6-AMINO-2,6-DIDEOXY- OR -2,3,6-TRIDEOXYHEXONO-1,6-LACTAMS: SYNTHESIS AND CONFORMATION

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6-Amino-2,6-dideoxy-D-*ribo*-hexono-1,6-lactam (**1a**), 6-amino-2,6-dideoxy-D-*arabino*-hexono-1,6-lactam (**2a**), 6-amino-2,3,6-trideoxy-L-*threo*-hexono-1,6-lactam (**3a**) and per-*O*-acetyl derivatives **1b**–**3b** were synthesized and their seven-membered lactam ring conformation was studied. ^{1}H and ^{13}C NMR spectra of the named lactams, measured at low temperature, always disclosed the presence of both $^{1,N}C_4$ and $^{4}C_{1,N}$ conformations in ratios which were affected mainly by the stereochemistry of cyclohexane. There were no CD extremes over 200 nm found in water solutions of the lactams **1a** and **2a**, probably owing to the symmetry of the C2–C6 parts of their seven-membered rings. These results contrast with those previously found for the lactams having OH or OAc at C2, and support a concept of the directive role of the C2 substituent in conformation equilibrium.

Keywords: Carbohydrates; Aminosugars; Lactams; Conformation analysis; CD spectroscopy; NMR spectroscopy.

Studying eight configurational isomers of 6-amino-6-deoxyhexono-1,6-lactams[1], four isomers of 5-amino-5-deoxypentono-1,5-lactams[2], and four isomers of 6-amino-3,6-dideoxyhexono-1,6-lactams[3], a dependence of conformation of the lactam ring on absolute configuration on C-2 was observed. The seven-membered chair[1,3] or six-membered half-chair[2] conformer with the equatorial hydroxy or acetoxy group at C-2 unequivocally

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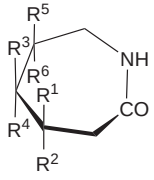
prevailed in solutions of the above-mentioned lactams and it was also found in the crystal lattice[4–6]. In the case of 6-amino-6-deoxy-L-gulono-1,6-lactam[1] and 6-amino-3,6-dideoxy-D-*xylo*-hexono-1,6-lactam[7], the decisive effect of equatorial C-2 group brought about a less favourable axial arrangement of remaining groups both in solution and in the solid state. This effect was observed in the previous studies of other lactams[8,9] and explained by the interaction of π-electrons of carbonyl group with the lone electron pair of the oxygen or nitrogen atom of the substituent on C-2.

To confirm the direct influence of the hydroxy or acetoxy group next to the carbonyl on the conformation of the lactam ring, we concentrated on several lactams bearing only hydrogen atoms at carbon atom C-2. For that reason, our study was focused on the synthesis and conformation of 6-amino-2,6-dideoxy-D-*ribo*-hexono-1,6-lactam (**1a**) (Scheme 1), 6-amino-2,6-dideoxy-D-*arabino*-hexono-1,6-lactam (**2a**) (Scheme 2), 6-amino-2,3,6-trideoxy-L-*threo*-hexono-1,6-lactam (**3a**) (Scheme 3), 6-amino-2,3,6-trideoxy-D-*erythro*-hexono-1,6-lactam[7] (**4a**) and their per-*O*-acetyl derivatives **1b**–**4b**.



	R^1	R^2	R^3	R^4	R^5	R^6
1a	H	OH	H	OH	H	OH
1b	H	OAc	H	OAc	H	OAc
2a	OH	H	H	OH	H	OH
2b	OAc	H	H	OAc	H	OAc
3a	H	H	H	OH	OH	H
3b	H	H	H	OAc	OAc	H
4a	H	H	H	OH	H	OH
4b	H	H	H	OAc	H	OAc

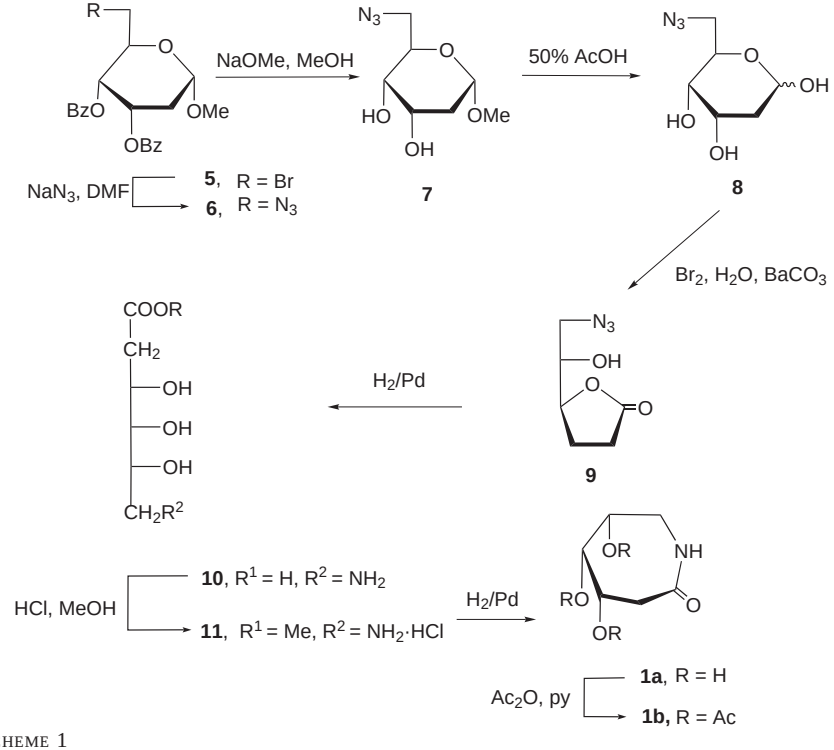
RESULTS AND DISCUSSION

Synthesis

6-Amino-2,6-dideoxy-D-*arabino*-hexono-1,6-lactam (**2a**) was prepared according to the described procedure[10], preparation of its triacetate **2b** is described in this paper (Scheme 2). 6-Amino-2,3,6-trideoxy-D-*erythro*-hexono-1,6-lactam (**4a**) and its diacetate **4b** were synthesized in our laboratory recently[7].

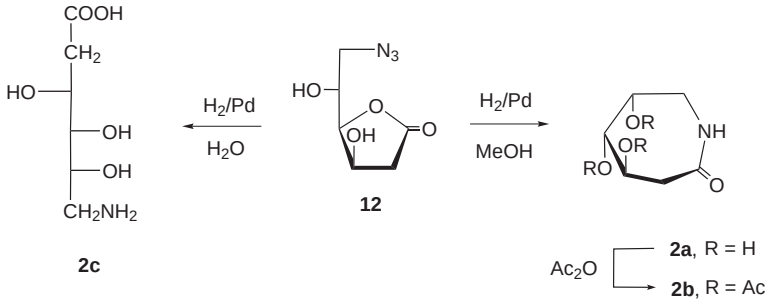
Synthesis of 6-amino-2,6-dideoxy-D-*ribo*-hexono-1,6-lactam (**1a**) (Scheme 1) started from methyl 3,4-di-*O*-benzoyl-6-bromo-2,6-dideoxy-α-D-*ribo*-hexopyranoside[11,12] (**5**). It was converted to methyl 6-azido-3,4-di-*O*-benzoyl-2,6-dideoxy-α-D-*ribo*-hexopyranoside (**6**) by treatment with sodium azide in

