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Synthesis and structure of 6-amino-2,3,6-trideoxy-D-*erythro*-hexono-1,6-lactam and 6-amino-3,6-dideoxy-D-*xylo*-hexono-1,6-lactam

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Abstract

Solid-state conformations of 6-amino-2,3,6-trideoxy-D-*erythro*-hexono-1,6-lactam (**3a**) and 6-amino-3,6-dideoxy-D-*xylo*-hexono-1,6-lactam (**7a**) were determined using X-ray diffraction. Conformations of the compounds **3a**, **7a**, and their per-*O*-acetyl derivatives 4,5-di-*O*-acetyl-6-amino-2,3,6-trideoxy-D-*erythro*-hexono-1,6-lactam (**3b**) and 2,4,5-tri-*O*-acetyl-6-amino-3,6-dideoxy-D-*xylo*-hexono-1,6-lactam (**7b**) in solutions were deduced from the analysis of NMR spectra using a modified Karplus equation and compared with the results of circular dichroism measurement of lactams **3a** and **7a**. Conformation $^{4}C_{1,N}$ was revealed for solid lactams **3a** and **7a** and for lactams **7a** and **7b** in solution, while lactams **3a** and **3b** in solution exist in the ~1:1 equilibrium of the conformers $^{4}C_{1,N}$ and $^{1,N}C_{4}$.

Keywords: Aminodeoxyhexonolactams; Crystal structure determination; Conformational analysis; Nuclear magnetic resonance; Circular dichroism

1. Introduction

In our previous papers, an important role of the C-2 substituent in equilibration of the conformation of 6-amino-6-deoxyhexono-1,6-lactams or 5-amino-5-deoxyhexono-1,5-lactams in solution [1,2] and also in a crystal lattice [3–5] has been demonstrated; all diastereoisomeric lactams and their per-*O*-acetyl derivatives in the measured sets prefer the chair or half-chair conformation with equatorial C-2 substituent (OH, OAc). Other dependence concerning the positions of the substituents on C-3 and C-4 was also indicated by the circular dichroism (CD) spectra of 6-amino-6-deoxyhexono-1,6-lactams [1]. A study of lactams with deoxy groups on C-2 and/or C-3 could be of interest to obtain further arguments for an explanation of the mentioned facts. In addition, lactams derived from aminodeoxyhexonic acids are receiving considerable attention as potential inhibitors

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of glycosidases [6–13]. The relationship between the structures of biologically active compounds and enzymes plays an important role in the mechanism of the effect.

In preliminary papers [14–16] we have reported on the syntheses and structural studies of some 6-amino-3,6-dideoxy hexono-1,6-lactams and 6-amino-2,6-dideoxy hexono-1,6-lactams. Their conformations were estimated from CD and NMR spectra as in the previous cases [1,2]. In this paper, we describe the synthesis and structure of 6-amino-2,3,6-trideoxy-D-*erythro*-hexono-1,6-lactam (**3a**) and 6-amino-3,6- dideoxy-D-*xylo*-hexono-1,6-lactam (**7a**), which were available in crystalline form suitable for X-ray diffraction.

As far as the seven-membered lactam ring is concerned, the chair $^{1,N}C_4$ and $^{4}C_{1,N}$ conformations (Fig. 1) can be taken into consideration when the idea of a planar arrangement of the amide segment C_2–C_1(=O)–N–C_6 is accepted. This theoretical assumption was supported by X-ray diffraction for the above-mentioned sugar lactams [3–5], as well as for ε-caprolactam [17]. Similar results were reported by other authors [18–22] in studies of variously substituted seven-membered lactams, either monocyclic or dicyclic. On the other hand, more conformational flexibility has been regarded for some similar seven-membered ring species having no lactam carbonyl group [23].

2. Results and discussion

Synthesis.—The preparation of 6-amino-2,3,6-trideoxy-D-*erythro*-hexono-1,6-lactam (**3a**) began with the catalytic hydrogenation of 2,6-dibromo-2,6-dideoxy-D-*mannono*-1,4-lactone [24] in ethanol to produce the 6-bromo-2,3,6-trideoxy-D-*erythro*-hexono-1,4-lactone [25]. Nucleophilic substitution at C-6 carried out by means of sodium azide in dimethylformamide led to 6-azido-2,3,6-trideoxy-D-*erythro*-hexono-1,4-lactone, which was reduced with hydrogen giving rise to crystalline lactam **3a**. Acetylation of **3a** yielded the 4,5-di-*O*-acetyl derivative **3b**. 6-Amino-3,6-dideoxy-D-*xylo*-hexono-1,6-lactam (**7a**) corresponding to the tri-*O*-acetyl derivative **7b** was prepared from 3-deoxy-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-*xylo*-hexofuranose [26]. Nucleophilic displacement of the tosyloxy group yielded 6-azido-3,6-dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexose (**4**). Deprotection of the hydroxyl groups led to 6-azido-3,6-dideoxy-D-*xylo*-hexose (**5**), which was oxidized to 6-azido-3,6-dideoxy-D-*xylo*-hexono-1,4-lactone (**6**). 6-Amino-3,6-dideoxy-D-*xylo*-hexono-1,6-lactam (**7a**) was formed as a result of the hydrogenation of lactone **6**. Conventional acetylation of **7a** yielded the tri-*O*-acetyl derivative **7b**.

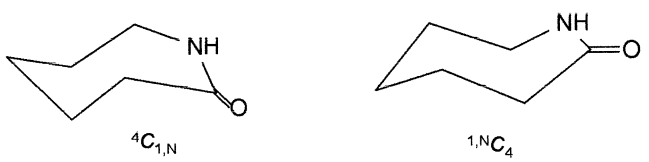


Fig. 1. Possible chair conformations of seven-membered lactam ring.

Structural studies.—The structures of the lactams **3a** and **7a** in the solid state were obtained from X-ray single-crystal analysis. The basic crystallographic data, parameters of hydrogen bonds and torsion angles for the ring atoms are collected in Tables 1–3 for both measured compounds. The ORTEP plots and packing schemes are in Figs. 2–5. Conformations of the lactams in solution were deduced from NMR and CD measurements and the structures of the corresponding acetates **3b** and **7b** only from NMR measurements. In order to determine the prevailing lactam conformation in solution, the values of the vicinal coupling constants $^{3}J_{H,H}$ were compared with those calculated for hydrogen atoms of the H–C–C–H segment in $^{1,N}C_4$ (D) and $^{4}C_{1,N}$ (D) conformations according to the Karplus-type equation with the Haasnoot–de Leeuw–Altona parameterization [27]. The molecular mechanics MM^{+} force field [28] was used for optimization of the geometry of $^{1,N}C_4$ (D) and $^{4}C_{1,N}$ (D) conformations of the studied lactams. Circular dichroism was interpreted according to the semi-empirical rules applicable for seven-membered lactams. A so-called lactam rule [29,30] associates the $^{1,N}C_4$ conformation with the negative Cotton effect and the $^{4}C_{1,N}$ form with the positive Cotton effect. An amide quadrant rule [31–33] deals with the influence of particular atoms on the sign of the Cotton effect.

