Studies towards a Conjugate Vaccine for Anthrax: Synthesis of the Tetrasaccharide Side Chain of the *Bacillus anthracis* Exosporium

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The first synthesis of β-L-glycoside **17** of the tetrasaccharide β-Ant-(1 → 3)-α-L-Rha*p*-(1 → 3)-α-L-Rha*p*-(1 → 2)-L-Rha*p* is described (*Schemes 1–3*). Its spacer can be functionalized to make it amenable to conjugation to proteins by different conjugation methods. The synthesis was performed in a stepwise manner starting from the aglycon-bearing terminal saccharide with thioglycosides as glycosyl donors. To attach the upstream terminal anthrose residue, the assembled linker-equipped trisaccharide was glycosylated with ethyl 4-azido-3-*O*-benzyl-2-*O*-(bromoacetyl)-4,6-dideoxy-1-thio-β-D-glucopyranoside (**11**). Further functionalization of the tetrasaccharide thus obtained, followed by deprotection gave the target substance **17**. Synthesis of substructures of **17** equipped with the same spacer, namely β-L-Rha*p*-1-*O*-$(CH_2)_5$COOMe (**21**), α-L-Rha*p*-(1 → 2)-β-L-Rha*p*-1-*O*-$(CH_2)_5$COOMe (**22**), and α-L-Rha*p*-(1 → 3)-α-L-Rha*p*-(1 → 2)-β-L-Rha*p*-1-*O*-$(CH_2)_5$COOMe (**23**), is also described (*Scheme 4*).

Introduction. – *Bacillus anthracis*, the causative agent of anthrax, is a spore-forming pathogen. One of the components of its exosporium is a collagen-like protein [1] whose carbohydrate portion is formed by the tetrasaccharide β-Ant-(1 → 3)-α-L-Rha*p*-(1 → 3)-α-L-Rha*p*-(1 → 2)-L-Rha*p* (*Fig.*) [2]. Anthrose (=4,6-dideoxy-4-[(3-hydroxy-3-methyl-1-oxobutyl)amino]-2-*O*-methyl-D-glucopyranose), which forms the upstream terminal residue of the tetrasaccharide, was first discovered as a component of the exosporium glycoprotein. In connection with our attempts to develop a conjugate vaccine for anthrax, we have recently synthesized this rare sugar, as well as its methyl glycosides [3]. Our approach to the vaccine is based on the premise that spores could be destroyed by antibodies specific for components on their surface. Such antibodies should be possible to elicit by immunization with, for example, immunogens prepared from the above-mentioned tetrasaccharide. Within a project aimed at immunogenic neoglycoconjugates, we have prepared tetrasaccharide glycoside **17**, whose aglycone makes it amenable to conjugation with suitable carriers. Here we report full details of the synthesis of **17**, together with complete assignment of ^{1}H- and ^{13}C-NMR spectra, that were not included in our preliminary report [4].

It has been proposed [2] that the tetrasaccharide is most probably attached to the glycoprotein through an *N*-acetyl-D-galactosamine linker, but the configuration of the glycosidic linkage providing that attachment to the linker is unknown. A prerequisite for obtaining a potent immunogen for anti exosporium antibodies from the spacer-

[1]) This work was presented at the 13th Eurocarb, August 22–26, 2005, Bratislava, Slovakia.

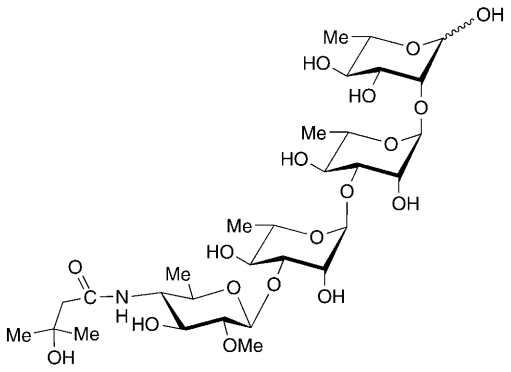
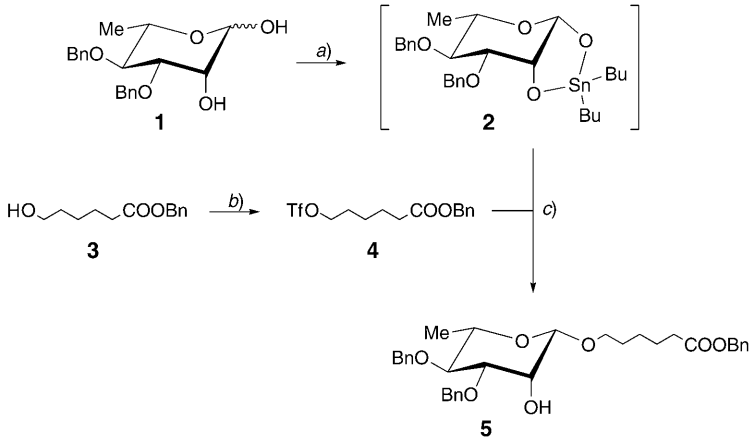


Figure. *Structure of the tetrasaccharide side chain of the collagen-like glycoprotein of the exosporium of* Bacillus anthracis

equipped tetrasaccharide is that its anomeric configuration in the glycoconjugate is the same as in the exosporium glycoprotein. With that information unavailable, conjugates made from both α- and β-linked tetrasaccharides will have to be prepared and tested for their immunogenicity. Described below is the first synthesis of tetrasaccharide **17** whose spacer is attached to the downstream β-L-rhamnosyl terminus (*Schemes 1–3*). Preparation of three structural fragments of **17**, namely the linker-equipped β-glycosides **21**–**23** (*Scheme 4*) is also described. These compounds will be used in binding and inhibition studies with anti exosporium antibodies. An independent synthesis of the tetrasaccharide equipped with a different, α-linked spacer has been published [5].

Results and Discussion. – Immune response to antigens is controlled by interaction of antigenic determinants with receptors of the complex immune system. With short-chain antigens, such as synthetic oligosaccharides, that interaction can be, presumably, facilitated when the oligosaccharide has sufficient translational and rotational freedom to access active sites on immunologically active cells. That can be achieved by linking the oligosaccharide antigen to a carrier through a flexible spacer moiety. Tetrasaccharide **17**, whose stepwise synthesis is presented here, is equipped with a β-L-linked C_6-chain spacer attached to the downstream terminal L-rhamnosyl residue. Depending on chemistry of conjugation, that spacer may become further extended when it is functionalized for conjugation. The stepwise synthesis of **17** started from the downstream rhamnose residue. In this way, fragments of **17**, which will be needed in connection with the development of the vaccine, were easily accessible. The initial glycosyl acceptor **5** was synthesized from the triflate **4** of benzyl 6-hydroxyhexanoate (**3**) [6] and the stannylidene acetal **2** of 3,4-di-*O*-benzyl-L-rhamnose (**1**) [7] (*Scheme 1*). The formation of the β-L-rhamnopyranosyl linkage was stereospecific [8][9], as manifested [10] in the ^{1}H-coupled ^{13}C-NMR spectrum of the sole glycoside formed (J(C(1),H–C(1)) = 156.4 Hz). To introduce the spacer, we preferred the use of benzyl ester **3** to the more commonly employed analogous methyl ester [11] since triflation of **3** (→ **4**) could be monitored by TLC with detection by UV light. The required, known [6] benzyl

Scheme 1



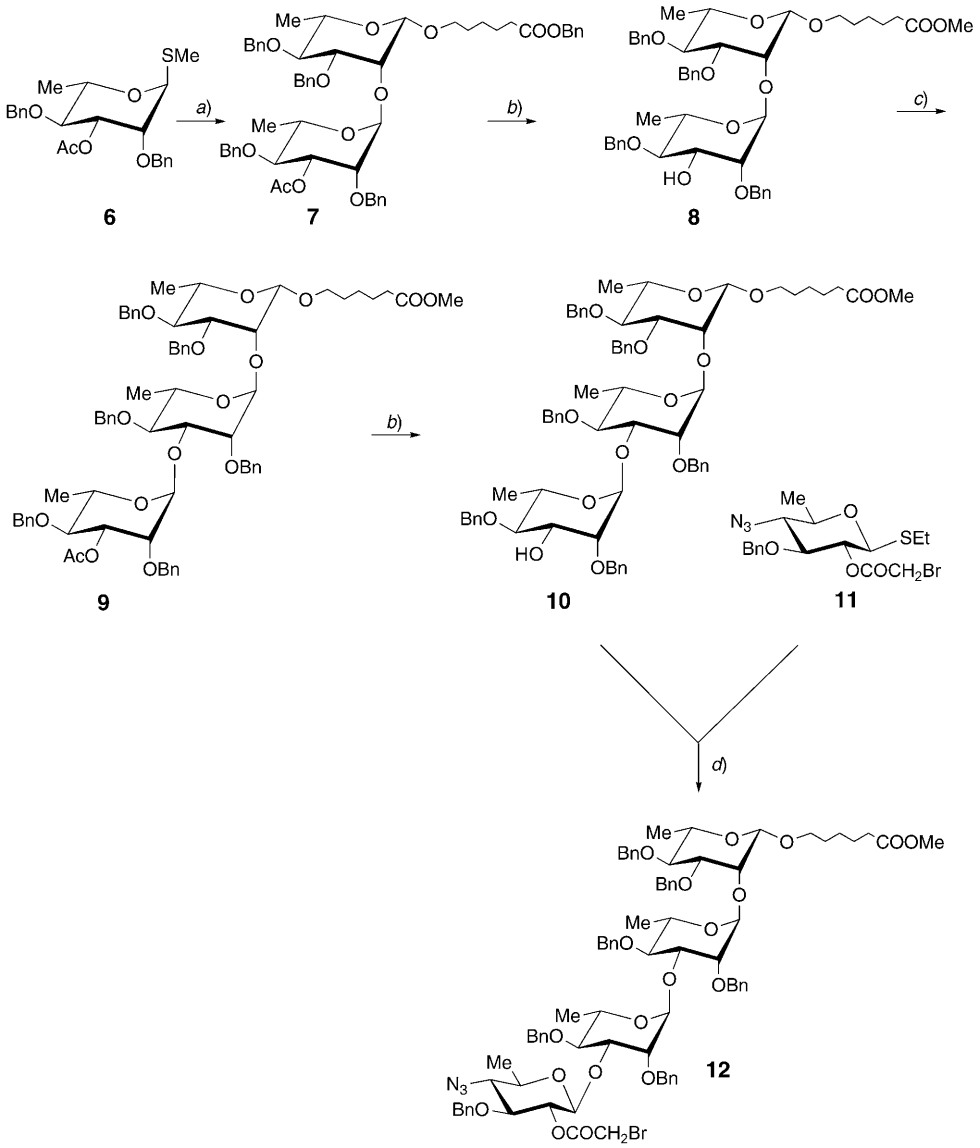
a) Bu_2SnO, toluene. *b*) Tf_2O, K_2CO_3, CH_2Cl_2. *c*) CsF, MeCN.

ester **3** was more conveniently made from commercially available ε-caprolactone (=oxepan-2-one) by transesterification with NaOBn in BnOH. The fully assigned ^{1}H-NMR data of **3** agreed with those reported [6], albeit not analyzed completely. Side reactions that occurred during subsequent triflation under standard conditions (Tf_2O, pyridine, not reported in the *Exper. Part*) were eliminated by the use of solid K_2CO_3 as a base [12]. In this way, pure (NMR) [4] triflate **4** was obtained from **3** in virtually theoretical yield. The compound is unstable, and should be freshly prepared before use.

