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Note

Homologation of methyl 2-azido- and 2-acetamido-3,4-di-*O*-benzyl-2-deoxy-D-hexopyranosides with allyloxymethylmagnesium chloride

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Dedicated to Professor Gerard Descotes on the occasion of his 68th birthday and in appreciation of his achievements in carbohydrate chemistry

Abstract

Methyl 2-azido-2-deoxy-hexodialdo-1,5-pyranosides of the α-, β-D-*gluco* and α-D-*manno* configuration as well as methyl 2-acetamido-2-deoxy-hexodialdo-1,5-pyranosides of the α- and β-D-*gluco* configuration, protected at positions 3 and 4 with *O*-benzyl groups were reacted with an excess of allyloxymethylmagnesium or (phenyldimethylsilyl)methylmagnesium chlorides to afford mixtures of C-6 stereoisomeric heptopyranosides. Configuration of the products separated by column chromatography was assigned by ^{1}H NMR data.

Keywords: Methyl 2-azido-3,4-di-*O*-benzyl-2-deoxy-α-, -β-D-*gluco*- and -α-D-*manno*-heptopyranosides; Methyl 2-acetamido-3,4-di-*O*-benzyl-2-deoxy-α- and -β-D-*gluco*-heptopyranosides; Allyloxymethylmagnesium chloride; (Phenyldimethylsilyl)methylmagnesium chloride; Homologation reaction

A convenient route to higher homologs of hexoses consists in reaction of properly protected dialdo-1,5-pyranosides with C_1 Grignard reagents of the type $ROCH_2MgCl$ or R_3SiCH_2MgCl followed by chromatographic separation of the resulting stereoisomeric heptosides.[1–4] The homologation reaction is compatible with a variety of protecting groups including ethers, acetals[1–3] and esters.[4] In this paper, we present our results on chain-elongation reactions of methyl hexopyranosides containing 2-azido- or 2-acetamido-2-deoxy groupings.

Natural 2-amino-2-deoxy-heptoses are only scarcely known. G. Weise et al.[5] found, among the sugars of *Anacystis nidulans* cell wall LPS, a minor component to which was assigned the structure of a 2-amino-2-deoxy-heptose with the D-*glycero*-D-*gulo*(*ido*?) (**1**) configuration. 2,6-Diamino-2,3,4,6,7-pentadeoxy-D-*ribo*-heptopyranose (purpurosamine B, **2**) was found as a component of the aminoglycoside antibiotic gentamycin C_2.[6] D-[7] and LD-[8] forms of this sugar have been obtained by synthesis.

Methyl 2-azido-3,4-di-*O*-benzyl-2-deoxy-hexopyranosides of α- and β-D-*gluco* (**3** and

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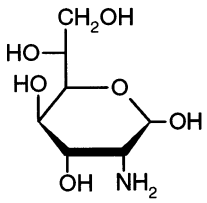

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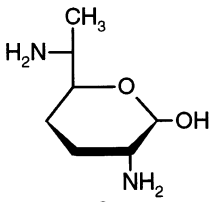

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4), and α-D-*manno* (**5**) configuration have been selected for the homologation experiments. For conversion to the corresponding dialdo-1,5-pyranosides (**6**–**8**), the Dess–Martin[9] oxidant proved to be the most efficient. Reaction of the freshly prepared aldehydes (**6**–**8**) with allyloxymethylmagnesium chloride occurred smoothly at low temperature and afforded mixtures of diastereoisomeric methyl heptosides in 58–60% overall yield. Both mixtures (**9**, **10** and **11**, **12**) stemming from the α- and β-D-*gluco* substrates (**6** and **7**) could be separated by simple-column chromatography. The mixture obtained from the α-D-*manno* aldehyde **8** resisted separation. However, after acetylation both 6-*O*-acetyl derivatives (**13**, **14**) were separated and characterized (Scheme 1).

From methyl 2-acetamido-3,4-di-*O*-benzyl-2-deoxy-α- and β-D-glucopyranosides (**15** and **16**) the corresponding hexodialdo-1,5-pyranosides (**17** and **18**) were prepared and reacted with allyloxymethylmagnesium chloride. From both reaction mixtures of diastereoisomeric heptosides, **19** (59%) and **20** (52%) were obtained. Their separation into components — directly after the reaction, as 6-*O*-acetyl derivatives, after de-allylation, and as 6,7-di-*O*-acetyl derivatives — was unsuccessful. Their NMR spectral and MS data characterized these mixtures only in part. Both aldehydes, **17** and **18**, were also reacted with (phenyldimethyl)silylmethylmagnesium chloride to furnish single heptosides (**21** and **22**, respectively) of L-*glycero*-D-*gluco* configuration in good yields. Oxidation of **21** and **22** (peroxyacetic acid, 0 °C) resulted in removal of the silyl group and formation of methyl heptosides **23** and **24**, respectively. However, when **21** was oxidized with the same reagent at −10 °C, a 'dimeric' product **25** was obtained.[10] The configuration of **23** and **24** was confirmed as LD on the basis of the CD spectra which showed a negative *E* band at 318.5 nm indicator of the LD configuration for the *glycero* moiety (Fig. 1).[11] 6,7-Diols **23** and **24** were next acetylated to yield 6,7-di-*O*-acetyl derivatives **26** and **27**, respectively. The results of chain elongation of aldehydes **6**–**8**, **17** and **18** are collected in Table 1.

The configuration of the methyl heptosides obtained was assigned on the basis of similarity of coupling constants $J_{5,6}$, $J_{6,7a}$, and $J_{6,7b}$ in the ^{1}H NMR spectra with the analogous data of heptosides of established configuration obtained earlier or with the CD spectra (Fig. 1). For compounds **11** and **12**, the configurational assignments are tentative, based on the observation of predominance of the DD stereoisomer over the LD counterpart in reactions of methyl hexodialdo-1,5-pyranosides with alkoxymethylmagnesium chloride.[3]

