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Synthesis of methyl α-glycosides of some higher oligosaccharide fragments of the O-antigen of *Vibrio cholerae* O1, serotype Inaba and Ogawa [1,2]

Jian Zhang, Pavol Kováč *

NIDDK, National Institutes of Health, 8 Center Drive, Bethesda, MD 20892-0815, USA

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Abstract

The title oligosaccharides, the tri- through the hexasaccharide in the Inaba series and the penta- and the hexasaccharide in the Ogawa series, have been synthesized using 1-thioglycosides of precursors to 3-*O*-benzyl-perosamine (4-amino-4,6-dideoxy-D-mannose) as building blocks and *N*-iodosuccinimide/silver triflate as a promoter. The azido groups in the assembled oligosaccharides were reduced to amino groups, which were then acylated using 2,4-*O*-benzylidene-3-deoxy-L-*glycero*-tetronic acid as the derivatizing reagent. Catalytic hydrogenolysis, simultaneously of the benzyl and benzylidene groups, gave the desired products that were characterized by ^{1}H and ^{13}C NMR spectroscopy. © 1997 Elsevier Science Ltd.

Keywords: *Vibrio cholerae* O1; 2,4-*O*-Benzylidene-3-deoxy-L-*glycero*-tetronic acid; *N*-Iodosuccinimide/silver triflate-promoted glycosylation; Synthetic oligosaccharides

1. Introduction

The serotype O1 and the recently discovered serotype O139 of *Vibrio cholerae* are causative agents of the disease in humans with symptoms of cholera. With growing number of pathogens that belong to the *Vibrio cholerae* species, the need for a potent vaccine against diseases caused by them is becoming more pressing. Clinically useful cellular vaccines against cholera elicit relatively short-lived, anti-LPS antibodies, but they are far from satisfactory [2]. It is hoped that conjugate vaccines, with their T-helper cell-directing protein component, will stimulate production of memory cells and, thus, long-lasting protective IgG antibodies, and so overcome this deficiency. Such immunogens, based on detoxified LPS of *Vibrio cholerae* O1, serotype Inaba, have already been described [2,3]. A similar conjugate material based on a synthetic carbohydrate antigen, let alone a synthetic carbohydrate-based vaccine against cholera, is yet to be prepared. Such materials are targets of our synthetic endeavor.

The serotype-specificity of Gram-negative bacteria, to which *Vibrio cholerae* species belong, resides in the O-polysaccharide (or O-antigen, O-PS) portion of lipopolysaccharides located on the outer membrane of smooth strains of such pathogens. The O-PSs of the two main strains of *Vibrio cholerae*, Ogawa

* Corresponding author.

[1] Synthesis of ligands related to the *Vibrio cholerae* O-specific antigen. Part 14. For Part. 13, see ref. [1].

[2] Dedicated to Professor Hans Paulsen on the occasion of his 75th birthday.

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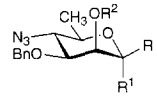
and Inaba, consist of a chain of about fifteen (1 → 2)-α-linked 4-amino-4,6-dideoxy-D-mannoses (D-perosamine), the amino group of which is acylated with 3-deoxy-L-*glycero*-tetronic acid. Only the Ogawa strain has the O-2 of its upstream, terminal end moiety of perosamine methylated.

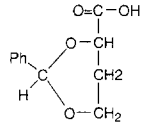
Detailed knowledge of the mode of binding of the O-PS and its homologous antibodies is a prerequisite for rational development of a medically useful immunogen. Within our efforts to obtain such information, we have synthesized a large number of fragments of the O-PS of both serotypes of *Vibrio cholerae* O1. Some of these were obtained in the form of glycosides whose aglycons make them suitable for linking to proteins [1,4]. Methyl α-glycosides of some lower oligosaccharides of the Inaba [5,6] and Ogawa [7] series have also been prepared. Here we describe synthesis of methyl α-glycosides of higher oligosaccharides of both series up to and including hexasaccharides.

2. Results and discussion

We have experienced a number of difficulties during our recent syntheses of oligosaccharides related to the O-PS of *Vibrio cholerae* O1. For example, in some cases, observed migration of acyl groups in some of the intermediates [6,7] made isolation of products difficult. Also, in the case of a dodecasaccharide [1], the conversion of the intermediate containing azido functions eventually to the corresponding 3-deoxy-L-*glycero*-teronamido derivative could only be achieved in low yield. Therefore, in the present work, we have modified some of the original chemistry. Firstly, to avoid complications due to acyl group migration, intermediate oligosacchrides containing azido groups, up to the pentasaccharide **11**, were prepared according to Bundle and co-workers [8–10]. That approach uses building blocks, such as **7**, where acyl migration cannot occur. In cases when ^{13}C NMR spectral data for these important intermediates had not been previously recorded, we have collected these data, and used them as an aid to confirm the structures of penta- and hexasaccharides (**12**, **16–18**, **22–24**), prepared and reported here for the first time following that strategy. Secondly, to convert azido to amino functions in the presence of O-benzyl groups using H_2S as the reagent, we applied the protocol of Peters and Bundle [10]. When comparing the outcome of that conversion in higher oligosaccharides effected by the method of Lemieux and co-workers [11] or according to Garegg and co-workers [12] (treatment in pyridine–trimethylamine at 0 °C to room temperatures for a few h, the protocol we previously followed) with that applied by Peters and Bundle [10] (treatment in pyridine–water at 40 °C overnight), the latter method was found to be more efficient. While the former gave us satisfactory results with mono- or disaccharides [5], the relatively minor change in reaction conditions made a substantial difference in the case of higher oligosaccharides. Finally, while 4-*O*-benzyl-3-deoxy-L-*glycero*-tetronic acid showed itself [4,13] to be a more powerful reagent for 3-deoxy-L-*glycero*-tetronylation of perosamine derivatives than 3-deoxy-L-*glycero*-tetronolactone [14], the former gave a low yield of 3-deoxy-L-*glycero*-tetronamidation in the case of a dodecasaccharide. When we examined the efficacy of *N*-3-deoxy-L-*glycero*-tetronylation with 2,4-*O*-benzylidene-3-deoxy-L-*glycero*-tetronic acid (**39**) the desired tetronamides were obtained in consistently high yields. A brief outline of the syntheses of the title compounds, together with a few salient points, follows.



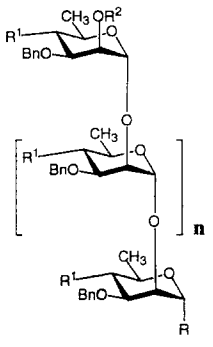
	R	R^1	R^2
1	H	OMe	H
2	H	OAc	Ac
3	OAc	H	Ac
4	H	SEt	Ac
5	H	SEt	OH
6	H	Cl	Ac

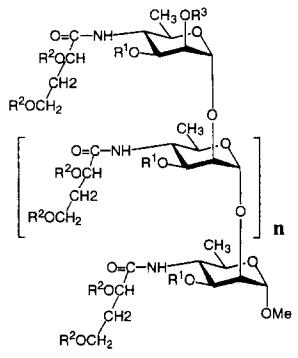


39

Acetolysis of the key monosaccharide intermediate **1** ([5,16] and papers cited therein), gave predominantly the α-acetyl derivative **2**. A small amount of the β-anomer **3** (previously unnoticed [8]) was also formed, as revealed by TLC. Both anomers were now obtained pure and fully characterized. Compounds **2** and **3** were converted [10] either to the thioglycoside **4** or to the glycosyl chloride **6** [5]. Condensation [5] of the glycosyl donor **6** with the glycosyl acceptor **5**, obtained by deacetylation of **4**, mediated by silver trifluoromethanesulfonate gave the disaccharide building block **7**. Oligosaccharides **9–12** were then assembled by reacting **1** or methyl 4-azido-2-*O*-(4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl)-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (**8**) [5] with **7**, or **7** with the requisite products **13** or **14**

(**1** + **7** → **9**, **7** + **8** → **10**, **7** + **13** → **11**, **7** + **14** → **12**). The coupling reactions were mediated by *N*-iodosuccinimide [17,18]. Deacetylation of **9–12** (Zemplén) then gave oligosaccharides **13-16** that were used to prepare haptens in the Inaba series. For the preparation of the penta- and the hexasaccharides in the Ogawa series, compounds **15** and **16** were methylated [19,20] to give **17** and **18**, respectively.





	R	R^1	R^2	n		R^1	R^2	R^3	n
7	SEt	N_3	Ac	0	25	Bn	PhCH<	H	1
8	OMe	N_3	H	0	26	Bn	PhCH<	H	2
9	OMe	N_3	Ac	1	27	Bn	PhCH<	H	3
10	OMe	N_3	Ac	2	28	Bn	PhCH<	H	4
11	OMe	N_3	Ac	3	29	Bn	PhCH<	Me	3
12	OMe	N_3	Ac	4	30	Bn	PhCH<	Me	4
13	OMe	N_3	H	1	31	H	H	H	1
14	OMe	N_3	H	2	32	H	H	H	2
15	OMe	N_3	H	3	33	H	H	H	3
16	OMe	N_3	H	4	34	H	H	H	4
17	OMe	N_3	Me	3	35	H	H	Me	3
18	OMe	N_3	Me	4	36	H	H	Me	4
19	OMe	NH_2	H	1	37	Bn	PhCH<	Ac	3
20	OMe	NH_2	H	2	38	Ac	Ac	Me	3
21	OMe	NH_2	H	3					
22	OMe	NH_2	H	4					
23	OMe	NH_2	OMe	3					
24	OMe	NH_2	OMe	4					

Next, the azido groups in compounds **13–18** were converted to amino groups (→ **19–24**, respectively). At this point, the utility of the new 3-deoxy-L-*glycero*-tetronylation reagent **39** [15] was tested in the reaction leading eventually to the known [6] trisaccharide in the Inaba series. Thus, reaction of **19** with **39**, mediated with 3-ethyl-1-(dimethylaminopropyl)carbodiimide (EDAC), followed by hydrogenolytic cleavage of benzyl and benzylidene groups in the product **25**, gave the deprotected methyl glycoside **31** in ~90% yield. The NMR characteristics found for the newly prepared substance were identical with those exhibited by the previously prepared [6] material and the specific optical rotation ($[\alpha]_D$ +4°) compared well with that reported ($[\alpha]_D$ +3.5°). Similar reactions of **20–24** with **39** (→ **26–30**, respectively), followed by hydrogenolysis, gave the target oligosaccharides **32–36**, respectively. We tried to obtain crystalline acetyl derivatives of **33** and **35**, but attempts to induce compounds **37** and **38** to crystallization failed.