Stepwise extension of the oligosaccharide chain, to give rhamnotrioside **9** was effected by repeated NIS (*N*-iodosuccinimide)/AgOTf-mediated glycosylation [13] with methyl 3-*O*-acetyl-2,4-di-*O*-benzyl-1-thio-α-L-rhamnopyranoside (**6**) [7], first of **5** ($\rightarrow$ **7**) and then of the product of deacetylation of **7**, alcohol **8** ($\rightarrow$ **9**) (*Scheme 2*). The α-L-linked products were obtained in high yield, as shown by the typical [10] large J(C(1),H–C(1)). Complete, unambiguous assignments of the NMR spectra of **6** were now made by 2-D correlation spectroscopy (see *Exper. Part*).

Positioning anthrose at the upstream terminus of the desired tetrasaccharide **17** required formation of the β-D-glucosidic linkage. Because of the presence of the 2-*O*-methyl group in the β-D-glucosyl residue of **17**, formation of such a linkage in a highly stereoselective manner could be problematic with a glycosyl donor derived from anthrose. Therefore, after deacetylation of **9**, the glycosyl acceptor **10** formed was glycosylated with the glucosyl donor **11** [14], obtained by 2-*O*-bromoacetylation of methyl 4-azido-3-*O*-benzyl-4,6-dideoxy-β-D-glucopyranoside [3] to give the fully protected tetrasaccharide **12** (*Scheme 2*). The general utility of glycosyl donor **11** is due to the presence of a protecting at group *O*-2 that can be selectively removed in the presence of other acyl groups. As such, it can also be used in alternate strategies towards analogs of **17** that involve acyl-protected intermediates.

Scheme 2

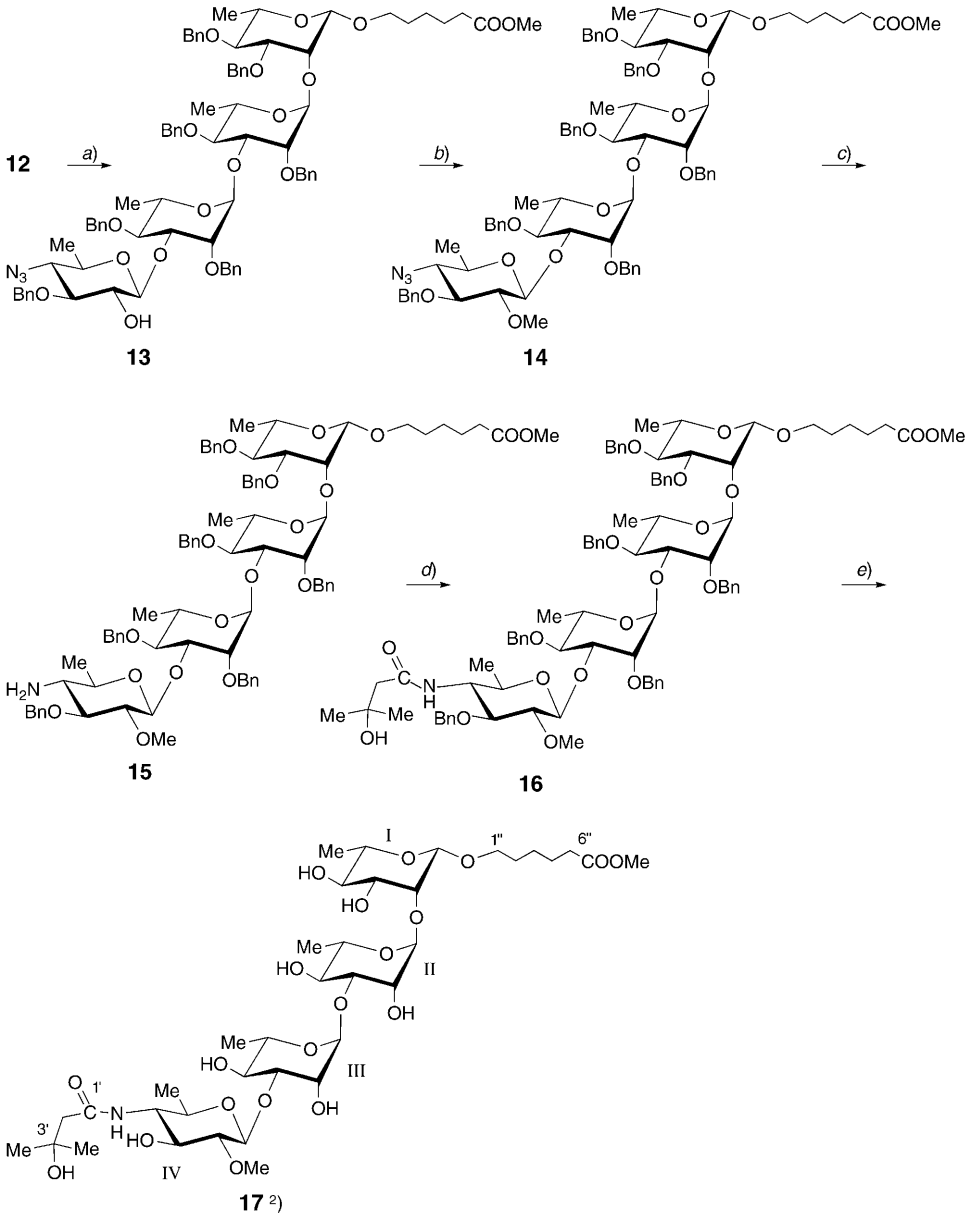


a) **5**, NIS, AgOTf, CH_2Cl_2. *b*) MeONa, MeOH. *c*) **6**, NIS, AgOTf, CH_2Cl_2. *d*) NIS, AgOTf, CH_2Cl_2.

Transformation of **12** into the target tetrasaccharide **17** was accomplished as shown in *Scheme 3*[2]). Accordingly, the protected tetrasaccharide **12** was debromoacetylated,

[2]) The aglycon spacer $(CH_2)_5COOMe$ is numbered with doubly primed locants. The sugar residue bearing the aglycon spacer is denoted by the Roman numeral I and the remaining sugar residues sequentially by II–IV, as required. The terminal butanamido group is numbered with primed locants.

Scheme 3



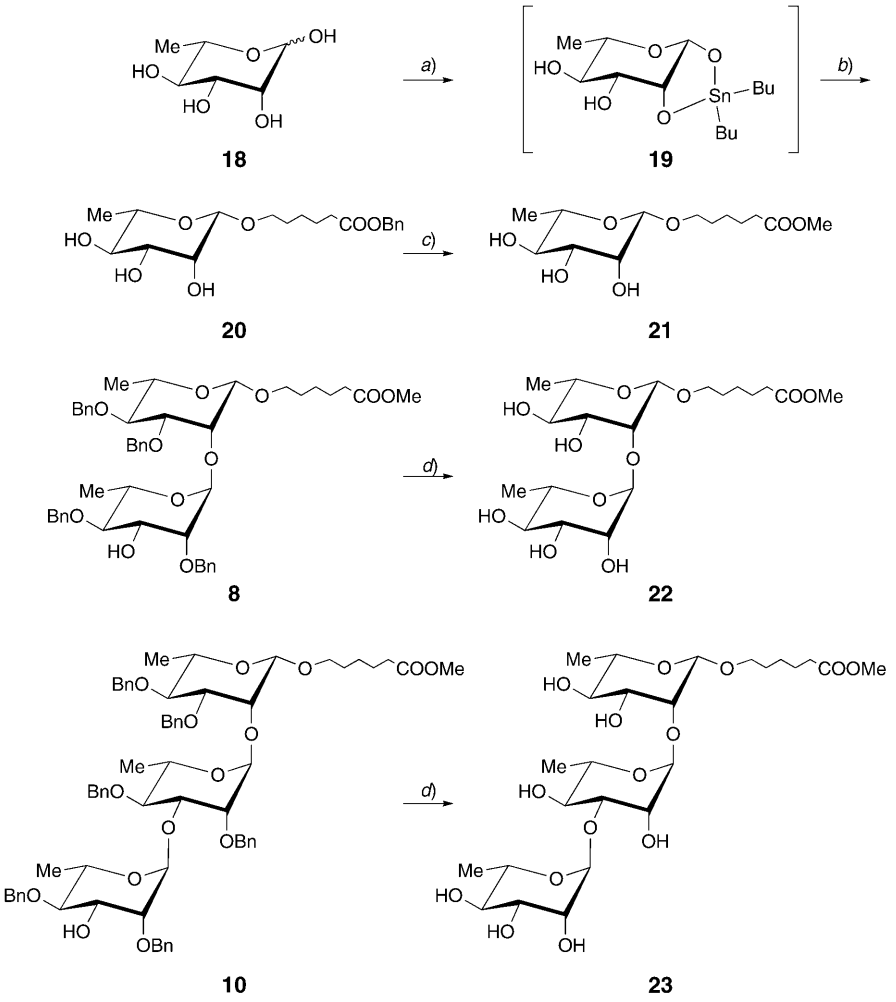
a) MeONa, MeOH. *b*) MeI, Me_2S, Ag_2O, CH_2Cl_2. *c*) H_2S, Py, H_2O. *d*) 3-Hydroxy-3-methylbutanoic acid, HATU, CH_2Cl_2. *e*) H_2, Pd/C, 2-methoxyethanol[2]).

and the formed alcohol **13** was methylated [15] (→ **14**). Selective reduction of the azido function in **14** with hydrogen sulfide [16] gave amine **15**, whose treatment with 3-hy-

droxy-3-methylbutanoic acid in the presence of HATU (= *O*-(1*H*-7-azabenzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate) yielded butanamido derivative **16**. Finally, hydrogenolytic debenzylation over 5% Pd/C catalyst gave the target tetrasaccharide **17** equipped with a spacer that makes it amenable to conjugation to proteins.

Future characterization of immunogenic epitopes in tetrasaccharide **17** and its α-L-glycoside analog [14] by carbohydrate microarray analysis will require fragments that mimic partial structures of both tetrasaccharides. Two such compounds, glycosides **22** and **23**, were obtained by catalytic debenzylation of intermediates **8** and **10** of the synthesis of **17**, respectively (*Scheme 4*).

Scheme 4



a) Bu_2SnO, MeOH. *b*) **4**, CsF, DMF. *c*) MeONa, MeOH. *d*) H_2, Pd/C, 2-methoxyethanol.

The β-L-rhamnopyranoside **21** was conveniently synthesized from benzyl ester **20**, obtained in turn from L-rhamnose (**18**) and triflate **4** by β-rhamnosylation *via* 1,2-*O*-stannylation [8][9], a method which does not require protection of the OH groups (*Scheme 4*). To insure an efficient use of the unstable triflate **4**, the reaction leading to **21** was carried out with excess stannylene acetal **19**. In view of the experimental simplicity of this method, we deem the relatively low yield (38%) of **20** satisfactory. Compound **20** was the only glycoside formed, and its β-L-configuration was confirmed by ^{1}H-coupled ^{13}C-NMR spectrum (J(C(1),H–C(1)) = 155.6 Hz). The desired methyl ester **21** was readily obtained from **20** by base-catalyzed transesterification.

