SYNTHESIS AND CONFORMATION OF 6-AMINO-3,6-DIDEOXYHEXONO-1,6-LACTAMS

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Three isomeric 6-amino-3,6-dideoxyhexono-1,6-lactams of D-*ribo* (**1a**), L-*lyxo* (**2a**) and L-*arabino* (**3a**) configuration were synthesized *via* the corresponding 6-azido-3,6-dideoxyhexoses starting from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose. Conformation of lactams **1a**, **2a** and **3a** and their tri-*O*-acetyl derivatives **1b**, **2b** and **3b** was studied using NMR spectroscopy. CD spectra of the lactams **1a**–**3a**, together with the D-*xylo* diastereoisomer **4a**, were measured and interpreted according to semiempirical rules. NMR and CD measurements confirmed the chair conformation with an equatorial substituent on C-2 as prevailing for the all measured lactams.

Keywords: Carbohydrates; Lactams; Amino sugars; Conformation analysis; NMR spectroscopy; Circular dichroism.

Conformation of aminodeoxyhexonolactams has been studied in our laboratory for a long period. Investigations have so far concentrated on 6-amino-6-deoxyhexono-1,6-lactams[1–9] and 5-amino-5-deoxypentono-1,5-lactams[10,11]. The conformational study of six- and seven-membered lactam rings performed by NMR, IR, CD spectroscopy[4,5,9,11] and X-ray measurements[6–8] opened discussion on the relationship between lactam configuration and conformation of the lactam ring especially with regard to interpretation of CD spectra[4]. In addition to the stereochemical aspects,

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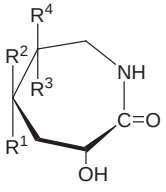
any knowledge of stereochemistry of lactam rings is significant also in connection with biological effects of these and related compounds, namely, with their potential action as inhibitors of glycosidases (see refs[12–14]).

Following our previous paper[9], we present here syntheses and conformational NMR studies of 6-amino-3,6-dideoxy-D-*ribo*-hexono-1,6-lactam (**1a**), 6-amino-3,6-dideoxy-L-*lyxo*-hexono-1,6-lactam (**2a**) and 6-amino-3,6-dideoxy-L-*arabino*-hexono-1,6-lactam (**3a**), and their 2,4,5-tri-*O*-acetyl derivatives **1b**, **2b** and **3b**, respectively. Conclusions from NMR are compared with CD measurement of the lactams **1a**–**3a** and of the previously described[9] 6-amino-3,6-dideoxy-D-*xylo*-hexono-1,6-lactam (**4a**).