3. Experimental

General methods.—Instruments and laboratory techniques used were the same as described previously in this series [6]. Unless stated otherwise, optical rotations were measured at ambient temperature for solutions in chloroform (*c* ~ 1), with a Perkin–Elmer automatic polarimeter, model 341. All reactions were monitored by thin-layer chromatography (TLC) on silica gel coated glass slides (Whatman or Analtech). Column chromatography was performed by gradient elution from columns of silica gel. Solvent mixtures slightly less polar than those used for TLC were used at the onset of development. Assignments of NMR signals were made by first-order analysis of the spectra, and by comparison with spectra of related substances reported previously in this series or elsewhere [10]. When the latter approach was used, to aid in the ^{13}C NMR signal–nuclei assignments, advantage was taken of variations of line intensity expected for oligosaccharides belonging to the same homologous series [21,22]. Thus, spectra showed close similarity of chemical shifts of equivalent carbon atoms of the internal residues, and an increase in the relative intensity of these signals with the increasing number of D-perosamine residues in the molecule. When feasible, the assignments were supported by homonuclear decoupling experiments or homonuclear and heteronuclear 2-dimensional correlation spectroscopy, run with the software supplied with the spectrometers. 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 indicates that those signals have not been individually assigned. Thus, for example, in a spectrum of a pen-

tasaccharide, a resonance denoted H-3 can be that of H-3 of either sugar residue. Palladium-on-charcoal catalyst (5%, ESCAT 103) was a product of Engelhard Industries.

General method for glycosylation with N-*iodosuccinimide / silver trifluoromethanesulfonate (NIS / AgOTf [18]).*—A mixture of the thioglycoside glycosyl donor (1.3 mmol), the glycosyl acceptor (1 mmol) and finely powdered 4 Å molecular sieves (0.5 g) in CH_2Cl_2 (10–15 mL, depending on the size of the glycosyl acceptor) was stirred under argon at 5–10 °C for 15 min. Solid NIS (1.4 mmol) was added, followed by a solution of AgOTf (0.4 mmol) in toluene (4 mL), and the mixture was stirred at the same temperature for 3 min. Cooling was terminated and, when TLC showed that the reaction was complete (~ 15 min), the mixture was neutralized with Et_3N, washed successively with aq $NaHCO_3$, to remove succinimide, and water, dried, and concentrated. Chromatography gave the desired products consistently in 85–95% yields.

General procedure for azido → amino conversions.—Hydrogen sulfide was passed, for 30 min at 40 °C, through a solution of an azido derivative in pyridine–water (2:1, v/v, 5 mL/100 mg). The mixture was kept at 40 °C in a loosely closed flask overnight when TLC showed that the starting material was no longer present, and that one, largely predominating product was formed. After concentration, the mixture was chromatographed, using for column preparation and elution a CH_2Cl_2–MeOH mixture of appropriately adjusted polarity containing ~ 1% of concentrated aqueous ammonia. The use of ammonia considerably reduced tailing. The desired products were obtained in 80–90% yields.

*General procedure for amidation with 2, 4-O-benzylidene-3-deoxy-*L-glycero-*tetronic acid* (**39**).—To a solution of carbohydrate amine (1 mmol) and **39** (1.2 equiv/amino group to be derivatized) in dichloromethane (10 mL) was added, dropwise and with stirring at room temperature, a suspension of EDAC (1.2 equiv/amino group to be derivatized) in dichloromethane (~ 3–5 mL). Stirring was continued and, after some time, a precipitate formed indicating progress of the reaction. When the conversion was complete (TLC), the mixture was filtered, the filtrate was concentrated, and chromatography of the residue gave the desired product in 80–90% yield.

*1,2-Di-*O*-acetyl-4-azido-3-*O*-benzyl-4,6-dideoxy-α-(2) and β-*D*-mannopyranose* (**3**).—Acetolysis of the methyl glycoside **1** was performed as described by Bundle et al. [8]. Chromatography yielded first the α-anomer (**2**, ~ 90%): $[\alpha]_D$ 111° (*c* 1.3, CH_2Cl_2); $[\alpha]_D$ +105.6° (*c* 1.7); ref. [8] $[\alpha]_D$ +89° (*c* 1, CH_2Cl_2). The ^1H NMR data agreed with those reported [8]. ^{13}C NMR ($CDCl_3$): δ 91.02 (C-1), 75.72 (C-3), 71.75 (CH_2Ph), 69.24 (C-5), 66.20 (C-2), 63.47 (C-4), 20.71, 20.63 (2 $COCH_3$), 18.37 (C-6). Anal. Calcd for $C_{17}H_{21}N_3O_6$: C, 56.20; H, 5.79; N, 11.57. Found: C, 56.07; H, 5.79; N, 11.50.

Eluted next was the β-anomer (**3**, ~ 5%), $[\alpha]_D$ +42.5° (*c* 1.4), $[\alpha]_D$ +45° (*c* 1.2, CH_2Cl_2); ^1H NMR ($CDCl_3$): δ 5.68 (d, 1 H, $J_{1,2}$ 1.3 Hz, H-1), 5.59 (dd, 1 H, $J_{2,3}$ 3.2 Hz, H-2), 4.72, 4.51 (2 d, 1 H each, ^2J 11.2 Hz, 2 CH_2Ph), 3.58 (dd, 1 H, $J_{3,4}$ 9.5 Hz, H-3), 3.42 (t, 1 H, H-4), 3.32 (m, 1 H, H-5), 2.19, 2.09 (2 s, 3 H each, 2 $COCH_3$), 1.40 (d, 3 H, $J_{5,6}$ 5.9 Hz, H-6); ^{13}C NMR ($CDCl_3$): δ 90.89 ($J_{C,H}$ 160.2 Hz, C-1), 78.04 (C-3), 72.04 (C-5), 71.5 (CH_2Ph), 66.31 (C-2), 63.30 (C-4), 20.83, 20.71 (2 $COCH_3$), 18.35 (C-6). Anal. Calcd for $C_{17}H_{21}N_3O_6$: C, 56.20; H, 5.79; N, 11.57. Found: C, 56.07; H, 5.88; N, 11.51.

*Ethyl 2-*O*-acetyl-4-azido-3-*O*-benzyl-4,6-dideoxy-1-thio-α-*D*-mannopyranoside* (**4**).—This compound was prepared as described by Peters and Bundle [10]. ^1H NMR data agreed with those reported. ^{13}C NMR ($CDCl_3$): δ 82.31 (C-1), 76.44 (C-3), 71.65 (CH_2Ph), 69.28 (C-2), 67.51 (C-5), 64.31 (C-4), 25.58 (SCH_2), 20.97 ($COCH_3$), 18.37 (C-6), 14.83 (CH_2CH_3).

*Ethyl 4-azido-3-*O*-benzyl-4,6-dideoxy-1-thio-α-*D*-mannopyranoside* (**5**).—This compound was prepared from **4**, as described by Peters and Bundle [10]. ^1H NMR data agreed with those reported. ^{13}C NMR ($CDCl_3$): δ 83.06 (C-1), 76.57 (C-3), 72.09 (CH_2Ph), 68.77 (C-2), 67.05 (C-5), 64.25 (C-4), 24.99 (SCH_2), 18.31 (C-6), 14.79 (CH_2CH_3).

*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-1-thio-α-*D*-mannopyranoside* (**7**).—This compound was prepared from **5** as described by Peters and Bundle [10], except that glycosyl chloride **6** [5] was used as the glycosyl donor. The NMR spectral data observed for the compound, obtained in 91% yield, agreed with those reported [10].

*Methyl 4, 6-dideoxy-4-(3-deoxy-*L*-glycero-tetronamido)-α-*D*-mannopyranosyl-(1 → 2)-4, 6-dideoxy-4-(3-deoxy-*L*-glycero-tetronamido)-α-*D*-mannopyranosyl-(1 → 2)-4,6-dideoxy-4-(3-deoxy-*L*-glycero-tetronamido)-α-*D*-mannopyranoside* (**31**).—Methyl 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-mannopyranoside (**9**)

was prepared by *NIS/AgOTf* glycosylation from **4** and **8** [5] as described above. The ^{1}H NMR spectral data agreed with those reported [8]. ^{13}C NMR ($CDCl_3$): δ 100.26, 99.79 (C-$1^{I,II}$), 99.09 (C-1^{III}), 77.50 (C-3^{I}), 76.77 (C-3^{II}), 75.42 (C-3^{III}), 73.40 (2 C, C-$2^{I,II}$), 72.06 (2 C), 71.52 (3 CH_2Ph), 67.71, 67.56, 67.05, 66.89 (C-2^{III},5^{I-III}), 64.29, 63.94, 63.70 (C-4^{I-III}), 20.86 ($COCH_3$), 18.48 (2 C), 18.22 (C-6^{I-III}).