The ^{1}H- and ^{13}C-NMR spectra of **17** (*Tables 1* and *2*), which were interpreted with the aid of two-dimensional techniques, fully confirmed the structure of the tetrasaccharide. Noteworthy in the ^{1}H-NMR spectrum ((D$_6$)DMSO) is the remarkable similarity of chemical shifts for signals associated with the anthrose residue of **17** with the corresponding resonances found in the spectrum of the reducing tetrasaccharide isolated from *Bacillus anthracis* [2] exosporium. Also, in addition to the resonances of H–C(1^{I}) to H–C(1^{IV})^2), the ^{1}H-NMR spectrum ((D$_6$)DMSO) of **17** showed eight signals in the

Table 1. *^{1}H-NMR Chemical Shifts* [ppm] *and Coupling Constants* [Hz] *for Tetrasaccharide* **17**[a])

Moiety[b])	H–C(1) or CH$_2$(1″)^2)	H–C(2), CH$_2$(2″) or CH$_2$(2′)	H–C(3) or CH$_2$(3″)^2)	H–C(4) or CH$_2$(4″)^2)	H–C(5) or CH$_2$(6″)^2)	H–C(6)
I[c])	4.641 (J(1,2) = 0.9)	4.002 (J(2,3) = 3.1)	3.691 (J(3,4) = 9.4)	3.400[d])	3.400	*ca.* 1.301[d])
	4.393[d])	*ca.* 3.755[d])	3.333[d])	2.091[d])	2.091	1.134[d])
II[e])	5.005 (J(1,2) = 1.8	4.186 (J(2,3) = 3.3)	3.902 (J(3,4) = 9.8)	3.508 (J = 10.0)	4.213	1.249 (J(5,6) = 6.3)
	4.906 (J(1,2) = 1.5	*ca.* 3.755[d])	3.615[d])	3.281[d])	3.939	1.028 (J(5,6) = 6.2)
III[f])	5.028 (J(1,2) = 1.7	4.285 (J(2,3) = 3.3)	4.002[d])	3.620 (J = 10.0)	3.876	*ca.* 1.315[d])
	4.894 (J(1,2) = 1.4	3.879[d])	*ca.* 3.755[d])	3.404[d])	3.628	1.129[d])
IV[g])	4.740 (J(1,2) = 8.0	3.135 (J(2,3) = 9.2)	3.543 (J = 10.0)	3.636 (J = 10.0)	3.561	1.223 (J(5,6) = 6.1)
	4.576 (J(1,2) = 7.9	2.850 (J(2,3) = 8.9)	3.275[d])	*ca.* 3.400[d])	3.270	1.067 (J(5,6) = 6.2)
Spacer[h])	3.840, 3.670	1.612	1.422	1.612	2.400 (J = 7.5)	
	3.695, 3.333	1.480	1.313	1.480	2.287 (J = 7.5)	
Amido group[i])		2.472, 2.446 2.208				

[a]) Measured at 600 MHz at 20°. Data in the first and second row for each moiety refer to measurements in D$_2$O and (D$_6$)DMSO, respectively. [b]) For notation of the sugar residues, see *Footnote 2*. [c]) δ ((D$_6$)DMSO) 5.030 (*d*, J = 4.2, OH–C(3)); 4.864 (br. *d*, J = 4.7, OH–C(4)). [d]) Coupling constant not determined. [e]) δ ((D$_6$)DMSO) 4.844 (*d*, J = 6.4, OH–C(4)); 4.643 (*d*, J = 4.7, OH–C(2)). [f]) δ ((D$_6$)DMSO) 4.704 (*d*, J = 5.3, OH–C(4)); 4.511 (*d*, J = 4.5, OH–C(2)). [g]) δ (D$_2$O) 3.632 (*s*, MeO). δ ((D$_6$)DMSO) 7.728 (*d*, J(NH,4) = 9.1, NH); 4.997 (*d*, J = 6.1, OH–CH(3)); 3.525 (*s*, MeO). [h]) δ (D$_2$O) 3.680 (*s*, COOMe). δ ((D$_6$)DMSO) 3.572 (*s*, COOMe). [i]) δ (D$_2$O) *ca.* 1.309, *ca.* 1.300 (2*s*, 2 Me). δ ((D$_6$)DMSO) 4.831 (*s*, OH–C(3′)); 1.158, 1.146 (2*s*, 2 Me).

Table 2. *^{13}C-NMR Chemical Shifts* [ppm] *for Tetrasaccharide* **17**[a])

Moiety[b])	C(1), C(1″), or C(1′)^2)	C(2), C(2″), or C(2′)^2)	C(3), C(3″), or C(3′)^2)	C(4) or C(4″)^2)	C(5) or C(5″)^2)	C(6) or C(6″)^2)
I	102.336	79.615	76.053	75.150[c])	74.979[c])	19.455[d])
	99.733	75.304	73.803	72.320[e])	72.132[e])	18.043
II	103.995	72.781	80.864	74.099	71.547	19.492
	100.756	70.196	79.966	71.527	68.099	17.678
III	104.929	72.606	82.392	73.912	72.047	19.424[d])
	101.476	69.634	79.585	71.633	68.187	17.678
IV[f])	106.431	86.030	75.620	59.345	73.536	19.806
	103.479	84.348	72.749	59.389	70.315	18.153
Spacer[g])	72.486	26.858	27.728	31.451	36.393	176.830
	68.414	29.024	25.224	24.424	33.261	171.401
Amido	180.399	51.687	72.990			
group[h])	173.445	48.645	68.674			

[a]) Measured at 150 MHz at 20°. Data in the first and second row for each moiety refer to measurements in D_2O and (D_6)DMSO, respectively. [b]) For the notation of the sugar residues, see *Footnote 2*. [c]) The assignment can be reversed. [d]) The assignment can be reversed. [e]) The assignment can be reversed. [f]) *Me*O–C(2): δ (D_2O) 62.811; δ ((D_6)DMSO) 59.989. [g]) COO*Me*: δ (D_2O) 54.855; δ ((D_6)DMSO) 51.213. [h]) Me: δ (D_2O) 31.040, 30.855; δ ((D_6)DMSO) 29.522, 29.418.

anomeric region whose presence in the spectrum of their material was not reported by *Daubenspeck et al.* [2]. Two-dimensional NMR spectra of **17** showed that these resonances, which did not produce cross-peaks in heteronuclear ^{1}H,^{13}C contour maps, arose from the eight OH groups present in the molecule. The attachment to their respective C-atoms could be individually assigned by homonuclear ^{1}H,^{1}H correlation spectroscopy.

This research was supported by the Intramural Research Program of the *NIH*, *NIDDK*.

Experimental Part

General. Pd/C Catalyst (5%; *ESCAT 103*) was a product of *Engelhard Industries*. HATU (= *O*-1*H*-7-azabenzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate) was purchased from *Applied Biosystems*. Solns. in org. solvents were dried with anh. Na_2SO_4, and evaporated at 40°/2 kPa. TLC: for reaction monitoring, silica gel *60* coated glass slides. Column chromatography (CC): silica gel, *CombiFlash Companion Chromatograph* (*Isco*, *Inc.*); solvent mixtures less polar than those used for TLC were used at the onset of separation. Optical rotations: unless stated otherwise at r.t. in $CHCl_3$; *Perkin-Elmer-341* automatic polarimeter. NMR Spectra[2]): *Varian-Gemini* or *Varian-Mercury* spectrometers at 300 (^{1}H) and 75 MHz (^{13}C); *Bruker-Avance-600* spectrometer at 600 (^{1}H) and 150 MHz (^{13}C); chemical shifts δ in ppm and coupling constants *J* in Hz; assignments by homonuclear and heteronuclear 2-D correlation spectroscopy, run with the software supplied with the spectrometers. MS: liquid chromatography electron-spray ionization (ESI-MS) with *Hewlett-Packard-1100-MSD* spectrometer; gas chromatography/electron impact ionization (GC/EI-MS) with *Hewlett-Packard-5898A* spectrometer. Microanalyses: some compounds tenaciously retained traces of solvents, despite exhaustive drying, and anal. figures for C could not be obtained within ±0.4%; their structures were established from the mode of synthesis and NMR and MS data.

*3,4-Di-*O*-benzyl-6-deoxy-*L*-mannopyranose* (**1**). H_2O (0.1 ml) was added to a stirred soln. of methyl 3,4-di-*O*-benzyl-6-deoxy-1-thio-α-L-mannopyranoside [17] (4 g, 10.7 mmol) in acetone (15 ml), followed by NIS (2.9 g, 12.8 mmol). After 1 h (TLC (hexane/AcOEt 3:2) monitoring), the mixture was evaporated, and the residue subjected to CC (toluene/AcOEt 4:1): 2.61 g (85%) of **1**. ^{1}H-NMR: in accord with that of independently synthesized material [7]. ^{13}C-NMR (75 MHz, $CDCl_3$): 93.68 (C(1) (α)); 93.55 (C(1) (β)); 81.50 (C(3) (β)); 79.89 (C(4) (α)); 79.53 (C(3) (α)); 79.43 (C(4) (β)); 75.38 (Ph*C*H$_2$ (β)); 75.36 (Ph*C*H$_2$ (β)); 72.14 (Ph*C*H$_2$ (α)); 72.05 (Ph*C*H$_2$ (β)); 71.16 (C(5) (α)); 68.88 (C(2) (β)); 68.60 (C(2) (α)); 67.48 (C(5) (α)); 17.94 (C(6) (β)); 17.89 (C(6) (α)).

Benzyl 6-Hydroxyhexanoate (**3**). ε-Caprolactone (29 g, 20 ml) was added to a soln. of Na (1 g) in BnOH (250 ml), and the mixture was stirred at r.t. overnight. After neutralization with *Amberlite IR-120*, the filtrate was concentrated, and the residue subjected to CC (CH_2Cl_2/MeOH 100:1). The product thus obtained was distilled at 145°/$1.3\cdot10^{-2}$ Torr: pure (NMR, TLC) **3** (22 g, 39%). ^{1}H-NMR (300 MHz, $CDCl_3$): 5.10 (*s*, PhC*H*$_2$); 3.57 (*t*, *J* = 6.5, CH$_2$(6)); 2.50 (br. *s*, OH–C(6)); 2.35 (*t*, *J* = 7.5, CH$_2$(2)); 1.71–1.61 (*m*, CH$_2$(3)); 1.59–1.50 (*m*, CH$_2$(5)); 1.42–1.34 (*m*, CH$_2$(4)). ^{13}C-NMR (75 MHz, $CDCl_3$): 173.44 (C=O); 65.94 (Ph*C*H$_2$); 62.10 (C(6)); 34.00 (C(2)); 32.02 (C(5)); 25.06 (C(4); 24.43 (C(3)). HR-ESI-MS: 245.1154 ([*M* + Na]$^+$; calc. 245.1151).

*6-(Benzyloxy)-6-oxohexyl 3,4-Di-*O*-benzyl-6-deoxy-β-*L*-mannopyranoside* (**5**). Trifluoromethanesulfonic acid anhydride (1.95 ml, 11.52 mmol) was added at −20° to a stirred mixture of **3** (2.13 g, 9.6 mmol) and finely powdered K_2CO_3 (1.6 g, 11.52 mmol) in CH_2Cl_2 (20 ml). After 1 h at −20° (TLC (hexane/AcOEt 4:1) monitoring), the mixture was filtered and washed quickly with ice-cold aq. $NaHCO_3$ soln. and the org. phase dried and concentrated at 15–20°: unstable *benzyl 6-{[(trifluoromethyl)sulfonyl]-oxy}hexanoate* (**4**; quant.), sufficiently pure for the next step. ^{1}H-NMR (600 MHz, $CDCl_3$): 5.13 (*s*, PhC*H*$_2$); 4.51 (*t*, *J* = 7.3, CH$_2$(6)); 2.39 (*t*, *J* = 7.3, CH$_2$(2)); 1.85–1.81 (*m*, CH$_2$(5)); 1.73–1.67 (*m*, CH$_2$(3)); 1.48–1.44 (*m*, CH$_2$(4)). ^{13}C-NMR (150 MHz, $CDCl_3$): 173.15 (C=O); 118.61 (*q*, CF_3SO_2); 77.16 (C(6)); 66.33 (Ph*C*H$_2$); 33.84 (C(2)); 28.93 (C(5)); 24.60 (C(4); 24.11 (C(3)). GC/EI-MS: 354 (*M*$^+$; calc. 354).