DMF. Azido derivative **6** exhibited in IR spectrum bands at 2104 (N_3), 1723 (C=O in ester), and 1602 cm^{-1} (aromatic ring). Structure of this compound and the prevailing $^4C_1$ (D) conformation was deduced from ^1H NMR spectrum, using chemical shifts of signals H-2, H-2′, H-6 and H-6′ (δ 2.32, 2.21, 3.47 and 3.47 ppm, respectively) and aromatic protons (7.86–8.07 ppm), and the low values of all vicinal coupling constants except *trans*-diaxial $J_{4,5}$ = 10.2 Hz. Deprotection of hydroxy groups in positions 3 and 4 with sodium methoxide in methanol led to methyl 6-azido-2,6-dideoxy-α-D-*ribo*-hexopyranoside (**7**). Its IR spectrum confirmed the presence of azido group (2103 cm^{-1}) and hydroxy group (3521 cm^{-1}). Similarly to **6**, also glycoside **7** exhibited in ^1H NMR only one large coupling constant $J_{4,5}$ = 9.4 Hz and, with regard to low values of remaining coupling constants, this fact gives the evidence of prevailing $^4C_1$ (D) conformation of this compound. Glycoside **7** was heated in 50% acetic acid to produce 6-azido-2,6-dideoxy-D-*ribo*-hexose (**8**). Azidohexose **8** was then oxidized with bromine in water in the presence of barium carbonate to give 6-amino-2,6-dideoxy-D-*ribo*-hexono-1,4-lactone (**9**) as a syrup. The evidence of a five-membered ring in **9** fol-



SCHEME 1

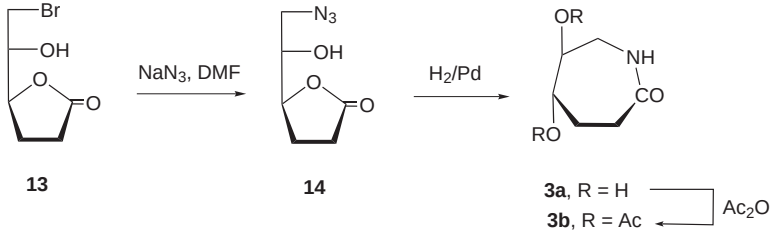
lows from the value of absorption band of C=O (1779 cm^{-1}) and from ^1H NMR spectrum, in particular from the chemical shift of H-4 (4.47 ppm) and the low value of the coupling constant $J_{3,4}$ of vicinal protons in gauche position. Hydrogenolysis of the azido group in lactone **9** yielded 6-amino-2,6-dideoxy-D-*ribo*-hexonic acid (**10**) as a foam. Associated amino and hydroxy groups (3431–3367 cm^{-1}), characteristic absorptions in the range 2916–2500 cm^{-1} and the band of carboxylate anion in the range 1646–1550 and 1402 cm^{-1} support the expected structure. Treatment with 5% hydrogen chloride in methanol converted the amino acid **10** to hydrochloride of the corresponding methyl ester **11**. 6-Amino-2,6-dideoxy-D-*ribo*-hexono-1,6-lactam (**1a**) arose spontaneously after liberation of the amino group of ester **11** and was isolated from the reaction mixture as 3,4,5-tri-*O*-acetyl-6-amino-2,6-dideoxy-D-*ribo*-hexono-1,6-lactam (**1b**).



SCHEME 2

6-Amino-2,6-dideoxy-D-*arabino*-hexono-1,6-lactam (**2a**) was prepared from calcium D-gluconate using the described[10] method to obtain the key compound – 6-azido-2,6-dideoxy-D-*arabino*-hexono-1,4-lactone (**12**). Lactam **2a** was obtained from **12** by catalytic hydrogenation in methanol (Scheme 2). If the catalytic hydrogenation was performed in water, a solid 6-amino-2,6-dideoxy-D-*arabino*-hexonic acid (**2c**) was formed. Acetylation of **2a** yielded the corresponding 3,4,5-tri-*O*-acetyl derivative **2b**.

Synthesis of 6-amino-2,3,6-trideoxy-L-*threo*-hexono-1,6-lactam (**3a**) started from 6-bromo-2,3,6-trideoxy-L-*threo*-hexono-1,4-lactone[13,14] (**13**) (Scheme 3). Nucleophilic substitution of bromine in **13** with azide gave 6-azido-2,3,6-trideoxy-L-*threo*-hexono-1,4-lactone (**14**). Its IR spectrum exhibited bands at 2108 cm^{-1} (azide) and 1774 cm^{-1} (carbonyl). Catalytic reduction of azidolactone **14** in methanol gave crystalline 6-amino-2,3,6-trideoxy-L-*threo*-hexono-1,6-lactam (**3a**). The 4,5-di-*O*-acetyl derivative **3b** was prepared by acetylation.



SCHEME 3

Conformational Analysis

Regarding the approximately planar arrangement of the bonds in the amide segment (C2–C1–N–C6), a seven-membered lactam ring can exist as $^{4}C_{1,N}$ or $^{1,N}C_{4}$ chair and $B_{N,1,4}$ or $^{4,1,N}B$ boat conformers (Fig. 1). Stereochemistry of lactams was studied on the basis of NMR and CD spectra.

Conformational analysis of lactams **1a**–**4a** and **1b**–**4b** was performed using modified Karplus equation[15]. Geometry of $^{4}C_{1,N}$ or $^{1,N}C_{4}$ conformers of all lactams was optimized using molecular mechanics MM^{+} [16]. The nuclear Overhauser effect observed between closed protons confirmed presence of corresponding conformer. The low-temperature NMR experiments made it possible to study conformational equilibrium between possible conformers.

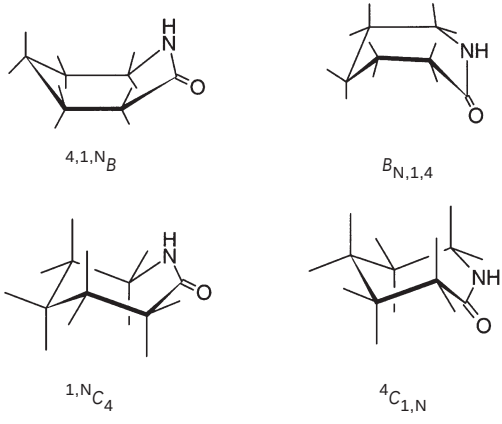


FIG. 1
Possible conformations of seven-membered lactam ring

NMR Measurements

^{1}H NMR spectra of 6-amino-2,6-dideoxy-D-*ribo*-hexono-1,6-lactam (**1a**) and its 3,4,5-triacetate **1b** recorded in D_2O and CD_3OD (Table I) exhibited signals of H-4 and H-3 at the lowest field (≈4 ppm). In signal of H-4, the couplings are not resolved, which is typical of the majority of lactams studied so far. NOE (Fig. 2) observed between H-2_{ax} and H-6_{ax}, H-3 and H-5 con-

TABLE I
^{1}H NMR spectra (500 MHz) of lactams **1a**, **1b** and **2a**, **2b** [a]