The foregoing compound **9** was deacetylated (Zemplén), to give methyl (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 (**13**) in virtually theoretical yield. The ^{1}H NMR data agreed with those reported [10]. ^{13}C NMR ($CDCl_3$): δ 100.45, 100.40 (C-$1^{II,III}$), 99.77 (C-1^{I}), 77.61, 77.46, 76.57 (C-3^{I-III}), 73.61 (C-2^{I}), 73.31 (C-2^{II}), 72.12, 72.09, 72.03 (3 CH_2Ph), 67.74 (C-2^{III}), 64.33, 64.14, 63.78 (C-4^{I-III}), 54.86 (OCH_3), 18.60, 18.54, 18.25 (C-6^{I-III}).

Compound **13** (350 mg, 0.43 mmol) was treated with H_2S as described above, to give methyl (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-amino-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (**19**). ^{1}H NMR ($CDCl_3$): δ 5.09, 4.99 (2 d, 1 H each, $J_{1,2}$ 1.9 and 1.7 Hz, respectively, H-$1^{II,III}$), 4.68–4.37 (7 H, 3CH_2Ph, incl d at 4.67 for H-1^{I}), 4.07–4.04 (m, 2 H, H-$2^{II,II}$), 3.85 (dd, 1 H, $J_{1,2}$ 1.9, $J_{2,3}$ 2.9 Hz, H-2^{I}), 3.65–3.54 (m, 6 H, H-3^{I-III},5^{I-III}), 3.31 (s, 3 H, OCH_3), 2.83 (m, 3 H, H-4^{I-III}), 1.63 (bs, 6 H, 3 NH_2), 1.21, 1.16 (2 d, 9 H, H-6^{I-III}); ^{13}C NMR ($CDCl_3$): δ 101.13, 100.94 (C-$1^{II,III}$), 100.30 (C-1^{I}), 79.60, 79.17, 79.03 (C-3^{I-III}), 72.84 (C-2^{II}), 72.68 (C-2^{I}), 71.41, 71.15 (2 C, 3 CH_2Ph), 70.20, 69.55, 69.44 (C-5^{I-III}), 66.42 (C-2^{III}), 54.62 (OCH_3), 53.64, 53.60, 53.23 (C-4^{I-III}), 18.21, 18.13, 17.93 (C-6^{I-III}); CIMS: *m/z* 738 ([M + 1]$^+$).

The foregoing compound **19** (130 mg, 0.18 mmol) was treated with **39** as described in the general procedure for amidation, to give methyl 3-*O*-benzyl-4-(2,4-*O*-benzylidene-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-3-*O*-benzyl-4-(2,4-*O*-benzylidene-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-3-*O*-benzyl-4-(2,4-*O*-benzylidene-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranoside (**25**, 184 mg, 82%): $[\alpha]_D$ −21° (*c* 1.2); ^{1}H NMR ($CDCl_3$): δ 6.33 (bd, 1 H, NH), 6.22 (bd, 2 H, 2 NH), 5.54 (s, 1 H, C*H*Ph), 5.51 (s, 2 H, 2 C*H*Ph), 5.02, 5.00 (2 d, 1 H each, $J_{1,2}$ 1.4 and 1.9 Hz, respectively, H-$1^{II,III}$), 4.67–4.47 (m, 7 H, 3 CH_2Ph, incl d at 4.55 for H-1^{I}), 4.39–3.66 (m, ring protons, incl m at ~4.32 for H-$2'^{I-III}$, m at ~4.17 for H-$2^{II,III}$, m at ~4.10 for 2 H-4, m at ~3.90 for H-2^{I}, m at ~3.86 for H-4, and m at ~3.70 for H-3^{I-III},5^{I-III}), 3.26 (s, 3 H, OCH_3), 2.06–1.78 (m, 6 H, H-$3'^{I-III}$), 1.18, 1.16, 1.08 (3 d, 3 H each, $J_{5,6}$ ~6.2 Hz, H-6^{I-III}); ^{13}C NMR ($CDCl_3$): δ 101.27, 101.19, 101.04 (3 *C*HPh), 100.97 (C-1^{III}), 100.42 (C-1^{II}), 100.02 (C-1^{I}), 76.57 (2 C), 76.36 (C-$2'^{I-III}$), 75.86, 75.33, 75.12 (C-3^{I-III}), 73.87, 72.80 (C-$2^{I,II}$), 71.50, 71.45, 71.14 (3 CH_2Ph), 68.56, 67.89, 67.29 (C-5^{I-III}), 67.19 (3 C, C-$4'^{I-III}$), 66.79 (C-2^{III}), 54.78 (OCH_3), 52.37, 51.70, 51.27 (C-4^{I-III}), 28.53 (2 C), 28.44 (C-$3'^{I-III}$), 18.08, 17.91, 17.73 (C-6^{I-III}). Anal. Calcd for $C_{73}H_{85}N_3O_{19}$: C, 67.01; H, 6.55; N, 3.21. Found: C, 67.15; H, 6.59; N, 3.17.

A mixture of compound **25** (236 mg) and palladium-on-charcoal catalyst (150 mg) in methanol (15 mL) was stirred in a hydrogen atmosphere until TLC showed that the reaction was complete. After processing and chromatography, a solution of the product in water was filtered through an Anotop 10 Plus 0.1-μm syringe filter and freeze-dried, to give the pure (TLC, NMR), hygroscopic compound **31** (124 mg, 89%): $[\alpha]_D$ +4° (*c* 1, H_2O); ref. [6], $[\alpha]_D$ +3.5° (*c* 0.7, H_2O); the NMR data were identical with those reported previously [6]. FABMS: *m/z* 774 ([M + 1]$^+$) and 796 ([M + Na]$^+$).

Methyl 4, 6 - dideoxy - 4 - (3 - deoxy - L - glycero - *tetronamido)* - α - D - *mannopyranosyl-(1 → 2)-bis[4,6-dideoxy-4-[(3-deoxy* - L - glycero - *tetronamido)* - α - D - *mannopyranosyl)-(1 → 2)]-4,6-dideoxy-4-(3-deoxy* - L - glycero - *tetronamido)* - α - D - *mannopyranoside* (**32**).— Methyl 2-*O*-acetyl-4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-bis[4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]-4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (**10**) was made by *NIS/AgOTf* glycosylation of **7** and **8**, as described above. The ^{1}H NMR spectral data agreed with those reported [8]. ^{13}C NMR ($CDCl_3$): δ 100.35, 100.06, 99.72 (C-1^{I-III}), 99.09 (C-1^{IV}), 77.42 (C-3^{I}), 76.79, 76.57 (C-$3^{II,III}$), 75.40 (C-3^{IV}), 73.50, 73.38 (2 C, C-2^{I-III}), 72.16, 72.07, 71.99, 71.48 (4 CH_2Ph), 67.74 (2 C), 67.57, 67.02, 66.85 (C-5^{I-IV},2^{IV}), 64.25, 64.16, 63.95, 63.74 (C-4^{I-IV}), 54.82 (OCH_3), 20.86 ($COCH_3$), 18.51 (2 C), 18.34, 18.26 (C-6^{I-IV}).

Deacetylation of **10** (Zemplén) gave methyl 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-bis[4-azido-3-*O*-benzyl-4,6- dideoxy-α-D-mannopyranosyl-(1 → 2)]-4-azido-3-*O*-benzyl-4,6-di-

deoxy-α-D-mannopyranoside (**14**) in theoretical yield. The ^{1}H NMR spectral data agreed with those reported [8]. ^{13}C NMR ($CDCl_3$): δ 100.43 (C-1^{IV}), 100.31, 100.18 (C-$1^{II,III}$), 99.68 (C-1^{I}), 77.58, 77.38, 76.87, 76.49 (C-3^{I-IV}), 73.46 (2 C), 73.08 (C-2^{I-III}), 72.12, 71.95 (3 C, 4CH_2Ph), 67.70 (2 C), 67.28, 67.02, 66.81 (C-2^{IV},5^{I-IV}), 64.20, 64.08 (2 C), 63.70 (C-4^{I-IV}), 54.78 (OCH_3), 18.42 (2 C), 18.34, 18.17 (C-6^{I-IV}).

Treatment of **14** (450 mg), as described above for other azido → amino conversions, gave methyl 4-amino-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-bis[4-amino-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]-4-amino-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (**20**, 334 mg, 82%). ^{1}H NMR ($CDCl_3$): δ 5.10 (2 d, partially overlapped, 2 H, H-$1^{II,III}$), 5.00 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1^{IV}), 4.70–4.63 (m, 5 H, 2 CH_2Ph, incl signal for H-1^{I} at 4.67), 4.50–4.37 (4 d, partially overlapped, 4 H, 2 CH_2Ph), 4.08–4.03 (m, 3 H, H-2^{II-IV}), 3.96 (bt, 1 H, H-2^{I}), 3.66–3.41 (m, 8 H, H-4^{I-IV},5^{I-IV}), 3.32 (s, 3 H, OCH_3), 1.47 (bs, 8 H, 4 NH_2), 1.26, 1.25, 1.17, 1.15 (4 d, 12 H, partially overlapped, $J_{5,6}$ ~ 6.2 Hz, H-6^{I-IV}); ^{13}C NMR ($CDCl_3$): δ 101.07 (C-1^{IV}), 100.84, 100.76 (C-$1^{II,III}$), 100.17 (C-1^{I}), 79.52, 78.55 (C-$3^{I,IV}$), 79.10, 79.03 (C-$3^{II,III}$), 72.97, 72.67 (C-2^{II-III}), 72.47 (C-2^{I}), 71.19, 71.03, 70.99, 70.92 (4 CH_2Ph), 70.13 (2 C), 69.52, 69.34 (C-5^{I-IV}), 66.26 (C-2^{IV}), 54.46 (OCH_3), 53.52 (2 C), 53.47, 53.11 (C-4^{I-V}), 18.07 (2 C), 18.01, 17.81 (C-6^{I-IV}); FABMS: *m/z* 973 ($[M + 1]^+$).