A mixture of **1** (1.1 g, 3.2 mmol) and dibutyloxostannane (0.95 g, 3.8 mmol) in dry toluene (5 ml) was stirred for 2 h under reflux in a *Soxhlet* apparatus. After addition of CsF (0.57 g, 3.8 mmol), the mixture was concentrated at 50°/0.1 Torr. Molecular sieves (3 Å, 1 g) and MeCN (15 ml) were added to the residue containing stannylene acetal **2**, the suspension was cooled to 0°, and triflate **4** (3.4 g, 9.6 mmol) was added slowly with vigorous stirring, which was continued for 2 h at r.t. (TLC (toluene/acetone 4:1) monitoring). The mixture was filtered through a *Celite* pad, the filtrate concentrated, and the residue chromatographed (toluene/acetone 6:1): **5** (0.82 g, 52%). $[\alpha]_D = +11.0$ ($c = 0.6$, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): 5.11 (*s*, PhC*H*$_2$OCO); 4.94 (*d*, *J* = 10.9, 1 H, PhC*H*); 4.76 (*d*, *J* = 11.9, 1 H, PhC*H*); 4.67 (*d*, *J* = 11.9, 1 H, PhC*H*); 4.64 (*d*, *J* = 10.9, 1 H, PhC*H*); 4.35 (*d*, *J*(1,2) = 1.0, H–C(1)); 4.09 (br. *s*, H–C(2)); 3.89, 3.88 (2*t*, *J* = 6.5, 1 H, H$_a$–C(1″)); 3.55–3.50 (*m*, H–C(4), H–C(3)); 3.47, 3.45 (2*t*, *J* = 6.5, 1 H, H$_b$–C(1″)); 3.33–3.28 (*m*, H–C(5)); 2.41 (br. *s*, OH–C(2)); 2.36 (*t*, *J* = 7.5, CH$_2$(5″)); 1.69–1.60 (*m*, CH$_2$(4″), CH$_2$(2″)); 1.41–1.36 (*m*, CH$_2$(3″)); 1.33 (*d*, *J*(5,6) = 6.2, Me(6)). ^{13}C-NMR (150 MHz, $CDCl_3$): 173.40 (C=O); 95.53 (*J*(C,H) = 156.4, C(1)); 81.35 (C(3)); 79.61 (C(4)); 75.43 (Ph*C*H$_2$); 71.37 (C(5)); 71.27 (Ph*C*H$_2$); 69.30 (C(1″)); 68.44 (C(2)); 66.05 (Ph*C*H$_2$OCO); 34.10 (C(5″)); 29.10 (C(2″)); 25.51 (C(3″)); 24.60 (C(4″)); 17.81 (C(6)). HR-ESI-MS: 571.2676 ([*M* + Na]$^+$; calc. 571.2672). Anal. calc. for $C_{33}H_{40}O_7$ (548.67): C 72.24, H 7.35; found: C 72.13, H 7.38.

*Methyl 3-*O*-Acetyl-2,4-di-*O*-benzyl-6-deoxy-1-thio-α-*L*-mannopyranoside* (**6**) was prepared as described [18]. ^{1}H-NMR (300 MHz, $CDCl_3$): 5.16–5.12 (*m*, 2 H; incl. br. *s* at 5.15, H–C(1)); 5.13 (*dd*, *J*(2,3) = 3.3, *J*(3,4) = 9.6, H–C(3)); 4.68 (*d*, *J* = 12.2, 1 H, PhC*H*); 4.56 (*d*, *J* = 11.4, 1 H, PhC*H*); 4.53 (*d*, *J* = 11.4, 1 H, PhC*H*); 4.50 (*d*, *J* = 12.2, 1 H, PhC*H*); 4.13–4.04 (*m*, H–C(5)); 3.95 (*dd*, *J*(1,2) = 1.9, H–C(2)); 3.66 (*t*, *J* = 9.5, H–C(4)); 2.10 (*s*, MeS); 1.95 (*s*, MeCO); 1.34 (*d*, *J*(5,6) = 6.3, Me(6)). ^{13}C-NMR (75 MHz, $CDCl_3$): 170.04 (C=O); 82.94 (C(1)); 79.21 (C(4)); 77.30 (C(2)); 74.84 (Ph*C*H$_2$); 73.78 (C(3)); 72.42 (Ph*C*H$_2$); 68.04 (C(5)); 20.97 (*Me*CO); 17.96 (C(6)); 13.64 (MeS).

*6-(Benzyloxy)-6-oxohexyl 2-*O*-[3-O-Acetyl-2,4-di-*O*-benzyl-6-deoxy-α-*L*-mannopyranosyl]-3,4-di-*O*-benzyl-6-deoxy-β-*L*-mannopyranoside* (**7**). A mixture of **5** (2.36 g, 4.37 mmol), **6** (2.2 g, 5.25 mmol), and 4-Å molecular sieves (1.35 g) in CH_2Cl_2 (30 ml) was stirred for 15 min at r.t. The mixture was cooled to 0°, and NIS (1.39 g, 6.16 mmol) was added, followed by solid AgOTf (0.45 g, 1.76 mmol). The mixture

turned immediately red, and stirring was continued for 30 min at r.t. when TLC (hexane/AcOEt 3:2) showed that the reaction was complete. The mixture was filtered through a *Celite* pad into a separatory funnel containing aq. $NaHCO_3$ and $Na_2S_2O_3$ soln., and the product was extracted with CH_2Cl_2. The combined org. phase was dried and concentrated and the residue subjected to CC (hexane/AcOEt 20:1 → 7:1): 3.23 g (82%) of **7**. $[\alpha]_D = +38.5$ ($c = 0.8$, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): 5.27 (*dd*, $J(2,3) = 3.5$, $J(3,4) = 9.5$, H–C(3^{II})); 5.14 (*d*, $J(1,2) = 1.6$, H–C(1^{II})); 5.09 (*s*, PhCH_2OCO); 4.90–4.61 (*m*, 6 H, PhC*H*); 4.41 (*d*, $J = 12.2$, 1 H, PhC*H*); 4.35–4.32 (*m*, 2 H, H–C(5^{II}), incl. *d* at 4.32, $J(1,2) = 0.8$, H–C(1^{I})); 4.18–4.16 (*m*, 2 H, PhC*H*; incl. signal at *ca.* 4.16, H–C(2^{I})); 3.96 (*dd*, H–C(2^{II})); 3.86, 3.84 (2*t*, $J = 6.5$, 1 H, H_a–C(1″)); 3.57 (*t*, $J = 9.4$, H–C(4^{II})); 3.50–3.47 (*m*, H–C(3^{I}), H–C(4^{I})); 3.37, 3.36 (2*t*, $J = 6.5$, 1 H, H_b–C(1″)); 3.30–3.27 (*m*, H–C(5^{I})); 2.36 (*t*, $J = 6.8$, CH_2(5″)); 1.90 (*s*, MeCO); 1.65–1.56 (*m*, CH_2(4″), CH_2(2″)); 1.40–1.34 (*m*, CH_2(3″)); 1.33 (*d*, $J(5,6) = 5.8$, Me(6^{II})); 1.27 (*d*, $J(5,6) = 6.2$, Me(6^{I})). ^{13}C-NMR (150 MHz, $CDCl_3$): 173.47, 170.06 (C=O); 99.74 (J(C,H) = 155.6, C(1^{I})); 98.40 (J(C,H) = 173.2, C(1^{II})); 82.79 (C(3^{I})); 80.37 (C(4^{I})); 79.26 (C(4^{II})); 76.05 (C(2^{II}); 75.49 (Ph*C*H_2); 74.49 (Ph*C*H_2); 73.62 (C(3^{II})); 73.60 (C(2^{I})); 72.72 (Ph*C*H_2); 72.24 (Ph*C*H_2); 71.75 (C(5^{I})); 69.29 (C(1″)); 67.32 (C(5^{II})); 66.02 (Ph*C*H_2OCO); 34.11 (C(5″)); 29.30 (C(2″); 25.62 (C(3″)); 24.70 (C(4″)); 21.07 (*Me*CO); 17.85 (C(6^{II})); 17.78 (C(6^{I})). HR-ESI-MS: 939.4394 ([M + Na]$^+$; calc. 939.4295). Anal. calc. for $C_{55}H_{64}O_{12}$ (917.09): C 72.03, H 7.03; found: C 72.10, H 7.08.

6-Methoxy-6-oxohexyl 3,4-Di-O-*benzyl-2*-O-*(2,4-di*-O-*benzyl-6-deoxy-α*-L-*mannopyranosyl)-6-deoxy-β*-L-*mannopyranoside* (**8**). Methanolic 0.1M MeONa was added to a soln. of **7** (3.35 g, 3.65 mmol) in MeOH (50 ml) until the soln. became strongly basic. After *ca.* 5 h (TLC (hexane/AcOEt 3:2) monitoring), the mixture was neutralized with *Amberlite IR-120* and filtered, the filtrate concentrated, and the residue subjected to CC (toluene/acetone 100:1 → 20:1): 2.73 g (94%) of pure **8**. Colorless oil. $[\alpha]_D = +13$ ($c = 0.6$, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): 5.26 (*d*, $J(1,2) = 1.2$, H–C(1^{II})); 4.92–4.63 (*m*, 6 H, PhC*H*); 4.42 (*d*, $J = 11.8$, 1 H, PhC*H*); 4.33 (*d*, $J(1,2) = 0.9$, H–C(1^{I})); 4.25–4.22 (*m*, 2 H, H–C(5^{II}); incl. *d* at 4.23, $J = 11.8$, PhC*H*); 4.20 (br. *d*, H–C(2^{I})); 4.07 (*ddd*, $J(2,3) = 3.7$, J(3,OH) = $J(3,4) = 9.1$, H–C(3^{II})); 3.86, 3.85 (2*t*, $J = 6.7$, 1 H, H_a–C(1″)); 3.79 (*dd*, H–C(2^{II})); 3.62 (*s*, MeOCO); 3.51 (*dd*, $J(2,3) = 2.7$, $J(3,4) = 9.3$, H–C(3^{I})); 3.44 (*t*, $J = 9.2$, H–C(4^{I})); 3.39–3.37 (2*t*, $J = 6.9$, 1 H, H_b–C(1″)); 3.31–3.27 (*m*, 2 H, H–C(5^{I}); incl. *t* at 3.30, $J = 9.3$, H–C(4^{I})); 2.33 (*d*, OH–C(3^{II})); 2.23 (*t*, $J = 7.4$, CH_2(5″)); 1.62–1.56 (*m*, CH_2(4″), CH_2(2″)); 1.39–1.35 (*m*, CH_2(3″)); 1.33 (*d*, $J(5,6) = 6.1$, Me(6^{I})); 1.28 (*d*, $J(5,6) = 6.3$, Me(6^{II})). ^{13}C-NMR (150 MHz, $CDCl_3$): 173.98 (C=O); 99.77 (C(1^{II})); 97.23 (C(1^{I})); 82.87 (C(3^{I})); 82.15 (C(4^{II})); 80.17 (C(4^{I})); 78.28 (C(2^{II}); 75.32 (Ph*C*H_2); 74.38, 72.55 (Ph*C*H_2); 72.44 (C(2^{I})); 72.04 (Ph*C*H_2); 71.61 (C(5^{I})); 71.08 (C(3^{II})); 69.27 (C(1″)); 66.88 (C(5^{II})); 51.25 (MeOCO); 33.78 (C(5″)); 29.24 (C(2″)); 25.57 (C(3″)); 24.60 (C(4″)); 17.79, 17.78 (C(6^{I}), C(6^{II})). HR-ESI-MS: 799.4048 ([M + 1]$^+$; calc. 799.4057). Anal. calc. for $C_{47}H_{59}O_{11}$ (798.96): C 70.65, H 7.32; found: C 70.52, H 7.41.