Parameter	**1a** 300 K		**1a** 200 K	**1b** 300 K	**2a** 300 K		**2a** 190 K, CD_3OD		W.M.[b]	**2b** 300 K
	D_2O	CD_3OD	CD_3OD $^{1,N}C_4$	$CDCl_3$	D_2O	CD_3OD	$^4C_{1,N}$	$^{1,N}C_4$		$CDCl_3$
					Chemical shifts δ, ppm					
H-2	3.08 m[c]	3.26 t	3.40 t	3.27 t	2.76 d	2.94 d	3.21[c]	2.33 m[c]	2.93	2.95 d
H-2′	2.37 d	2.25 d	2.06 d	2.45 d	2.66 dd	2.49 dd	2.33 m[c]	2.86 m[c]	2.50	2.80 dd
H-3	4.04 d	3.89 d	3.83 d	5.22 d	3.93 dd	3.93 dd	3.95 m[c]	3.76 m[c]	3.81	5.18 dd
H-4	3.99 s	3.99 s	4.08 s	5.57 s	3.79 dd	3.81 bs	3.95 m[c]	3.45 m	3.80	5.35 dd
H-5	3.83 d	3.63 m[c]	3.57 d	4.97 d	3.99 ddd	3.88 dd	3.76 m[c]	3.95 m[c]	3.82	5.15 ddd
H-6	3.56 dd	3.63 m[c]	3.72 dd	3.76 ddd	3.49 dd	3.57 dd	3.76 m[c]	3.21 m[c]	3.59	3.74 ddd
H-6′	3.08 m[c]	2.92 d	2.76 d	3.10 dd	3.24 d	3.02 d	2.78[c]	3.30	2.94	3.18 dd
CH_3CO	–	–	–	2.19 s; 2.05 s; 2.04 s	–	–	–	–	–	2.15 s; 2.11 s; 2.08
NH	–	–	–	6.40 bs	–	–	–	–	–	6.18 bs
					Coupling constants ^3J and ^2J, Hz					
$J_{2,3}$	10.5	11.0	11.3	11.6	<0.5	<0.5	[d]	[d]	–	<0.5
$J_{2',3}$	<0.5	<0.5	<0.5	<0.5	9.4	8.6	[d]	[d]	–	8.2
$J_{2,2'}$	11.8	11.0	13.3	14.1	14.4	13.6	[d]	[d]	–	14.3
$J_{3,4}$	<0.5	<0.5	<0.5	<0.5	7.6	7.0	[d]	[d]	–	6.1
$J_{4,5}$	<0.5	<0.5	<0.5	<0.5	2.2	2.7	[d]	[d]	–	2.3
$J_{5,6}$	8.7	10.7	11.3	9.7	8.2	9.1	[d]	[d]	–	9.2
$J_{5,6'}$	<0.5	<0.5	<0.5	<0.5	1.4	<0.5	[d]	[d]	–	<0.5
$J_{6,6'}$	14.9	10.2	13.8	14.6	15.0	14.6	[d]	[d]	–	15.0
$J_{6,NH}$	–	–	–	5.0	–	–	–	–	–	5.7
$J_{6',NH}$	–	–	–	3.1	–	–	–	–	–	6.9

[a] CH_2 hydrogen atoms over the reference plane (C2–C3–C5–C6) are primed. [b] Weighted mean corresponding with the ratio $^4C_{1,N}/^{1,N}C_4$ 7:3. [c] Overlapping signals. [d] Values were not determined owing to overlap and unresolved multiplets.

firmed the prevailing $^{1,N}C_4$ conformer, while interactions between H-2 and H-3, H-2′ and H-6′, characteristic of $^4C_{1,N}$ conformer, were not found. Comparison of the measured coupling constants with the computed ones (Table II) also supported the idea of prevailing $^{1,N}C_4$ conformer with two equatorial and one axial hydroxy (acetoxy) group. ^{1}H NMR spectrum of lactam **1a** recorded at 200 K exhibited changes in chemical shifts in comparison with the spectrum recorded at 300 K, and some new signals with unresolved splitting belonging to conformer $^4C_{1,N}$ at 4.18, 3.97, 2.65, and doublet at 2.88 ppm. Owing to a small coupling and intensity of the signals, they could not be assigned to certain H-atoms in the chains. An

TABLE II
Calculated[a] values of $^3J_{H,H}$ of lactams **1a** and **2a**

Lactam	Conformation	Coupling constants					
		$J_{2,3}$	$J_{2',3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$
1a	$^4C_{1,N}$	6.7	0.9	2.5	1.9	5.8	0.9
	$^{1,N}C_4$	11.6	2.3	2.2	2.5	10.9	2.9
	W.M.[b]	11.3	2.2	2.2	2.4	10.6	2.7
2a	$^4C_{1,N}$	2.5	11.6	8.6	2.4	5.9	0.9
	$^{1,N}C_4$	0.9	6.9	4.6	2.4	10.9	2.4
	W.M.[c]	1.8	10.2	7.4	2.4	7.4	1.4

[a] Karplus equation in the modification of Altona and co-workers[15] with the data of optimized[16] forms were used for calculation of the theoretical values. [b] Weighted mean corresponding with the ratio $^{1,N}C_4/^4C_{1,N} \approx 13:1$. [c] Weighted mean corresponding to the ratio $^4C_{1,N}/^{1,N}C_4 \approx 7:3$.

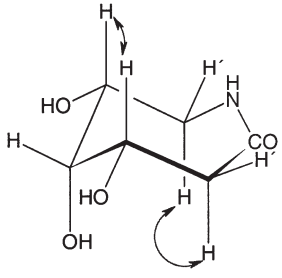


FIG. 2
The most important NOE contacts of lactam **1a**

approximate ratio of $^{1,N}C_4$ and $^4C_{1,N}$ conformers ≈13:1 corresponded to the ratio of the average intensities of the signals in both conformations.

In the spectrum of 6-amino-2,6-dideoxy-D-*arabino*-hexono-1,6-lactam (**2a**) and 3,4,5-triacetate **2b** recorded in D_2O, the signal of proton H-5 was found at the lowest field (3.99 ppm). The signal of H-4 was a broad singlet. The prevailing $^4C_{1,N}$ conformation could be presumed from a comparison of the experimental (Table I) and calculated coupling constants (Table II). Nevertheless, the population of the second possible $^{1,N}C_4$ conformer must also be considered. NOE experiment (Fig. 3) confirmed the presence of both conformers. The prevailing conformer $^4C_{1,N}$ was determined by NOE between signals H-6′$_{ax}$, H-4$_{ax}$ and H-2′$_{ax}$, the less favourable conformer $^{1,N}C_4$ with one equatorial and two axial hydroxy groups exhibited interactions between H-2′ and H-3, H-6 and H-2, H-6′ and H-5.

^{1}H NMR spectra, recorded at low temperature (200 K), confirmed the equilibrium between conformers $^4C_{1,N}$ and $^{1,N}C_4$ in the ratio ≈7:3. Using COSY spectrum and the equation

$$\nu = p_1\nu_1 + p_2\nu_2 ,$$

where $p_1 = 0.3$, $p_2 = 0.7$, all signals were identified. The weighted mean of experimental chemical shifts of both conformers is in accordance with experimental shifts of most signals with maximum deviation ±0.06 ppm.

^{13}C NMR spectra of lactams **1a**, **1b** and **2a**, **2b** are collected in the Table III. At 300 K the values of the chemical shifts corresponding to the conformers are averaged by a chemical exchange.