Condensation of **20** (334 mg) with **39**, as described above, gave methyl 3-*O*-benzyl-(2,4-*O*-benzylidene-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-bis[3-*O*-benzyl-4-(2,4-*O*-benzylidene-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]-3-*O*-benzyl-(2,4-*O*-benzylidene-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranoside (**26**, 480 mg 81%): $[\alpha]_D$ −32° (*c* 1.2). Definite signals in the ^{1}H NMR spectrum ($CDCl_3$) were at δ 6.45, 6.31, 6.23, 6.19 (4 d, 4 H, $J_{4,NH}$ ~ 10 Hz, 4 NH), 5.53 (s, 2 H, 2 C*H*Ph), 5.52, 5.51 (2 s, 2 H, 2 C*H*Ph), 5.02, 5.01, 4.93 (3 bd, 1 H each, H-1^{II-IV}), 4.68–4.41 (m, 9 H, 4 CH_2Ph, incl signal for H-1^{I} at ~ 4.55), 4.18–4.15 (m, 2 H, H-2,2^{IV}), 3.79–3.61 (8 H, H-3^{I-IV},5^{I-IV}), 3.25 (s, 3 H, OCH_3), 2.10–1.80 (m, 8 H, H-$3'^{I-IV}$a,b), 1.18–1.03 (4 d, partially overlapped, 12 H, $J_{5,6}$ ~ 6.2 Hz, H-6^{I-IV}); ^{13}C NMR ($CDCl_3$): δ 101.26, 101.17, 101.09 (2 C, 4 *C*HPh), 100.81 (C-1^{IV}), 100.34 (C-$1^{II,III}$), 99.90 (C-1^{I}), 76.54 (2 C), 76.47, 76.38 (C-$2'^{I-IV}$), 75.91 (C-3^{IV}), 75.26, 75.09, 74.65 (C-3^{I-III}), 73.58 (C-2^{I}), 73.05, 72.94 (C-$2^{II,III}$), 71.34 (2 C), 71.25, 71.17 (4 CH_2Ph), 68.54, 68.49, 67.92, 67.36 (H-5^{I-IV}), 67.19 (4 C, H-$4'^{I-IV}$), 66.84 (C-2^{IV}), 54.81 (OCH_3), 52.17, 51.73 (2 C), 51.27 (C-4^{I-IV}), 28.51 (4 C, C-$3'^{I-IV}$), 18.01, 17.97, 17.90, 17.77 (C-6^{I-IV}); FABMS: *m/z* 1733 ($[M + 1]^+$), 1755 ($[M + Na]^+$). Anal. Calcd for $C_{97}H_{112}N_4O_{25}$: C, 67.19; H, 6.51; N, 3.23. Found: C, 67.24; H, 6.52; N, 3.22.

Catalytic hydrogenolyis of **26**, as described above, gave the pure (TLC, NMR), title substance **32** in virtually theoretical yield: $[\alpha]_D$ +4.3° (*c* 1.0, H_2O); ^{1}H NMR (D_2O): δ 5.17, 5.15 (2 d, 1 H each, $J_{1,2}$ 1.4 Hz, H-$1^{II,III}$), 5.04 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1^{IV}), 4.78 (d, 1 H, $J_{1,2}$ 1.4 Hz, H-1^{I}), 4.32–4.26 (m, 4 H, H-$2'^{I-IV}$), 4.18–4.13 (m, 4 H, 2 H-2, 2 H-3), 4.12–4.10 (dd, 1 H, $J_{2,3}$ 3.3 Hz, H-2^{IV}), 4.05–4.00 (m, 2 H, 2 H-3), 3.98–3.84 (m, 9 H, H-2,4^{I-IV},5^{I-IV}), 3.76–3.70 (m, 8 H, H-$4'^{I-IV}$a,b), 3.39 (s, OCH_3), 2.10–1.98, 1,90–1.78 (2 m, 4 H each, H-$3'^{I-IV}$a,b), 1.25–1.14 (m, 12 H, H-6^{I-IV}); ^{13}C NMR (D_2O): δ 102.27 (C-1^{IV}), 100.89, 100.82 (C-$1^{II,III}$), 99.72 (C-1^{I}), 77.55, 77.40, 77.25 (C-2^{I-III}), 69.21 (C-2^{IV}), 69.06 (C-$2'^{I-IV}$), 68.36 (2 C), 68.14, 67.85, 67.75, 67.54 (3 C, C-3^{I-IV},5^{I-IV}), 57.92 (C-$4'^{I-IV}$), 54.98 (OCH_3), 53.11, 53.10 (2 C), 52.82 (C-4^{I-IV}), 36.03 (C-$3'^{I-IV}$), 16.87 (6 C, C-6^{I-IV}); FABMS: *m/z* 1021 ($[M + 1]^+$), 1043 ($[M + Na]^+$).

Methyl 4, 6 - dideoxy - 4 - (3 - deoxy - L - glycero - *tetronamido)-α-D-mannopyranosyl-(1 → 2)-tris[4,6-dideoxy-4-(3-deoxy*-L-glycero-*tetronamido)-α-D-mannopyranosyl-(1 → 2)]-4,6-dideoxy-4-(3-deoxy*-L-glycero-*tetronamido)-α-D-mannopyranoside* (**33**).— Methyl 2-*O*-acetyl-4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-tris[4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]-4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (**11**) was prepared from **7** and **9** as described above. The ^{1}H NMR data agreed with those reported [10]. ^{13}C NMR ($CDCl_3$): δ 100.28, 100.12, 100.00, 99.68 (C-1^{I-IV}), 99.05 (C-1^{V}), 77.39 (C-3^{I}), 76.74, 76.57 (2 C, C-3^{II-IV}), 75.33 (C-3^{V}), 73.51 (2 C), 73.32 (2 C, C-2^{I-IV}), 72.10 (3 C), 71.95, 71.44 (5 CH_2Ph), 67.71 (3 C), 67.45, 67.10, 66.81 (C-2^{V},5^{I-V}), 64.22, 64.05 (2 C), 63.91, 63.67 (C-4^{I-V}), 54.76 (OCH_3), 20.80 ($COCH_3$), 18.40 (2 C), 18.30 (2 C), 18.21 (C-6^{I-V}).

Deacetylation (Zemplén) of **11** gave in virtually theoretical yield methyl 4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-tris[4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]-4-azido-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (**15**), whose ^{1}H NMR data agreed with those reported

[10]. ^{13}C NMR ($CDCl_3$): δ 100.43 (C-1^{V}), 100.25, 100.14, 100.10 (C-1^{II-IV}), 99.68 (C-1^{I}), 77.55, 77.40 (C-$3^{I,V}$), 76.86, 76.48 (2 C, C-3^{II-IV}), 73.64, 73.56 (C-$2^{I,IV}$), 73.44 (C-2^{III}), 73.21 (C-2^{II}), 72.11 (2 C), 72.05 (2 C), 71.96 (5 CH_2Ph), 67.76 (2 C), 67.71, 67.31, 66.87 (C-5^{I-V}), 67.09 (C-2^{V}), 64.30, 64.14 (3 C, C-4^{I-IV}), 63.76 (C-4^{V}), 54.80 (OCH_3), 18.54, 18.49, 18.44, 18.42, 18.23 (C-6^{I-V}).

The foregoing compound **15** (480 mg) was treated with H_2S as described for the preparation of **19** to give **21** (380 mg, 88%). FABMS: *m/z* 1208 ([M + 1]$^+$), 1340 ([M + Cs]$^+$).

Compound **21** (380 mg) was treated with **39** as described for the preparation of **25** to give methyl 3-*O*-benzyl-(2,4-*O*-benzylidene-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-tris[3-*O*-benzyl-4-(2,4-*O*-benzylidene-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]-3-*O*-benzyl-(2,4-*O*-benzylidene-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranoside (**27**, 530 mg, 78%): $[\alpha]_D$ −32°; ^{1}H NMR ($CDCl_3$): δ 6.5–6.16 (5 d, partially overlapped, $J_{4,NH}$ ~ 9.0 Hz, 5 NH), 5.55, 5.53, 5.52, 5.50 (4 s, 5 H total, 5 C*H*Ph), 5.51–5.50 (2 d, 2 H, partially overlapped, H-1,1^{V}), 4.97, 4.95 (2 d, 1 H, each, 2 H-1), 4.68–4.20 (m, 16 H, 5 CH_2Ph, H-$2'^{I-V}$, incl bd for H-1^{I} at ~ 4.53), 4.17–3.80 (m, 20 H, H-2^{II-IV},4^{I-V},$4'^{I-V}$, incl m at ~ 4.15 for H-2^{V}, and bt at ~ 3.85 for H-2^{I}), 3.75–3.55 (m, 10 H, H-3^{I-V},5^{I-V}), 3.25 (s, 3 H, OCH_3), 2.08–1.80 (m, 10 H, H-$3'^{I-V}$), 1.12–1.02 (5 d, partially overlapped, 15 H, H-6^{I-V}); ^{13}C NMR ($CDCl_3$): δ 101.24, 101.18 (3 C), 101.14 (5 *C*HPh), 100.89 (C-1^{V}), 100.35 (2 C), 100.26 (C-1^{II-IV}), 99.94 (C-1^{I}), 76.58 (4 C), 76.43 (C-$2'^{I-V}$), 76.03 (C-3^{V}), 75.25, 75.18, 74.77, 74.57 (C-3^{I-IV}), 73.75 (C-2^{I}), 73.00 (2 C), 72.79 (C-2^{II-IV}), 71.42, 71.28, 71.20 (3 C, 5 CH_2Ph), 68.60 (2 C), 68.51, 67.98, 67.41 (C-5^{I-V}), 67.22 (5 C, C-$4'^{I-V}$), 66.88 (C-2^{V}), 54.84 (OCH_3), 52.16, 51.88, 51.83, 51.64, 51.27 (C-4^{I-V}), 28.54 (C-$3'^{I-V}$), 18.04 (2 C), 17.97, 17.95, 17.18 (C-6^{I-V}); FABMS: *m/z* 2158 ([M + 1]$^+$), 2180 ([M + Na]$^+$). Anal. Calcd for $C_{121}H_{139}N_5O_{31}$: C, 67.32; H, 6.44; N, 3.25. Found: C, 67.35; H, 6.48; N, 3.13.