6-Methoxy-6-oxohexyl O-*3*-O-*Acetyl-2,4-di*-O-*benzyl-6-deoxy-α*-L-*mannopyranosyl-(1 → 3)*-O-*2,4-di*-O-*benzyl-6-deoxy-α*-L-*mannopyranosyl-(1 → 2)-3,4-di*-O-*benzyl-6-deoxy-β*-L-*mannopyranoside* (**9**). As described for **7**, with **8** (2.65 g, 3.31 mmol), **6** (1.66 g, 3.98 mmol), 4-Å molecular sieves (1 g), AgOTf (0.34 g, 1.32 mmol), and NIS (1.05 g, 4.63 mmol). After *ca.* 30 min (TLC (toluene/AcOEt 9:1) monitoring), the mixture was worked up as described for **7**: 3.6 g (92%) of amorphous **9**. $[\alpha]_D = +21.9$ ($c = 1.2$, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): 5.28 (*dd*, $J(2,3) = 3.4$, $J(3,4) = 9.7$, H–C(3^{III})); 5.18 (*d*, $J(1,2) = 1.7$, H–C(1^{II})); 5.17 (*d*, $J(1,2) = 1.6$, H–C(1^{III})); 4.88 (*d*, $J = 10.9$, 1 H, PhC*H*); 4.81 (*d*, $J = 11.9$, 1 H, PhC*H*); 4.68–4.65 (*m*, 3 H, PhC*H*); 4.61 (*d*, $J = 10.9$, 1 H, PhC*H*); 4.58 (*d*, $J = 11.2$, 1 H, PhC*H*); 4.48 (*d*, $J = 12.2$, 1 H, PhC*H*); 4.43 (*d*, $J = 12.2$, 1 H, PhC*H*); 4.36 (*d*, $J = 12.2$, 1 H, PhC*H*); 4.34 (br. *s*, H–C(1^{I})); 4.30–4.28 (*m*, H–C(5^{II})); 4.23 (*dd*, $J(2,3) = 3.0$, $J(3,4) = 9.5$, H–C(3^{II})); 4.18 (*dd*, $J(1,2) = 0.8$, $J(2,3) = 2.6$, H–C(2^{I})); 4.13 (*d*, $J = 12.2$, 1 H, PhC*H*); 3.90, 3.88 (2*t*, $J = 6.2$, 1 H, H_a–C(1″)); 3.83 (*dd*, $J(2,3) = 2.9$, H–C(2^{II})); 3.82 (*dd*, $J(2,3) = 3.2$, H–C(2^{III})); 3.81–3.77 (*m*, H–C(5^{III})); 3.63 (*s*, MeOCO); 3.59 (*t*, $J \approx 9.8$, H–C(4^{II}), H–C(4^{III})); 3.50 (*dd*, $J(3,4) = 9.3$, H–C(3^{I})); 3.41 (*t*, $J = 9.3$, H–C(4^{I})); 3.41, 3.39 (2*t*, $J = 6.2$, 1 H, H_b–C(1″)); 3.32–3.27 (*m*, H–C(5^{I})); 2.27 (*t*, $J = 7.5$, CH_2(5″)); 1.91 (*s*, MeCO); 1.65–1.59 (*m*, CH_2(4″), CH_2(2″)); 1.42–1.38 (*m*, CH_2(3″)); 1.32 (*d*, $J(5,6) = 6.1$, Me(6^{I})); 1.24 (*d*, $J(5,6) = 6.4$, Me(6^{II})); 1.21 (*d*, $J(5,6) = 6.1$, Me(6^{III})). ^{13}C-NMR (150 MHz, $CDCl_3$): 174.07, 170.07 (C=O); 99.90 (C(1^{I})); 99.17 (C(1^{III})); 98.07 (C(1^{II})); 82.72 (C(3^{I})); 80.68 (C(4^{II})); 80.29 (C(4^{I})); 79.00 (C(4^{III})); 77.96 (C(2^{II}); 77.84 (C(3^{II})); 76.86 (C(2^{III})); 75.41, 74.59, 74.36 (Ph*C*H_2); 73.53 (C(3^{III}));

73.21 (C(2^{I})); 72.57, 72.51, 71.97 (Ph*C*H$_2$); 71.64 (C(5^{I})); 69.44 (C(1′); 67.96 (C(5^{II})); 67.93 (C(5^{III})); 51.39 (*Me*OCO); 33.89 (C(5′)); 29.33 (C(2′)); 25.63 (C(3′)); 24.69 (C(4′)); 21.03 (*Me*CO); 17.91 (C(6^{III})); 17.87 (C(6^{II})); 17.71 (C(6^{I})). HR-ESI-MS: 1189.5505 ([*M*+Na]$^+$; calc. 1189.5501). Anal. calc. for $C_{69}H_{82}O_{16}$ (1167.38): C 70.99, H 7.08; found: C 70.96, H 7.24.

6-Methoxy-6-oxohexyl O-*2,4-Di*-O-*benzyl-6-deoxy-α*-L-*mannopyranosyl-(1 → 3)*-O-*2,4-di*-O-*benzyl-6-deoxy-α*-L-*mannopyranosyl-(1 → 2)-3,4-di*-O-*benzyl-6-deoxy-β*-L-*mannopyranoside* (**10**). As described for **8**, with **9** (3.73 g, 3.31 mmol) and 0.1M MeONa. The mixture was neutralized with dry ice and concentrated and the residue subjected to CC (hexane/AcOEt 10:1 → 5:1): 3.45 g (96%) of syrupy **10**. $[\alpha]_D = +13.7$ ($c = 0.4$, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): 5.22 (br. *s*, H–C(1^{III})); 5.18 (*d*, *J*(1,2) = 1.6, H–C(1^{II})); 4.89–4.39 (*m*, 10 H, PhC*H*); 4.34–4.25 (*m*, 3 H, H–C(5^{II}), PhC*H*; incl. *d* at 4.34, *J*(1,2) = 0.8, H–C(1^{I})); 4.24 (*dd*, *J*(2,3) = 2.9, *J*(3,4) = 9.5, H–C(3^{II})); 4.17 (*d*, *J*(2,3) = 2.6, H–C(2^{I})); 4.03 (*d*, *J* = 11.8, 1 H, PhC*H*); 3.93 (*ddd*, H–C(3^{III})); 3.90, 3.89 (2*t*, *J* = 6.4, 1 H, H$_a$–C(1′)); 3.80 (*dd*, *J*(1,2) = 1.9, H–C(2^{II})); 3.72–3.68 (*m*, H–C(5^{III})); 3.67 (*dd*, *J*(1,2) = 1.4, *J*(2,3) = 3.5, H–C(2^{III})); 3.64 (*s*, MeOCO); 3.57 (*t*, *J* = 9.5, H–C(4^{II})); 3.50 (*dd*, *J*(3,4) = 9.2, H–C(3^{I})); 3.41 (*t*, *J* = 9.2, H–C(4^{I})); 3.42, 3.39 (2*t*, *J* = 6.4, 1 H, H$_b$–C(1′)); 3.31–3.28 (*m*, H–C(5^{I})); 3.26 (*t*, *J* = 9.3, H–C(4^{III})); 2.28 (*t*, *J* = 7.4, CH$_2$(5′)); 2.25 (*d*, *J*(3,OH) = 10.1, OH–C(3^{III})); 1.65–1.60 (*m*, CH$_2$(4′), CH$_2$(2′)); 1.42–1.38 (*m*, CH$_2$(3′)); 1.32 (*d*, *J*(5,6) = 6.1, Me(6^{I})); 1.25 (*d*, *J*(5,6) = 6.2, Me(6^{II})); 1.21 (*d*, *J*(5,6) = 6.3, Me(6^{III})). ^{13}C-NMR (150 MHz, $CDCl_3$): 174.07 (C=O); 99.93 (C(1^{I})); 98.30 (C(1^{III})); 98.15 (C(1^{II})); 82.69 (C(3^{I})); 82.17 (C(4^{III})); 80.99 (C(4^{II})); 80.41 (C(4^{I})); 79.18 (C(2^{III})); 78.06 (C(2^{II})); 77.00 (C(3^{II})); 75.46, 74.74, 74.35 (Ph*C*H$_2$); 73.31 (C(2^{I})); 72.61, 72.32, 72.00 (Ph*C*H$_2$); 71.68 (C(3^{III})); 71.62 (C(5^{I})); 69.50 (C(1′)); 67.98 (C(5^{II})); 67.35 (C(5^{III})); 51.42 (MeOCO); 33.91 (C(5′)); 29.33 (C(2′)); 25.63 (C(3′)); 24.71 (C(4′)); 17.93 (C(6^{II})); 17.90, (C(6^{I})); 17.79 (C(6^{III})). HR-ESI-MS: 1147.5372 ([*M*+Na]$^+$; calc. 1147.5395). Anal. calc. for $C_{67}H_{80}O_{15}$ (1125.34): C 71.51, H 7.17; found: C 71.56, H 7.16.