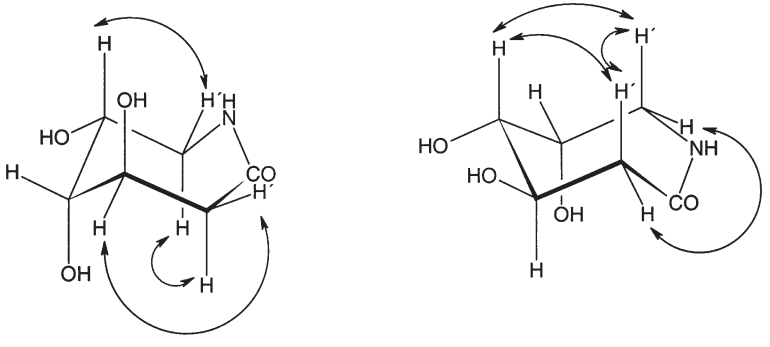


FIG. 3
The most important NOE contacts of lactam **2a**

Structures of 6-amino-2,3,6-trideoxy-L-*threo*-hexono-1,6-lactam (**3a**) and the corresponding 4,5-diacetate **3b** in CD_3OD solutions were deduced from the NMR spectra measured at 300, 200 or 190 K (Table IV), and from NOE experiments (Fig. 4).

^{1}H NMR spectra of lactams **3a** and **3b** in CD_3OD exhibited the most shielded signal of H-3, which is split into a double triplet (at 300 K) or into a quartet (at 200 K). The latter quartet corresponds to the H-3 in anti-periplanar arrangement to the atoms H-2′ and H-4 of the $^4C_{1,N}$ (L) conformation (i.e., with two ^3J and one large ^2J coupling constants), while the former double triplet corresponds to the signal of the same atom with ^3J coupling constants averaged by the chemical exchange. All spectral data

TABLE III
^{13}C NMR spectra (75 MHz, 300 K) of lactams **1a**, **2a** (D_2O) and **1b**, **2b** ($CDCl_3$)

Lactam	C-1	C-2	C-3	C-4	C-5	C-6	$COCH_3$	$COCH_3$
1a	179.37	39.53	69.77	76.59	72.15	43.44	–	–
1b	171.91	36.57	67.46	71.75	70.51	40.17	170.45 170.05 170.01	21.39 21.35 21.39
2a	179.29	39.45	67.56	76.98	69.21	42.56	–	–
2b	172.97	36.57	67.04	71.88	69.71	40.46	170.24 169.89 169.77	21.36

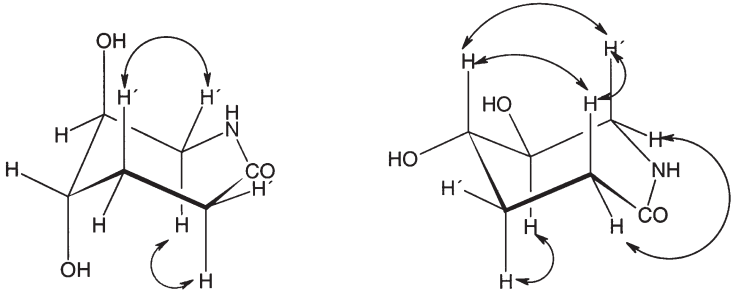


FIG. 4
The most important NOE contacts of lactam **3a**

TABLE IV
^{1}H NMR spectra (500 MHz, CD_3OD) of lactams **3a** and **3b**[a]

Parameter	**3a** 300 K	**3a**, 200 K		**3b** 300 K	**3b**, 190 K	
		$^{1,N}C_4$	$^4C_{1,N}$		$^{1,N}C_4$	$^4C_{1,N}$
			Chemical shift δ, ppm			
H-2	2.37 t	3.0 t[b]	2.23 dd	2.68 dd	3.05 t	2.28 dd[b]
H-2′	2.54 t	1.97 d[b]	2.68 t	2.43 dd	2.09[b]	2.80 t
H-3	1.66 dt	2.00 dd[b]	1.53 q	1.88 m	2.03 bd[b]	1.68 q
H-3′	2.06 tt	1.80 dd	2.10 t	2.04 ddt	1.95 t	2.20[b]
H-4	3.64 bs	3.90 bs	3.48 dt	5.07 dt	5.07 bs[b]	5.07 bs[b]
H-5	3.40 t	3.62 t	3.24 t	4.78 dt	4.77 s[b]	4.72 t[b]
H-6	3.34 d	3.76 d	3.30 d[b]	3.41 dd	3.33[b]	3.20 d
H-6′	3.17 dd	3.32[b]	3.06 dd[b]	3.51 dd	3.78 d	3.46 dd
NH		–	–	6.16 bs		
other		–	–	2.10 s, 2.09 s	2.14 s 2.09 s	
			Coupling constants ^3J and ^2J, Hz			
$J_{2,3}$	≈0	≈0	≈0	1.7	≈0	≈0
$J_{2,3'}$	11.4	11.3	12.8	10.8	13.3	5
$J_{2,2'}$	13.5	12.5	13.5	13.6	13.3	13.6
$J_{2',3}$	10.3	≈0	12.3	9.9	≈0	11.9
$J_{2',3'}$	≈0	4.5	0	1.8	≈0	≈0
$J_{3,4}$	11.2	≈0	12.3	9	<1	12.2
$J_{3',4}$	[c]	4	0–1	3.7	[c]	<1
$J_{3,3'}$	14.3	13.5	12.8	14.8	14.3	14.3
$J_{4,5}$	7.7	4	12	8.3	[c]	10.2
$J_{5,6}$	≈0	4.5	0	1.7	[c]	≈0
$J_{5,6'}$	8.4	3.5	10.5	7.6	≈0	11
$J_{6,6'}$	14.3	14.9	13.9	15.3	15.7	14.2

[a] CH_2 hydrogen atoms over the reference plane (C2–C3–C5–C6) are primed. [b] Overlapping signals. [c] Values were not determined owing to overlap and unresolved multiplets.

(Table IV) confirmed the presence of both chair conformations in CD_3OD solutions with the prevaling $^4C_{1,N}$ (L) in the ratio ≈2:1 for lactam **3a** and $^{1,N}C_4$ (L) in the ratio ≈1.4:1 for the lactam **3b**. A NOE (Fig. 4) also exhibited interactions in both conformations. ^{1}H NMR spectra of **3a** were also recorded in D_2O and of the **3b** in CD_3Cl (Table V). In CD_3Cl solution of lactam **3b**, the ratio of the conformers was ≈1:1. In the ^{13}C NMR spectrum of **3a** recorded at 200 K, the signals of all carbon atoms in both chair conformations (ratio ≈2:1) were well resolved (Table VI, Fig. 5).

Concerning 6-amino-2,3,6-trideoxy-D-*erythro*-hexono-1,6-lactam (**4a**) and its 2,4-di-*O*-acetyl derivative **4b**, we published[7] data about their conformation in solutions. The ratio of $^4C_{1,N}$ and $^{1,N}C_4$ ≈ 1:1 was deduced[7] from ^{1}H NMR measurements of the lactams **4a** and **4b** in CD_3OD and $CDCl_3$ solutions, respectively. Now, we are able to give results of ^{13}C NMR spectra of the lactam **4a** measured in CD_3OD at 300 and 200 K. The values of chemical shifts of the corresponding C-signals recorded at low and room temperatures (Table VI, Fig. 5) were consistent with the values of the population parameters $p_1 = p_2 = 0.5$ in the above-mentioned equation.