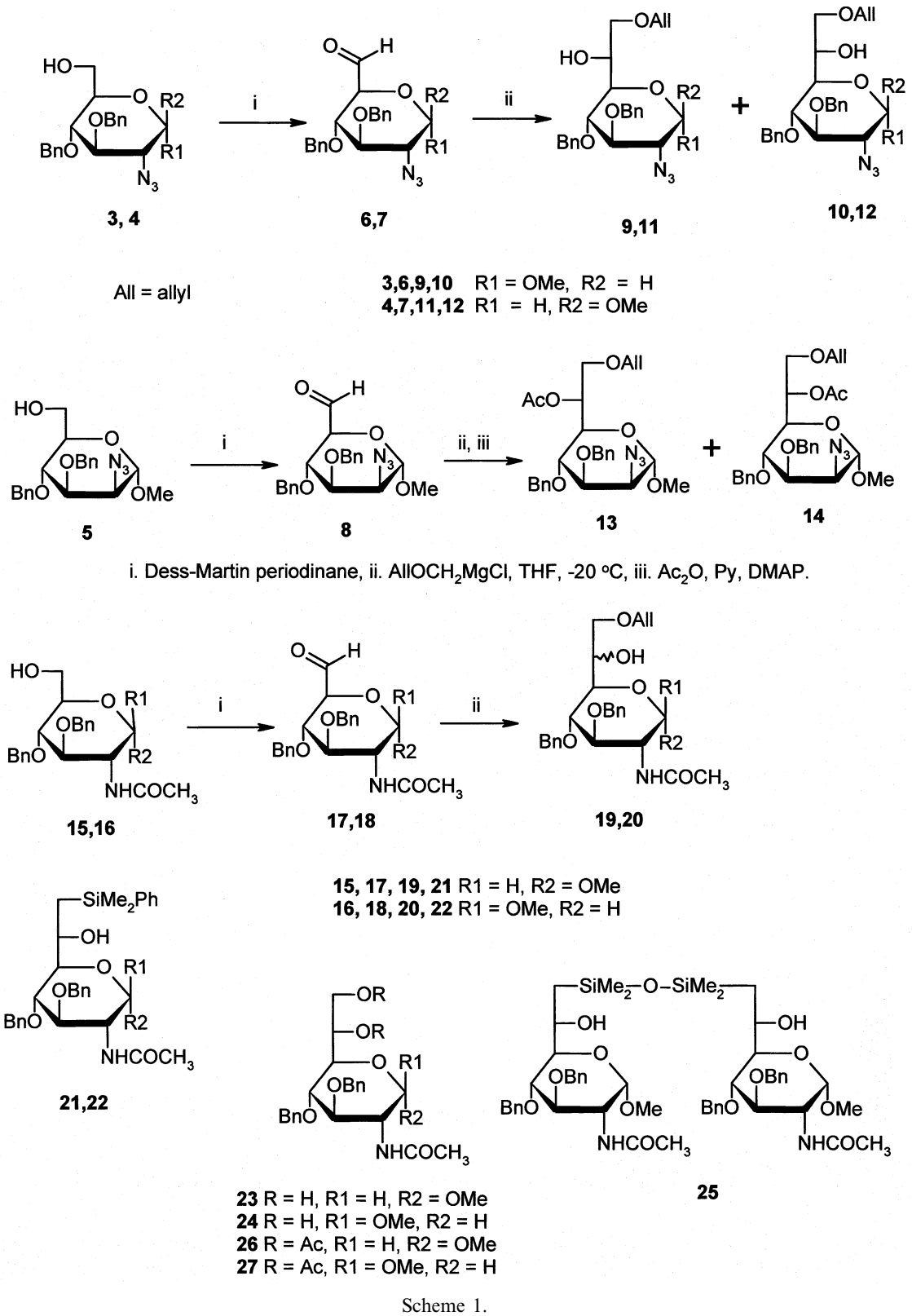
In summary, chain-elongation reactions with allyloxymethylmagnesium chloride led to the expected heptosides in moderate yields. Although the separation of diastereoisomers formed could be effected by simple chromatography, in some cases difficulties were encountered. Also, the stereoselectivities of these reactions were rather low, furnishing the DD stereoisomer in a light predominance over the LD form. Only in the case of 2-acetamido-2-deoxy aldehyde (**17**), the LD stereoisomer dominated over the DD partner. The chain-elongation reactions with the silyl reagent were superior, affording single diastereoisomeric (LD) heptosides in good yields.

The ^{1}H NMR spectrum of the aldehyde **18** deserves a short comment. The ^3J coupling constants recorded are not typical for a compound of the β-D-*gluco* configuration: $J_{1,2}$ 3.2, $J_{2,3}$ 4.3, and $J_{3,4}$ 4.2 Hz point at an equilibrium of both chair forms, $^4C_1$ and $^1C_4$. Epimerization of the formyl group at C-5 was excluded by reduction of **18** back to the substrate **16**. MM calculations (SYBYL, MMFF-94[12]) indicated a small strain energy difference between both chair forms with a small preference for the $^1C_4$ conformer. The ^{1}H NMR spectrum of the aldehyde **18** has been recorded earlier in literature and all coupling constants were found in agreement.[13] It is possible that the hydrated form of the aldehyde **18** is responsible for these abnormalities. The elemental analysis values point at a hemihydrate. Never-

theless, in the ^{1}H NMR spectrum of **18** a peak of the aldehyde proton is present at δ 9.80. Non-typical ^3J values were also noted by Paulsen[14] for the β anomer of the aldehyde **8**.

1. Experimental

Optical rotations were measured with a JASCO DIP 360 automatic polarimeter at



Scheme 1.

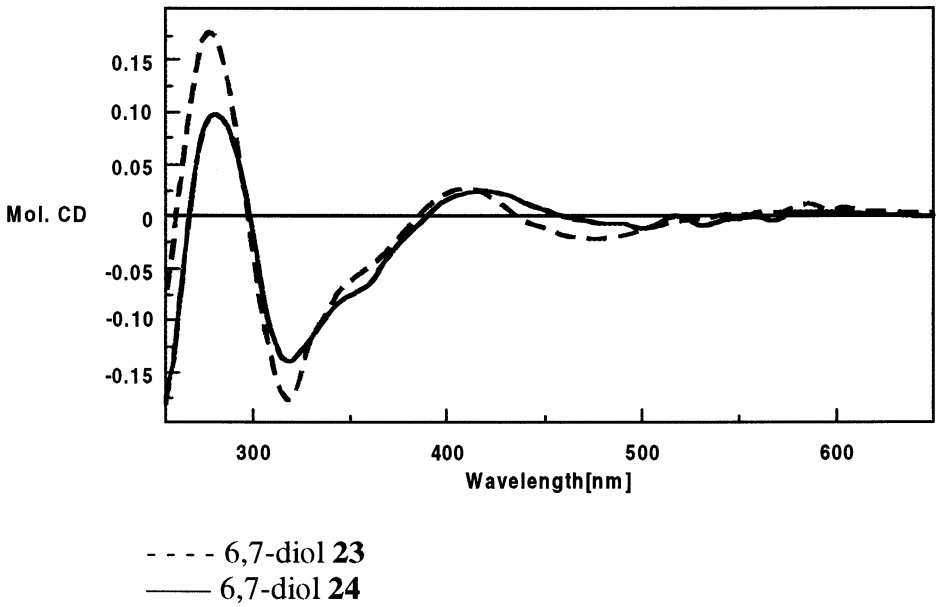


Fig. 1. CD spectra for compounds **23** and **24**.

Table 1
The results of chain-elongation reactions of methyl 2-azido- (**6**–**8**) and 2-acetamido- (**17**, **18**) -3,4-di-*O*-benzyl-2-deoxy-hexodialdo-1,5-pyranosides

Aldehyde no.	$AllOCH_2MgCl$				$PhMe_2SiCH_2MgCl$	
	Compound no.	DD (%)	Compound no.	LD (%)	Compound no.	LD (%)
6	9	34.4	10	24.4		
7	11	34.7	12	22.7		
8	13 [a]	37.8	14 [a]	11.1		
17			19 (59%) [b]		21	70
18			20 (51.7%) [b]		22	63

[a] 6-*O*-Acetyl derivatives.
[b] Unresolved mixture of stereoisomers.

