 (OCH$_2$$CH_2$), 26.70 (OCH$_2CH_2$$CH_2$), 25.60 (OCH$_2CH_2CH_2$$CH_2$), 18.32, 18.22 (C-6^{I,II}); FABMS: *m/z* 641 [M + 1]$^+$.

*5-(Carboxy)pentyl 2-*O*-[4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl]-4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**19**).—2 M NaOH (1 mL) was added to a solution of **18** (18 mg) in MeOH (1 mL), and the mixture was kept at room temperature for 2 h, when TLC (solvent D) showed that the reaction was complete. After processing, as described for the preparation of **18**, the pure (NMR), amorphous **19** (14 mg, 80%) was obtained: [α]$_D$ +11° (*c* 1, MeOH); ^{1}H NMR (CD$_3$OD): δ 4.95 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1^{II}), 4.84 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1^{I}), 4.18 (dd, 2 H, $J_{2',3'a}$ 3.9, $J_{2',3'b}$ 8.0 Hz, H-2′^{I,II}), 4.02 (bt, 1 H, H-2^{II}), 3.98–3.64 (m, 12 H, H-3^{I,II},4^{I,II},5^{I,II},OCH_a, incl bt at 3.79, H-2^{I}, and m at 3.72 for H-4′^{I,II}a,b), 3.45–3.28 (m, 1 H, OCH$_b$), 2.32–2.24 (m, 2 H, CH$_2$CO), 2.06–2.15, 1.87–1.78 (2 m, 2 H each, C-3′^{I,II}), 1.67–1.57 (m, 4 H, OCH$_2$CH_2CH$_2$CH_2), 1.48–1.36 (m, 2 H, OCH$_2$CH$_2$CH_2), 1.16, 1.15 (2 d, partially overlapped, $J_{5,6}$ 6.2 Hz, H-6^{I,II}); ^{13}C NMR (CDCl$_3$): δ 104.14 (C-1^{II}), 100.31 (C-1^{I}), 79.67 (C-2^{I}), 70.99 (C-2^{II}), 70.76 (2 C, C-2′^{I,II}), 70.06, 69.70, 69.32, 68.80 (C-3^{I,II},5^{I,II}), 68.57 (OCH$_2$), 59.46 (2 C, C-4′^{I,II}), 54.74, 54.19 (C-4^{I,II}), 38.24 (2 C, C-3′^{I,II}), 34.77 (CH$_2$CO), 30.17 (OCH$_2$$CH_2$), 26.80 (OCH$_2CH_2$$CH_2$), 25.74 (OCH$_2CH_2CH_2$$CH_2$), 18.34, 18.23 (C-6^{I,II}); FABMS: *m/z* 649 [M + Na]$^+$, [M + 1]$^+$.

*5-(Hydrazinocarbonyl)pentyl 2-O-[4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl]-4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**20**).—To a solution of **18** (20 mg) in EtOH (0.5 mL) was added hydrazine hydrate (0.1 mL), and the mixture was kept at room temperature overnight, when TLC (solvent *D*) showed that the starting material was no longer present. After concentration, the product was purified by elution with MeOH from a column of Sephadex LH-20, to give pure (NMR) **20** (17 mg, 85%): $[\alpha]_D$ +7° (*c* 1, MeOH); ^{1}H NMR (CD_3OD): δ 4.94 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{II}), 4.83 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.20–4.15 (2 m, partially overlapped, 2 H, H-2′^{I,II}), 4.03 (dd, 1 H, $J_{2,3}$ 2.7 Hz, H-2^{II}), 3.98–3.54 (m, 12 H, H-3^{I,II},4^{I,II},5^{I,II},OCH_a, incl dd, 3.78 for H-2^{I}, and m, 3.74 for H-4′^{I,II}a,b), 3.44–3.33 (m, 1 H, OCH_b), 2.16 (t, 2 H, *J* 7.1 Hz, CH_2CO), 2.06–1.94, 1.89–1.77 (2 m, 2 H each, H-3′^{I,II}a,b), 1.70–1.53 (m, 4 H, $OCH_2CH_2CH_2CH_2$), 1.46–1.35 (m, 2 H, $OCH_2CH_2CH_2$), 1.16, 1.15 (2 d, partially overlapped, 6 H, $J_{5,6}$ 5.9 and 6.1, respectively, H-6^{I,II}); ^{13}C NMR (CD_3OD): δ 104.17 C-1^{II}), 100.24 (C-1^{I}), 79.75 (C-2^{I}), 70.97 (C-2^{II}), 70.75 (2C, C-2′^{I,II}), 70.04, 69.65, 69.33, 68.71, (C-3^{I,II},5^{I,II}), 68.28 (OCH_2), 59.44 (2 C, C-4′^{I,II}ab), 54.77, 54.17 (C-4^{I,II}), 38.28, 38.25 (C-3′^{I,II}), 34.76 (CH_2CO), 30.06 (OCH_2CH_2), 26.76 ($OCH_2CH_2CH_2$), 26.20 ($OCH_2CH_2CH_2CH_2$), 18.35, 18.24 (C-6^{I,II}); FABMS: *m/z* 641 $[M + 1]^+$.