The foregoing compound gave the amorphous 2^{V}-*O*-acetyl derivative, methyl 2-*O*-acetyl-3-*O*-benzyl-(2,4-*O*-benzylidene-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-tris[3-*O*-benzyl-4-(2,4-*O*-benzylidene-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]-3-*O*-benzyl-(2,4-*O*-benzylidene-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranoside (**37**). Definite signals in the ^{1}H NMR ($CDCl_3$) spectrum were at: δ 6.44–6.16 (m, 5 H, 5 NH), 5.55, 5.54, 5.52, 5.50 (4 s, 5 H, 5 C*H*Ph), 5.46 (bt, 1 H, H-2^{V}), 5.02, 4.95, 4.92, 4.80 (4 bd, 1 H each, H-1^{II-V}), 4.58–5.52 (m, 11 H, H-1^{I}, 5 CH_2Ph), 3.25 (s, 3 H, OCH_3), 2.08 (s, overlapped, $COCH_3$), 2.08–1.80 (m partially overlapped, H-$3'^{I-V}$), 1.25–1.04 (5 d, 15 H, partially overlapped, H-6^{I-V}); ^{13}C NMR ($CDCl_3$): δ 101.30, 101.23 (4 C, 5 *C*HPh), 100.91, 100.46, 100.21 (C-1^{II-IV}), 99.97 (C-1^{I}), 99.26 (C-1^{V}), 76.68 (2 C), 76.61, 76.57, 76.50 (C-$2'^{I-V}$), 75.23, 74.99, 74.82, 74.59 (C-3^{I-IV}), 73.97, 73.82 (3 C), 73.09, 72.92 (C-2^{I-IV},3^{V}), 71.42, 71.38, 71.26, 71.22, 71.12 (5 CH_2Ph), 68.66, 68.62, 68.55, 68.43, 67.46 (2 C, C-5^{I-V}, incl C-2^{V} at 67.46), 67.28 (5 C, C-$4'^{I-V}$), 54.89 (OCH_3), 52.21 (2 C), 51.94, 51.78, 51.71 (C-4^{I-V}), 28.57 (5 C, C-$3'^{I-V}$), 21.07 $COCH_3$), 18.08 (2 C), 17.98 (3C, C-6^{I-V}).

Hydrogenolysis of compound **27** (104 mg), as described above, gave pure (TLC, NMR) **33** (56 mg, 91%), $[\alpha]_D$ +2.2° (*c* 1.0, H_2O); ^{1}H NMR (D_2O, 60°C): δ 5.15–5.13 (m, 3 H, H-1^{II-IV}), 5.03 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1^{V}), 4.77 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1^{I}), 4.32–4.26 (m, 5 H, H-$2'^{I-V}$), 3.75–3.69 (m, 10 H, H-$4'^{I-V}$a,b), 3.38 (s, 3 H, OCH_3), 2.08, 1.75 (2 m, 10 H, H-$3'^{I-V}$a,b), 1.18–1.12 (m, 15 H, H-6^{I-V}); ^{13}C NMR (D_2O): δ 102.20 (C-1^{V}), 100.80 (3 C, C-1^{II-IV}), 99.68 (C-1^{I}), 77.49, 77.37, 77.32, 77.20 (C-2^{I-IV}), 69.21 (C-2^{V}), 69.09 (5 C, C-$2'^{I-V}$), 68.34 (3 C), 68.13, 67.88, 67.78, 67.54 (4 C, C-3^{I-V}, 5^{I-V}), 57.95 (5 C, C-$4'^{I-V}$), 54.98 (OCH_3), 53.06 (4 C), 52.83 (C-4^{I-V}), 36.07 (5 C, C-$3'^{I-V}$), 16.94 (5 C, C-6^{I-V}); FABMS: *m/z* 1268 ([M + 1]$^+$), 1290 ([M + Na]$^+$).

Methyl 4-azido-3-O-benzyl-4,6-dideoxy-2-O-methyl-α-D-mannopyranosyl-(1 → 2)-tris[4-azido-3-O-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]-4-azido-3-O-benzyl-4,6-dideoxy-α-D-mannopyranoside (**17**).—Iodomethane (35 μL, 0.56 mmol, 1.5 equiv) was added to a suspension of the pentasaccharide **15** (0.5 g, 0.37 mmol) and powdered KOH (62 mg, 3 equiv) in Me_2SO (5 mL), and the mixture was stirred at room temperature until TLC showed that the reaction was complete (~ 1 h). After filtration through a sintered glass funnel, the filtrate was neutralized with aqueous AcOH and partitioned between water and CH_2Cl_2. The organic phase was dried and concentrated, and the residue was chromatographed to give **17** (450 mg, 89%): $[\alpha]_D$ +80° (*c* 1.2), ^{1}H NMR ($CDCl_3$): δ 4.91 (bd, 2 H, 2 H-1, incl H-1^{V}), 4.89, 4.87 (2 d, 1 H each, $J_{1,2}$ 1.8 Hz, 2 H-1), 4.75–4.53 (m, 10 H, 5 CH_2Ph), 4.51 (d, 1 H, $J_{1,2}$1.8 Hz, H-1^{I}), 3.96, 3.84, 3.81 (3 dd, 4 H, H-2^{I-IV}),

3.72–3.64 (m, 5 H, H-3^{I-V}), 3.50–3.16 (m, 17 H, H-4^{I-V},5^{I-V}, incl m at ~ 3.39 for H-2^{V}, 2 s at 3.27 and 3.20 for OCH_3-2^{V} and OCH_3-1^{I}), 1.29–1.14 (5 d, 15 H, partially overlapped, H-6^{I-V}); ^{13}C NMR ($CDCl_3$): δ 100.22, 100.15, 100.10 (C-1^{II-IV}), 99.65 (C-1^{I}), 98.70 (C-1^{V}), 77.41, 77.35, 77.07, 76.56, 76.48 (C-3^{I-V}), 76.28 (C-2^{V}), 73.55, 73.53, 73.20, 73.10 (C-2^{I-IV}), 72.26, 72.10 (2 C), 72.03, 71.93 (5 CH_2Ph), 67.76 (2 C), 67.69 (2 C), 66.84 (C-5^{I-V}), 64.24 (2 C), 64.10 (2 C), 64.02 (C-4^{I-V}), 58.80 (OCH_3-2^{V}), 54.78 (OCH_3-1^{I}), 18.50, 18.46, 18.39 (2 C), 18.31 (C-6^{I-V}); FABMS: *m/z* 1484 ([M + Cs]$^+$). Anal. Calcd for $C_{67}H_{81}N_{15}O_{16}$: C, 59.49; H, 6.04; N, 15.54. Found: C, 59.24; H, 6.05; N, 15.44.

*Methyl 2-O-methyl-3-O-benzyl-(2,4-O-benzylidene-3-deoxy-*L-glycero*-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)-tris[3-O-benzyl-4-(2,4-O-benzylidene-3-deoxy-*L-glycero*-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]-3-O-benzyl-(2,4-O-benzylidene-3-deoxy-*L-glycero*-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**29**).—Compound **17** (385 mg) was treated with H_2S, as described above, to give methyl 4-amino-3-*O*-benzyl-4,6-dideoxy-2-*O*-methyl-α-D-mannopyranosyl-(1 → 2)-tris[4-amino-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]-4-amino-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (**23**, 310 mg, 87%); ^1H NMR ($CDCl_3$): δ 5.10, 5.06, 4.99 (bd, 2 H, 2 bd 1 H each, H-1^{II-V}), 4.72–4.39 (m, 11 H, H-1^{I}, 5 CH_2Ph), 4.09, 4.05 (bt, 1 H, bs, 2 H, H-2^{II-IV}), 3.96 (bt, 1 H, H-2^{I}), 3.67–3.40 (m, 11 H, H-2^{V},3^{I-V},5^{I-V}), 3.32, 3.28 (2 s, 3 H each, 2 OCH_3), 2.93–2.82 (m, 5 H, H-4^{I-V}), 1.28–1.15 (m, 15 H, H-6^{I-V}); ^{13}C NMR ($CDCl_3$): δ 100.91, 100.84, 100.76 (C-1^{II-IV}), 100.20 (C-1^{I}), 99.03 (C-1^{V}), 79.43, 79.11, 79.00, 78.61, 78.50 (C-3^{I-V}), 75.72 (C-2^{V}), 72.97, 72.92, 72.54, 72.46 (C-2^{I-IV}), 71.50, 71.15, 71.02 (3 C, 5 CH_2Ph), 70.17 (4 C), 69.39 (C-5^{I-V}), 58.72 (OCH_3-2^{V}), 54.51 (OCH_3-1^{I}), 53.70, 53.51(2 C), 53.46 (2 C, C-4^{I-V}), 18.10 (3 C), 18.04, 17.94 (C-6^{I-V}); FABMS: *m/z* 1222 ([M + 1]$^+$).