20 ± 2 °C. NMR spectra were recorded with Varian Gemini AC-200 (200 MHz) or Bruker AM-500 (500 MHz) spectrometers in $CDCl_3$ solutions with Me_4Si as an internal standard unless otherwise noted. ^1H signals of aromatic groups occurred at the expected chemical shifts and are omitted in the description of spectra. ^{13}C NMR spectra were recorded in the DEPT 135 mode. TLC was performed on Silica Gel HF-254 ready plates and column chromatography on Silica Gel 230–400 or 70–230 mesh (E. Merck). Mass spectra (LSIMS, positive mode) were recorded on an AMD-604 mass spectrometer and on a Per Septive Biosystems Mariner™ mass spectrometer (ESI/TOF, positive mode). HPLC was carried out on a Shimadzu instrument: central unit C-R4A, pump unit LC-8A, UV-detector STD 250-6A on a column LiChroCART® 250-10 with ChiraSpher® NT (5 μm) (E. Merck). CD spectra were measured with JASCO 715 CD spectrometer for solutions of heptose 6,7-diols **23** and **24** in Me_2SO which the $(CH_3COO)_4Mo_2$ complex was added (molar ratio 1.25:1).

Methyl 2-azido-3,4-di-*O*-benzyl-2-deoxy-α- and -β-D-glucopyranosides (**3** and **4**),[14,15] and methyl 2-azido-3,4-di-*O*-benzyl-2-deoxy-α-D-mannopyranoside (**5**)[16] were obtained by azidonitration of 3,4,6-tri-*O*-acetyl-1,5-anhydro-2-deoxy-D-*arabino*-hex-1-enitol and the subsequent conventional steps.[14] Methyl 2-acetam-

ido-3,4-di-*O*-benzyl-2-deoxy-α- and -β-D-glucopyranosides (**15** and **16**) were prepared according to literature.[17,18]

Methyl 2-azido-3,4-di-O-*benzyl-2-deoxy-α*-D-gluco-*hexodialdo-1,5-pyranoside* (**6**).—To a solution of **3** (0.297 g) in $CHCl_2$ (15 mL), the Dess–Martin periodinane reagent[9] (0.379 g) was added and the solution was stirred 17 min at rt. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and saturated aq solutions of $Na_2S_2O_3$ (20 mL) and $NaHCO_3$ (25 mL) were added. The mixture was stirred for 15 min, the organic layer was separated, dried, and concentrated to dryness. The residue (0.350 g) was purified by chromatography in 1:1 → 1:2 hexane–EtOAc to yield **6** (0.279 g, 95%). ^{1}H NMR (200 MHz): δ 9.66 (d, 1 H, $J_{6,5}$ 0.4 Hz, C*H*O).

Methyl 7-O-*allyl-2-azido-3,4-di*-O-*benzyl-2-deoxy*-D- *and* -L-glycero-α-D-gluco-*heptopyranosides* (**9** and **10**).—To dry magnesium turnings (0.097 g, 4.06 mmol) under freshly distilled THF (0.1 mL), sublimed $HgCl_2$ (50 mg) was added and a few drops of neat pure allyloxymethyl chloride, freshly distilled before the reaction, were added while lowering the temperature to ca. −10 to −15 °C. When formation of the Grignard reagent has started, the rest of allyloxymethyl chloride (0.433 g, 4.06 mmol) in THF (2 mL) was added at −18 to −20 °C, and stirring was continued for 2 h. The temperature was then lowered to −30 °C and a solution of aldehyde **6** (0.233 g, 0.59 mmol) in abs THF (3 mL) was dropped in. The mixture was stirred at −20 °C for 1.5 h and slowly brought to rt while stirring for another 12 h. A cold (0 °C) aq satd solution of NH_4Cl (20 mL) was added and the products were extracted with ether. Ether extract was dried, concentrated to dryness and the residue was chromatographed with 3:2 hexane–EtOAc to give a mixture of **9** and **10** (0.162 g, 59%). Proportion of diastereoisomers **9** and **10** was determined to be 1.4:1 on the basis of ^{1}H NMR spectral OMe signals. The mixture was separated by HPLC using 4:1 hexane–EtOAc as eluent.

The configuration of stereoisomeric methyl heptosides **9**, **10** was determined by comparison of coupling constants ^3J of protons at C-6, -7A, and -7B. For D-*glycero*-D-*gluco* stereoisomers $J_{6,5}$ 3.5–4.2, $J_{6,7A} \sim 7.0$, $J_{6,7B}$ 3.5–4.0 Hz, and for L-*glycero*-D-*gluco* stereoisomers $J_{6,5} < 1.5$, $J_{6,7A} \sim 8.0$, $J_{6,7B}$ 4.9–5.3 Hz.[3] The values of analogous coupling constants were used also for configurational determination of the D- and L-*glycero*-D-*manno* stereoisomers **13** and **14**.[19]

Compound **9**: Yield (34.4%), colorless oil, $[\alpha]_D$ +68° (*c* 1.2, $CHCl_3$); ^{1}H NMR: δ 5.91–5.81 (m, 1 H, CH_2=C*H*), 5.25–5.12 (m, 2 H, CH_2=CH), 4.95–4.69 (2 × ABq, 4 H, 2 × CH_2Ph), 4.78 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.05 (ddd, 1 H, H-6), 3.99 (dd, 1 H, $J_{3,4}$ 8.8, $J_{3,2}$ 10.2 Hz, H-3), 3.96–3.93 (m, 2 H, CH_2–CH=CH_2), 3.82 (dd, 1 H, $J_{5,6}$ 3.6, $J_{5,4}$ 10.0 Hz, H-5), 3.64 (dd, 1 H, H-4), 3.52 (dd, 1 H, $J_{7A,6}$ 6.8, $J_{7A,7B}$ 9.9 Hz, H-7A), 3.50 (dd, 1 H, $J_{7B,6}$ 4.0 Hz, H-7B), 3.43 (s, 3 H, OCH_3), 3.38 (dd, 1 H, H-2), 2.68 (d, 1 H, $J_{OH,6}$ 3.5 Hz, O*H*); ^{13}C NMR: δ 134.47 (CH_2=*C*H), 117.34 (*C*H_2=CH), 98.45 (C-1), 81.02, 79.23, 72.35, 70.59 (C-3, 4, 5, 6), 75.51, 74.72 (2 × *C*H_2Ph), 72.35 (CH_2=CH–*C*H_2O), 70.62 (C-7), 63.80 (C-2), 55.25 (O*C*H_3); LSIMS HRMS for $C_{25}H_{31}N_3O_6 + Na^+$ ($[M + Na]^+$) Calcd: 492.21106. Found: 492.21145.