6-Methoxy-6-oxohexyl O-*4-Azido-3*-O-*benzyl-4,6-dideoxy-β*-D-*glucopyranosyl-(1 → 3)*-O-*2,4-di*-O-*benzyl-6-deoxy-α*-L-*mannopyranosyl-(1 → 3)*-O-*2,4-di*-O-*benzyl-6-deoxy-α*-L-*mannopyranosyl-(1 → 2)-3,4-di*-O-*benzyl-6-deoxy-β*-L-*mannopyranoside* (**13**). As described for **9**, with ethyl 4-azido-3-*O*-benzyl-2-*O*-(bromoacetyl)-4,6-dideoxy-1-thio-*β*-D-glucopyranoside (**11**) [14] (0.72 g, 1.6 mmol), **10** (2 g, 1.78 mmol), NIS (0.5 g, 2.24 mmol), and AgOTf (0.16 g, 0.64 mmol). After the usual workup, chromatography gave 1.72 g of **12** (66%). $[\alpha]_D = +17.9$ ($c = 1$, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): 5.17 (*d*, *J*(1,2) = 1.8, H–C(1^{II})); 5.11 (br. *s*, H–C(1^{III})); 5.04 (*dd*, *J*(1,2) = 8.0, *J*(2,3) = 9.6, H–C(2^{IV})); 4.89–4.32 (*m*, 16 H, 14 PhC*H*; incl. *d* at 4.64, H–C(1^{IV}) and *s* at 4.34, H–C(1^{I})); 4.32–4.28 (*m*, H–C(5^{II})); 4.19 (*dd*, *J*(2,3) = 3.1, *J*(3,4) = 9.4, H–C(3^{II})); 4.16 (*d*, *J*(2,3) = 2.5, H–C(2^{I})); 4.08 (*dd*, *J*(2,3) = 3.0, *J*(3,4) = 9.6, H–C(3^{III})); 3.88, 3.87 (2*t*, *J* = 6.5, 1 H, H$_a$–C(1′)); 3.86 (*dd*, H–C(2^{II})); 3.83–3.79 (*m*, 2 H, H–C(5^{III}); incl. *dd* at 3.82, *J*(1,2) = 1.8, H–C(2^{III})); 3.63 (*s*, MeOCO); 3.55 (*t*, *J* = 9.5, H–C(4^{III})); 3.52–3.49 (*m*, H–C(4^{II}), H–C(3^{I})); 3.43 (*t*, *J* = 9.2, H–C(4^{I})); 3.41, 3.39 (2*t*, *J* = 6.5, 1 H, H$_b$–C(1′)); 3.37 (*t*, *J* = 9.4, H–C(3^{IV})); 3.32, 3.30 (2*d*, *J* = 12.6, C*H*$_2$Br)); 3.31–3.28 (*m*, H–C(5^{I})); 3.12 (*t*, *J* = 9.5, H–C(4^{IV})); 3.02–2.90 (*m*, H–C(5^{IV})); 2.25 (*t*, *J* = 7.8, CH$_2$(5′)); 1.62–1.58 (*m*, CH$_2$(4′), CH$_2$(2′)); 1.40–1.36 (*m*, CH$_2$(3′)); 1.31 (*d*, *J*(5,6) = 6.1, Me(6^{I})); 1.23 (*d*, *J*(5,6) = 6.2, Me(6^{II})); 1.21 (*d*, *J*(5,6) = 6.2, Me(6^{III})); 1.10 (*d*, *J*(5,6) = 6.1, Me(6^{IV})). ^{13}C-NMR (150 MHz, $CDCl_3$): 174.00, 165.53 (C=O); 100.59 (*J*(C,H) = 160.9, C(1^{IV})); 99.97 (br. *s*, *J*(C,H) = 171.2, C(1^{III})); 98.84 (*J*(C,H) = 152.3, C(1^{I})); 97.90 (br. *s*, *J*(C,H) = 169.9, C(1^{II})); 82.69 (C(3^{I})); 80.98 (C(3^{IV})); 82.42 (C(4^{III})); 80.37 (C(4^{II})); 80.29 (C(4^{I})); 79.14 (C(3^{III})); 78.59 (C(2^{III}), C(3^{II})); 78.29 (C(2^{II})); 75.40, 75.04, 74.93, 74.51, 74.42 (Ph*C*H$_2$); 73.48 (br. *s*, C(2^{I})); 73.15, 72.57, 71.70 (Ph*C*H$_2$); 71.63 (C(5^{I})); 70.51 (C(5^{IV})); 69.42 (C(1′)); 68.14 (C(5^{III})); 67.72 (C(5^{II})); 67.63 (C(4^{IV})); 51.40 (*Me*OCO); 33.87 (C(5′)); 29.31 (C(2′)); 25.63 (C(3′)); 25.22 (CH$_2$Br); 24.70 (C(4′)); 18.15 (C(6^{IV})); 17.86, 17.83, 17.79 (C(6^{I}), C(6^{II}), C(6^{III})). HR-ESI-MS: 1528.5813 ([*M*+Na]$^+$; calc. 1528.5719), 1506.5923 ([*M*+1]$^+$; calc. 1506.5900).

As described for **6**, the fully protected **12** (1.47 g, 1.39 mmol) was treated with 0.1M MeONa for 1 h (TLC (toluene/acetone 9:1) monitoring). CC (toluene/acetone 30:1) gave amorphous **13** (1.2 g, 91%). $[\alpha]_D = +40$ ($c = 0.4$, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): 5.18 (*d*, *J*(1,2) = 1.8, H–C(1^{II})); 5.10 (br. *s*, H–C(1^{III})); 4.90–4.40 (*m*, 13 H, PhC*H*); 4.34–4.32 (*m*, 3 H, PhC*H*; incl. *d* at 4.34, *J*(1,2) = 0.8, H–C(1^{I}), and *d* at 4.33, *J*(1,2) = 8.0, H–C(1^{IV})); 4.27–4.22 (*m*, 1 H, H–C(5^{II})); 4.19–4.16 (*m*, H–C(3^{II}), H–C(2^{I})); 4.04 (*dd*, *J*(2,3) = 3.1, *J*(3,4) = 9.5, H–C(3^{III})); 3.89, 3.87 (2*t*, *J* = 6.3, 1 H, H$_a$–C(1′)); 3.84–3.83 (*m*, H–C(2^{II}), H–C(2^{III})); 3.81–3.76 (*m*, H–C(5^{III})); 3.63 (*s*, MeOCO); 3.61 (*t*, *J* = 9.6, H–

C(4^{III})); 3.52–3.48 (*m*, H–C(3^{I}), H–C(2^{IV}), H–C(4^{II})); 3.43 (*t*, *J* = 9.2, H–C(4^{I})); 3.41, 3.39 (2*t*, *J* = 6.3, 1 H, H$_b$–C(1″)); 3.32–3.27 (*m*, 2 H, H–C(5^{I}); incl. *t* at 3.30, *J* = 9.2, H–C(3^{IV})); 3.04 (*t*, *J* = 9.2, H–C(4^{IV})); 3.03–2.98 (*m*, H–C(5^{IV})); 2.70 (br. *s*, OH–C(2^{IV})); 2.25 (*t*, *J* = 7.8, H–CH$_2$(5″)); 1.61–1.58 (*m*, 4 H, CH$_2$(4″), CH$_2$(2″)); 1.38–1.33 (*m*, CH$_2$(3″)); 1.32 (*d*, *J*(5,6) = 6.1, Me(6^{I})); 1.24 (*d*, *J*(5,6) = 6.3, Me(6^{III})); 1.20 (*d*, *J*(5,6) = 6.2, Me(6^{II})); 1.14 (*d*, *J*(5,6) = 5.8, Me(6^{IV})). ^{13}C-NMR (150 MHz, $CDCl_3$): 174.07 (C=O); 103.67 (C(1^{IV})); 99.89 (C(1^{I})); 99.77 (br. *s*, C(1^{III})); 97.88 (br. *s*, C(1^{II})); 82.72 (C(3^{I})); 82.01 (C(3^{IV})); 80.65 (C(4^{III})); 80.44 (C(4^{II})); 80.40 (C(4^{I})); 80.08 (C(3^{III})); 78.31 (C(2^{II}), C(2^{III})); 78.15 (C(3^{II})); 75.73 (C(2^{IV})); 75.47, 75.16, 74.75, 74.41 (Ph*C*H$_2$); 73.40 (br. *s*, C(2^{I})); 73.04 , 72.63, 71.78 (Ph*C*H$_2$); 71.68 (C(5^{I})); 70.61 (C(5^{IV})); 69.49 (C(1″)); 68.28 (C(5^{III})); 67.76 (C(5^{II})); 67.00 (C(4^{IV})); 51.40 (*Me*OCO); 33.87 (C(5″)); 29.30 (C(2″)); 25.61 (C(3″)); 24.68 (C(4″)); 18.46 (C(6^{IV})); 18.04 (C(6^{III})); 17.87 (C(6^{II})); 17.80 (C(6^{I})). HR-ESI-MS: 1408.6567 ([*M* + Na]$^+$; calc. 1408.6508). Anal. calc. for $C_{80}H_{95}N_3O_{18}$ (1386.62): C 69.29, H 6.91, N 3.03; found: C 69.44, H 7.04, N 3.05.

6-Methoxy-6-oxohexyl O-*4-Azido-3*-O-*benzy-4,6-dideoxy-2*-O-*methyl-β*-D-*glucopyranosyl-(1 → 3)*-O-*2,4-di*-O-*benzyl-6-deoxy-α*-L-*mannopyranosyl-(1 → 3)*-O-*2,4-di*-O-*benzyl-6-deoxy-α*-L-*mannopyranosyl-(1 → 2)-3,4-di*-O-*benzyl-6-deoxy-β*-L-*mannopyranoside* (**14**). A soln. of **13** (440 mg, 0.32 mmol) in 1,2-dimethoxyethane (10 ml) was treated with MeI (18 ml, 288 mmol) and Ag_2O (16.9 g, 65.8 mmol) in the presence of a cat. amount of Me_2S [15]. After stirring for 24 h at r.t. (TLC (toluene/acetone 10 : 1) monitoring), the mixture was filtered, the solids were washed with toluene, the filtrate was concentrated, and the residue subjected to CC (toluene/acetone 1 : 1): syrupy **14** (400 mg, 90%). $[\alpha]_D = +28.9$ (*c* = 0.4, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): 5.16 (*d*, *J*(1,2) = 1.7, H–C(1^{II})); 5.12 (br. *s*, H–C(1^{III})); 4.96–4.36 (*m*, 15 H, 14 PhC*H*; incl. *d* at 4.58, *J*(1,2) = 8.0, H–C(1^{IV})); 4.33 (*d*, *J*(1,2) = 0.8, H–C(1^{I})); 4.28–4.24 (*m*, H–C(5^{II})); 4.20 (*dd*, *J*(2,3) = 3.1, *J*(3,4) = 9.4, H–C(3^{II})); 4.16 (*d*, *J*(2,3) = 2.3, H–C(2^{I})); 4.10 (*dd*, *J*(2,3) = 3.1, *J*(3,4) = 9.5, H–C(3^{III})); 3.89, 3.88 (2*t*, *J* = 6.9, 1 H, H$_a$–C(1″)); 3.87–3.80 (*m*, H–C(2^{II}), H–C(2^{III}), H–C(5^{III})); 3.63 (*s*, 2 MeO); 3.61 (*t*, *J* = 9.5, H–C(4^{III})); 3.54–3.49 (*m*, 2 H, H–C(4^{II}); incl. *dd* at 3.50, *J*(3,4) = 9.3, H–C(3^{I})); 3.43 (*t*, *J* = 9.2, H–C(4^{I})); 3.40, 3.38 (2*t*, *J* = 6.9, 1 H, H$_b$–C(1″)); 3.33–3.28 (*m*, 2 H, H–C(5^{I}), incl. *t* at 3.31, *J* = 9.2, H–C(3^{IV})); 3.11 (*dd*, *J*(2,3) = 9.0, H–C(2^{IV})); 3.02 (*t*, *J* = 9.8, H–C(4^{IV})); 2.95–2.99 (*m*, H–C(5^{IV})); 2.26 (*t*, *J* = 7.8, H–CH$_2$(5″)); 1.64–1.57 (*m*, CH$_2$(4″), CH$_2$(2″)); 1.41–1.36 (*m*, CH$_2$(3″)); 1.33 (*d*, *J*(5,6) = 6.2, Me(6^{I})); 1.27 (*d*, *J*(5,6) = 6.0, Me(6^{III})); 1.21 (*d*, *J*(5,6) = 6.2, Me(6^{II})); 1.07 (*d*, *J*(5,6) = 5.9, Me(6^{IV})). ^{13}C-NMR (150 MHz, $CDCl_3$): 174.03 (C=O); 103.44 (C(1^{IV})); 100.03 (br. *s*, C(1^{III})); 99.84 (C(1^{I})); 98.04 (C(1^{II})); 84.66 (C(2^{IV})); 82.68 (C(3^{I})); 82.59 (C(3^{IV})); 80.85 (C(4^{III})); 80.44 (C(4^{II})); 80.33 (C(4^{I})); 79.28 (C(2^{III})); 78.55 (C(3^{III})); 78.25 (C(2^{II})); 78.21 (C(3^{II})); 75.42, 75.32, 74.45 (Ph*C*H$_2$); 73.44 (br. *s*, C(2^{I})); 73.15, 72.53, 71.81 (Ph*C*H$_2$); 71.64 (C(5^{I})); 70.08 (C(5^{IV})); 69.41 (C(1″)); 68.12 (C(5^{III})); 67.79 (C(5^{II})); 67.50 (C(4^{IV})); 60.04 (MeO); 51.37 (*Me*OCO); 33.87 (C(5″)); 29.28 (C(2″)); 25.60 (C(3″)); 24.67 (C(4″)); 17.98 (C(6^{IV})); 17.92 (C(6^{III})); 17.83 (C(6^{II})); 17.76 (C(6^{IV})). HR-ESI-MS: 1422.6680 ([*M* + Na]$^+$; calc. 1422.6665). Anal. calc. for $C_{81}H_{97}N_3O_{18}$ (1400.65): C 69.46, H 6.98, N 3.00; found: C 69.74, H 7.04, N 2.94.