TABLE V
^{1}H NMR spectra (500 MHz): chemical shifts δ (ppm) for lactams **3a** and **3b**

Proton	**3a** 300 K, D_2O	**3b** 300 K, $CDCl_3$	**3b**, $CDCl_3$, 205 K		
			$^{1,N}C_4$	$^4C_{1,N}$	W.M.[a]
H-2	2.57 d	2.67 dd	2.86	2.41	2.64
H-2′	2.37 t	2.40 dd	2.23[b]	2.54	2.39
H-3	2.05 d	1.91 dt	2.02[b]	1.74	1.88
H-3′	1.64 dd	2.13[b]	2.0[b]	2.16	2.08
H-4	3.63 bs	5.07 dt	5.08	4.95	5.02
H-5	3.40 t	4.87 t	4.75[b]	4.85[b]	4.80
H-6	3.38 d	3.51 dd	3.24	3.70	3.47
H-6′	3.16 dd	3.38 dt	3.38[b]	3.31[b]	3.35
OAc	–	2.10[b], 2.09[b]	2.16–2.08[b]		–
NH	–	6.16 s	7.14	7.82	–

[a] Weighted mean coresponding to the ratio $^{1,N}C_4/^4C_{1,N}$ 1:1. [b] Overlapping signals.

TABLE VI
^{13}C NMR spectra (125.75 MHz, CD_3OD): chemical shifts δ (ppm) for lactams **3a** and **4a** [a]

Carbon	**3a** 300 K	**3a**, 200 K		W.M.[b]	**4a** 300 K	**4a**, 200 K		W.M.[b]
		$^{1,N}C_4$	$^{4}C_{1,N}$			$^{1,N}C_4$	$^{4}C_{1,N}$	
C-1	180.70	181.4	180.4	180.73	180.74	181.46	180.02	180.74
C-2	30.82	28.93	31.42	30.60	30.41	28.70	32.26	30.48
C-3	28.81	25.32	30.60	28.86	28.16	29.60	25.54	27.57
C-4	75.30	70.71	77.43	75.21	73.04	70.67	75.67	73.17
C-5	73.65	69.36	75.47	73.45	71.85	72.77	69.68	71.23
C-6	44.16	41.28	45.45	44.07	42.88	41.62	43.99	42.81

[a] For data of **3b**, see Experimental. [b] Weighted mean for the lactam **3a** coresponding with the ratio $^{1,N}C_4/^{4}C_{1,N} \approx 1{:}2$ and for the lactam **4a** coresponding to the ratio $^{1,N}C_4/^{4}C_{1,N} \approx 1{:}1$.

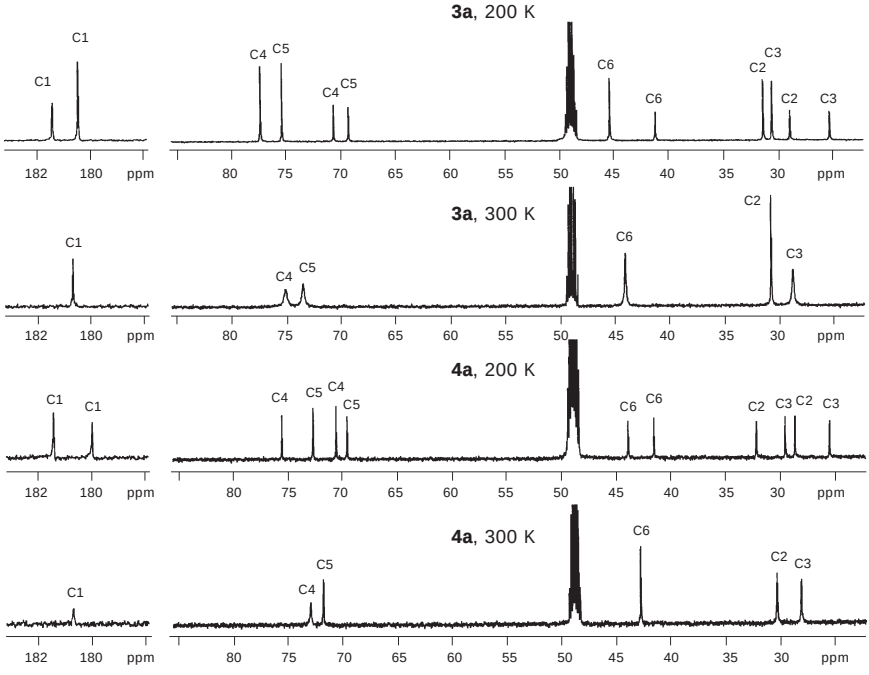


FIG. 5
^{13}C NMR (500 MHz) spectra of lactams **3a**, **4a**

CD Measurements

In the previous series of 6-amino-6-deoxyhexono-1,6-lactams[1] and 6-amino-3,6-dideoxyhexono-1,6-lactams[3] it was found that signs of extremes in the 204–220 nm range correspond, according to the lactam[17–19] and amide[20–22] rule, to the observed $^{4}C_{1,N}$ (D) or $^{1,N}C_{4}$ (D) conformation. According to X-ray analysis[7], the amide segment in the crystalline 6-amino-3,6-dideoxy-D-*xylo*-hexono-1,6-lactam is not quite planar, exhibiting a torsion angle (C6–N–C1–C2) Φ = +5°. When in the solid state and in solution lactam conformations are identical, this fact supports the validity of spiral rule[23,24], according to which the positive Cotton effect corresponds to the positive torsion angle of amide non-planarity. On the contrary, lactams bearing only hydrogen atoms at C-2 position exhibit in CD spectra only minima below 200 nm belonging to π–π^* transitions so that they are not interpretable according to any rule. Explanation of non-existence of extremes above 200 nm can lie in the higher symmetry of chromophore. For instance, 6-amino-2,3,6-trideoxy-D-*erythro*-hexono-1,6-lactam (**4a**) has, according to the amide[20] rule, the same number of atoms in both positive and negative quadrants in both possible chairs. Interpreting according to this rule it is also important to consider the atom weight and the distance of atom from the imaginary axial cross; also this fact may play the decisive role in resulting symmetry of lactams **1a** and **2a**.

It may be accepted that the hydroxy group at C-2 is a part of lactam chromophore[8,9]. Semi-empirical rules proposed under these circumstances are probably not valid for lactams chromophores with hydrogen atom in position C-2. Based on X-ray analysis of 6-amino-2,3,6-trideoxy-D-*erythro*-hexono-1,6-lactam (**4a**), it was found that amidic segment C6–N–C1–C2 is almost planar (Φ = ±1°). The spiral rule[23,24] does not predict for this arrangement any Cotton effect, which is in accordance with CD spectrum where no extreme above 200 nm was measured.

Contrary to the previously studied sets of hexono-1,6-lactams[1,3], all the seven-membered 2-deoxylactams examined here were found to exist as a mixture of conformers in solution. Conformation equilibrium of the $^{1,N}C_{4}$ and $^{4}C_{1,N}$ in solution of these lactams is mainly directed by usual stereochemical rules known from the stereochemistry of the cyclohexane ring, and it does not depend on the close environment of the carbonyl group.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Optical rotations were measured with an Opton photoelectric polarimeter at 20 °C and are given in

10^{-1} deg cm^2 g^{-1}. NMR spectra (δ, ppm; *J*, Hz) in $CDCl_3$, CD_3OD and D_2O were recorded with the instruments: Bruker AMX3 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz), 300HC Varian Gemini 2000 (^{1}H at 300 MHz, ^{13}C at 75 MHz) and Bruker AVANCE DRX 500 (^{1}H at 500 MHz, ^{13}C at 125 MHz). Assignment of signals was provided by means of 2D homonuclear and heteronuclear correlated spectra (COSY, HMQC, HMBC) or based on APT experiments. NOE experiments were made using the DPFGSE-NOE method[25]. Infrared spectra (wave numbers in cm^{-1}) were measured with a Nicolet 750 FT IR instrument in chloroform solutions, KBr pellets or at neat liquids. UV spectra were obtained with an M 40 Carl Zeiss Jena instrument in water. CD spectra of lactams measured in the 190–260 nm range in water (concentration ca. 1 × 10^{-3} mol l^{-1}) were obtained using a Jobin–Yvon dichrograph Mark V. The data are given as the differences of molar absorption coefficients for the left and right polarized light, $\Delta\varepsilon = \varepsilon_L - \varepsilon_R$ (cm^2 mmol^{-1}).