Compound **10**: Yield (24.2%), colorless oil, $[\alpha]_D$ +61° (*c* 1.0, $CHCl_3$); ^{1}H NMR: δ 5.94–5.85 (m, 1 H, CH_2=C*H*), 5.31–5.16 (m, 2 H, CH_2=CH), 4.91–4.73 (2 × ABq, 4 H, 2 × CH_2Ph), 4.79 (d, 1 H, $J_{1,2}$ 3.5 Hz, H-1), 4.13–4.09 (m, 1 H, H-6), 4.06–4.00 (m, 2 H, CH_2–CH=CH_2), 3.97 (dd, 1 H, $J_{3,4}$ 9.0, $J_{3,2}$ 10.1 Hz, H-3), 3.79 (dd, 1 H, $J_{4,5}$ 9.9 Hz, H-4), 3.72 (bd, 1 H, $J_{5,6} < 1$, H-5), 3.60 (dd, 1 H, $J_{7A,6}$ 7.9, $J_{7A,7B}$ 9.4 Hz, H-7A), 3.50 (dd, 1 H, $J_{7B,6}$ 5.4 Hz, H-7B), 3.39 (dd, 1 H, H-2), 3.37 (s, 3 H, OCH_3), 2.04 (d, 1 H, $J_{OH,6}$ 6.6 Hz, O*H*); ^{13}C NMR: δ 134.38 (CH_2=*C*H), 117.33 (*C*H_2=CH), 98.77 (C-1), 80.46, 77.73, 69.96, 67.37 (C-3, 4, 5, 6), 75.45, 75.09 (2 × *C*H_2Ph), 72.30 (CH_2=CH–*C*H_2O), 71.19 (C-7), 63.56 (C-2), 55.11 (O*C*H_3); LSIMS HRMS for $C_{25}H_{31}N_3O_6 + Na^+$ ($[M + Na]^+$) Calcd: 492.21106. Found: 492.20958.

Methyl 2-azido-3,4-di-O-*benzyl-2-deoxy-β*-D-gluco-*hexodialdo-1,5-pyranoside* (**7**).—The procedure used was analogous to the one described for **6**. Alcohol **4** (0.353 g) was converted to **7** (0.324 g, 92%), ^{1}H NMR: δ 9.68 (d, 1 H, $J_{5,6}$ 0.9 Hz, C*H*O).

Methyl 7-O-*allyl*-2-*azido*-3,4-*di*-O-*benzyl*-2-*deoxy*-D-glycero- *and* -L-glycero-β-D-gluco-*heptopyranosides* (**11** and **12**).—The procedure used was analogous to the one described for **9** and **10**. Starting from aldehyde **7** (0.264 g), **11** (0.108 g, 34.7%), and **12** (0.071 g, 22.7%) were obtained.

Compound **11**: White solid, mp 40–41 °C, $[\alpha]_D$ −11.3° (*c* 1.3, $CHCl_3$); ^1H NMR: δ 5.91–5.82 (m, 1 H, CH_2=C*H*), 5.26–5.13 (m, 2 H, CH_2=CH), 4.93–4.69 (2 × ABq, 4 H, 2 × CH_2Ph), 4.18 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.09–4.04 (m, 1 H, H-6), 3.97–3.93 (m, 2 H, CH_2–CH=CH_2), 3.63 (dd, 1 H, $J_{4,3}$ 8.8, $J_{4,5}$ 9.6 Hz, H-4), 3.56–3.42 (m, 4 H, H-3, -5, -7A, -7B), 3.55 (s, 3 H, OCH_3), 3.36 (dd, 1 H, $J_{2,3}$ 9.8 Hz, H-2); ^{13}C NMR: δ 134.5 (CH_2=*C*H), 117.3 (*C*H_2=CH), 103.05 (C-1), 83.60, 78.74, 74.77, 71.44 (C-3, 4, 5, 6), 75.56, 74.77 (2 × *C*H_2Ph), 72.33 (CH_2=CH–*C*H_2O), 70.62 (C-7), 66.43 (C-2), 57.10 (O*C*H_3); LSIMS HRMS for $C_{25}H_{31}N_3O_6 + Na^+$ ([M + Na]$^+$) Calcd: 492.21106. Found 492.21054. Anal. Calcd for $C_{25}H_{31}N_3O_6$: C, 63.95; H, 6.66; N, 8.95. Found: C, 63.95; H, 6.62; N, 8.81.

Stereoisomer **11** was also characterized as the 6-*O*-acetyl derivative **11Ac** obtained as a colorless oil, $[\alpha]_D$ −33° (*c* 0.6, $CHCl_3$); ^1H NMR: δ 5.88–5.79 (m, 1 H, CH_2=C*H*), 5.41 (ddd, 1 H, $J_{6,5}$ 1.9 Hz, H-6), 5.24–5.11 (m, 2 H, CH_2=CH), 4.90–4.71 (2 × ABq, 4 H, 2 × CH_2Ph), 4.15 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 3.97–3.88 (m, 2 H, CH_2–CH=CH_2), 3.65 (t, 1 H, $J_{4,3}$ 9.8, $J_{4,5}$ 8.9 Hz, H-4), 3.65 (dd, 1 H, $J_{7A,6}$ 6.1, $J_{7A,7B}$ 10.2 Hz, H-7A), 3.57 (s, 3 H, OCH_3), 3.54 (dd, 1 H, $J_{7B,6}$ 6.3 Hz, H-7B), 3.45 (dd, 1 H, H-2), 3.43 (t, 1 H, $J_{3,2}$ 9.9 Hz, H-3), 2.05 (s, 3 H, COCH_3); ^{13}C NMR: δ 134.38 (CH_2=*C*H), 117.16 (*C*H_2=CH), 102.87 (C-1), 83.53, 78.06, 74.70, 71.25, 66.25 (C-2, -3, -4, -5, -6), 67.50 (C-7), 75.67, 74.67, 72.07 (2 × *C*H_2Ph, CH_2=CH–*C*H_2O), 56.99 (O*C*H_3), 21.06 (CO*C*H_3); ESI HRMS for $C_{27}H_{33}N_3O_7 + Na^+$ ([M + Na]$^+$) Calcd: 534.2216. Found 534.2198.

Compound **12**: Colorless oil, $[\alpha]_D$ +34° (*c* 0.6, $CHCl_3$); ^1H NMR: δ 5.94–5.83 (m, 1 H, CH_2=C*H*), 5.30–5.14 (m, 2 H, CH_2=CH), 4.89–4.73 (2 × ABq, 4 H, 2 × CH_2Ph), 4.17 (d, 1 H, $J_{1,2}$ 8.1 Hz, H-1), 4.14–3.95 (m, 3 H, H-6, CH_2–CH=CH_2), 3.59 (t, 1 H, $J_{3,2}$ 7.2 Hz, H-3), 3.53 (s, 3 H, OCH_3), 3.46 (t, 1 H, $J_{4,3}$ 9.1 Hz, H-4), 3.37 (dd, 1 H, H-2), 3.34 (dd, 1 H, $J_{5,6}$ 1.5, $J_{5,4}$ 9.7 Hz, H-5); ^{13}C NMR: δ 134.47 (CH_2=*C*H), 117.33 (*C*H_2=CH), 103.06 (C-1), 83.12, 77.14, 74.00, 67.55, 66.24 (C-2, 3, 4, 5, 6), 75.52, 75.36 (2 × *C*H_2Ph), 72.32 (CH_2=CH–*C*H_2O), 70.92 (C-7), 57.03 (O*C*H_3); LSIMS HRMS for $C_{25}H_{31}N_3O_6 + Na^+$ ([M + Na]$^+$) Calcd: 492.21106. Found 492.21023.