6-Methoxy-6-oxohexyl O-*3*-O-*Benzyl-4,6-dideoxy-4-[(3-hydroxy-3-methyl-1-oxobutyl)amino]-2*-O-*methyl-β*-D-*glucopyranosyl-(1 → 3)*-O-*2,4-di*-O-*benzyl-6-deoxy-α*-L-*mannopyranosyl-(1 → 3)*-O-*2,4-di*-O-*benzyl-6-deoxy-α*-L-*mannopyranosyl-(1 → 2)-3,4-di*-O-*benzyl-6-deoxy-β*-L-*mannopyranoside* (**16**). H_2O (*ca.* 4 ml) was added to a mixture of **14** (440 mg, 0.31 mmol) and pyridine (16 ml) until slight turbidity, followed by a few drops of pyridine until a clear soln. was formed. A slow stream of H_2S gas was passed through this soln. for 0.5 h. The mixture was stirred overnight at 40° (TLC (hexane/AcOEt 2 : 1) monitoring). After concentration, the residue was subjected to CC (hexane/AcOEt 3 : 1 → 2 : 5): pure (TLC, NMR) **15** (310 mg, 72%). ^{1}H-NMR (600 MHz, $CDCl_3$): 5.15 (*d*, *J*(1,2) = 1.7, H–C(1^{II})); 5.13 (br. *s*, H–C(1^{III})); 4.98 (*d*, *J* = 10.5, 1 H, PhC*H*); 4.97 (*d*, *J* = 11.3, 1 H, PhC*H*); 4.88 (*d*, *J* = 10.8, 1 H, PhC*H*); 4.71 (*d*, *J* = 11.5, 1 H, PhC*H*); 4.68–4.37 (*m*, 11 H, 10 PhC*H*; incl. *d* at 4.67, *J*(1,2) ≈ 9.8, H–C(1^{IV})); 4.32 (br. *s*, H–C(1^{I})); 4.27–4.23 (*m*, H–C(5^{II})); 4.19 (*dd*, *J*(2,3) = 3.1, *J*(3,4) = 9.2, H–C(3^{II})); 4.15 (*dd*, *J*(2,3) = 2.5, H–C(3^{III})); 4.12 (br. *s*, H–C(2^{I})); 3.90 (*dd*, *J*(1,2) = 1.7, H–C(2^{III})); 3.88, 3.86 (2*t*, *J* = 6.5, 1 H, H$_a$–C(1″)); 3.84 (*dd*, H–C(2^{II})); 3.83–3.79 (*m*, H–C(5^{III})); 3.65 (*s*, MeO); 3.63 (*s*, MeOCO); 3.62 (*t*, *J* = 9.5, H–C(4^{III})); 3.54–3.51 (*m*, H–C(4^{II})); 3.49 (*dd*, *J*(2,3) = 2.5, *J*(3,4) = 9.4, H–C(3^{I})); 3.42 (*t*, *J* = 9.3, H–C(4^{I})); 3.39–3.37 (2*t*, *J* = 6.5, 1 H, H$_b$–C(1″)); 3.30–3.26 (*m*, H–C(5^{I})); 3.14–3.11 (*m*, H–C(2^{IV}), H–C(3^{IV})); 3.05–3.01 (*m*, H–C(5^{IV})); 2.48–2.45 (*m*, H–C(4^{IV})); 2.26 (*t*, *J* = 7.8, CH$_2$(5″)); 1.65–1.58 (*m*, CH$_2$(4″), CH$_2$(2″)); 1.40–1.36 (*m*, CH$_2$(3″)); 1.31 (*d*, *J*(5,6) = 6.1,

Me(6^{I})); 1.26 (*d*, *J*(5,6) = 6.2, Me(6^{III})); 1.20 (*d*, *J*(5,6) = 6.2, Me(6^{II})); 1.03 (*d*, *J*(5,6) = 6.1, Me(6^{IV})). ^{13}C-NMR (150 MHz, $CDCl_3$): 174.12 (C=O); 103.75 (C(1^{IV})); 100.17 (br. *s*, C(1^{III})); 99.87 (C(1^{I})); 98.13 (C(1^{II})); 85.28 (C(3^{IV}); 83.95 (C(2^{II})); 82.70 (C(3^{I})); 80.99 (C(4^{III})); 80.50 (C(4^{II})); 80.38 (C(4^{I})); 79.44 (C(2^{III})); 78.25 (C(2^{II})); 78.17 (C(3^{III}); 78.10 (C(3^{II})); 75.46, 74.95, 74.52, 74.43 (Ph*C*H_2); 73.52 (br. *s*, C(2^{I})); 73.20, 72.55 (Ph*C*H_2); 72.36 (C(5^{IV})); 71.86 (Ph*C*H_2); 71.66 (C(5^{I})); 69.42 (C(1″)); 68.16 (C(5^{III})); 67.86 (C(5^{II})); 60.41 (MeO); 58.04 (C(4^{IV})); 51.43 (*Me*OCO); 33.90 (C(5″)); 29.31 (C(2″)); 25.63 (C(3″)); 24.68 (C(4″)); 17.99 (C6^{IV})); 17.94 (C(6^{III})); 17.86 (C(6^{I})); 17.75 (C(6^{II})). HR-ESI-MS: 1374.6906 ($[M+1]^+$; calc. 1374.6900).

HATU (83 mg, 0.22 mmol) followed by $^{i}Pr_2NEt$ (0.05 ml, 0.27 mmol) was added to a soln. of **15** (205 mg, 0.15 mmol) and 3-hydroxy-3-methylbutanoic acid (23 mg, 0.22 mmol) in CH_2Cl_2 (6 ml). The mixture was stirred for 1 h at r.t., when the soln. became clear (TLC (CH_2Cl_2/AcOEt 4 : 1) monitoring). After concentration, the residue was subjected to CC (CH_2Cl_2/MeOH 100 : 1): syrupy **16** (195 mg, 89%). $[\alpha]_D = +14$ (*c* = 0.3, $CHCl_3$). ^{1}H-NMR (600 MHz, $CDCl_3$): 5.35 (*d*, *J*(4,NH) = 8.9, NH); 5.15 (*d*, *J*(1, 2) = 1.7, H–C(1^{II})); 5.11 (br. *s*, H–C(1^{III})); 5.00–4.37 (*m*, 15 H, 14 PhC*H*; incl. *d* at 4.58, *J*(1,2) = 8.0, H–C(1^{IV})); 4.32 (*d*, *J*(1,2) = 0.8, H–C(1^{I})); 4.27–4.23 (*m*, H–C(5^{II})); 4.19 (*dd*, *J*(2,3) = 3.1, *J*(3,4) = 9.4, H–C(3^{II})); 4.15 (br. *d*, H–C(2^{I})); 4.11 (*dd*, *J*(2,3) = 3.1, *J*(3,4) = 9.5, H–C(3^{III})); 3.89 (*dd*, *J*(1,2) = 1.8, H–C(2^{III})); 3.88, 3.87 (2*t*, *J* = 6.8, 1 H, H_a–C(1″)); 3.86–3.81 (*m*, 2 H, H–C(5^{III}); incl. *dd* at 3.85, *J*(1, 2) = 2.0, H–C(2^{II})); 3.65 (*t*, *J* = 9.9, H–C(4^{IV})); 3.63 (*s*, MeOCO); 3.62 (*s*, MeO); 3.52–3.48 (*m*, 2 H, H–C(4^{II}); incl. *t* at 3.62, *J* = 9.5, H–C(4^{III})); 3.49 (*dd*, *J*(2,3) = 2.6, *J*(3,4) = 9.3, H–C(3^{I})); 3.42 (*t*, *J* = 9.2, H–C(4^{I})); 3.39, 3.38 (2*t*, *J* = 6.8, 1 H, H_b–C(1″)); 3.31–3.26 (*m*, 2 H, H–C(5^{I}); incl. *dd* at *ca.* 3.28, H–C(3^{IV})); 3.16 (*dd*, *J*(2,3) = 8.9, H–C(2^{IV})); 3.12–3.08 (*m*, H–C(5^{IV})); 2.26 (*t*, *J* = 7.8, CH_2(5″)); 2.19 (*d*, *J* = 15.0, H_a–C(1′)); 2.08 (*d*, *J* = 15.0, H_b–C(1′)); 1.63–1.57 (*m*, CH_2(4″), CH_2(2″)); 1.40–1.36 (*m*, CH_2(3″)); 1.32 (*d*, *J*(5,6) = 6.1, Me(6^{I})); 1.27 (*d*, *J*(5,6) = 6.3, Me(6^{III})); 1.21 (*s*, Me–C(3′)); 1.20 (*d*, *J*(5,6) = 6.3, Me(6^{II})); 1.18 (*s*, Me–C(3′)); 1.00 (*d*, *J*(5,6) = 6.2, Me(6^{IV})). ^{13}C-NMR (150 MHz, $CDCl_3$): 174.10, 172.31 (C=O); 103.68 (C(1^{IV})); 100.15 (br. *s*, C(1^{III})); 99.86 (C(1^{I})); 98.08 (C(1^{II})); 84.82 (C(2^{IV}); 82.69 (C(3^{I})); 80.82 (C(4^{III})); 80.44 (C(4^{II})); 80.36 (C(4^{I})); 80.03 (C(3^{IV})); 79.24 (C(2^{III})); 78.91 (C(3^{III}); 78.23 (C(2^{II}), C(3^{II})); 75.44 (Ph*C*H_2); 74.43 (2 Ph*C*H_2); 73.65, (Ph*C*H_2); 73.46 (br. *s*, C(2^{I})); 73.27, 72.52, 71.83 (Ph*C*H_2); 71.66 (C(5^{I})); 70.78 (C(5^{I})); 69.42 (C(3′)); 69.39 (C(1′)); 68.15 (C(5^{III})); 67.80 (C(5^{II})); 60.54 (MeO); 55.47 (C(4^{IV})); 51.43 (*Me*OCO); 47.68 (C(2′)); 33.92 (C(5″)); 29.29 (C(2″)); 29.28, 29.26 (*Me*$_2$C(3′)); 25.64 (C(3″)); 24.71 (C(4″)); 18.04 (C(6^{IV})); 17.96 (C(6^{III})); 17.84 (C(6^{I})); 17.78 (C(6^{II})). HR-ESI-MS: 1496.7227 ($[M+Na]^+$; calc. 1496.7284). Anal. calc. for $C_{86}H_{107}NO_{20}$ (1474.76): C 70.04, H 7.31, N 0.95; found: C 69.83, H 7.31, N 0.85.

6-Methoxy-6-oxohexyl O-*4,6-Dideoxy-4-[(3-hydroxy-3-methyl-1-oxobutyl)amino]-2*-O-*methyl-β*-D-*glucopyranosyl-(1 → 3)*-O-*6-deoxy-α*-L-*mannopyranoyl-(1 → 3)*-O-*6-deoxy-α*-L-*mannopyranosyl-(1 → 2)-6-deoxy-β*-L-*mannopyranoside* (**17**). A soln. of **16** (140 mg, 0.1 mmol) in 2-methoxyethanol (5 ml) was added to a suspension of 5% Pd/C catalyst (140 mg) in the same solvent (5 ml), and the mixture was stirred overnight under H_2 (TLC (CH_2Cl_2/MeOH 4 : 1) monitoring: 1 product). After filtration through a *Celite* pad, the filtrate was concentrated, and the residue subjected to CC (CH_2Cl_2/MeOH 4 : 1). After freeze-drying, **17** (75 mg, 94%) was obtained as a white amorphous solid. $[\alpha]_D = -31$ (*c* = 0.4, H_2O). HR-ESI-MS: 866.3970 ($[M+Na]^+$; calc. 866.3998). NMR: *Tables 1* and *2*.