The geometry of lactams was optimized using the MM$^+$ molecular mechanics[16]. Column chromatography was carried out on silica gel (Lachema Brno, 100–200 μm). Reactions were monitored by TLC on silica gel G (Merck, 10–40 μm), using 1% solution of cerium(IV) sulfate in 10% sulfuric acid for detection. Solutions were evaporated on a rotatory vacuum evaporator at 40–50 °C.

Methyl 6-Azido-3,4-di-*O*-benzoyl-2,6-dideoxy-α-D-*ribo*-hexopyranoside (**6**)

To a solution of hexopyranoside[11,12] **5** (3.50 g, 7.8 mmol) in DMF (105 ml), sodium azide (3.5 g, 53.8 mmol) was added. The mixture was stirred for 4.5 h at 90 °C under nitrogen and monitored by TLC (azide gave positive reaction with Buchanan reagent). Reaction mixture was cooled, butanol (30 ml) added and solvents were evaporated. Product was extracted with diethyl ether and then washed with water. Organic layer was dried over anhydrous magnesium sulfate, filtered and concentrated. Syrupy product (3.18 g, 99%) was recrystallized from an ether–petroleum ether mixture yielding crystalline product **6** (2.86 g, 89%), m.p. 53–55 °C, $[\alpha]_D^{20}$ +194 (*c* 0.8, ethanol). IR (chloroform): 2934 (CH_2); 2104 (N_3); 1723 (C=O, C_6H_5COO); 1602 (aromatic ring); 1452 (CH_3). ^{1}H NMR (400 MHz, $CDCl_3$): 4.91 d, 1 H, *J*(1,2) ≈ 4.1, *J*(1,2′) < 0.5 (H-1); 2.32 dd, 1 H, *J*(2,2′) ≈ 15.3, *J*(2,3) ≈ 3.3 (H-2); 2.21 m, 1 H (H-2′); 5.74 dd, 1 H, *J*(3,4) ≈ 6.6 (H-3); 5.22 dd, 1 H, *J*(4,5) ≈ 10.1 (H-4); 4.61 dd, 1 H, *J*(5,6) ≈ 6.4, *J*(5,6′) ≈ 3.0 (H-5); 3.47 dd, 1 H, *J*(6,6′) ≈ 10.8 (H-6); 3.42 dd, 1 H (H-6′). ^{13}C NMR (100 MHz, $CDCl_3$): 98.01 (C-1); 34.05 (C-2); 67.23, 68.95, 66.47 (C-3, C-4, C-5); 52.43 (C-6); 3.49 (CH_3); 156.88 (CO); 8.07–7.86 (Ar). For $C_{21}H_{21}N_3O_6$ (411.4) calculated: 61.31% C, 5.14% H, 10.21% N; found: 61.33% C, 5.26% H, 10.23% N.

Methyl 6-Azido-2,6-dideoxy-α-D-*ribo*-hexopyranoside (**7**)

To a solution of hexopyranoside **6** (1.33 g, 3.2 mmol) in methanol (80 ml) sodium methoxide in methanol (1 M solution, 5 ml) was added dropwise. The mixture was left at room temperature and monitored by TLC in the benzene–ethanol (20:1) system (**6**: R_F 0.8, **7**: R_F 0.38). After 90 min the solution was neutralized by stream of carbon dioxide (30 min). Then the solvent was evaporated and the rest was repeatedly evaporated with water (50 ml) to remove methyl benzoate. Product was extracted with diethyl ether and the organic layer was dried with anhydrous magnesium sulfate. Syrupy azido derivative **7** (0.59 g, 89.6 mmol) was obtained, which after chromatography on silica gel in chloroform–methanol (50:1) yielded product **7** as a syrup (0.38 g, 57.8%), $[\alpha]_D^{20}$ +76 (*c* 1.01, H_2O). IR (chloroform): 3521 (OH);

2940 (CH_2); 2640 (OCH_3); 2103 (N_3). ^{1}H NMR (400 MHz, D_2O): 4.85 d, 1 H, J(1,2) < 0.5, J(1,2′) ≈ 3.1 (H-1); 2.93 dd, 1 H, J(2,2′) ≈ 14.8, J(2,3) ≈ 2.8 (H-2); 3.42 m, 2 H (H-3, H-4); 3.80 m, 1 H, J(5,6) ≈ 2.0 (H-5); 3.62 dd, 1 H, J(6,6′) ≈ 13.0 (H-6); 3.51 dd, 1 H (H-6′). ^{13}C NMR (100 MHz, D_2O): 98.93 (C-1); 35.35 (C-2); 38.51 (C-3); 69.61 (C-4); 67.68 (C-5); 52.69 (C-6); 3.42 (CH_3). For $C_7H_{13}N_3O_4$ (203.2) calculated: 41.38% C, 6.45% H, 20.68% N; found: 41.78% C, 6.65% H, 20.21% N.

6-Azido-2,6-dideoxy-D-*ribo*-hexono-1,4-lactone (**9**)

Hexopyranoside **7** (378 mg, 1.9 mmol) was heated in a 50% solution of acetic acid (50 ml) at 80 °C. The course of hydrolysis was monitored by TLC in benzene–ethanol (10:1) (**7**: R_F 0.76; **8**: R_F 0.36). After 8 h the reaction mixture was cooled, diluted with water and purified by charcoal treatment. The filtrate was evaporated and the product was dried over sodium hydroxide to remove the rest of acetic acid yielding syrupy 6-azido-2,6-dideoxy-D-*ribo*-hexose (**8**; 0.33 g, 96%), $[\alpha]_D^{20}$ +47 (*c* 0.7, H_2O). A solution of hexose **8** (0.39 g, 1.9 mmol) in water (12 ml) was mixed without isolation with bromine (100 µl, 3.9 mmol) in the presence of barium carbonate (1 g, 5.1 mmol) in ice bath. Oxidation was monitored by TLC in the chloroform–methanol (10:2) system (**8**: R_F 0.68, **9**: R_F 0.73). After 3.5 h extra bromine (100 µl, 3.9 mmol) was added and the mixture was stirred at room temperature overnight. When TLC showed completion the reaction, excess of bromine was removed with a stream of air and barium carbonate was filtered off. The solution was stirred at room temperature for 2 h with freshly prepared silver carbonate (1 g). After removing the salts and thorough washing with water, the solution was passed through the column of Dowex 50WX4 in H^+ cycle and water was evaporated. After evaporation the product was dried and yielded syrupy lactone **9** (0.36 g, 92%), $[\alpha]_D^{20}$ +10 (*c* 0.7, H_2O). IR (neat): 3409 (OH); 2938 (CH_2); 2110 (N_3); 1779 (C=O). ^{1}H NMR (400 MHz, D_2O): 3.14 dd, 1 H, J(2,2′) ≈ 18.7, J(2,3) ≈ 7.0 (H-2); 2.58 dd, 1 H, J(2′,3) ≈ 2.4 (H-2′); 4.67, 1 H, J(3,4) ≈ 2.2 (H-3); 4.47, 1 H, J(4,5) ≈ 5.5 (H-4); 4.00 ddd, 1 H, J(5,6) ≈ 3.8, J(5,6′) ≈ 7.0 (H-5); 3.56 dd, 1 H, J(6,6′) ≈ 13.2 (H-6); 3.47 dd, 1 H (H-6′). ^{13}C NMR (100 MHz, D_2O): 180.01 (C-1); 38.29 (C-2); 70.27 (C-3); 89.22 (C-4); 68.42 (C-5); 53.38 (C-6). For $C_6H_9N_3O_4$ (187.2) calculated: 38.51% C, 4.85% H, 22.45% N; found: 38.19% C, 4.90% H, 22.26% N.