Table 1
Data collection and structure refinement parameters for 6-amino-2,3,6-trideoxy-D-*erythro*-hexono-1,6-lactam (**3a**) and 6-amino-3,6-dideoxy-D-*xylo*-hexono-1,6-lactam (**7a**)

	3a	**7a**
Crystal dimensions (mm)	$0.25\times0.22\times0.14$	$0.29\times0.14\times0.11$
Diffractometer	Enraf–Nonius CAD4	
Radiation used (Å)	Cu K_α, $\lambda = 1.54178$ Å	
Temperature (K)	293	
Scan technique	ω–2θ	
θ Range (°)	6.74–74.82	5.71–74.68
Range of h, k, l	$0\rightarrow6$, $0\rightarrow8$, $-24\rightarrow0$	$0\rightarrow8$, $0\rightarrow8$, $-19\rightarrow19$
No. of reflections	819	1592
Used for refinement	819	1391
Function minimized	$\Sigma\omega(F_o^2-F_c^2)$	
Weighting scheme	$\omega = 1/[\sigma^2F_o^2+(0.05431P)^2+0.1382P]$, where $P=(F_o^2+2F_c^2)/3$	$\omega = 1/[\sigma^2F_o^2+(0.0584P)^2+0.2024P]$, where $P=(F_o^2+2F_c^2)/3$
Parameters refined	136	145
R_1 ($F>4\sigma(F)$)	0.034	0.035
wR_2 (all data)	0.087	0.096
S	1.111	1.109
Ratio of max least-squares shift to e.s.d. in the last cycle	<0.001	0.001
Max. and min. heights in final $\Delta\rho$ map (e Å^3)	0.16, -0.19	0.24, -0.16

*Lactams **3a** and **3b**.*—The crystal structure analysis revealed the chair $^4C_{1,N}$(D) conformation for the lactam **3a** (Fig. 2) and the planar character of its amidic segment (value of torsion angle C-6–N–C-1–C-2 is 0.1° (3)). The hydroxyl groups on C-4 and C-5 are equatorial and axial, respectively. The crystal packing of the molecule of **3a** in the unit cell is displayed in Fig. 4. Amide, carbonyl and all secondary hydroxyl groups are involved in hydrogen bonding, forming three-dimensional networks (for geometric characteristics of these interactions see Table 2).

Considering a generally acceptable fact that an equatorial substituent contributes to the total molecular energy less than the axial one, it was not possible to predict the preferred conformation for lactam **3a** possessing one axial and one equatorial hydroxyl group invariably. A ^{1}H NMR spectrum recorded at 300 K (Table 4) could not provide any convincing information on the prevailing conformation. Table 5 shows that the values of theoretical coupling constants $J_{2,3}$, $J_{2',3'}$ $J_{3,4}$, $J_{4,5}$ and $J_{5,6'}$ calculated for the $^{1,N}C_4$ (D) and $^4C_{1,N}$ (D) conformers are similar. The remaining coupling constants found in the spectrum ($J_{2,3'}$, $J_{2',3}$, $J_{3,4}$, $J_{4,5}$ and $J_{5,6}$) in all cases represented the arithmetical average from the values calculated for these two conformers. This fact together with the NOE observed between H-6, H-6′ and H-2, H-2′ indicated that both conformers are present in the solution. In the spectrum recorded at 200 K we distinguished

Table 2
Hydrogen bonds for 6-amino-2,3,6-trideoxy-D-*erythro*-hexono-1,6-lactam (**3a**) and 6-amino-3,6-dideoxy-D-*xylo*-hexono-1,6-lactam (**7a**)

D–H…A	*d*(D-H) (Å)	*d*(H…A) (Å)	*d*(D…A) (Å)	D–H…A (°)
Lactam **3a** [a]				
O4–H1O4…O4 [b]	0.84(4)	1.93(4)	2.746(2)	163(3)
O5–H1O5...O1 [c]	0.85(3)	1.93(3)	2.717(2)	155(3)
N–H1N…O5 [d]	0.89(3)	2.47(3)	3.298(2)	155(2)
Lactam **7a** [a]				
N–H1N…O5 [e]	0.85(3)	2.02(3)	2.833(2)	162(3)
O4–H1O4…O2 [f]	0.84(4)	2.05(4)	2.887(2)	172(4)
O2–H1O2…O1 [g]	0.85(3)	2.10(3)	2.896(2)	155(3)
O5–H1O5…O1 [h]	0.92(3)	1.83(3)	2.735(2)	167(2)

[a] Symmetry transformations used to generate equivalent atoms: **3a**: [a] $x+1/2$, $-y+3/2$, $-z$; [b] x, $y+1$, z; [c] $-x+2$, $y-1/2$, $-z+1/2$; **7a**: [d] $x+1/2$, $-y+3/2$, $-z+2$; [e] $-x$, $y-1/2$, $-z+3/2$; [f] $x-1/2$, $-y+5/2$, $-z+2$; [g] x, $y-1$, z.

Table 3
Torsion angles (°) for ring atoms in lactams **3a** and **7a**

Atoms	Angle	
	3a	**7a**
C-1–C-2–C-3–C-4	−81.6(2)	−80.8(2)
C-2–C-3–C-4–C-5	63.3(2)	64.5(2)
C-3–C-4–C-5–C-6	−60.5(2)	−58.6(2)
C-4–C-5–C-6–N	76.8(2)	75.7(2)
C-1–N–C-6–C-5	−65.4(3)	−69.2(2)
C-6–N–C-1–C-2	0.1(3)	4.9(3)
N–C-1–C-2–C-3	65.3(2)	61.3(2)

both conformers in a 1:1 ratio (coalescence temperature 250 K). The data are summarized in Table 6. Some signals overlap and in most cases they are not split very well. Only $J_{5,6}$ in signals of H-6 was detectable (5.7 for $^{4}C_{1,N}$, 10.0 for $^{1,N}C_{4}$), being in accordance with the theoretical calculations. The chemical shifts at 300 K represent the average of the chemical shifts of the considered conformers. The spectra recorded at 300 K in deuterium oxide, methanol-d_4 and dimethylsulfoxide-d_6 differ slightly in the chemical shifts and in the coupling constants. Downfield shifts of H-4, H-2′

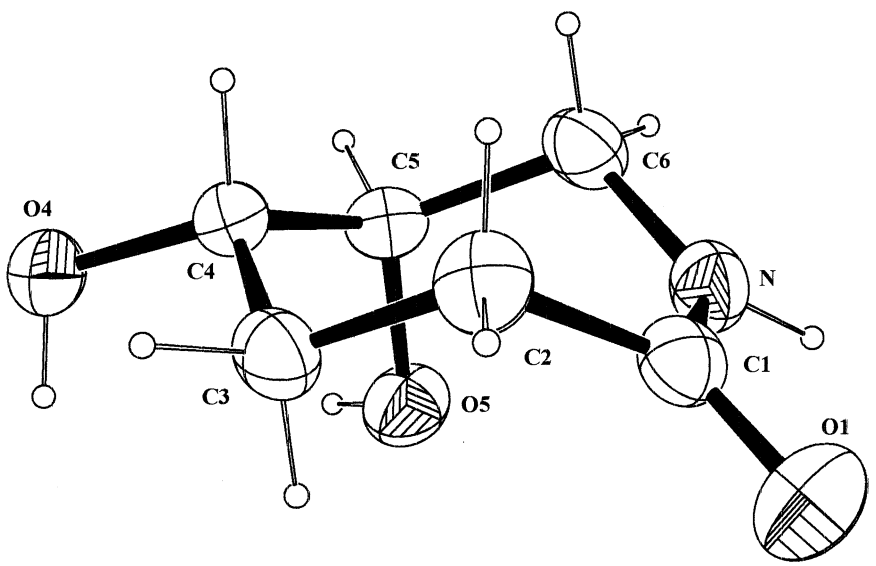


Fig. 2. ORTEP plot of 6-amino-2,3,6-trideoxy-D-*erythro*-hexono-1,6-lactam (**3a**). Thermal ellipsoids at 50% probability.