Treatment of amine **23** (300 mg) with **39**, as described above, gave the title fully protected compound **29** (440 mg, 82.5%): $[\alpha]_D$ −29° (*c* 1.2), ^1H NMR ($CDCl_3$): δ 6.42, 6.30, 6.25, 6.19, 6.18 (5 bd, partially overlapped, 5 NH), 5.54, 5.52, 5.50 (3 s, 5 H, 5 C*H*Ph), 5.00 (d, 1H, $J_{1,2}$ 1.4 Hz, H-1^{V}), 4.97, 4.92 (bs, 2 H, d, 1 H, $J_{1,2}$ 1.4 Hz, H-1^{II-IV}), 4.70–4.24 (m, 16 H, m, 5 CH_2Ph, H-$2'^{I-V}$, incl H-1^{I} at 4.53), 4.20–3.84 (m, 9 H, H-2^{II-IV},4^{I-V}, incl bt for H-2^{I} at 3.86), 3.82–3.58 (m, 16 H, H-3^{I-V},$4'^{I-V}$, incl m for H-2^{V} at 3.68), 3.26 (s, 3 H, OCH_3-2^{V}), 3.24 (s, 3 H, OCH_3-1^{I}), 2.06–1.80 (m, 10 H, H-$3'^{I-V}$), 1.16–1.03 (5 d, 15 H, partially overlapped, H-6^{I-V}); ^{13}C NMR ($CDCl_3$): δ 101.14 (3 C), 101.06 (2 C, 5 *C*HPh), 100.75, 100.29 (2 C, C-1^{II-IV}), 99.84 (C-1^{I}), 99.05 (C-1^{V}), 76.53 (3 C), 76.44, 76.34 (C-$2'^{I-V}$), 75.75 (2 C), 75.48, 75.14, 74.65, 74.45 (C-3^{I-V},2^{V}), 73.62 (C-2^{I}), 72.88 (2 C), 72.78 (C-2^{II-IV}), 71.84, 71.13 (2 C), 71.05, 70.94 (5 CH_2Ph), 68.53 (2 C), 68.48 (2 C), 67.37 (C-5^{I-V}), 67.14 (5 C, C-$4'^{I-V}$), 58.90 (OCH_3-2^{V}), 54.77 (OCH_3-1^{I}), 52.03, 51.95, 51.70 (2 C), 51.56 (C-4^{I-V}), 28.45 (5 C, C-$3'^{I-V}$), 17.97, 17.89 (4 C, C-6^{I-V}); FABMS: *m/z* 2172 ([M + 1]$^+$). Anal. Calcd for $C_{122}H_{141}N_5O_{31}$: C, 67.43; H, 6.49; N, 3.27. Found: C, 67.23; H, 6.54; N, 3.26.

*Methyl 4,6-dideoxy-(3-deoxy-*L*-glycero-tetronamido)-2-O-methyl-α-*D*-mannopyranosyl-(1 → 2)-tris[4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**35**).—Compound **29** (236 mg) was treated with hydrogen, as described for the preparation of **31**, to give after freeze-drying the pure, (TLC, NMR), title glycoside **35** (124 mg, 89%) as a white hygroscopic solid: $[\alpha]_D$ +4.4° (*c* 1.1, H_2O). Definite signals in the ^1H NMR spectrum (D_2O) were at δ 5.17–5.13 (m, 4 H, H-1^{II-V}), 4.77 (bd, 1 H, $J_{1,2}$ ~ 1.2 Hz, H-1^{I}), 4.29–4.24 (m, 5 H, H-$2'^{I-V}$), 3.75–3.62 (m, 9 H, H-2^{V},$4'^{I-V}$a,b), 3.45 (s, 3 H, OCH_3-2^{V}),3.36 (OCH_3-1^{I}), 2.08–1.75 (2 m, 10 H, H-$3'^{I-V}$a,b), 1.18–1.10 (m, 15 H, H-6^{I-V}); ^{13}C NMR (D_2O): δ 100.84 (3 C, C-1^{II-IV}), 99.69 (C-1^{I}), 99.04 (C-1^{V}), 79.02 (C-2^{V}), 77.64, 77,52, 77.34, 77.27 (C-2^{I-IV}), 69.10 (5 C, C-$2'^{I-V}$), 68.38 (3 C), 68.03, 67.78, 67.57 (5 C, C-3^{I-V},5^{I-V}), 58.58 (OCH_3-2^{V}), 57. 96 (5 C, C-$4'^{I-V}$), 55.00 (OCH_3), 53.26, 53.06 (4 C, C-4^{I-V}), 36.09 (5 C, C-$3'^{I-V}$), 16.97 (3 C), 16.91 (2 C, C-6^{I-V}); FABMS: *m/z* 774 ([M + 1]$^+$), 796 ([M + Na]$^+$).

In search for a possible crystalline derivative, a portion of compound **35** was acetylated with 1:1 Ac_2O–pyridine, to give methyl 2-*O*-methyl-3-*O*-acetyl-(2,4-di-*O*-acetyl-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-tris[3-*O*-acetyl-4-(2,4-di-*O*-acetyl-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]-3-*O*-acetyl-(2,4-di-*O*-acetyl-3-deoxy-L-*glycero*-tetronamido)-4,6-dideoxy-α-D-mannopyranoside (**38**), but it could not be induced to crystallize. ^1H NMR ($CDCl_3$): δ 6.66, 6.55, 6.10 (3 d, 5 H, $J_{4,NH}$ ~ 9.5 Hz, 5 NH), 5.30–5.20 (m, 5 H, H-3^{I-V}), 5.08–5.03 (m, 7 H, H-$1^{IV,V}$,$2'^{I-V}$), 4.99 (d, 1 H, $J_{1,2}$ ~ 1.6 Hz, H-1^{III}), 4.95 (d, 1 H, $J_{1,2}$ ~ 1.5 Hz, H-1^{II}), 4.70 (d, 1 H, $J_{1,2}$

~ 1.5 Hz, H-1^{I}), 4.35–4.03 (m, 18 H, H-2^{II-IV},4^{I-V},4'$^{I-V}$), 3.91 (bt, 1 H, H-2^{I}), 3.83–3.57 (m, 6 H, H-2^{V},5^{I-V}), 3.53 (OCH_3-2^{V}), 3.39 (OCH_3-1^{I}), 2.20–2.04 (m, 55 H, 15 $COCH_3$ overlapping signals for H-3'$^{I-V}$), 1.25–1.17 (m, 15 H, H-6^{I-V}); ^{13}C NMR ($CDCl_3$): δ 100.24, 100.11 (2 C, C-1^{II-IV}), 99.53 (C-1^{I}), 99.38 (C-1^{V}), 77.78 (C-2^{V}), 75.66, 75.50, 75.29, 75.19 (C-2^{I-IV}), 70.92 (2 C), 70.89 (3 C, 2'$^{I-V}$), 70.78, 69.96, 69.71 (2 C), 69.47, 69.42, 69.18, 69.06, 68.91 (C-3,$^{I-V}$,5^{II-V}), 68.22 (C-5^{I}), 59.93 (4 C), 59.83 (C-4'$^{I-V}$), 59.73 (OCH_3-2^{V}), 55.16 (OCH_3-1^{I}), 52.01, 51.70 (2 C), 51.58, 51.40 (C-4^{I-V}), 30.63 (4 C), 30.56 (C-3'$^{I-V}$), 17.92 (2 C), 17.81 (3 C, C-6^{I-V}).

Methyl 2-O-acetyl-4-azido-3-O-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-tetrakis[4-azido-3-O-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]-4-azido-3-O-benzyl-4,6-dideoxy-α-D-mannopyranoside (**12**).—Condensation of **7** (840 mg, 1.34 mmol) with **14** (1.09 g, 1.02 mmol), as described for the preparation of **9**, gave amorphous **12** (1.464 g, 88%): $[\alpha]_D$ +115° (*c* 0.7). Definite signals in the ^{1}H NMR spectrum ($CDCl_3$) were at δ 5.42 (dd, 1 H, $J_{1,2}$ 1.9, $J_{2,3}$ 3.3 Hz, H-2^{VI}), 4.98 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{II}), 4.89 (d, 1 H, $J_{1,2}$ 1.7, H-1^{III}), 4.88 (m, 3 H, H-1^{IV-VI}), 4.75-4.50 (7 d, partially overlapped, 13 H, 6 C*H*$_2$Ph, incl d at 4.51 for H-1^{I}), 3.88, 3.84 (2 bt, 1 H each, 2 H-2), 3.82–3.79 (m, 3 H, 3 H-2), 3.75 (dd, 1 H, $J_{2,3}$ 3.3 Hz, $J_{3,4}$ 10.4 Hz, H-3), 3.27 (s, 3 H, OCH_3), 1.29–1.11 (6 d, partially overlapped, 18 H, $J_{5,6}$ ~ 6.2 Hz, H-6^{I-VI}), ^{13}C NMR ($CDCl_3$): δ 100.23, 100.06 (2 C), 99.98, 99.66 (C-1^{I-V}), 99.02 (C-1^{VI}), 77.38 (C-3^{I}), 76.72, 76.57, 76.45 (2 C, C-3^{II-V}), 75.32 (C-3^{VI}), 73.49 (2 C), 73.32 (2 C), 73.24 (C-2^{I-V}), 72.08 (3 C), 72.01, 71.93, 71.43 (6 *C*H$_2$Ph), 67.71 (4 C), 67.54, 67.00, 66.81 (C-2^{VI}, 5^{I-VI}), 64.21, 64.10, 64.06 (2 C), 63.91, 63.68 (C-4^{I-VI}), 54.77 (OCH_3), 20.83 ($COCH_3$), 18.47, 18.41, 18.34 (3C), 18.24 (C-6^{I-VI}); FABMS: *m/z* 1773 ([M + Cs]$^+$). Anal. Calcd for $C_{81}H_{96}N_{18}O_{20}$: C, 59.27; H, 5.85; N, 15.37. Found: C, 59.19; H, 5.92; N, 15.24.