*2-[2-(Methoxycarbonyl)ethylthio]ethyl 2-O-[4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl]-4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**21**).—Compound **21** (81 mg, 98%): $[\alpha]_D$ +15° (*c* 1, MeOH) was prepared from **17** (120 mg) as described for **18**. ^{1}H NMR (CD_3OD): δ 4.97 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1^{II}), 4.90 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.19 (2 dd, overlapped, $J_{2',3'a}$ 3.9, $J_{2',3'b}$ 8.0 Hz, H-2′^{I,II}), 4.06 (dd, $J_{2,3}$ 2.9 Hz, H-2^{II}), 4.02–3.79 (m, 8 H, incl bt at 3.84 for H-2^{I},3^{I,II},4^{I,II},5^{I,II},OCH_a), 3.76–3.59 (m, 8 H, incl bt at 3.73 for H-4′^{I,II}a,b, and s at 3.70 for OCH_3, OCH_b), 2.92–2.79 (m, 2 H, $SCH_2CH_2COOCH_3$), 2.78–2.74 (m, 2 H, OCH_2CH_2), 2.68–2.41 (m, 2 H, CH_2CO), 2.07–1.96, 1.90–1.77 (2 m, 2 H each, H-3′^{I,II}a,b), 1.17, 1.16 (2 d, partially overlapped, $J_{5,6}$ ~ 6.0 Hz, H-6^{I,II}); ^{13}C NMR (CD_3OD): δ 177.98, 177.90 (2 CONH), 174.20 ($COOCH_3$), 104.06 (C-1^{II}), 100.42 (C-1^{I}), 79.36 (C-2^{I}), 70.94 (C-2^{II}), 70.71 (2 C, C-2′^{I,II}), 70.00 (C-5), 69.58, 69.32 (C-3^{I,II}), 68.99 (C-5), 68.80 (OCH_2), 59.42 (2 C, C-4′^{I,II}ab), 54.61, 54.15 (C-4^{I,II}), 52.33 (OCH_3), 38.21 (2 C, C-3′^{I,II}), 35.62 (CH_2COOCH_3), 32.53 (OCH_2CH_2S), 28.47 ($SCH_2CH_2COOCH_3$), 18.34, 18.25 (C-6^{I,II}); FABMS: *m/z* 659 $[M + 1]^+$.

*2-[2-(Carboxy)ethylthio]ethyl 2-O-[4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl]-4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**22**).—The title compound [35 mg, 95%, $[\alpha]_D$ +15° (*c* 1, MeOH)] was obtained from **21** (38 mg), as described for the preparation of **19**. ^{1}H NMR (CD_3OD): δ 4.96 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{II}), 4.90 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{I}), 4.20–4.16 (2 dd, partially overlapped, $J_{2',3'a}$ 3.9, $J_{2',3'b}$ 7.9 Hz, H-2′^{I,II}), 4.02 (dd, 1 H, $J_{2,3}$ 3.0 Hz, H-2^{II}), 3.99–3.70 (m, 12 H, H-3^{I,II},4^{I,II},5^{I,II},OCH_a, incl dd at 3.83, $J_{2,3}$ 2.8 Hz, H-2^{I}, and m at 3.73, H-4′^{I,II}a,b), 3.68–3.59 (m, 1 H, OCH_b), 2.85–2.79 (2 dd, 2 H, SCH_2CH_2CO), 2.76 (t, 2 H, *J* 6.3 Hz, OCH_2CH_2), 2.58 (m, 2 H, CH_2CO), 2.06–1.96, 1.89–1.76 (2 m, 2 H each, H-3′^{I,II}), 1,17, 1.16 (2 d, partially overlapped, 6 H, H-6^{I,II}); ^{13}C NMR ($CDCl_3$): δ 104.07 (C-1^{II}), 100.43 (C-1^{I}), 79.35 (C-2^{I}), 70.96 (C-2^{II}), 70.72 (2 C, C-2′^{I,II}), 70.01, 69.61, 69.34, 69.03 (C-3^{I,II},5^{I,II}), 68.72 (OCH_2), 59.43 (2 C, C-4′^{I,II}),