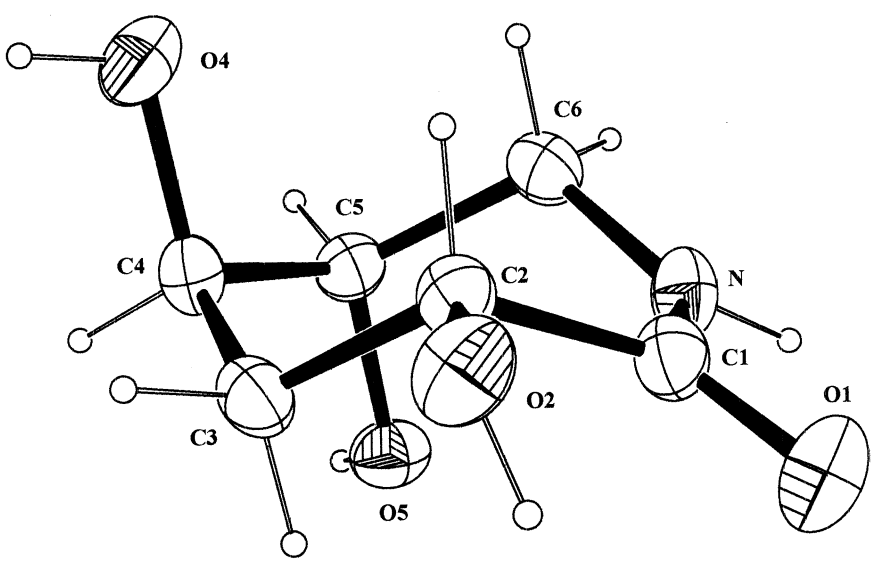


Fig. 3. ORTEP plot of 6-amino-3,6-dideoxy-D-*xylo*-hexono-1,6-lactam (**7a**). Thermal ellipsoids at 50% probability.

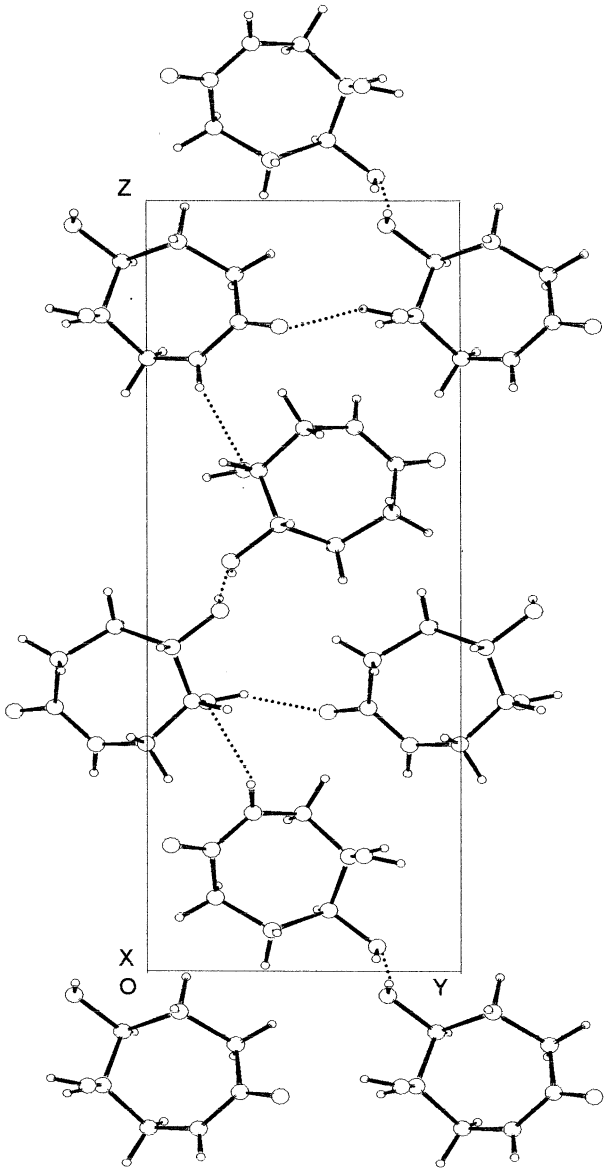


Fig. 4. Packing scheme of 6-amino-2,3,6-trideoxy-D-*erythro*-hexono-1,6-lactam (**3a**). Dashed lines indicate hydrogen bonds.

and upfield shifts of H-5, H-2 in the case of the $^{1,N}C_4$ (D) conformer in comparison with $^4C_{1,N}$ (D) form are in accordance with the general experience, i.e., signals of the axial protons are located more upfield than those of equatorial ones. For signals of H-6 and H-6′ the situation is reversed. This effect has also been previously reported in 6-amino-6-deoxy-hexono-1,6-lactams or for H-5 and H-5′ in 5-amino-5-deoxypentono-1,5-lactams [1,2]. In the CD spectrum of **3a** no Cotton effect was observed in the area 200–260 nm. This fact interpreted according to the lactam rule indicates that both conformers are present approximately in equal amount. According to the amide quadrant rule, the contributions in 'positive' and in 'negative' quadrants are therefore the same and no CD band in this region can be observed.

In the case of the acetate **3b** the NMR spectrum is similar to that of the lactam **3a**. In the spectrum recorded at 300 K a NOE was observed between H-4 and H-2′, H-6′ and H-2′ suggesting the axial orientation of H-6′ and H-2′, which indicates the $^4C_{1,N}$ (D) conformation. At the same time the NOE observed between H-6 and H-2 provides evidence that the $^{1,N}C_4$ (D) conformation is also present in solution. In the spectrum recorded at 215 K the signals of the two conformers are separated in a 1:1 ratio $^{1,N}C_4$ (D):$^4C_{1,N}$ (D) (coalescent temperature 240 K). The signals are not split and the arithmetical average of the chemical shifts of particular signals nearly corresponds to the signals in the spectrum recorded at 300 K. The data are summarized in Tables 4 and 6.