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

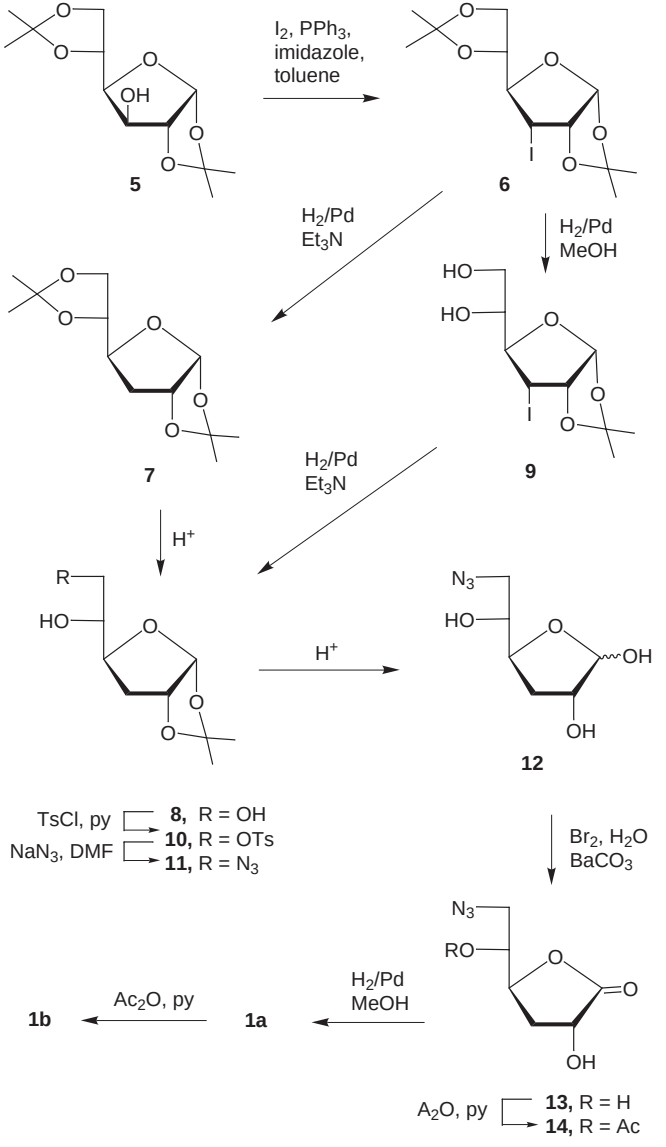
RESULTS AND DISCUSSION

Synthesis

Three new studied lactams **1a**–**3a** were prepared *via* corresponding 6-azido-3,6-dideoxyhexoses. 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (**5**) was used as starting compound for synthesis of lactam **1a** (Scheme 1). The hydroxy group in position 3 of was displaced by iodine with the inversion of configuration using iodine, triphenylphosphine and imidazole in toluene[15]. 3-Deoxy-3-iodo-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**6**) was reduced with hydrogen on 5% Pd/C in the presence of triethylamine to 3-deoxy-1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranose (**7**). Partial hydrolysis of this compound with dilute acetic acid led to 3-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranose (**8**) with the physical constants identical with those in literature[15].

We modified the two-step process from **6** to **8** to an "one-pot" synthesis using acidity of hydrogen iodide forming during the reduction to produce directly the partially hydrolysed product **8**. Reduction of starting iodo derivative **6** in methanol without triethylamine resulted in a small amount of deoxy derivative **7**. The presence of hydrogen iodide in this step deceler-

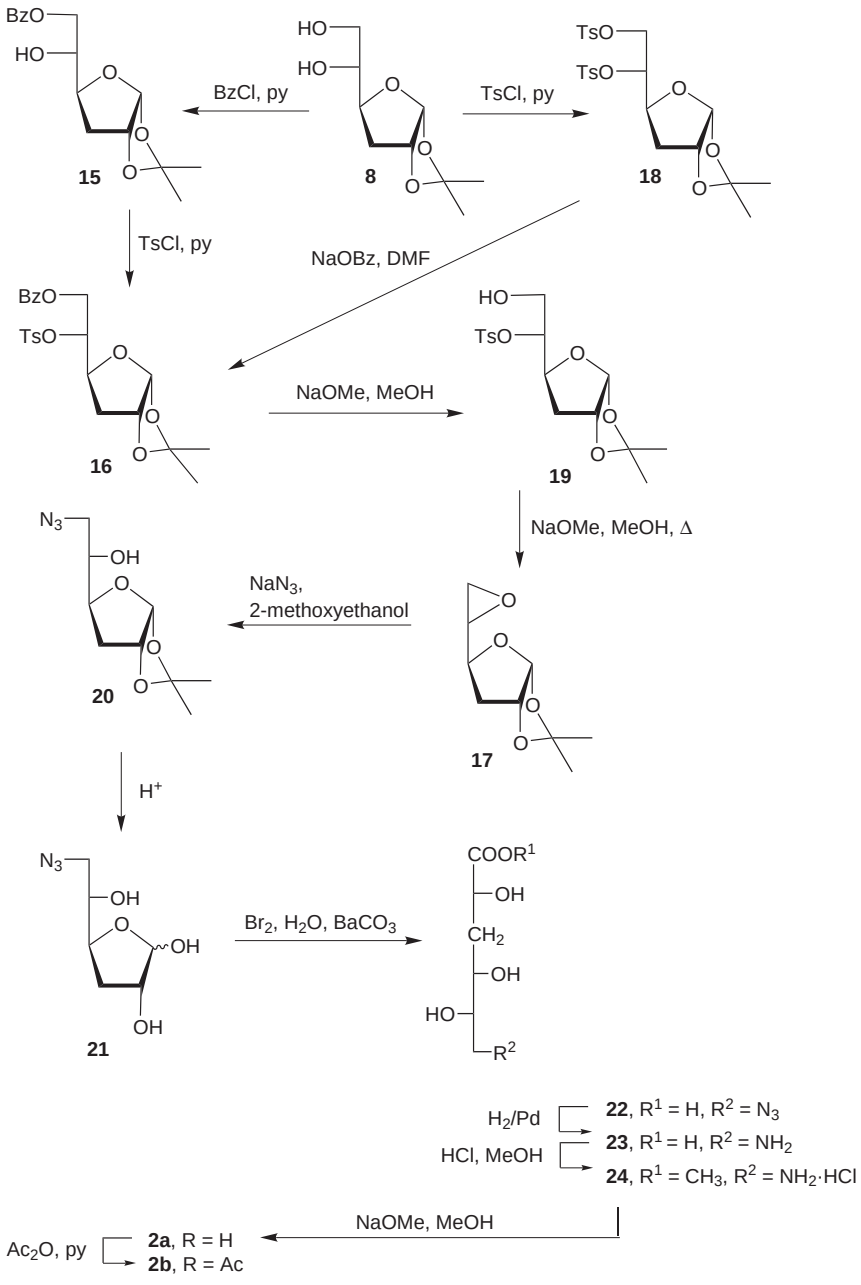
ated the reduction and caused the partial hydrolysis of **6** to 3-deoxy-3-iodo-1,2-*O*-isopropylidene-α-D-allofuranose (**9**) which was complete in several hours. Then, triethylamine and the fresh 5% Pd/C were added to the reaction mixture. Hydrogenolysis gave a single product **8**. Selective tosylation of compound **8** afforded[16] 3-deoxy-1,2-*O*-isopropylidene-