Stereoisomer **12** was characterized also as the 6-*O*-acetyl derivative **12Ac** obtained as a colorless oil, $[\alpha]_D$ −65° (*c* 1.0, $CHCl_3$); ^1H NMR: δ 5.90–5.81 (m, 1 H, CH_2=C*H*), 5.46 (ddd, 1 H, $J_{6,5}$ 1.5 Hz, H-6), 5.28–5.15 (m, 2 H, CH_2=CH), 4.94–4.41 (2 × ABq, 4 H, 2 × CH_2Ph), 4.16 (d, 1 H, $J_{1,2}$ 8.0 Hz, H-1), 4.04–3.95 (m, 2 H, CH_2–CH=CH_2), 3.64 (dd, 1 H, $J_{7A,6}$ 7.5, $J_{7A,7B}$ 9.5 Hz, H-7A), 3.62 (dd, 1 H, $J_{7B,6}$ 6.6 Hz, H-7B), 3.57 (s, 3 H, OCH_3), 3.57 (dd, 1 H, H-5), 3.52 (t, 1 H, $J_{4,3}$ 8.2, $J_{4,5}$ 9.3 Hz, H-4), 3.48 (t, 1 H, $J_{3,2}$ 9.6 Hz, H-3), 3.40 (t, 1 H, H-2), 2.09 (s, 3 H, COCH_3); ^{13}C NMR: δ 134.35 (CH_2=*C*H), 117.22 (*C*H_2=CH), 103.26 (C-1), 83.67, 76.77, 72.37, 68.46, 66.31 (C-2, -3, -4, -5, -6), 66.92 (C-7), 75.64, 75.14, 72.14 (2 × *C*H_2Ph, CH_2=CH–*C*H_2O), 57.17 (O*C*H_3), 21.01 (CO*C*H_3); LSIMS HRMS for $C_{27}H_{33}N_3O_7 + Na^+$ ([M + Na]$^+$) Calcd: 534.22162. Found 534.22292.

Methyl 2-*azido*-3,4-*di*-O-*benzyl*-2-*deoxy*-α-D-manno-*hexodialdo*-1,5-*pyranoside* (**8**).—The procedure used was analogous to the one described for **6**. Alcohol **5** (0.513 g) was converted to **8** (0.497 g, 96%), ^1H NMR δ: 9.72 (d, 1 H, $J_{5,6}$ 1.1 Hz, C*H*O).

Methyl 6-O-*acetyl*-7-O-*allyl*-2-*azido*-3,4-*di*-O-*benzyl*-2-*deoxy*-D-glycero- *and* -L-glycero-α-D-manno-*heptopyranosides* (**13** and **14**).—The procedure was analogous to the one described for **9** and **10**. Starting from aldehyde **8** (0.436 g), an inseparable diastereomeric mixture of methyl heptosides (0.308 g, 60%) was obtained. This mixture was acetylated in the conventional manner (Ac_2O–Py) and the 6-*O* acetyl derivatives **13** and **14** were separated by column chromatography using 2:1 hexane–EtOAc as eluent.

Compound **13**: Colorless oil, $[\alpha]_D$ −38.2° (*c* 1.2, $CHCl_3$); ^1H NMR: δ 5.90–5.80 (m, 1 H,

CH_2=C*H*), 5.44 (ddd, 1 H, $J_{6,5}$ 2.0 Hz, H-6), 5.26–5.12 (m, 2 H, CH_2=CH), 4.96–4.65 (2 × ABq, 4 H, 2 × CH_2Ph), 4.33 (d, 1 H, $J_{1,2}$ 1.2 Hz, H-1), 3.99–3.89 (m, 2 H, CH_2–CH=CH_2), 3.88 (dd, 1 H, H-2), 3.86 (t, 1 H, H-4), 3.68 (dd,1 H, $J_{7A,6}$ 5.4, $J_{7A,7B}$ 10.4 Hz, H-7A), 3.64 (dd, 1 H, $J_{3,4}$ 9.6, $J_{3,2}$ 3.6 Hz, H-3), 3.61 (dd, 1 H, $J_{7B,6}$ 6.7 Hz, H-7B), 3.47 (dd, 1 H, $J_{5,4}$ 9.9 Hz, H-5), 3.51 (s, 3 H, OCH_3), 2.04 (s, 3 H, COCH_3); ^{13}C NMR: δ 134.52 (CH_2=*C*H), 117.02 (*C*H_2=CH), 100.46 (C-1), 81.57, 75.22, 74.48, 71.58 (C-3, 4, 5, 6), 74.99, 72.29, 72.03 (2 × *C*H_2Ph, CH_2=CH–*C*H_2O), 67.70 (C-7), 61.49 (C-2), 56.97 (O*C*H_3); 21.09 (CO*C*H_3); LSIMS HRMS for $C_{27}H_{33}N_3O_7 + Na^+$ ([M + Na]$^+$) Calcd: 534.22162. Found: 534.22315

Compound **14**: Colorless oil, $[\alpha]_D$ −71.2° (*c* 1.6, $CHCl_3$); ^{1}H NMR: δ 5.89–5.80 (m, 1 H, CH_2=C*H*), 5.50 (ddd, 1 H, H-6), 5.27–5.12 (m, 2 H, CH_2=CH), 4.87–4.45 (2 × ABq, 4 H, 2 × CH_2Ph), 4.35 (d, 1 H, $J_{1,2}$ 1.1 Hz, H-1), 4.03–3.93 (m, 2 H, CH_2–CH=CH_2), 3.90 (dd, 1 H, $J_{2,3}$ 3.1 Hz, H-2), 3.72 (t, 1 H, $J_{4,5}$ 8.7 Hz, H-4), 3.69 (dd, 1 H, $J_{3,4}$ 8.6 Hz, H-3), 3.67 (dd, 1 H, $J_{7A,6}$ 7.6, $J_{7A,7B}$ 9.5 Hz, H-7A), 3.62 (dd, 1 H, $J_{7B,6}$ 6.5 Hz, H-7B), 3.52 (s, 3 H, OCH_3), 3.50 (dd, 1 H, $J_{5,6}$ 1.5 Hz, H-5), 2.18 (s, 3 H, COCH_3); ^{13}C NMR: δ 134.64 (CH_2=CH), 117.32 (*C*H_2=CH), 101.16 (C-1), 81.83, 73.51, 73.17, 68.70 (C-3, 4, 5, 6), 75.64, 72.47, 72.34 (2 × *C*H_2Ph, CH_2=CH–*C*H_2O), 67.25 (C-7), 61.84 (C-2), 57.26 (O*C*H_3), 21.26 (CO*C*H_3); LSIMS HRMS for $C_{27}H_{33}N_3O_7 + Na^+$ ([M + Na]$^+$) Calcd: 534.22162. Found: 534.22051.

Methyl 2-acetamido-3,4-di-O-*benzyl-2-deoxy*-α-D-gluco-*hexodialdo*-*1,5*-*pyranoside* (**17**).—The procedure used was analogous to the one described for **6**. Alcohol **15** (0.831 g) was converted to the aldehyde **17** (0.800 g, 97%). ^{1}H NMR: δ 9.66 (d, 1 H, $J_{6,5}$ 1.2 Hz, C*H*O).