Methyl 4-azido-3-O-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-tetrakis[4-azido-3-O-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]-4-azido-3-O-benzyl-4,6-dideoxy-α-D-mannopyranoside (**16**).—Deacetylation of **12** gave **16** in virtually theoretical yield: $[\alpha]_D$ +104° (*c* 1.2). Definite signals in the ^{1}H NMR spectrum ($CDCl_3$) were at δ 4.97 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{VI}), 4.95 (d, 1 H, $J_{1,2}$ 1.9 Hz, H-1^{II}), 4.88, 4.86, 4.84 (3 d, 1 H each, $J_{1,2}$ ~ 1.5 Hz, H-1^{III-V}), 4.71–4.55 (12 d, partially overlapped, 12 H, 6 C*H*$_2$Ph), 4.51 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{I}), 3.97 (bs, 1 H, H-2^{VI}), 3.92 (bt, 1 H, H-2^{II}), 3.82 (bt, 1 H, H-2^{III}), 3.81–3.77 (m, 3 H, H-2^{I,IV,V}), 3.25 (s, partially overlapped, OCH_3), 1.27, 1.25, 1.21, 1.19, 1.16, 1.13 (6 d, partially overlapped, 18 H, H-6^{I-VI}); ^{13}C NMR ($CDCl_3$): δ 100.37 (C-1^{VI}), 100.15, 100.04, 99.97 (2 C, C-1^{II-V}), 99.56 (C-1^{I}), 77.42, 77.31 (C-3^{I,VI}), 76.68, 76.36 (3 C, C-3^{II-V}), 73.46 (2 C), 73.27 (2 C), 72.97 (C-2^{I-V}), 71.93 (4 C), 71.82, 71.76 (6 *C*H$_2$Ph), 67.60 (4 C), 67.19, 68.90, 66.71 (C-2^{VI},5^{I-VI}), 64.09, 63.94 (4 C, C-4^{I-V}), 63.55 (C-4^{VI}), 54.64 (OCH_3), 18.36, 18.32, 18.26 (3 C), 18.06 (C-6^{I-VI}); FABMS: *m/z* 1731 ([M + Cs]$^+$). Anal. Calcd for $C_{79}H_{94}N_8O_{19}$: C, 59.32; H, 5.88; N, 15.77. Found: C, 59.55; H, 5.97; N, 15.82.

Methyl 4-azido-3-O-benzyl-4,6-dideoxy-2-O-methyl-α-D-mannopyranosyl-(1 → 2)-tetrakis[4-azido-3-O-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]-4-azido-3-O-benzyl-4,6-dideoxy-α-D-mannopyranoside (**18**).—The foregoing compound **16** was methylated, as described for the preparation of **17**, to give compound **18** in ~95% yield: $[\alpha]_D$ +138° (*c* 0.7). Definite signals in the ^{1}H NMR spectrum ($CDCl_3$) were at δ 4.93–4.91 (3 d, partially overlapped, 3 H, 3 H-1, incl H-1^{VI}), 4.87–4.85 (2 d, partially overlapped, 2 H, 2 H-1), 4.76–4.58 (6 d, partially overlapped, 12 H, 6 C*H*$_2$Ph), 4.51 (d, 1 H, $J_{1,2}$ 1.7 Hz, H-1^{I}), 3.97, 3.85, 3.82, 3.80 (4 bt, 5 H, H-2^{I-V}), 3.72–3.63 (m, 6 H, H-3^{I-VI}), 3.51–3.14 (m, 19 H, (H-2^{VI},4^{I-VI},5^{I-VI}, incl 2 s at 3.28 and 3.20 for OCH_3-1^{I} and OCH_3-2^{VI}, respectively), 1.28, 1.25, 1.19, 1.18, 1.17, 1.13 (6 d, 18 H, partially overlapped, C-6^{I-VI}); ^{13}C NMR ($CDCl_3$): d 100.29, 100.22, 100.13 (2 C, C-1^{II-V}), 99.71 (C-1^{I}), 98.76 (C-1^{VI}), 77.42 (2 C), 77.12, 77.00, 76.56, 76.49 (C-3^{I-VI}), 76.31 (C-2^{VI}), 73.60, 73.50, 73.36, 73.15, 73.10 (C-2^{I-V}), 72.35, 72.14 (3 C), 72.05 (2 C, 6 *C*H$_2$Ph), 67.79 (3 C), 67.72 (2 C), 66.87 (C-5^{I-VI}), 64.26 (2 C), 64.12 (3 C), 64.04 (C-4^{I-VI}), 58.87 (OCH_3-2^{V}), 54.84 (OCH_3-1^{I}), 18.51, 18.43, 18.39 (3 C), 18.31 (C-6^{I-VI}); FABMS: *m/z* 1745 ([M + Cs]$^+$). Anal. Calcd for $C_{80}H_{96}N_{18}O_{19}$: C, 59.55; H, 5.96; N, 15.63. Found: C, 59.82; H, 6.00; N, 15.57.

Methyl 3-O-benzyl-(2,4-O-benzylidene-3-deoxy-L-glycero-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-tetrakis[3-O-benzyl-4-(2,4-O-benzylidene-3-deoxy-L-glycero-tetronamido)-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]-3-O-benzyl-(2,4-O-benzylidene-3-deoxy-L-glycero-tetronamido)-4,6-dideoxy-α-D-mannopyranoside (**28**).—Compound **16** (450 mg) was treated with H_2S, as described for the preparation of **19**, to give methyl 4-amino-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)-tetra-

kis[4-amino-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranosyl-(1 → 2)]-4-amino-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (**22**, 370 mg, 91%). ^{1}H NMR ($CDCl_3$): δ 5.10, 5.08, 5.07, 5.01 (4 bd, 5 H, H-1^{II-VI}), 4.71–4.38 (m, 13 H, H-1^I, 6 CH_2Ph), 4.08–4.03 (m, 5 H, H-2^{II-VI}), 3.95 (bdd, 1 H, H-2^I), 3.65–3.44 (m, 12 H, H-3^{I-VI},5^{I-VI}), 3.32 (s, 3 H, OCH_3), 2.89–2.79 (m, 6 H, H-4^{I-VI}), 1.27–1.15 (6 d, partially overlapped, 18 H, H-6^{I-VI}); ^{13}C NMR ($CDCl_3$): δ 101.08 (C-1^{VI}), 100.85 (3 C), 100.79 (C-1^{II-V}), 100.21 (C-1^I), 79.48, 78.97 (2 C), 78.53, 78.44, 78.38 (C-3^{I-VI}), 73.01, 72.89 (2 C), 72.77 (C-2^{II-V}), 72.44 (C-2^I), 71.25, 71.01 (5 C, 6 CH_2Ph), 70.11 (4 C), 69.45, 69.30 (C-5^{I-VI}), 66.29 (C-2^{VI}), 54.53 (OCH_3), 53.48 (4 C), 53.29, 53.11 (C-4^{I-VI}), 18.05 (4 C), 17.99, 17.78 (C-6^{I-VI}); FABMS: *m/z* 1443 ([M + 1]$^+$).

Compound **22** (370 mg, 0.26 mmol) was treated, with **39**, as described for the preparation of **25**, to give **28** (424 mg, 64%): $[\alpha]_D$ −41.5°. Definite signals in the ^{1}H NMR ($CDCl_3$) spectrum were at δ 6.42–6.09 (6 d, partially overlapped, 6 H, 6 NH), 5.54, 5.53, 5.52 (double intensity), 5.50, 5.47 (5 s, 6 H, 6 C*H*Ph), 5.00 (bs, 2 H), 4.93, 4.92 (2 d, partially overlapped, 2 H), 4.89 (d, 1 H, $J_{1,2}$ 1.8 Hz, H-1^{II-VI}), 3.24 (s, 3 H, OCH_3), 2.41 (s, 1 H, OH), 2.08–1.80 (m, 12 H, H-$3'^{I-VI}$a,b), 1.13, 1.12, 1.10, 1.06, 1.04, 1.01 (6 d, partially overlapped, H-6^{I-VI}); ^{13}C NMR ($CDCl_3$): δ 101.23, 101.20 (2 C), 101.17, 101.11, 101.05 (6 *C*HPh), 100.89 (C-1^{VI}), 100.38, 100.27 (3 C, C-1^{II-V}), 99.81 (C-1^I), 76.55 (5 C), 76.42 (C-$2'^{I-VI}$), 76.05 (C-3^{VI}), 75.32, 75.13, 74.85, 74.78, 74.63 (C-3^{I-V}), 73.80 (C-2^I), 73.02, 72.92, 72.87, 72.79 (C-2^{II-V}), 71.42, 71.28, 71.17 (2 C), 71.03 (2 C, 6 *C*H_2Ph), 68.61 (3 C), 68.54, 67.99, 67.39 (C-5^{I-VI}), 67.21 (6 C, C-$4'^{I-VI}$), 66.86 (C-2^{VI}), 54.80 (OCH_3), 52.15, 51.83 (2 C), 51.77, 51.54, 51.21 (C-4^{I-VI}), 28.52 (6 C, C-3^{I-VI}), 18.03 (2 C), 17.98 (2 C), 17.94, 17.78 (C-6^{I-VI}); FABMS: *m/z* 2583 ([M + 1]$^+$), 2605 ([M + Na]$^+$).