SCHEME 1

6-*O*-tosyl-α-D-*ribo*-hexofuranose (**10**). Treatment of **10** with sodium azide in dimethylformamide yielded 6-azido-3,6-dideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranose (**11**). ^{1}H NMR spectrum of this compound was in accord with the described one[17]. Acid hydrolysis of azido derivative **11** gave[17] the syrupy 6-azido-3,6-dideoxy-D-*ribo*-hexose (**12**). Oxidation of **12** by means of bromine in water in the presence of barium carbonate led to 6-azido-3,6-dideoxy-D-*ribo*-hexono-1,4-lactone (**13**). The stretching absorption on 1 744 cm^{-1} would give evidence rather for the six-membered lactone ring, but the ^{1}H NMR spectrum confirmed the five-membered ring, especially because of the chemical shift of H-4 (≈4.7 ppm) and the great coupling constants between H-2, H-3′, H-3, H-4. In the ^{1}H NMR spectrum of 2,5-di-*O*-acetyl-6-azido-3,6-dideoxy-D-*ribo*-hexono-1,4-lactone (**14**), the signals of H-2 and H-5 were deshielded, which made the spectrum easily "readable" and confirmed also the five-membered lactone ring. Lactone **13** was reduced by means of hydrogen on 5% Pd/C in methanol to 6-amino-3,6-dideoxy-D-*ribo*-hexono-1,6-lactam (**1a**), which was recrystallized from hot methanol. Conventional acetylation of lactam **1a** with acetic anhydride in pyridine gave tri-*O*-acetyl derivative **1b**.