Methyl 2-acetamido-7-O-*allyl-3,4-di*-O-*benzyl-2-deoxy*-D-glycero- *and* -L-glycero-α-D-gluco-*heptopyranoside* (**19**).—To dry magnesium turnings (0.111 g 4.64 mmol) under freshly distilled THF (0.1 mL) sublimed $HgCl_2$ (50 mg) was added and a few drops of neat pure allyloxymethyl chloride (freshly distilled before the reaction) were added while lowering the temperature −10 to −15 °C. When the formation of the Grignard reagent had started, the rest of allyloxymethyl chloride (0.494 g, 4.64 mmol) in THF (2 mL) was added at −18 to −20 °C, and stirring was continued for 2 h. The temperature was then lowered to −30 °C and a solution of aldehyde **17** (0.340 g, 0.77 mmol) in abs THF (10 mL) was dropped in. The mixture was stirred at −20 °C for 2 h. A cold (0 °C) aq satd solution of NH_4Cl (20 mL) was added and the products were extracted with CH_2Cl_2. The organic extract was dried, concentrated to dryness, and the residue was chromatographed with 1:1 hexane–acetone to give a mixture of diastereoisomers **19** (0.235 g, 59%). The approximate proportion of diastereoisomeric heptosides in **19** was determined to be 1:1.5 on the basis of ^{1}H NMR spectrum. Some selected data from the spectrum of **19** are listed below: inter alia δ 4.61 (d, 1 H, $J_{1,2}$ 3.6 Hz) and 4.67 (d, 1 H, $J_{1,2}$ 3.7 Hz): two H-1, 4.07 (ddd, 1 H, $J_{6,5}$ 3.9 Hz) and 4.11 (ddd, 1 H, $J_{6,5}$ 0.9, $J_{6,7A}$ 7.2, $J_{6,7B}$ 6.2 Hz): two H-6, 3.54 (dd, 1 H, $J_{7A,6}$ 6.6, $J_{7A,7B}$ 9.9 Hz, H-7A), 3.50 (dd, 1 H, $J_{7B,6}$ 3.7 Hz, H-7B) and 3.58 (dd, 1 H, $J_{7A,7B}$ 9.4 Hz, H-7A), 3.50 (dd, 1 H, H-7B): two pairs of H-7, 3.38 (s, 3 H) and 3.28 (s, 3 H): two OCH_3; ^{13}C NMR: inter alia δ 98.61 and 98.87 (two C-1).

Other signals 5.94–5.83 (m, 2 H, 2 × CH_2=C*H*), 5.29–5.13 (m, 4 H, 2 × CH_2=CH), 4.94–4.60 (4 × ABq, 8 H, 4 × CH_2Ph), 4.05–3.95 (m, 4 H, 2 × CH_2–CH=CH_2), 3.74–3.63 (m, 4 H, H-3, 2 × H-4, H-5); LSIMS HRMS for $C_{27}H_{35}NO_7 + Na^+$ ([M + Na]$^+$) Calcd 508.23112. Found 508.23022.

Methyl 2-acetamido-3,4-di-O-*benzyl-2,7-dideoxy-7-(phenyldimethylsilyl)*-L-glycero-α-D-gluco-*heptopyranoside* (**21**).—To dry magnesium turnings (0.105 g 4.36 mmol) and sublimed $HgCl_2$ (50 mg) in freshly distilled dry THF (7 mL) was added dropwise (chloromethyl)dimethylphenylsilane (0.805 g, 4.36 mmol). The mixture was heated until the reaction started. The remaining solution of (chloromethyl)dimethylphenylsilane in THF was now added dropwise at such rate as to maintain a gentle reflux. After the Grignard reagent formation was complete the temperature was lowered to −20 °C and a solution of

aldehyde **17** (0.300 g, 0.726 mmol) in abs THF (15 mL) was added dropwise and stirring was continued for 2 h. A cold (0 °C) aq satd solution of NH_4Cl (20 mL) was added and the products were extracted with CH_2Cl_2. The organic extract was dried, concentrated to dryness, and the residue was purified by column chromatography with 1:1 hexane–acetone to give **21** (0.287 g, 70%) as a white solid, mp 113–114 °C, $[\alpha]_D$ +78.2° (*c* 0.8, $CHCl_3$); ^{1}H NMR: δ:5.23 (d, 1 H, $J_{NH,2}$ 9.2 Hz, N*H*), 4.88–4.59 (2 × ABq, 4 H, 2 × CH_2Ph), 4.66 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.14 (ddd, 1 H, $J_{2,3}$ 10.4 Hz, H-2), 4.05 (dt, 1 H, $J_{6,7A}$ 10.7, $J_{6,7B}$ 3.5, $J_{6,5} < 1.0$ Hz, H-6), 3.70 (t, 1 H, $J_{4,5}$ 9.5, $J_{4,3}$ 9.2 Hz, H-4), 3.63 (dd, 1 H, H-3), 3.35 (dd, 1 H, H-5), 3.27 (s, 3 H, OCH_3), 1.82 (s, 3 H, COCH_3), 1.36 (dd, 1 H, $J_{7A,7B}$ 14.9 Hz, H-7A), 0.90 (dd, 1 H, H-7B); ^{13}C NMR: δ 98.69 (C-1), 80.04, 78.71, 74.69, 66.70 (C-3, -4, -5, -6), 75.29, 74.67 (2 × *C*H_2Ph), 55.00 (O*C*H_3), 52.52 (C-2), 23.39 (CO*C*H_3), 21.47 (C-7); LSIMS HRMS for $C_{32}H_{41}NO_6Si + Na^+$ ($[M + Na]^+$) Calcd: 586.26009. Found: 586.26243. Anal. Calcd for $C_{32}H_{41}NO_6Si$: C, 68.17; H, 7.52; N, 2.19. Found: C, 68.10; H, 7.54; N, 2.29.

Methyl 2-acetamido-3,4-di-O-*benzyl-2-deoxy*-L-glycero-α-D-gluco-*heptopyranoside* (**23**).—To a solution of **21** (100 mg, 0.98 mmol) in AcOH (1.5 mL) were added KBr (0.025 g) and CH_3COONa (0.184 g). The mixture was cooled to 0 °C and stirred with exclusion of light. AcOH (0.97 mL of a 30% solution in AcOH) was added to the mixture. After stirring for 2 h at 0 °C the mixture was brought to rt. An aq 15% solution of $Na_2S_2O_5$ was added to reduce the remaining peroxyacetic acid. The product was extracted with CH_2Cl_2 and the organic extract was washed with water, aq 10% $NaHCO_3$ and water again, dried, and concentrated. The residue was chromatographed with 1:2 hexane–EtOAc to yield **23** (73 mg, 96%) as a colorless oil, $[\alpha]_D$ +105° (*c* 1.2, $CHCl_3$); ^{1}H NMR: δ 5.23 (d, 1 H, $J_{NH,2}$ 9.2 Hz, N*H*), 4.87–4.66 (2 × ABq, 4 H, 2 × CH_2Ph), 4.67 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.17 (ddd, 1 H, $J_{2,3}$ 10.6 Hz, H-2), 3.97 (bt, 1 H, H-6), 3.83 (t, 1 H, $J_{3,4}$ 9.4 Hz, H-3), 3.54 (dd, 1 H, $J_{7A,6}$ 6.3, $J_{7A,7B}$ 11.3 Hz, H-7A), 3.69 (t, 1 H, H-4), 3.65 (dd, 1 H, $J_{5,6}$ 1.5, $J_{5,4}$ 10.0 Hz, H-5), 3.68 (dd, 1 H, $J_{7B,6}$ 4.7 Hz, H-7B), 3.30 (s, 3 H, OCH_3), 1.82 (s, 3 H, COCH_3); ^{13}C NMR: δ 98.77 (C-1), 79.71, 78.01, 71.78, 68.83 (C-3, C-4, C-5, C-6), 75.15, 74.73 (2 × *C*H_2Ph), 64.80 (C-7), 55.09 (O*C*H_3), 52.42 (C-2), 23.35 (CO*C*H_3); LSIMS HRMS for $C_{24}H_{31}NO_7 + H^+$ ($[M + H]^+$) Calcd: 446.21788. Found: 446.21798.