6-Methoxy-6-oxohexyl 6-Deoxy-β-L-*mannopyranoside* (**21**). A mixture of 6-deoxy-L-mannose monohydrate (1 g, 5.39 mmol) and dibutyloxostannane (1.3 g, 5.31 mmol) in dry MeOH (25 ml) was stirred for 2 h at 60° until a clear soln. was obtained. Toluene (5 ml) and CsF (1 g, 6.62 mmol) were added, and the mixture was concentrated. The residue was dried at 50°/0.3 kPa for 2 h, then dissolved in DMF (8 ml), molecular sieves (3 Å, 0.75 g) were added, and the mixture was cooled to 0°. Freshly prepared benzyl 6-{[(trifluoromethyl)sulfonyl]oxy}hexanoate (**4**; 1.3 g, 3.66 mmol) was added, and the mixture was stirred at 0° for 2 h (TLC (CH_2Cl_2/MeOH 4 : 1) monitoring of **4**). The mixture was filtered and concentrated, and the residue subjected to CC (CH_2Cl_2/acetone 4 : 1): 0.52 g (38%) of 6-(benzyloxy)-6-oxohexyl 6-deoxy-β-L-mannopyranoside (**20**). ^{1}H-NMR (300 MHz, $CHCl_3$): 5.11 (*s*, PhCH_2OCO); 4.45 (*s*, H–C(1)); 3.98 (br. *s*, H–C(2)); 3.93, 3.90 (2*t*, *J* = 6.4, 1 H, H_a–C(1″)); 3.53, 3.50 (2*t*, *J* = 6.4, 1 H, H_b–C(1″)); 3.44–3.41 (*m*, H–C(3), H–C(4)); 3.29–3.25 (*m*, H–C(5)); 2.52 (*d*, *J*(3,OH) = 8.6, OH–C(3)); 2.48 (*d*, *J*(2,OH) = 2.5, OH–C(2)); 2.37 (*t*, *J* = 7.2, CH_2(5″)); 2.33 (br. *s*, OH–C(4)); 1.73–1.58 (*m*, CH_2(4″), CH_2(2″)); 1.45–1.35 (*m*, 5 H, CH_2(3″); incl. *d* at 1.36, *J*(5,6) = 6.1, Me(6)). ^{13}C-NMR (75 MHz, $CHCl_3$): 175.82

(C=O); 99.46 (C(1)); 74.40 (C(3)); 73.62 (C(4)); 71.51 (C(5)); 70.83 (C(2)); 69.34 (Ph*C*H$_2$OCO); 66.18 (C(1″)); 34.11 (C(5″)); 29.03 (C(2″)); 27.40 (C(3″)); 24.62 (C(4″)); 18.02 (C(6)). HR-ESI-MS: 391.1741 ([*M*+Na]$^+$; calc. 391.1733).

Ester **20** (0.5 g, 1.35 mmol) was dissolved in MeOH (25 ml), and the soln. was made strongly basic by addition of 0.1M MeONa/MeOH. After stirring overnight at r.t. (TLC (CH$_2$Cl$_2$/acetone 4:1) monitoring of the UV-positive **20**, formation of a single charring product) and usual workup, chromatography gave **21** (370 mg, 93%). M.p. 87–88° (from AcOEt). $[\alpha]_D = +42.0$ ($c = 0.3$, CHCl$_3$). ^{1}H-NMR (600 MHz, CD$_3$OD): 4.47 (*d*, *J*(1.2) = 1.0, H–C(1)); 3.88–3.85 (*m*, H$_a$–C(1″)); 3.87 (br. *d*, H–C(2)); 3.67 (*s*, MeOCO); 3.55, 3.53 (2*t*, *J* = 6.7, 1 H, H$_b$–C(1″)); 3.42 (*dd*, *J*(2,3) = 3.2, *J*(3,4) = 9.4, H–C(3)); 3.39 (*t*, *J* = 9.3, H–C(4)); 3.26–3.22 (*m*, H–C(5)); 2.36 (*t*, *J* = 7.4, CH$_2$(5″)); 1.68–1.62 (*m*, CH$_2$(4″), CH$_2$(2″)); 1.46–1.41 (*m*, CH$_2$(3″)); 1.32 (*d*, *J*(5,6) = 6.2, Me(6)). ^{13}C-NMR (150 MHz, CD$_3$OD): 175.80 (C=O); 100.58 (*J*(C,H) = 155.6)); 74.95 (C(3)); 73.84 (C(4)); 73.51 (C(5)); 72.49 (C(2)); 70.16 (C(1″)); 34.66 (C(5″)); 30.29 (C(2″)); 26.59 (C(3″)); 25.73 (C(4″)); 17.98 (C(6)). HR-ESI-MS: 315.1411 ([*M*+Na]$^+$; calc. 315.1420). Anal. calc. for C$_{13}$H$_{24}$NO$_7$ (292.33): C 53.41, H 8.28; found: C 53.11, H 8.27.

*6-Methoxy-6-oxohexyl 6-Deoxy-2-*O*-[6-deoxy-α-*L*-mannopyranosyl]-β-*L*-mannopyranoside* (**22**). As described for **17**, **8** (200 mg, 0.25 mmol) was treated with H$_2$. The product was eluted from a small silica gel column, mainly to remove residual catalyst. After freeze-drying, amorphous **22** (105 mg, 95%) was obtained. White solid. $[\alpha]_D = +66.6$ ($c = 0.5$, H$_2$O). ^{1}H-NMR (600 MHz, D$_2$O): 5.03 (*d*, *J*(1,2) = 1.7, H–C(1^{II})); 4.62 (*d*, *J*(1,2) = 0.9, H–C(1^I)); 4.17–4.13 (*m*, H–C(5^{II})); 4.08 (*dd*, *J*(2,3) = 3.4, H–C(2^{II})); 4.00 (*dd*, *J*(2,3) = 3.1, H–C(2^I)); 3.85–3.81 (*m*, 2 H, H$_a$–C(1″); incl. *dd* at 3.84, *J*(3,4) = 9.8, H–C(3^{II})); 3.68–3.66 (*m*, 4 H, H–C(3^I); incl. *s* at 3.68, MeOCO); 3.57, 3.55 (2*t*, *J* = 6.5, 1 H, H$_b$–C(1″)); 3.42–3.37 (*m*, 3 H, H–C(5^I); incl. *t* at 3.41, *J* = 9.8, H–C(4^{II}) and *t* at 3.40, *J* = 9.3, H–C(4^I)); 2.40 (*t*, *J* = 7.5, CH$_2$(5″)); 1.64–1.57 (*m*, CH$_2$(4″), CH$_2$(2″)); 1.40–1.36 (*m*, CH$_2$(3″)); 1.29 (*d*, *J*(5,6) = 5.9, Me(6^{II})); 1.23 (*d*, *J*(5,6) = 6.3, Me(6^I)). ^{13}C-NMR (150 MHz, D$_2$O): 181.75 (C=O); 105.55 (*J*(C,H) = 170.8, C(1^{II})); 103.94 (*J*(C,H) = 158.4, C(1^I)); 80.86 (C(2^I)); 77.68 (C(3^I)); 76.66 (C(5^{II})); 76.42, 76.38 (C(4^{I,II})); 74.49 (C(2^{II}); 74.28 (C(3^{II})); 73.97 (C(1″)); 72.80 (C(5^I)); 56.39 (*Me*OCO); 37.92 (C(5″)); 32.99 (C(2″)); 29.73 (C(3″)); 28.42 (C(4″)); 21.03 (C(6^I)); 21.01 (C(6^{II})). HR-ESI-MS: 461.1979 ([*M*+Na]$^+$; calc. 461.1999).

6-Methoxy-6-oxohexyl O*-6-Deoxy-α-L-mannopyranosyl-(1 → 3)-*O*-6-deoxy-α-L-mannopyranosyl-(1 → 2)-6-deoxy-β-L-mannopyranoside* (**23**). As described for **22**, from **10** (110 mg, 0.1 mmol). Elution of the crude product from a small silica gel column (CH$_2$Cl$_2$/MeOH 4:1) and freeze-drying yielded **23** (55 mg, 96%). White amorphous solid. $[\alpha]_D = +3.3$ ($c = 0.4$, H$_2$O). ^{1}H-NMR (600 MHz, D$_2$O): 5.02 (*d*, *J*(1,2) = 1.7, H–C(1^{III})); 5.00 (*d*, *J*(1,2) = 1.8, H–C(1^{II})); 4.63 (*d*, *J*(1,2) = 0.9, H–C(1^I)); 4.23–4.19 (*m*, H–C(5^{II})); 4.18 (*dd*, *J*(2,3) = 3.3, H–C(2^{III})); 4.07 (*dd*, *J*(2,3) = 3.4, H–C(2^{II})); 4.00 (*dd*, *J*(2,3) = 2.9, H–C(2^I)); 3.90 (*dd*, *J*(3,4) = 9.8, H–C(3^{II})); 3.91–3.82 (*m*, H–C(3^{III}), H–C(5^{III}), H$_a$–C(1″)); 3.70–3.67 (*m*, 4 H, H–C(3^I); incl. *s* at 3.68, MeOCO); 3.58, 3.56 (2*t*, *J* = 6.5, 1 H, H$_b$–C(1″)); 3.50 (*t*, *J* = 9.8, H–C(4^{II})); 3.46 (*t*, *J* = 9.8, H–C(4^{III})); 3.42–3.39 (*m*, 2 H, H–C(5^I); incl. *t* at 3.40, *J* = 9.4, H–C(4^I)); 2.40 (*t*, *J* = 7.5, CH$_2$(5″)); 1.65–1.58 (*m*, CH$_2$(4″), CH$_2$(2″)); 1.40–1.35 (*m*, CH$_2$(3″)); 1.31 (*d*, *J*(5,6) = 6.3, Me(6^{III})); 1.30 (*d*, *J*(5,6) = 5.8, Me(6^I)); 1.24 (*d*, *J*(5,6) = 6.2, Me(6^I)). ^{13}C-NMR (150 MHz, D$_2$O): 180.33 (C=O); 105.19 (*J*(C,H) = 172.7, C(1^{III})); 103.94 (*J*(C,H) = 173.8, C(1^{II})); 102.34 (*J*(C,H) = 155.0, C(1^I)); 80.93 (C(3^{II})); 79.52 (C(2^I)); 76.07 (C(3^I)); 75.14 (C(5^I)); 74.97 (C(4^I)); 74.73 (C(4^{III})); 74.08 (C(4^{II})); 72.91 (C(2^{III})); 72.87 (C(2^{II})); 72.79 (C(3^{III})); 72.46 (C(1″)); 71.84 (C(5^{III})); 71.51 (C(5^I)); 54.85 (*Me*OCO); 36.38 (C(5″)); 31.44 (C(2″)); 27.72 (C(3″)); 26.85 (C(4″)); 19.49 (C(6^{II})); 19.46 (C(6^I)); 19.43 (C(6^{III})). HR-ESI-MS: 607.2599 ([*M*+Na]$^+$; 607.2578).

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Received December, 30, 2005