For the preparation of 6-amino-6-deoxy-L-*lyxo*-hexono-1,6-lactam (**2a**) (Scheme 2), we used the inversion of configuration on C-5 of compound **8** *via* 5,6-anhydro-3-deoxy-1,2-*O*-isopropylidene-β-L-*lyxo*-hexofuranose (**17**). According to the described[18] procedure, **17** was prepared by alkaline cyclization of 6-*O*-benzoyl-3-deoxy-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-*ribo*-hexofuranose (**16**) obtained from 6-*O*-benzoyl-3-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranose (**15**). We were successful in the preparation of **16** also by regioselective displacement of a tosyloxy group in 3-deoxy-1,2-*O*-isopropylidene-5,6-di-*O*-tosyl-α-D-*ribo*-hexofuranose (**18**) with benzoyloxy group using sodium benzoate in dimethylformamide. The formation of anhydro compound **17** included two steps: debenzoylation followed by nucleophilic cyclization of 3-deoxy-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-*ribo*-hexofuranose (**19**). Provided that the reaction was performed at room temperature, we were able to isolate intermediate **19**. Treatment of compound **17** with sodium azide in dimethylformamide caused the nucleophilic opening of the anhydro ring to produce 6-azido-3,6-dideoxy-1,2-*O*-isopropylidene-β-L-*lyxo*-hexofuranose (**20**). Acid hydrolysis of **20** led to 6-azido-3,6-dideoxy-L-*lyxo*-hexose (**21**). In oxidation of **21** with bromine in water, the corresponding lactone was formed (according to TLC), but it was rapidly hydrolyzed so that only 6-azido-3,6-dideoxy-L-*lyxo*-hexonic acid (**22**) was isolated. Structure of **22** was confirmed by IR spectra exhibiting bands of associated OH groups (3 438, 3 340, 3 295 cm^{-1}), a characteris-

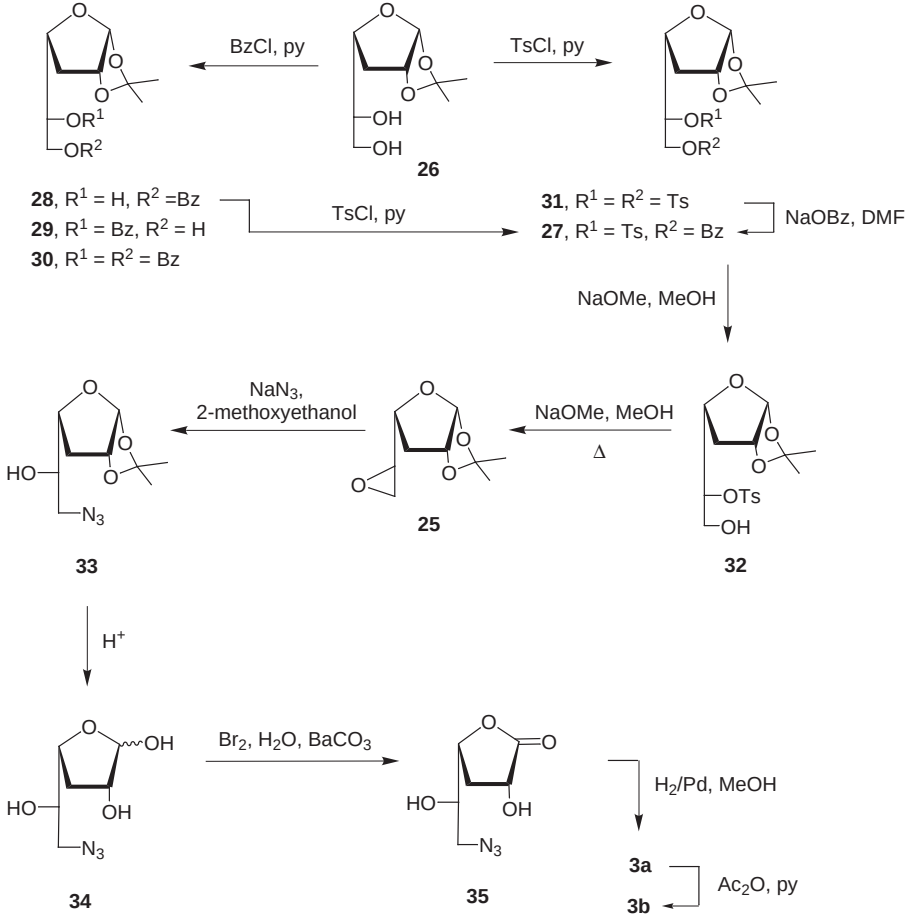

BzO
HO
15
BzCl, py
HO
HO
8
TsCl, py
TsO
TsO
18
TsCl, py
NaOBz, DMF
BzO
TsO
16
NaOMe, MeOH
HO
TsO
19
NaOMe, MeOH, Δ
N3
OH
20
NaN3,
2-methoxyethanol
17
H+
N3
OH
OH
21
Br2, H2O, BaCO3
COOR1
OH
CH2
OH
HO
R2
H2/Pd
HCl, MeOH
22, R1 = H, R2 = N3
23, R1 = H, R2 = NH2
24, R1 = CH3, R2 = NH2·HCl
NaOMe, MeOH
Ac2O, py
2a, R = H
2b, R = Ac