*Methyl 4,6-dideoxy-(3-deoxy-*L*-glycero-tetronamido)-α-*D*-mannopyranosyl-(1 → 2)-tetrakis[4-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]-(3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**34**). —Compound **28** (134 mg) was treated with hydrogen, as described for the preparation of **31**, to give after freeze-drying the pure (TLC, NMR), title glycoside **34** (75 mg, 95%) as a white hygroscopic solid: $[\alpha]_D$ +0.3° (H_2O). Definite signals in the ^{1}H NMR spectrum (D_2O) were at δ 5.15 (bs, 4 H, H-1^{II-V}), 5.04 (bd, 1 H, $J_{1,2}$ ~ 1.7 Hz, H-1^{VI}), 4.78 (bd, 1 H, $J_{1,2}$ ~ 1.6 Hz, H-1^I), 4.31–4.25 (m, 6 H, H-$2'^{I-VI}$), 3.76–3.70 (m, 12 H, H-$4'^{I-VI}$), 3.38 (s, 3 H, OCH_3), 2.09–1.98, 1.89–1.78 (2 m, 6 H each, H-$3'^{I-VI}$), 1.19–1.12 (m, 18 H, H-6^{I-VI}); ^{13}C NMR ($CDCl_3$): δ 102.33 (C-1^{VI}), 100.93 (4 C, C-1^{II-IV}), 99.77 (C-1^I), 77.57, 77.43, 77.36 (2 C), 77.27 (C-2^{I-V}), 69.25 (C-2^{VI}), 69.10 (6 C, C-$2'^{I-VI}$), 68.40 (4 C), 68.19, 67.91, 67.81, 67.58 (5 C, C-3^{I-VI},5^{I-VI}), 57.96 (6 C, C-$4'^{I-VI}$), 54.99 OCH_3), 53.31, 53.07 (4 C), 52.86 (C-4^{I-VI}), 36.09 (6 C, C-$3'^{I-VI}$), 16.91 (6 C, C-6^{I-VI}); FABMS: *m/z* 1515 ([M + 1]$^+$), 1537 ([M + Na]$^+$).

*Methyl 3-O-benzyl-(2,4-O-benzylidene-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-2-O-methyl-α-*D*-mannopyranosyl-(1 → 2)-tetrakis[3-O-benzyl-4-(2,4-O-benzylidene-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranosyl-(1 → 2)]-3-O-benzyl-(2,4-O-benzylidene-3-deoxy-*L*-glycero-tetronamido)-4,6-dideoxy-α-*D*-mannopyranoside* (**30**).—Compound **18** (320 mg) was treated with H_2S, as described for the preparation of **19**, to give methyl 4-amino-3-*O*-benzyl-4,6-dideoxy-2-*O*-methyl-α-D-mannopyranosyl- (1 → 2)-tetrakis[4-amino-3-*O*-benzyl-4,6-dideoxy-α- D-mannopyranosyl-(1 → 2)]-4-amino-3-*O*-benzyl-4,6-dideoxy-α-D-mannopyranoside (**24**, 284 mg, 84%). ^{1}H NMR ($CDCl_3$): δ 5.11–5.06 (4 d, partially overlapped, 4 H, $J_{1,2}$ ~ 1.5 Hz, 4 H-1), 4.99 (d, 1 H, $J_{1,2}$ 1.5 Hz, H-1), 4.72–4.38 (m, 13 H, H-1^I, 6 CH_2Ph), 4.10–4.03 (m, 5 H, H-2^{II-VI}), 3.96 (bdd, 1 H, H-2^I), 3.61–3.44 (m, 12 H, H-3^{I-VI},5^{I-VI}), 3.32, 3.29 (2 s, 3 H each, OCH_3-1^I, OCH_3-2^{VI}), 2.90–2.80 (m, 6 H, H-4^{I-VI}), 1.37 (bs, 12 H, 6 NH_2), 1.27–1.14 (m, 18 H, H-6^{I-VI}); ^{13}C NMR ($CDCl_3$): δ 100.93, 100.85 (2 C), 100.80 (C-1^{II-V}), 100.23 (C-1^I), 99.04 (C-1^{VI}), 79.46, 79.07, 78.98, 78.60, 78.53, 78.48 (C-3^{I-VI}), 75.69 (C-2^{VI}), 72.89 (3 C), 72.47, 72.43 (C-2^{I-V}), 71.51, 71.15, 70.99 (4 C, 6*C*H_2Ph), 70.17 (4 C), 70.11 (C-5^{II-VI}), 69.39 (C-5^I), 58.73 (OCH_3-2^{VI}), 54.50 (OCH_3-1^I), 53.70, 53.60, 53.50, 53.43 (3 C, C-4^{I-VI}),18.06 (4 C), 18.00, 17.89 (C-6^{I-VI}); FABMS: *m/z* 1457 ([M + 1]$^+$), 1479 ([M + Na]$^+$).

Compound **24** (284 mg, 0.2 mmol) was treated with **39**, as described for the preparation of **25**, to give **30** (420 mg, 83%), mp 118–119 °C (from ethyl acetate–hexane); $[\alpha]_D$ −44° (*c* 0.7). Definite signals in the ^{1}H NMR ($CDCl_3$) spectrum were at δ 6.45–6.18 (m, incl 3 d at 6.31, 6.21, 6.18, partially overlapped, $J_{4,NH}$ ~ 9.6 Hz, 6 H, 6 NH), 5.55, 5.54, 5.53, 5.51 (double intensity), 5.50 (5 s, 6 H, 6 *C*HPh), 4.98, 4.96, 4.95, 4.93, 4.89 (5 d, partially overlapped, $J_{1,2}$ ~ 1.8 Hz, H-1^{II-VI}), 4.19 (bt, 1 H, H-2), 3.25, 3.24 (2 s, 3 H each, 2 OCH_3), 2.06–1.84 (m, 12 H, H-$3'^{I-VI}$), 1.14–1.00 (6 d, 18 H, H-6^{I-VI}); ^{13}C NMR

($CDCl_3$): δ 101.28 (2 C), 101.25, 101.19, 101.17, 101.14 (6 *C*HPh), 100.88, 100.47, 100.40, 100.33 (C-1^{II-V}), 99.92 (C-1^{I}), 99.16 (C-1^{VI}), 76.64 (2 C), 76.57 (3 C), 76.45 (C-$2'^{I-VI}$), 75.91, 75.86, 75.62, 75.16, 74.82, 74.58, 74.45 (C-2^{VI},3^{I-VI}), 73.85 (C-2^{I}), 73.12, 73.04, 72.93 (2 C, C-2^{II-V}), 71.99, 71.30, 71.21, 71.07 (2 C), 71.04 (6 CH_2Ph), 68.62 (3 C), 68.55 (2 C), 67.43 (C-5^{I-VI}), 67.25 (6 C, C-$4'^{I-VI}$), 58.98 (OCH_3-2^{VI}), 54.86 (OCH_3-1^{I}), 52.15, 52.03, 51.87 (2 C), 51.81, 51.87 (C-4^{I-VI}), 28.54 (6 C, C-$3'^{I-VI}$), 18.05, 18.00 (4 C), 17.94 (C-6^{I-VI}); FABMS: *m/z* 2597 ($[M + 1]^+$). Anal. Calcd for $C_{146}H_{168}N_6O_{37}$: C, 67.47; H, 6.52; N, 3.25. Found: C, 67.77; H, 6.58; N, 3.18.

*Methyl 4,6-dideoxy-2-O-methyl-(3-deoxy-*L-glycero-*tetronamido)-α-*D-*mannopyranosyl-(1 → 2)-tetrakis[4-(3-deoxy-*L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranosyl-(1 → 2)]-(3-deoxy-*L-glycero-*tetronamido)-4,6-dideoxy-α-*D-*mannopyranoside* (**36**). —Compound **30** (240 mg) was treated with hydrogen, as described for the preparation of **31**, to give after freeze-drying the pure (TLC, NMR), title glycoside **36** (124 mg, 88%) as a white hygroscopic solid: $[\alpha]_D$ −1.6° (H_2O). Definite signals in the ^1H NMR spectrum (D_2O) were at δ 5.18, 5.16, 5.14 (3 bs, 5 H, H-1^{II-VI}), 4.78 (bs, 1 H, H-1^{I}), 4.30–4.24 (m, 6 H, H-$2'^{I-VI}$), 3.46 (s, 3 H, OCH_3-2^{VI}), 3.37 (s, 3 H, OCH_3-1^{I}), 2.08–1.96, 1.88–1.77 (2 m, 6 H each, H-$3'^{I-VI}$), 1.19–1.10 (m, 18 H, H-6^{I-VI}); ^{13}C NMR ($CDCl_3$): δ 100.90 (4 C, C-1^{II-V}), 99.75 (C-1^{I}), 99.09 (C-1^{VI}), 79.04 (C-2^{VI}), 77.65, 77.53, 77.32 (3 C, C-2^{I-V}), 69.07 (6 C, C-$2'^{I-VI}$), 68.38 (5 C), 68.05, 67.78, 67.58 (5 C, C-3^{I-VI},5^{I-VI}), 58.85 (OCH_3-2^{VI}), 57.94 (6 C, C-$4'^{I-VI}$), 54.99 (OCH_3-1^{I}), 53.24, 53.10, 53.03 (4 C, C-4^{I-VI}), 36.05 (6 C, C-$3'^{I-VI}$), 16.89 (6 C, C-6^{I-VI}); FABMS: *m/z* 1529 ($[M + 1]^+$).

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