*Lactams **7a** and **7b**.*—X-ray diffraction analysis confirmed the $^4C_{1,N}$ (D) conformation of lactam **7a** (Fig. 3). The amide segment is nearly planar (the value of torsion angle C-6–N–C-1–C-2 is 4.9° (3)). The crystal packing of the molecule in the cell unit is displayed in Fig. 5. Amide, carbonyl and all secondary hydroxyl groups are involved in hydrogen bonding, forming three-dimensional networks (for geometric characteristics of these interactions see Table 2). The hydroxyl on C-2 is oriented equatorially in spite of the energetically disadvantageous axial orientation of hydroxyl groups on C-4 and C-5. The conformational analysis of lactam **7a** in solution using the modified Karplus equation demonstrates the requirement of the equatorial arrangement of the substituent on the carbon next to the carbonyl. This fact has already been observed during the investigation of 6-amino-6-deoxyhexono-1,6-lactams [1] and 5-amino-5-deoxypentono-1,5-lactams [2]. The $^4C_{1,N}$ (D) conformation for lactam **7a** is unequivocally supported not only by the conformational analysis (Tables 7 and 8), but also by the NOE observed between C-2 and C-6′. During NMR measurement in deuterium oxide, we noticed an easy lactam hydrolysis,

which could be a result of the instability of the molecule bearing two axial hydroxyl groups. A similar behaviour was observed [1] in the case of the $^{1,N}C_4$ (D) conformer of 6-amino-6-deoxy-L-gulono-1,6-lactam. Lactam **7a** exhibited in CD measurements a positive Cotton effect at 212 nm ($\Delta\varepsilon = 1.8$ cm^2 mmol^{-1}, water), which interpreted according to the lactam and amide rules also provides evidence of the $^4C_{1,N}$ (D) conformation of the studied lactam and reflects the crucial effect of the substituent on the C-2 on the conformation. Japanese authors [34,35] reporting the dependence of the conformation of lactam on the absolute configuration on C-2 assumed a hypothesis that the substituent bond by a heteroatom on C-2 interacts with the amide carbonyl, giving rise to an inherently chiral chromophore.

The results of the conformational analysis of acetate **7b** are in agreement with the conclusions concerning the free lactam **7a**. A NOE observed between H-2 and H-6′ confirms the $^4C_{1,N}$ (D) conformation. Chemical shifts of the protons of the lactam **7b** in the

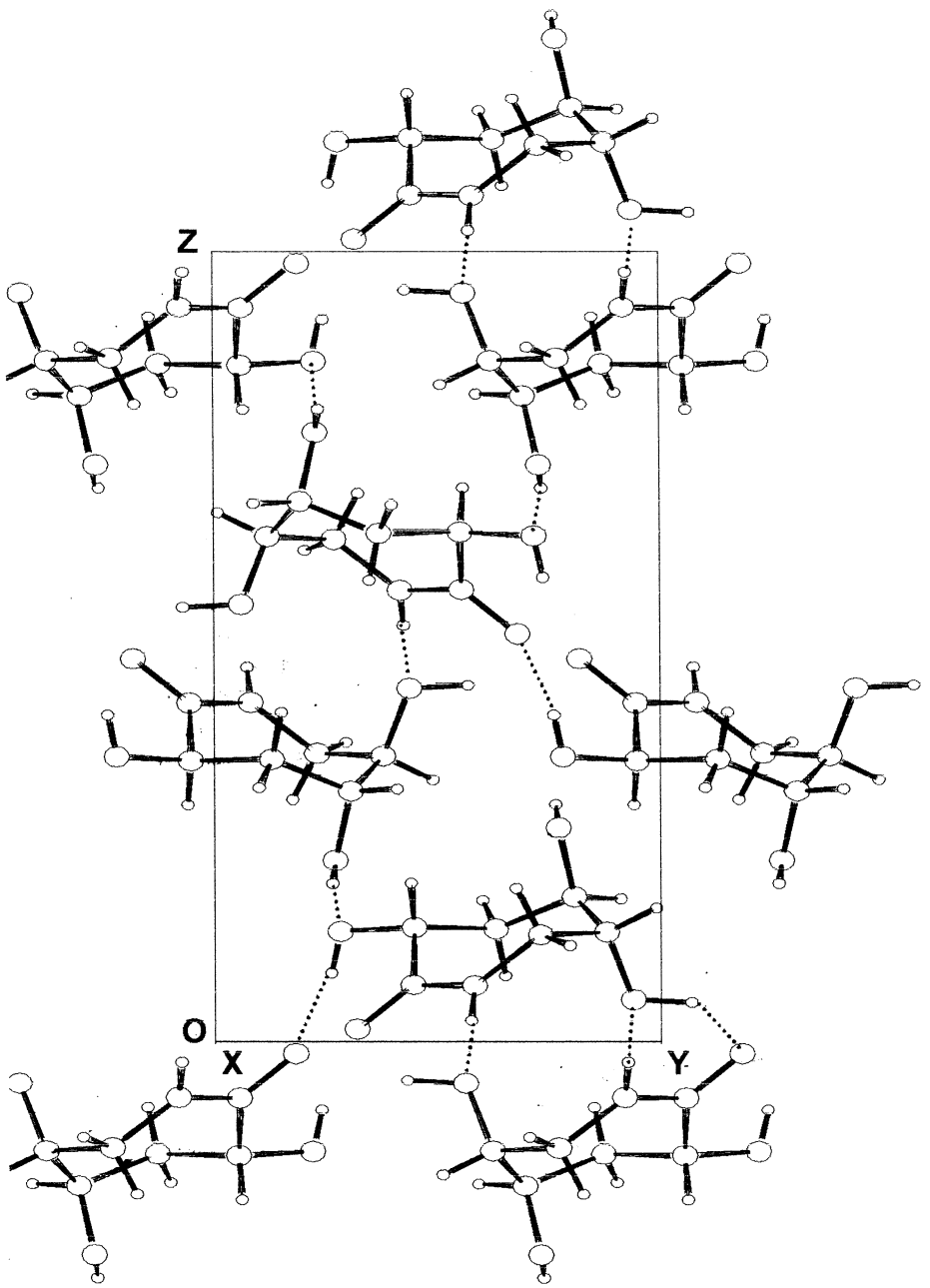


Fig. 5. Packing scheme of 6-amino-3,6-dideoxy-D-*xylo*-hexono-1,6-lactam (**7a**). Dashed lines indicate hydrogen bonds.