SCHEME 2

tic series of absorptions at 2 930–2 500 cm^{-1} and carboxylate bands at 1 730–1 636 and 1 404 cm^{-1}. 6-Amino-3,6-dideoxy-L-*lyxo*-hexonic acid (**23**) was prepared by catalytic reduction of **22**. IR spectrum exhibited an expressive band of associated amino and hydroxy groups at 3 600–2 500 cm^{-1}, and a carboxylate band (1 765–1 615, 1 405 cm^{-1}). Amino acid **23** was treated with hydrogen chloride in methanol to form methyl ester hydrochloride **24** which was transformed without isolation to 2,4,5-tri-*O*-acetyl-6-amino-3,6-dideoxy-L-*lyxo*-hexono-1,6-lactam (**2b**) with sodium methanolate in methanol and acetylated. Acetate **2b** after chromatographic purification was treated with sodium methanolate in methanol and the resulting solution neutralized with ion exchanger in H^+ generation. Structure of syrupy 6-amino-3,6-dideoxy-L-*lyxo*-hexono-1,6-lactam (**2a**) was confirmed by NMR, IR and elemental analysis.

In the preparation of 6-amino-6-deoxy-L-*arabino*-hexono-1,6-lactam (**3a**), 5,6-anhydro-3-deoxy-1,2-*O*-isopropylidene-β-L-*arabino*-hexofuranose (**25**) was the key intermediate (Scheme 3). 3-Deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose[19,20] (**26**) was converted to 6-*O*-benzoyl-3-deoxy-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-*xylo*-hexofuranose (**27**). We suggested two pathways for this preparation. The first procedure included partial benzoylation of **26** yielding mainly 6-*O*-benzoyl-3-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (**28**) as expected, but also 8% of 5-*O*-benzoyl-3-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (**29**), 4% of 5,6-di-*O*-benzoyl-3-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (**30**) and the unreacted starting material. Tosylation of 6-benzoate **28** led to 5-*O*-tosyl derivative **27**. Structures of compounds **27**, **28**, **29** and **30** were confirmed by NMR. The number of aromatic protons could be observed in the region 7–9 ppm, the positions of benzoyloxy groups resulted on the deshieldings of signals H-5 and H-6. A better route to the preparation of compound **27** started from 3-deoxy-1,2-*O*-isopropylidene-5,6-di-*O*-tosyl-α-D-*xylo*-hexofuranose (**31**). Treatment of **31** with sodium benzoate in dimethylformamide yielded 90% of compound **27** which after alkaline debenzoylation afforded 74% of 5,6-anhydro derivative **25** and 10% of 3-deoxy-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-*xylo*-hexofuranose (**32**) at room temperature or 80% of **25** at 50 °C. The formation of the anhydro ring in positions 5 and 6 was in ^1H NMR accompanied by the upfield shift of signals H-6 and H-6′ by 2 ppm and by the reduction of the geminal spin–spin coupling constants between protons H-6 and H-6′ in α-position to the oxirane oxygen to the value $^2J_{6,6'} \approx 5$ Hz. Nucleophilic opening of the oxirane ring by an azide anion led to 6-azido-3,6-dideoxy-1,2-*O*-isopropylidene-β-L-*arabino*-hexofuranose (**33**). This compound exhibited IR absorp-

tions at 2 107 cm^{-1} (azide), 3 466 cm^{-1} (hydroxyl) and a bending doublet on 1 377 and 1 374 cm^{-1} (isopropylidene). The structure was confirmed by NMR and by comparison of the data with those described[17] for D-enantiomer. Compound **33** was quantitatively hydrolyzed under acid conditions to produce 6-azido-3,6-dideoxy-L-*arabino*-hexose (**34**). It was oxidized similarly – as mentioned above – to 6-azido-3,6-dideoxy-L-*arabino*-hexono-1,4-lactone (**35**). The five-membered lactone was characterized in IR spectrum by the elevated wavenumber of a carbonyl band (1 776 cm^{-1}). In ^1H NMR spectrum this fact is evident from the increased chemical shift of H-4. The great spin–spin interactions between protons H-2, H-3 and H-3, H-4 give evidence of the prevailing E_3 conformation of the lactone ring. Azidolactone