6-Amino-2,6-dideoxy-D-*ribo*-hexonic Acid (**10**)

Azidolactone **9** (0.78 g, 4.2 mmol) in water (70 ml) was hydrogenated on 5% Pd/C (0.16 g). The reaction was monitored by TLC in the toluene–acetone (7:3) system (**9**: R_F 0.45, **10**: R_F 0). After 6 h the catalyst was removed and the solvent was evaporated and dried to give foamy amino acid **10** (0.63 g, 85.1%), $[\alpha]_D^{20}$ –8 (*c* 1, H_2O). IR (KBr): 3431 (OH); 3367 (NH); 2916–2500 (COOH); 1646–1550, 1402 (COO). For $C_6H_{13}NO_5$ (179.2) calculated: 40.22% C, 7.31% H, 7.82% N; found: 39.90% C, 6.99% H, 7.40% N.

6-Amino-2,6-dideoxy-D-*ribo*-hexono-1,6-lactam (**1a**) and
3,4,5-Tri-*O*-acetyl-6-amino-2,6-dideoxy-D-*ribo*-hexono-1,6-lactam (**1b**)

6-Amino-6-deoxyhexonic acid **10** (0.3 g, 1.67 mmol) was dissolved in methanol (20 ml) with addition of 5% solution HCl in methanol (9 ml) and refluxed for 5 h. Methanol was evaporated and methyl ester hydrochloride **11** (0.38 g) was alkalized without isolation and purification with sodium methoxide dissolved in methanol (1.67 mmol). After evaporation of

methanol, lactam **1a** in a mixture with salts was treated with acetic anhydride (3 ml) in pyridine (5 ml) at room temperature for 24 h. Tri-*O*-acetyl derivative **1b** (0.35 g, 79%) was isolated as usually, then it was purified on a silica gel column in toluene–acetone (7:3), $[\alpha]_D^{20}$ –2 (*c* 0.8, $CHCl_3$). For NMR, see Tables I–III. For $C_{12}H_{17}NO_7$ (287.1) calculated: 50.21% C, 5.92% H, 4.88% N; found: 50.11% C, 5.66% H, 4.98% N. Deacetylation of acetate **1b** (0.3 g, 1.04 mmol) using sodium methoxide (10 ml of 0.055 M solution in methanol) for 12 h followed by neutralization with Dowex 50WX4 (H^+) produced lactam **1a** (0.07 g, 42%), m.p. 194–195 °C with decomposition, $[\alpha]_D^{20}$ –37 (*c* 0.53, water). IR (KBr): 3447 (OH); 1637 (CONH). UV, λ_{max}: 201 nm. For NMR, see Tables I–III. For $C_6H_{11}NO_4$ (161.1) calculated: 44.74% C, 6.83% H, 8.69% N; found: 44.75% C, 6.89% H, 8.55% N.

6-Azido-2,6-dideoxy-D-*arabino*-hexono-1,4-lactone[10] (**12**)

M.p. 108–110 °C, $[\alpha]_D^{20}$ +75 (*c* 0.56, EtOAc); lit.[10] gives: m.p. 106–108 °C, $[\alpha]_D^{20}$ +74.2 (*c* 1.7, EtOAc). IR (KBr): 3397 (OH); 2931 (CH_2); 2128 (N_3); 1738 (C=O). ^{1}H NMR (400 MHz, D_2O): 3.07 dd, 1 H, *J*(2,2′) ≈ 18.1, *J*(2,3) ≈ 5.1 (H-2); 2.59 d, 1 H, *J*(2′,3) ≈ 0.5 (H-2′); 4.71 dd, 1 H, *J*(3,4) ≈ 2.5 (H-3); 4.50 dd, 1 H, *J*(4,5) ≈ 11.6 (H-4); 4.18 ddd (1 H, *J*(5,6) ≈ 2.1, *J*(5,6′) ≈ 5.6 (H-5); 3.67 dd, 1 H, *J*(6,6′) ≈ 13.3 (H-6); 3.51 dd (H-6′). ^{13}C NMR (100 MHz, D_2O): 180.19 (C-1); 68.49, 84.37, 67.83 (C-4, C-5, C-3); 39.82 (C-2); 54.98 (C-6). For $C_6H_9N_3O_4$ (187.2) calculated: 38.51% C, 4.85% H, 22.45% N; found: 38.47% C, 4.96% H, 22.27% N.

6-Amino-2,6-dideoxy-D-*arabino*-hexono-1,6-lactam[10] (**2a**)

M.p. 202–203 °C, $[\alpha]_D^{20}$ –92 (*c* 0.4, H_2O); lit.[10] gives: m.p. 206–207 °C, $[\alpha]_D^{20}$ –41 (*c* 0.8, H_2O). IR (KBr): 3450 (OH); 3270 (NH); 1656, 1633 (CONH). UV, λ_{max}: 195 nm. For NMR, see Tables I–III. For $C_6H_{11}NO_4$ (161.1) calculated: 44.74% C, 6.83% H, 8.69% N; found: 44.40% C, 6.70% H, 8.39% N.

3,4,5-Tri-*O*-acetyl-6-amino-2,6-dideoxy-D-*arabino*-hexono-1,6-lactam (**2b**)

Acetylation of lactam **2a** (100 mg, 0.62 mmol) with acetic anhydride (0.5 ml) in pyridine (2 ml) yielded triacetate **2b** (150 mg, 84%), m.p. 151–153 °C (ethanol), $[\alpha]_D^{20}$ –14 (*c* 0.4, $CHCl_3$). For NMR, see Tables I–III. For $C_{12}H_{17}NO_7$ (287.1) calculated: 50.21% C, 5.92% H, 4.88% N; found: 50.30% C, 6.13% H, 4.64% N.

6-Amino-2,6-dideoxy-D-*arabino*-hexonic Acid (**2c**)

Lactone **12** (1 g, 5.3 mmol) was hydrogenated in a water solution (100 ml) on 5% Pd/C (300 mg) at room temperature and atmospheric pressure. After 16.5 h, no starting compound was present in the reaction mixture (TLC, $CHCl_3$–MeOH (10:1), lactone: R_F 0.49, **2c**: R_F 0). Catalyst was removed by filtration and filtrate evaporated. By recrystallization of a residue from a water–methanol mixture, acid **2c** (0.9 g, 94%) was obtained, m.p. 192–205 °C with decomposition, $[\alpha]_D^{22}$ –1 (*c* 0.7, water). IR (KBr): 3262, 3206 (COOH, OH); 2926 (CH_2); 1632 (NH); 1460 (CH). For $C_6H_{13}NO_5$ (179.2) calculated: 40.22% C, 7.31% H, 7.82% N; found: 39.94% C, 7.61% H, 7.59% N.