Table 4
^{1}H NMR (500 MHz, 300 K): chemical shifts δ (ppm) and the coupling constants $^3J_{H,H}$ (Hz) for lactams **3a**, **3b** (**3a** in deuterium oxide, MeOH-d_4, Me_2SO-d_6, **3b** in $CDCl_3$)

Parameter	**3a** (D_2O)	**3a** (MeOH-d_4)	**3a** (Me_2SO-d_6)	**3b** ($CDCl_3$)
H-2	2.44dd	2.73t	2.52m	2.71dd
H-2′	2.28ddd	2.20dd	1.95dd	2.35ddd
H-3	1.75m	1.94dddd	1.73ddd	2.06dddd
H-3′	1.75m	1.80dddd	1.59dddd	1.93dddd
H-4	3.81m	3.9m	3.72d	5.18m
H-5	3.81m	3.68d	3.42d	4.97d
H-6	3.37dd	3.55dd	3.31ddd	3.66ddd
H-6′	3.15d	3.04d	2.77dd	3.18dd
H–N			7.22s	6.41bs
OH			4.62s	
OAc				2.10s, 2.07s
$J_{2,3}$	0.0	1.4	1.8	0.0
$J_{2,3'}$	8.9	9.7	12.3	10.0
$J_{2',3}$	10.1	8.7	8.7	9.8
$J_{2',3'}$	1.7	1.7	1.5	1.2
$J_{2,2'}$	14.8	13.5	13.5	14.0
$J_{3,4}$	[a]	7.7	6.6	10.0
$J_{3',4}$	[a]	2.9	1.6	0.0
$J_{3,3'}$	[a]	13.0	13.0	11.0
$J_{4,5}$	[a]	0.0	0.0	0.0
$J_{5,6}$	7.5	8.8	9.2	8.6
$J_{5,6'}$	0.0	0.0	0.0	0.0
$J_{6,6'}$	15.3	14.9	14.9	15.0
$J_{6,NH}$			5.3	6.6
$J_{6',NH}$			5.1	6.6

[a] Overlapping signals.

spectrum recorded at 210 K were consistent with those recorded at 300 K. These observations demonstrate that the $^4C_{1,N}$ (D) conformer prevails in solution (Table 7). ^{13}C NMR data of the lactams **3a** and **3b**, or **7a** and **7b** are presented in Section 3.

Table 6
^{1}H NMR (500 MHz): chemical shifts δ (ppm) for lactams **3a** (CH_3OH-d_4, 200 K) and **3b** ($CDCl_3$, 215 K)

Parameter	**3a**	**3a**	**3b**	**3b**
	$^4C_{1,N}$	$^{1,N}C_4$	$^4C_{1,N}$	$^{1,N}C_4$
H-2	3.05m	2.53m	2.90bs	2.10m [a]
H-2′	1.83m [a]	2.25m	2.10m [a]	2.46
H-3	1.98m [a]	1.98m [a]	2.10m [a]	2.10m [a]
H-3′	1.83m [a]	1.83m [a]	2.10m [a]	2.10m [a]
H-4	3.66bs	4.09bs	4.86bs	5.43bs
H-5	3.89bs	3.53d $J_{5,6}$ 9.7 Hz	5.14bs	4.75bs
H-6	3.23dd $J_{6,6'}$15.4 Hz $J_{6,5}$ 5.7 Hz	3.76dd $J_{6,6'}$ 13.2 Hz $J_{6,5}$ 10.0 Hz	3.47bs	3.81bs
H-6′	3.38d	2.77d	3.39bs	2.96bs
H–N			8.11 [b]bs	7.44 [b]bs

[a] Overlapping signals.
[b] Values could be reversed; bs, broad singlet.

3. Experimental

General methods.—The studied compounds, 6-amino-2,3,6-trideoxy-D-*erythro*-hexono-1,6-lactam (**3a**), 6-amino-3,6-dideoxy-D-*xylo*-hexono-1,6-lactam (**7a**) and corresponding acetates **3b** and **7b** were prepared as is described below. The melting points were determined with a Kofler apparatus and are not corrected. NMR spectra in $CDCl_3$, Me_2SO-d_6, MeOH-d_6 and D_2O were measured on a Bruker AM 400 instrument (^{1}H at 400 MHz, ^{13}C at 100 MHz), Gemini 2000 (300HC Varian) instrument (^{1}H at 300 MHz, ^{13}C at 75 MHz) and on a Bruker Avance DRX 500 (^{1}H at 500 MHz, ^{13}C at 125 MHz). The majority of the measurements were performed at 300 K; low-temperature experiments are men-

Table 5
Calculated values of vicinal coupling constants $^3J_{H,H}$ (Hz) for the corresponding torsion angles $\Phi_{H,H}$ (°) in the $^{1,N}C_4$ (D) and $^4C_{1,N}$ (D) conformations of the lactams **3a** and **3b**

Lactam	$J_{2,3}/\Phi_{2,3}$	$J_{2,3'}/\Phi_{2,3'}$	$J_{2',3}/\Phi_{2',3}$	$J_{2',3'}/\Phi_{2',3}$	$J_{3,4}/\Phi_{3,4}$	$J_{3',4}/\Phi_{3',4}$	$J_{4,5}/\Phi_{4,5}$	$J_{5,6}/\Phi_{5,6}$	$J_{5,6'}/\Phi_{5,6}$
	$^{1,N}C_4$	$^{1,N}C_4$	$^{1,N}C_4$	$^{1,N}C_4$	$^{1,N}C_4$	$^{1,N}C_4$	$^{1,N}C_4$	$^{1,N}C_4$	$^{1,N}C_4$
	$^4C_{1,N}$	$^4C_{1,N}$	$^4C_{1,N}$	$^4C_{1,N}$	$^4C_{1,N}$	$^4C_{1,N}$	$^4C_{1,N}$	$^4C_{1,N}$	$^4C_{1,N}$
3a	0.7/−74	7.3/41	14.7/170	0.6/−75	11.2/174	4.3/59	2.3/−59	5.8/−43	0.9/75
	0.7/74	14.6/−169	7.1/−42	0.6/75	4.5/56	1.8/−61	2.3/60	10.9/170	2.9/−72
3b	0.7/−74	7.3/41	14.7/170	0.6/−75	11.4/177	3.8/62	2.4/−60	5.8/−43	0.9/74
	0.6/74	16.6/−169	2.1/−42	0.6/75	4.8/54	1.6/−63	2.1/64	10.8/168	2.7/−74

Table 7
^{1}H NMR (500 MHz, 300 K): chemical shifts δ (ppm) and the coupling constants $^3J_{H,H}$ (Hz) for lactams **7a** and **7b** (**7a** in deuterium oxide, Me_2SO-d_6, **7b** in $CDCl_3$)

Parameter	**7a** (D_2O)	**7a** (Me_2SO-d_6)	**7b** ($CDCl_3$)	**7b** ($CDCl_3$, 210 K)
H-2	4.65dd	4.32d	5.52d	5.42d
H-3	2.05ddd	1.82ddd	2.33ddd	2.31t
H-3′	1.88dddd [a]	1.67ddd	2.12m	2.02m
H-4	3.95m	3.68bs	5.16m	5.12bs
H-5	3.67t	3.39t	4.77t	4.77bs
H-6	3.61d	2.91ddd	3.78dd	3.75m
H-6′	3.18dd	3.41dd	3.49ddd	3.50m
H–N		7.56t	5.85bs	6.84bs
H–O		5.03bs		
		4.84bs		
		4.19s		
$COCH_3$			2.19	2.19
			2.17	2.17
			2.12	2.12
$J_{2,3}$	11.6	11.5	11.7	12.2
$J_{2,3'}$	2.6	2.1	0.0	0.0
$J_{3,4}$	3.0	2.2	2.1	0.0
$J_{3',4}$	5.0	5.0	4.4	[b]
$J_{3,3'}$	14.7	13.7	14.7	[b]
$J_{4,5}$	4.9	3.9	4.5	[b]
$J_{5,6}$	4.5	6.1	4.5	[b]
$J_{5,6'}$	0.0	0.0	0.0	[b]
$J_{6,6'}$	15.7	14.4	15.9	[b]
$J_{6,NH}$		5.1	6.6	[b]
$J_{6',NH}$		5.1	6.6	