Methyl 2-acetamido-6,7-di-O-*acetyl-3,4-di*-O-*benzyl-2-deoxy*-L-glycero-α-D-gluco-*hepto-pyranoside* (**26**).—Compound **23** was acetylated in the conventional manner (Ac_2O–Py) to give **26** as a colorless oil, $[\alpha]_D$ +48° (*c* 1.2, $CHCl_3$); ^{1}H NMR: δ 5.59 (ddd, 1 H, $J_{6,5}$ 1.3, $J_{6,7A}$ 6.7, $J_{6,7B}$ 8.1 Hz, H-6), 5.29 (d, 1 H, $J_{NH,2}$ 9.4 Hz, N*H*), 4.87–4.44 (2 × ABq, 4 H, 2 × CH_2Ph), 4.67 (d, 1 H, H-1), 4.27 (ddd, 1 H, $J_{2,1}$ 3.6, $J_{2,3}$ 10.5 Hz, H-2), 4.28–4.25 (m, 2 H, H-7A, H-7B), 3.82 (t, 1 H, $J_{5,4}$ 10.0 Hz, H-5), 3.72 (dd, 1 H, $J_{3,4}$ 8.8 Hz, H-3), 3.55 (dd,1 H, H-4), 3.31 (s, 3 H, OCH_3), 2.15, 2.04, 1.84 (3 × s, 9 H, 3 × COCH_3); ^{13}C NMR: δ 98.77 (C-1), 80.59, 77.41, 69.01, 67.88 (C-3, -4, -5, -6), 75.23, 75.13 (2 × *C*H_2Ph), 62.16 (C-7), 55.05 (O*C*H_3), 52.25 (C-2), 23.37, 20.87, 20.68 (3 × CO*C*H_3); LSIMS HRMS for $C_{28}H_{35}NO_9 + Na^+$ ($[M + Na]^+$) Calcd: 552.22095. Found: 552.22173.

Methyl 2-acetamido-3,4-di-O-*benzyl-2-deoxy*-β-D-gluco-*hexodialdo*-*1,5*-*pyranoside* (**18**).—To a solution of alcohol **16** (0.603 g) in CH_2Cl_2 (40 mL), the Dess–Martin periodinane reagent (0.738 g) was added and the solution was stirred 5 days at 32 °C. The reaction mixture was diluted with CH_2Cl_2 (20 mL), a saturated aq solution of $Na_2S_2O_3$ (20 mL) and a saturated aq solution of $NaHCO_3$ (25 mL) were added. After the mixture was stirred for 15 min, the organic layer was separated, dried, and concentrated to dryness. The residue (0.621 g) was purified by chromatography with 1:1 hexane–acetone to yield **18** (0.415 g, 69%); mp 197–198 °C, $[\alpha]_D$ −22.3° (*c* 0.4, $CHCl_3$); ^{1}H NMR: δ 9.80 (d, 1 H, $J_{6,5}$ 0.3 Hz, C*H*O), 6.45 (d, 1 H, $J_{NH,2}$ 8.9 Hz, N*H*), 4.71 (d, 1 H, $J_{1,2}$ 3.2 Hz, H-1), 4.70–4.53 (2 × ABq, 4 H, 2 × CH_2Ph), 4.28 (d, 1 H, $J_{5,4}$ 3.4 Hz, H-5), 4.19 (ddd, 1 H, $J_{2,3}$ 4.3 Hz, H-2), 3.98 (t, 1 H, $J_{4,3}$ 4.2 Hz, H-4), 3.76 (t, 1 H, H-3), 3.53 (s, 3 H, OCH_3), 1.82 (s, 3 H, COCH_3); ^{13}C NMR: δ 101.5 (C-1), 79.03, 75.46, 73.42 (C-3,

-4, -5), 73.05, 71.96 ($2 \times CH_2Ph$), 57.08 (OCH_3), 49.17 (C-2), 23.53 ($COCH_3$); LSIMS HRMS for $C_{23}H_{27}NO_6 + H^+$ ($[M+H]^+$) Calcd: 414.19166. Found: 414.19263. Anal. Calcd for $C_{23}H_{27}NO_6 \cdot 1/2\ H_2O$: C, 65.39; H, 6.68; N, 3.32. Found: C, 65.08; H, 6.81; N, 3.61.

*Methyl 2-acetamido-7-*O*-allyl-3,4-di-*O*-benzyl-2-deoxy-*D*-glycero- and -*L*-glycero-β-*D*-gluco-heptopyranosides* (**20**).—Starting from aldehyde **18** (0.327 g), an inseparable diastereomeric mixture of heptosides (**20**, 0.199 g, 52%) was obtained in the form of a colorless oil. The proportion of stereoisomers in **20** was close to 1:1 on the basis of ^{1}H NMR data. Selected data from the ^{1}H NMR spectrum are given below: inter alia δ 4.74 (d, 1 H, $J_{1,2}$ 8.1 Hz) and 4.64 (d, 1 H, $J_{1,2}$ 7.4 Hz): two H-1, 3.45 (s, 3 H) and 3.44 (s, 3 H): two OCH_3; ^{13}C NMR: δ 101.31, 101.06 ($2 \times$ C-1); LSIMS HRMS for $C_{27}H_{35}NO_7 + Na^+$ ($[M+Na]^+$) Calcd: 508.23112. Found 508.23075.