6-Azido-2,3,6-trideoxy-L-*threo*-hexono-1,4-lactone (**14**)

A solution of 6-bromo-2,3,6-trideoxy-L-*threo*-hexono-1,4-lactone[14] (**13**; 1.1 g, 5.3 mmol) in DMF (17 ml) was stirred with sodium azide (1.1 g, 16.9 mmol) at 90 °C for 3 h. Reaction was monitored by TLC in the ethyl acetate–petroleum ether (1:1) system (**13**: R_F 0.40, **14**: R_F 0.37). Solvent was evaporated, the residue was suspended in water (30 ml) and product was extracted with chloroform (5 × 25 ml). Organic phases were concentrated to yield syrupy azidolactone **14** (0.9 g, 98%), $[\alpha]_D$ +65.1 (*c* 1.1, $CHCl_3$). IR ($CHCl_3$): 3424 (OH); 2935 (CH_2); 2108 (N_3); 1774 (CO). ^{1}H NMR (500 MHz, $CDCl_3$): 2.64 ddd, 1 H, *J*(2,2′) ≈ 15.9, *J*(2,3) ≈ 10.0, *J*(2,3′) ≈ 5.7 (H-2); 2.55 dd, 1 H, *J*(2′, 3) ≈ 8.2, *J*(2′,3′) ≈ 9.6 (H-2′); 2.23–2.32 m, 2 H (H-3, H3′); 4.59 dddd, 1 H, *J*(4,3) ≈ 7.3, *J*(4,3′) ≈ 7.3, *J*(4,5) ≈ 3.3 (H-4); 3.78 s, 1 H, *J*(5,6) ≈ 5.1, *J*(5,6′) ≈ 7.0 (H-5); 3.51 dd, 2 H, *J*(6,6′) ≈ 12.6 (H-6); 3.47 dd, 1 H (H-6′). ^{13}C NMR (125.75 MHz, $CDCl_3$): 178.36 (C-1); 29.08 (C-2); 24.41 (C-3); 80.97 (C-4); 72.96 (C-5); 53.83 (C-6). For $C_6H_9N_3O_3$ (171.2) calculated: 42.11% C, 5.30% H, 24.55% N; found: 41.83% C, 5.54% H, 23.91% N.

6-Amino-2,3,6-trideoxy-L-*threo*-hexono-1,6-lactam (**3a**)

Azidolactone **14** (0.64 g, 3.7 mmol) dissolved in methanol (75 ml) was hydrogenated on 5% Pd/C (0.19 g) at room temperature and atmospheric pressure. According to TLC (toluene–acetone (7:3), **14**: R_F 0.73, **3a**: R_F 0.17), starting material disappeared during 2 h. Catalyst was removed by filtration on a Supercel layer. Methanol was evaporated and the product was recrystallized from hot methanol to give lactam **3a** (0.434 g, 80%), m.p. 165–167 °C with decomposition, $[\alpha]_D$ –2.6 (*c* 1.05, H_2O). IR (KBr): 3430 (OH); 3365 (NH); 2984 (CH_2); 1627 (CO). For NMR, see Tables IV–VI. For $C_6H_{11}NO_3$ (145.2) calculated: 49.65% C, 7.64% H, 9.65% N; found: 49.72% C, 9.75% H, 7.72% N.

4,5-Di-*O*-acetyl-6-amino-2,3,6-trideoxy-L-*threo*-hexono-1,6-lactam (**3b**)

Lactam **3a** (0.04 g, 0.3 mmol) dissolved in pyridine (1 ml) was treated with acetic anhydride (0.19 ml, 2 mmol). Reaction mixture was left at room temperature for 24 h. Then according to TLC (toluene–acetone (7:3), **3a**: R_F 0.16, **3b**: R_F 0.26), starting material was converted completely to product. The solution was poured to ice water and product extracted with chloroform (5 × 5 ml). After washing with water, combined organic layers were dried with anhydrous magnesium sulfate, filtered and evaporated. A residue was recrystallized from diethyl ether to give pure product **3b** (0.05 g, 84%), m.p. 164–166 °C, $[\alpha]_D^{22}$ +78.3 (*c* 1.0, $CHCl_3$). ^{13}C NMR (125.75 MHz, $CDCl_3$): 177.0 (C-1); 29.91 (C-2); 24.79 (C-3); 72.08 (C-4); 70.47 (C-5); 40.59 (C-6). For further NMR data, see Tables IV–VI. For $C_{10}H_{15}NO_5$ (229.1) calculated: 52.42% C, 6.55% H, 6.11% N; found: 52.38% C, 6.50% H, 5.95% N.

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REFERENCES

1. Kefurt K., Kefurtová Z., Trška P., Bláha K., Frič I., Jarý J.: *Collect. Czech. Chem. Commun.* **1989**, *54*, 2156.
2. Kefurt K., Havlíček J., Hamerníková M., Kefurtová Z., Votavová H.: *Collect. Czech. Chem. Commun.* **1997**, *62*, 1919.
3. Hamerníková M., Havlíček J., Votavová H., Kefurt K.: *Collect. Czech. Chem. Commun.* **2002**, *67*, 622.
4. Ondráček J., Novotný J., Kefurt K., Havlíček J.: *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *48*, 929.
5. Ondráček J., Havlíček J., Kefurt K., Jarý J., Novotný J., Kratochvíl B.: *Collect. Czech. Chem. Commun.* **1993**, *58*, 1600.
6. Takayanagi H., Ogura H.: *Croat. Chem. Acta* **1989**, *62*, 135.
7. Hamerníková M., Pakhomova S., Havlíček J., Votavová H., Kefurt K.: *Carbohydr. Res.* **2000**, *325*, 56.
8. Konno T., Meguro H., Tuzimura K.: *Tetrahedron Lett.* **1975**, 1305.
9. Meguro H., Konno T., Tuzimura K.: *Tetrahedron Lett.* **1975**, 1309.
10. Bock K., Lundt. I., Pedersen C.: *Acta Chem. Scand., Ser. B* **1987**, *41*, 435.
11. Horton D., Chewing T.-M., Weekerle W.: *Methods Carbohydr. Chem.* **1980**, *8*, 135.
12. Hanessian S., Plessas N. R.: *J. Org. Chem.* **1969**, *34*, 1035.
13. Bock K., Lundt I., Pedersen Ch., Refn S.: *Acta Chem. Scand., Ser. B* **1986**, *40*, 740.
14. Pedersen Ch., Schubert L.: *Acta Chem. Scand.* **1993**, *47*, 885.
15. Haasnoot C. A. G., de Leeuw F. A. A. M., Altona C.: *Tetrahedron* **1980**, *36*, 2783.
16. *HyperChem for Windows*, Rel 2, 1992, Autodesk, Inc.
17. Ogura H., Takayanagi H., Kerbo K., Furuhata K.: *J. Am. Chem. Soc.* **1973**, *95*, 8056.
18. Ogura H., Takayanagi H., Furuhata K.: *Chem. Lett.* **1973**, 387.
19. Ogura H., Takayanagi H., Furuhata K.: *J. Chem. Soc., Perkin Trans. 1* **1976**, 665.
20. Schellman J. A., Oriel P.: *Chem. Phys.* **1962**, *37*, 2114.
21. Litman J., Schellman J. A.: *J. Phys. Chem.* **1965**, *67*, 978.
22. Schellman J. A.: *Acc. Chem. Res.* **1968**, *1*, 144.
23. Frič I., Maloň P., Tichý M.: *Collect. Czech. Chem. Commun.* **1977**, *42*, 678.
24. Maloň P., Bláha K.: *Collect. Czech. Chem. Commun.* **1977**, *42*, 687.
25. Scott K., Stonehouse J., Keeler J., Hwang T., Shaka A. J.: *J. Am. Chem. Soc.* **1995**, *117*, 4199.