[a] $J_{3',5} = 0.8$ Hz.
[b] Indistinguishable.

tioned in the text. The assignment of signals was confirmed using 2D homonuclear and heteronuclear correlated spectra (^{1}H–^{1}H COSY, ^{1}H–^{13}C HETCOR). The IR spectra were measured in $CHCl_3$, in KBr pellet or in a film of substance on a Nicolet 750 FTIR spectrometer. The UV spectra were measured on the M 40 Carl Zeiss Jena spectrometer in water. The CD spectra of lactams **3a** and **7a** were obtained on a Jobin–Yvon Dichrographe Mark V instrument equipped with a data processor. The measurements were carried out at room temperature (rt) in a 0.1-cm cell in the range 190–260 nm. Lactam concentration was about 1×10^{-3} mol L^{-1}, samples were dissolved in distilled water. The data are given as the difference of molar absorption coefficient for the left and right polarized light $\Delta\varepsilon = \varepsilon_L - \varepsilon_R$ (cm^2 $mmol^{-1}$). For X-ray diffraction measurements see Table 1.

6-Bromo-2,3,6-trideoxy-D-erythro-*hexono-1,4-lactone* (**1**).—Prepared according to Lundt and Pedersen [25] starting from 2,6-dibromo-2,6-dideoxy-D-mannono-1,4-lactone (5 g, 16.4 mmol). The product was isolated as colourless crystals (2.4 g, 70%): mp 74–75 °C, lit. 76–78 °C [25]; R_f 0.64 (1:2 EtOAc–petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.59 (q, 1 H, $J_{4,5} \sim J_{4,3} \sim J_{4,3'}$ 6.4 Hz, H-4), 3.98 (ddd, 1 H, $J_{5,6} \sim J_{5,6'}$ 6.1 Hz, H-5), 3.58 (dd, 1 H, $J_{6,6'}$ 10.7 Hz, H-6), 3.52 (dd, 1 H, H-6), 2.91 (1 H, s, OH), 2.64 (ddd, 1 H, $J_{2',3}$ 9.2, $J_{2',3'}$ 8.2, $J_{2',2}$ 17.8 Hz, H-2′), 2.56 (ddd, 1 H, $J_{2,3}$ 6.0, $J_{2,3'}$ 10.0 Hz, H-2), 2.36 (dddd, 1 H, $J_{3,3'}$ 12.9 Hz, H-3), 2.28 (dddd, 1 H, H-3′); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) in accordance with Ref. [25].

6-Azido-2,3,6-trideoxy-D-erythro-*hexono-1,4-lactone* (**2**).—Bromolactone **1** (1.5 g, 7 mmol) was dissolved in dry dimethylformamide (15 mL), NaN_3 (1.5 g, 23.1 mmol) was added and the reaction mixture was heated to 90 °C avoiding air moisture. After 2 h the suspension was cooled, dimethylformamide was evaporated and the residue partitioned between water and $CHCl_3$. The combined organic layers were dried over

Table 8
Calculated values of vicinal coupling constants $^3J_{H,H}$ (Hz) for the corresponding torsion angles $\Phi_{H,H}$ (°) in the $^{1,N}C_4$ (D) and $^4C_{1,N}$ (D) conformations of the lactams **7a** and **7b**

Lactam	$J_{2,3}/\Phi_{2,3}$	$J_{2,3'}/\Phi_{2,3'}$	$J_{3,4}/\Phi_{3,4}$	$J_{3',4}/\Phi_{3',4}$	$J_{4,5}/\Phi_{4,5}$	$J_{5,6}/\Phi_{5,6}$	$J_{5,6'}/\Phi_{5,6'}$
	$^{1,N}C_4$	$^{1,N}C_4$	$^{1,N}C_4$	$^{1,N}C_4$	$^{1,N}C_4$	$^{1,N}C_4$	$^{1,N}C_4$
	$^4C_{1,N}$	$^4C_{1,N}$	$^4C_{1,N}$	$^4C_{1,N}$	$^4C_{1,N}$	$^4C_{1,N}$	$^4C_{1,N}$
7a	11.5/169	2.2/−75	1.9/60	4.5/−56	4.6/55	5.8/−43	0.9/75
	6.6/−42	1.0/74	4.4/−58	11.2/−174	8.5/174	10.9/171	2.9/−72
7b	11.4/165	1.7/−80	1.9/60	4.8/−54	4.2/57	5.7/−44	0.9/73
	6.6/−42	1.0/73	4.0/−61	11.3/−176	8.9/177	10.8/168	2.6/−75

$MgSO_4$ and evaporated. The yellow syrupy residue (1.2 g) was chromatographed on silica gel (1:1 EtOAc–petroleum ether) yielding the colourless syrupy product **2** (1 g, 83%); $[\alpha]_D^{20}$ 14° (*c* 0.64, $CHCl_3$); R_f 0.57 (1:2 EtOAc–petroleum ether); IR (subst) 1777 (CO), 2108 (N_3), 3418, 3604 (OH) cm^{-1}; ^1H NMR (500 MHz, D_2O): δ 4.62 (q, 1 H, $J_{4,5} \sim J_{4,3} \sim J_{4,3'}$ 7.2 Hz, H-4), 3.99 (ddd, 1 H, $J_{5,6}$ 4.0, $J_{5,6'}$ 5.1, Hz, H-5), 3.46 (dd, 1 H, $J_{6,6'}$13.2 Hz, H-6), 3.52 (1 H, dd, H-6′), 2.61 (m, 2 H, $J_{2,2'}$ 18.3 Hz, H-2,H-2′), 2.32 (1 H, dddd, $J_{3',4}$ 6.5, $J_{3',3}$ 13.5, $J_{3',2}$ 6.5, $J_{3',2'}$ 8.1 Hz, H-3′), 2.16 (1 H, dddd, $J_{3,4}$ 9.2, $J_{3,2}$ 6.0, $J_{3,2'}$ 9.2 Hz, H-3); ^{13}C NMR (400 MHz, D_2O): δ 182.6 (C-1), 82.6 (C-5), 71.8 (C-4), 53.5 (C-6), 29.3 (C-2), 23.3 (C-3). Anal. Calcd for $C_6H_9N_3O_3$: C, 42.12; H, 5.26. Found: C, 41.82; H, 5.48.