54.63, 54.16 (C-4^{I,II}), 38.22 (2 C, C-3'^{I,II}), 35.82 (CH_2CO), 32.60 (OCH_2CH_2), 28.54 (SCH_2CH_2CO), 18.34, 18.25 (C-6^{I,II}); FABMS: m/z 645 $[M + 1]^+$.

*2-[2-(Hydrazinocarbonyl)ethylthio]ethyl 2-O-[4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl]-4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**23**).—Compound **23** [38 mg, 83%, $[\alpha]_D$ +13° (*c* 1, MeOH)] was prepared from **21** (46 mg), as described for the preparation of **20**. ^{1}H NMR (CD_3OD): δ 4.97 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1^{II}), 4.89 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{I}), 4.21–4.16 (m, 2 H, H-2'^{I,II}), 4.03 (dd, 1 H, $J_{2,3}$ 2.7 Hz, H-2^{II}), 4.01–3.79 (m, 8 H, H-2^{I},3^{I,II},4^{I,II},5^{I,II},OCH_a), 3.76–3.70 (m, 4 H, 4'^{I,II}a,b), 3.68–3.59 (m, 1 H, OCH_b), 2.98–2.80 (2 m, partially overlapped, 2 H, CH_2CH$_2$CO), 2.75 (t, 2 H, *J* 6.0 Hz, OCH_2CH_2), 2.52–2.35 (m, 2 H, CH_2CO), 2.07–1.95, 1.88–1.78 (2 m, 2 H each, H-3'^{I,II}), 1.17, 1.16 (2 d, partially overlapped, $J_{5,6}$ 5.9 Hz, H-6^{I,II}); ^{13}C NMR (CD_3OD): d 173.16 (CONH), 104.06 (C-1^{II}), 100.40 (C-1^{I}), 79.40 (C-2^{I}), 70.94 (C-2^{II}), 70.72 (2 C, C-2'^{I,II}), 69.96, 69.48, 60.34 (C-3^{I,II},5), 69.00 (2 C, C-5,OCH_2), 59.41 (2 C, C-4'^{I,II}), 38.21 (2 C, C-3'^{I,II}), 35.28 (CH_2CO), 32.54 (OCH_2CH_2) 29.18 (SCH_2CH_2CO), 18.35, 18.27 (C-6^{I,II}); FABMS: m/z 659 $[M + 1]^+$.

Methyl 2-(2-hydroxyethylthio)propionate (**26**).—Ethyl 3-mercaptopropionate (6 g, 50 mmol), followed by 2-bromoethanol (6.25 g, 50 mmol), was added to a solution of Na (1.15 g) in MeOH (40 mL), and the mixture was stirred under reflux for 4 h. After concentration, a solution of the residue in CH_2Cl_2 was washed in water, dried, and concentrated. Chromatography of the residue (solvent *E*) gave the title, oily compound **26** (7.1 g, 88%). ^{1}H NMR ($CDCl_3$): δ 3.75 (bq, 2 H, *J* ~ 5.8 Hz, OCH_2), 3.71 (s, 3 H, OCH_3), 2.82 (t, 2 H, *J* 7.1 Hz, SCH_2CH_2CO), 2.75 (t, 2 H, *J* 5.8 Hz, OCH_2CH_2S), 2.63 (t, 2 H, *J* 7.5 Hz, CH_2CO), 2.29 (bt, 1 H, *J* ~ 5.9 Hz, OH); ^{13}C NMR ($CDCl_3$): δ 172.37 (CO), 60.49 (OCH_2), 51.86 (OCH_3), 35.35, 34.59 (OCH_2CH_2S, CH_2CO), 26.55 (SCH_2CH_2CO); CIMS: m/z 165 $[M + 1]^+$, 182 $[M + 18]^+$. Anal. Calcd for $C_6H_{12}O_3S$: C, 43.88; H, 7.36; S, 19.53. Found: C, 43.96; H, 7.31; S, 19.46.

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