*Methyl 2-acetamido-3,4-di-*O*-benzyl-2,7-dideoxy-7-(phenyldimethylsilyl)-*L*-glycero-β-*D*-gluco-heptopyranoside* (**22**).—The procedure used was analogous to the one described for **21**. Starting from aldehyde **18** (0.495 g), **22** (0.426 g, 63%) was obtained as a colorless oil, $[\alpha]_D$ −10.6° (*c* 1.01, $CHCl_3$); ^{1}H NMR: δ 5.43 (d, 1 H, $J_{NH,2}$ 7.8 Hz, N*H*), 4.87–4.60 ($2 \times$ ABq, 4 H, $2 \times CH_2Ph$), 4.58 (d, 1 H, $J_{1,2}$ 8.2 Hz, H-1), 4.10–4.02 (m, 1 H, H-6), 4.00 (t, 1 H, $J_{3,4}$ 9.3 Hz, H-3), 3.67 (t, 1 H, $J_{4,5}$ 9.1 Hz, H-4), 3.45 (s, 3 H, OCH_3), 3.31 (ddd, 1 H, $J_{2,3}$ 9.9 Hz, H-2), 3.12 (d, 1 H, $J_{5,6} < 1.0$ Hz, H-5), 1.85 (s, 3 H, $COCH_3$), 1.35 (dd, 1 H, $J_{7A,6}$ 9.2, $J_{7A,7B}$ 14.7 Hz, H-7A), 1.10 (dd, 1 H, $J_{7B,6}$ 5.6 Hz, H-7B), 0.36, 0.34 (2s, 6 H, $(CH_3)_2Si$); ^{13}C NMR: δ 101.09 (C-1), 80.48, 78.97, 77.90, 67.01 (C-3, -4, -5, -6), 74.91, 74.67 ($2 \times CH_2Ph$), 57.22, 55.89 (OCH_3, C-2), 23.59 ($COCH_3$), 22.04 (C-7), −2.05, −2.56 $(CH_3)_2Si$; LSIMS HRMS for $C_{32}H_{41}NO_6Si + Na^+$ ($[M+Na]^+$) Calcd: 586.26009 Found: 586.26274.

*Methyl 2-acetamido-3,4-di-*O*-benzyl-2-deoxy-L-glycero-β-D-gluco-heptopyranoside* (**24**).—The procedure used was analogous to the one described for **23**. From **22** (107 mg), **24** (50 mg, 59%) was obtained as a colorless oil, $[\alpha]_D$ −42.8° (*c* 0.8, CH_3OH); ^{1}H NMR (CD_3OD): δ 4.83–4.34 (m, 6 H, H-1, N*H*, $2 \times CH_2Ph$), 3.96 (ddd, $J_{5,6}$ 1.4, $J_{6,7A}$ 6.9, $J_{6,7B}$ 8.2 Hz, H-6), 3.81 (dd, 1 H, $J_{4,3}$ 8.6, $J_{4,5}$ 8.5 Hz, H-4), 3.78 (dd, 1 H, $J_{3,4}$ 9.0, $J_{3,2}$ 9.6 Hz, H-3), 3.62–3.71 (m, 3 H, H-5, H-7A, H-7B), 3.45 (s, 3 H, OCH_3), 1.88 (s, 3 H, $COCH_3$); ^{13}C NMR (CD_3OD): δ 102.15 (C-1), 82.97, 77.92, 73.52, 68.97 (C-3, -4, -5, -6), 74.64, 74.48 ($2 \times CH_2Ph$), 62.42 (C-7), 55.53, 55.25 (OCH_3, C-2), 21.62 ($COCH_3$); LSIMS HRMS for $C_{24}H_{31}NO_7 + Na^+$ ($[M+Na]^+$) Calcd: 468.19982. Found: 468.20018.

*Methyl 2-acetamido-6,7-di-*O*-acetyl-3,4-di-*O*-benzyl-2-deoxy-L-glycero-β-D-gluco-heptopyranoside* (**27**).—Compound **24** was acetylated in the conventional manner (Ac_2O/Py) to give **27** as a colorless oil, $[\alpha]_D$ +13.0° (*c* 1.0, $CHCl_3$); ^{1}H NMR: δ 5.58–5.47 (m, 2 H, N*H*, H-6), 4.89–4.42 ($2 \times$ ABq, 4 H, $2 \times CH_2Ph$), 4.74 (d, 1 H, $J_{1,2}$ 7.9 Hz, H-1), 4.38 (dd, 1 H, $J_{7A,6}$ 6.0, $J_{7A,7B}$ 11.1 Hz, H-7A), 4.21 (dd, 1 H, $J_{7B,6}$ 7.1 Hz, H-7B), 4.18 (t, 1 H, H-3), 3.59 (bd, 1 H, $J_{5,4}$ 9.8 Hz, H-5), 3.53 (t, 1 H, $J_{4,3}$ 8.7 Hz, H-4), 3.47 (s, 3 H, OCH_3), 3.34 (ddd, 1 H, $J_{2,NH}$ 8.2, $J_{2,3}$ 9.1 Hz, H-2), 1.87 (s, 3 H, $COCH_3$); ^{13}C NMR: δ 101.99 (C-1), 81.08, 77.68, 72.68, 68.15 (C-3, -4, -5, -6), 74.94, 74.92 ($2 \times CH_2Ph$), 62.09 (C-7), 57.43, 56.86 (OCH_3, C-2), 23.58 ($COCH_3$), 20.95, 20.74 ($COCH_3$); LSIMS HRMS for $C_{28}H_{35}NO_9 + Na^+$ ($[M+Na]^+$) Calcd: 552.22095. Found: 552.22372

*1,3-Di-[methyl 2-acetamido-3,4-di-*O*-benzyl-2,7-dideoxy-L-glycero-α-D-gluco-heptopyranos-7-yl]-1,1,3,3-tetramethyl-disiloxane* (**25**).—The procedure used was analogous to the one described for **23** except for the temperature (−10 °C). From **21** (93 mg) **25** (80 mg, 50%) was obtained as a white solid; mp 212–214 °C, $[\alpha]_D$ +63° (*c* 0.7, $CHCl_3$); ^{1}H NMR: δ 5.27 (d, 1 H, $J_{NH,2}$ 9.1 Hz, N*H*), 4.92–4.64 ($2 \times$ ABq, 4 H, $2 \times CH_2Ph$), 4.69 (d, 1 H, $J_{1,2}$ 3.6 Hz, H-1), 4.17 (ddd, 1 H, $J_{2,3}$ 10.1 Hz, H-2), 3.73 (t, 1 H, $J_{4,5}$ 9.4, $J_{4,3}$ 9.1 Hz, H-4), 3.67 (dd, 1 H, H-3), 3.40 (dd, 1 H, $J_{5,6}$ 1.0 Hz, H-5), 3.31 (s, 3 H, OCH_3), 1.83 (s, 3 H, $COCH_3$), 0.89 (dd, 1 H, $J_{7A,6}$ 7.5 Hz, H-7A), 0.69 (dd, 1 H, $J_{7B,6}$ 3.6, $J_{7B,7A}$ 14.8 Hz, H-7B), 0.19, 0.17 (2 s, 6 H, $[(CH_3)_2Si]$); ^{13}C NMR: δ 98.89 (C-1), 80.38, 78.84, 774.72, 62.01 (C-3, -4, -5, -6), 75.46, 75.39 ($2 \times CH_2Ph$), 55.24,

55.21 ($2 \times OCH_3$), 52.86, 52.82 ($2 \times$ C-2), $2 \times$ 23.59 ($2 \times COCH_3$), 22 99 (C-7), 0.73, 0.42 [$(CH_3)_2Si$]; ESI HRMS for $C_{52}H_{72}N_2O_{13}Si_2 + Na^+$ ($[M + Na]^+$) Calcd: 1011.4474. Found: 1011.4465. Anal. Calcd for $C_{52}H_{72}N_2O_{13}Si_2$: C, 63.13; H, 7.34; N, 2.83. Found: C, 63.07; H, 7.51; N, 2.72.

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