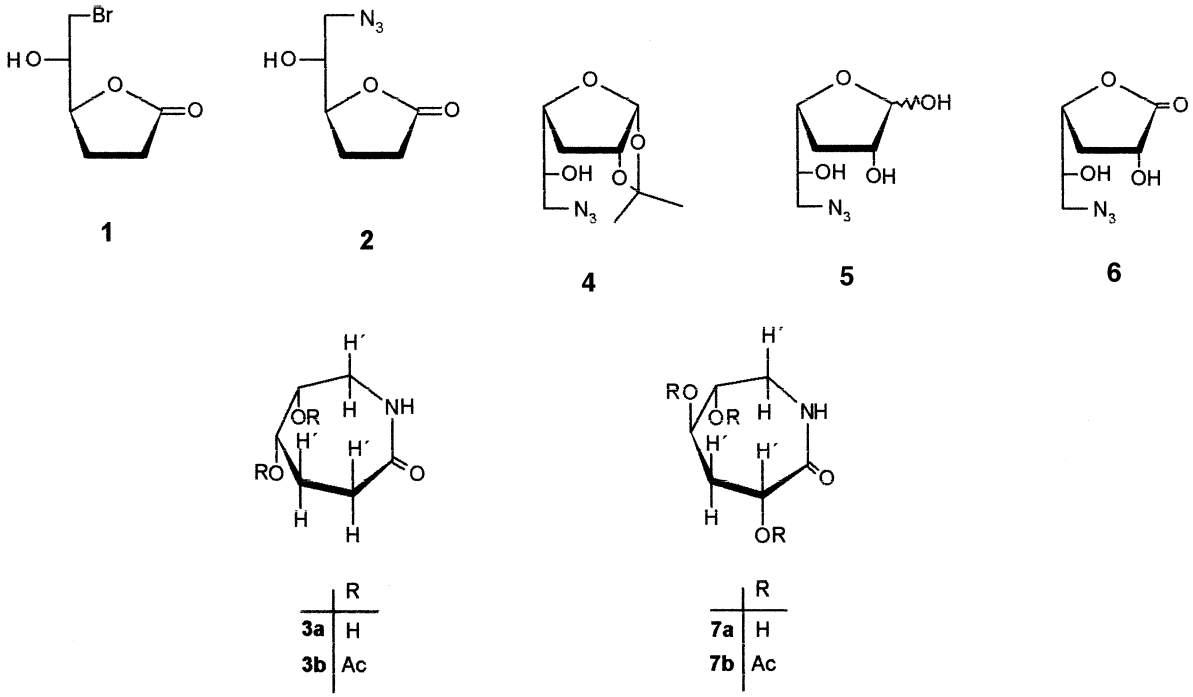
6-Amino-2,3,6-trideoxy-D-erythro-*hexono-1,6-lactam* (**3a**).—Azidolactone **2** (0.17 g, 0.99 mmol) was dissolved in MeOH (20 mL) and reduced by means of H_2 on 5% Pd–C (0.05 g). After 2 h the starting material was consumed and the reaction mixture was evaporated. A syrupy product (0.14 g) was isolated and recrystallized from MeOH to give pure **5a** as white crystals (0.12 g, 83%): mp above 200 °C (decomp); $[\alpha]_D^{20}$ −58.6° (*c* 0.84, water); IR (KBr): 1646, 1619 (CO), 3364 (OH), 3315 (NH) cm^{-1}; UV: 195 nm; ^{13}C NMR (D_2O): δ 183.4 (C-1), 75.1 (C-4), 71.6 (C-5), 44.4 (C-6), 32.1 (C-2), 27.6 (C-3). Anal. Calcd for $C_6H_{11}NO_3$: C, 49.64; H, 7.58; N, 9.64. Found: C, 49.59; H, 7.60; N, 9.61.

4,5-Di-O-*acetyl-6-amino-2,3,6-trideoxy*-D-erythro-*hexono-1,6-lactam* (**3b**).—Lactam **3a** (0.04 g, 0.27 mmol) was dissolved in pyridine (1 mL) and Ac_2O (1 mL) was added. After 2 h at rt the reaction mixture was poured into water (10 mL) and $CHCl_3$ (10 mL) was added. The product was extracted several times with $CHCl_3$. The combined organic layers were dried over $MgSO_4$ and evaporated. The syrupy product was subjected to silica gel chromatography in EtOAc to give the colourless syrupy **3b** (0.03 g, 50%): $[\alpha]_D^{20}$ −4.3° (*c* 0.29, $CHCl_3$); R_f 0.14 (7:3 toluene–acetone); ^{13}C NMR ($CDCl_3$): δ 177.6 (C-1), 170.55 ($COCH_3$), 72.8 (C-4), 71.1 (C-5), 41.1 (C-6), 31.1 (C-2), 25.3 (C-3), 21.7 (CH_3CO). Anal. Calcd for $C_{10}H_{15}NO_5$: C, 52.43; H, 6.55. Found: C, 52.57; H, 6.75.

6-Azido-3,6-dideoxy-1,2-O-*isopropylidene*-α-D-xylo-*hexofuranose* (**4**).—3-Deoxy-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-*xylo*-hexofuranose (2.46 g, 6.88 mmol) [26] was dissolved in dry Me_2SO (35 mL). Sodium azide (1.33 g, 20.4 mmol) was added and the stirred reaction mixture was heated at 80 °C for 30 min avoiding air moisture. After evaporation of Me_2SO the residue was partitioned between water and $CHCl_3$. The organic layer was dried with anhyd $MgSO_4$, evaporated and the syrup was chromatographed on silica gel in 1:2 EtOAc–petroleum ether yielding the pure syrupy product **4** (1.6 g, 100%): $[\alpha]_D^{20}$ −32.3° (*c* 0.8 $CHCl_3$); R_f 0.38 (1:3 EtOAc–petroleum ether); IR ($CHCl_3$): 1375 ($(CH_3)_2C$), 2106 (N_3), 3567, 3483 (OH) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.82 (d, 1 H, $J_{1,2}$ 3.8 Hz, H-1), 4.76 (ddd, 1 H, $J_{2,3}$ 6.0, $J_{2,3'}$ 1.1 Hz, H-2), 4.20 (ddd, 1 H, $J_{4,5}$ 10.4, $J_{4,3}$ 7.1, $J_{4,3'}$ 3.3 Hz, H-4), 3.94 (ddd, 1 H, $J_{5,6}$ 4.4, $J_{5,6'}$ 6.0, Hz, H-5); 3.39 (dd, 1 H, $J_{6,6'}$ 12.6 Hz, H-6), 3.29 (dd, 1 H, H-6′), 2.25 (ddd, 1 H, $J_{3,3'}$14.3 Hz, H-3), 2.05 (dd, 1 H, H-3′); ^{13}C NMR (100 MHz, $CDCl_3$): δ 113.3 ($C(CH_3)_2$), 116.9 (C-1), 82.05, 81.2, 72.6 (C-2, C-4, C-5, the values could be reversed), 53.8 (C-6), 33.97 (C-3), 27.5, 26.4 ($C(CH_3)_2$ Anal. Calcd for $C_9H_{15}N_3O_4$: C, 47.15; H, 6.54. Found: C, 47.41; H, 6.64.

6-Azido-3,6-dideoxy-D-xylo-*hexose* (**5**).—Compound **4** (1.6 g, 6.9 mmol) was stirred at 60 °C with the cation-exchanger resin (Dowex WX 4 100–200 mesh, H^+ form, 5 mL in 16 mL of water). The starting material completely hydrolysed in 15 min. Then the ion exchanger was removed and the filtrate was evaporated. The colourless crystalline product (0.83 g, 60%) was obtained after evaporation of water and chromatography of the crude product on silica gel in EtOAc. The compound melted in the range 44–47 °C; $[\alpha]_D^{20}$ 30° (5 min) → 20° (24 h) (*c* 1, water); IR (KBr): 2106 (N_3), 3365 (OH) cm^{-1}. Anal. Calcd for $C_6H_{11}N_3O_4$: C, 38.09; H, 5.86. Found: C, 38.21; H, 5.68 (Scheme 1).

6-Azido-3,6-dideoxy-D-xylo-*hexono-1,4-lactone* (**6**).—6-Azido-3,6-dideoxy-D-*xylo*-hexose (**5**) (0.78 g, 4.1 mmol) was dissolved in water (50 mL). Subsequently, $BaCO_3$ (5.6 g) was added and Br_2 (1 mL) was dropped into the solution at 0 °C and the reaction mixture was



Scheme 1.

stirred. After 1.5 h of stirring at rt thin-layer chromatography (TLC) confirmed consumption of the starting material. Excess Br_2 was removed by an air stream. After filtration and careful washing the aqueous solution (250 mL) was stirred for 2 h with Ag_2CO_3 (8 g) to remove Br^-. The suspension was filtered and washed with water. The remaining salts were removed on a column of Dowex 50 in H^+ form (20 mL). After evaporation of water the colourless syrupy product **6** (0.67 g, 87%) was obtained: $[\alpha]_D^{20}$ −14.1° (*c* 0.5 water); R_f 0.63 (EtOAc); IR (subst): 2108 (N_3), 3401 (OH), 1777 (CO) cm^{-1}; ^1H NMR (500 MHz, deuterium oxide): δ 4.74 (dd, 1 H, $J_{2,3}$ 8.5, $J_{2,3'}$ 11.0 Hz, H-2), 4.58 (m, 1 H, $J_{4,5}$ 5.0 Hz, H-4), 3.91 (q, 1 H, $J_{5,6}$ 5.5, $J_{5,6'}$ 5.5 Hz, H-5), 3.51 (s, 1 H, H-6), 3.49 (s, 1 H, H-6′), 2.69 (ddd, 1 H, $J_{3,4}$ 5.5, $J_{3,3'}$ 11.0 Hz, H-3), 2.09 (q, 1 H, $J_{3',4}$ 11.0 Hz, H-3′), ^{13}C NMR (125.77 MHz, D_2O): δ 180.1 (C-1), 79.0, 71.8, 68.85 (C-2, C-4, C-5), 53.6 (C-6), 33.3 (C-3). Anal. Calcd for $C_6H_9N_3O_4$: C, 38.50; H, 4.81. Found: C, 38.27; H, 4.97.

6-Amino-3,6-dideoxy-D-xylo-*hexono-1,4-lactam* (**7a**).—6-Azido-3,6-dideoxy-D-*xylo*-hexono-1,4-lactone (**6**) (0.57 g, 3 mmol) was hydrogenated in MeOH (100 mL) on 5% Pd–C. After 15 min the reaction was completed (according to TLC), the reaction mixture was filtered and MeOH was evaporated. Yellowish foamy lactam **7a** (0.48 g, 98%) was recrystallized from MeOH; melted in the range 178–182 °C; $[\alpha]_D^{20}$ −16.3° (*c* 0.95, water); IR (KBr): 1648 (CO), 3284, 3222 (NH), 3422, 3353 (OH) cm^{-1}; UV: 195 nm; ^{13}C NMR (D_2O): δ 177.7 (C-1), 67.0 (C-5), 66.2 (C-4), 62.1 (C-2), 38.0 (C-6), 32.1 (C-3); Anal. Calcd for $C_6H_{11}NO_4$: C, 44.74; H, 6.83; N, 8.69. Found: C, 44.58; H, 6.75; N, 8.45.

2,4,5-Tri-O-*acetyl-6-amino-3,6-dideoxy*-D-xylo-*hexono-1,6-lactam* (**7b**).—Lactam **7a** (0.3 g, 1.8 mmol) was dissolved in dry pyridine (10 mL) and Ac_2O (5 mL) was added. The reaction was left to run at rt for 12 h and then the mixture poured into ice water and extracted with $CHCl_3$. The organic layer was washed with a satd soln of $KHCO_3$ and water, dried with anhyd $MgSO_4$ and evaporated giving the syrupy product (0.4 g, 77%), which after chromatography on silica gel in 9:1 $CHCl_3$–MeOH yielded tri-*O*-acetate **7b** as a colourless syrup: $[\alpha]_D^{20}$ −60.1° (*c* 1.3 $CHCl_3$); R_f 0.36 (1:1 toluene–acetone); ^{13}C NMR ($CDCl_3$): δ 173.0 (C-1), 170.9, 170.2, 169.9 ($COCH_3$), 66.9 (C-2), 68.6 (C-4), 68.3 (C-5), 39.0 (C-6), 30.2 (C-3), 21.5, 21.3, 21.2 (CH_3CO). Anal. Calcd for $C_{12}H_{17}NO_7$: C, 50.21; H, 5.92; N, 4.88. Found: C, 50.35; H, 5.70; N, 4.69.

Crystal structure analysis.—Crystals of **3a** and **7a** suitable for X-ray analysis were grown by slow evaporation from a methanolic solution at rt.

*6-Amino-2,3,6-trideoxy-*D-erythro-*hexono-1,6-lactam* (**3a**). $C_6H_{11}NO_3$; $M_r = 145.16$; orthorhombic space group $P2_12_12_1$ (no. 19), $a = 4.861(1)$, $b = 6.972(2)$, $c = 19.677(2)$ Å, $V = 666.9(2)$ Å^3, $Z = 4$, $D_{calcd} = 1.446$ g cm^{-3}, μ(Cu K_α) = 0.98 mm^{-1}. The structure was solved by direct methods and anisotropically refined by full-matrix least-squares on F^2. Hydrogen atoms were found from difference synthesis maps and refined isotropically. A semi-empirical correction for absorption based on the ψ-scan [36] was applied.

*6-Amino-3,6-dideoxy-*D-xylo-*hexono-1,6-lactam* (**7a**). $C_6H_{11}NO_4$; $M_r = 161.16$; orthorhombic space group $P2_12_12_1$ (no. 19), $a = 6.546(1)$, $b = 7.002(1)$, $c = 15.485(1)$ Å, $V = 709.7(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.508$ g cm^{-3}, μ(Cu K_α) = 1.09 mm^{-1}. The structure was solved by direct methods and anisotropically refined by full-matrix least-squares on F^2. Hydrogen atoms were found from difference synthesis maps and from expected geometry and were refined isotropically. No correction for absorption was applied.

Programs used were SDP [37], SHELXS86 [38] and SHELXL97 [39].

Supplementary material

Tables of atomic coordinates, bond lengths, and bond angles have been deposited with the Cambridge Crystallographic Data Centre. These tables may be obtained on request from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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