SCHEME 3

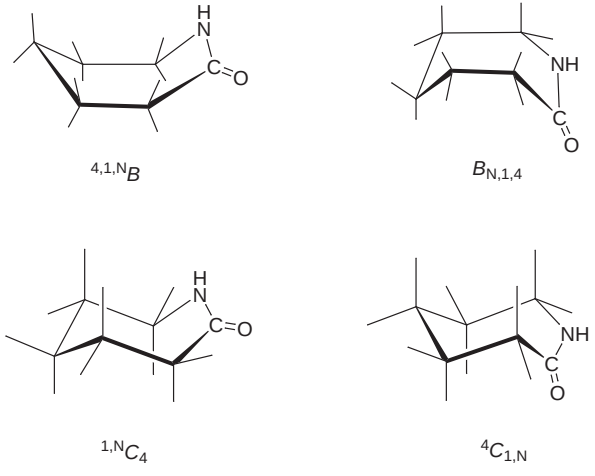
35 was reduced with hydrogen on 5% Pd/C in methanol to give 6-amino-3,6-dideoxy-L-*arabino*-hexono-1,6-lactam (**3a**). Conventional acetylation afforded the corresponding tri-*O*-acetyl derivative **3b**.

Conformational Analysis

Because of the approximately planar arrangement of the amide segment, a seven-membered lactam ring is able to exist as a $^{4}C_{1,N}$ or $^{1,N}C_{4}$ chair and $B_{N,1,4}$ or $^{4,1,N}B$ boat conformers (Fig. 1).

NMR Measurements

The conformational study of cyclic compounds is based on modified Karplus's equation[21]. For each substituted $H^{a}R^{1}R^{2}C\text{-}CR^{3}R^{4}H^{b}$ segment in a lactam molecule it is possible, according to modified Karplus's equation[21], to calculate the coupling constants for an arbitrary torsion angle $H^{a}R^{1}R^{2}C\text{-}CR^{3}R^{4}H^{b}$. A comparison of the coupling constants, found in the ^{1}H NMR spectra, with the values calculated for $^{4}C_{1,N}$ and $^{1,N}C_{4}$ conformers makes it possible to determine the prevailing conformer. Eight configuration isomers of 6-amino-6-deoxyhexonolactams[4] and four isomers of 5-amino-5-deoxypentonolactams[11] have been studied previously. ^{1}H NMR conformational analysis revealed the predominance of the conformer with



$^{4,1,N}B$ $B_{N,1,4}$ $^{1,N}C_{4}$ $^{4}C_{1,N}$

FIG. 1
Possible conformation of seven-membered lactam ring

equatorial hydroxy or acetoxy group on C-2, even in the case of 6-amino-6-deoxy-L-gulonolactam with three remaining axial groups. Similar situation was observed studying 5-amino-5-deoxypentonolactams[11]. This fact was discovered previously[22,23] and has been explained by the interaction of π-electrons of a carbonyl group with the lone electron pair of the heteroatom of the neighbouring substituent. A plane arrangement desirable for interacting atoms is available rather for equatorial than for axial substituent on C-2. In order to study the solution conformer equilibrium in our set of lactams, we performed low-temperature NMR spectroscopy. Geometries of $^4C_{1,N}$ and $^{1,N}C_4$ conformers were optimized using molecular mechanics (MM^+) in vacuum[24] to obtain the theoretical values of torsion angles between vicinal protons. Conformation of 6-amino-3,6-dideoxy-D-*xylo*-hexono-1,6-lactam (**4a**) and its tri-*O*-acetyl derivative **4b** has been studied recently[9] and the $^4C_{1,N}$ (D) conformer was found both in solutions of lactams **2a**, **2b** or in the solid **2a**. The decisive effect of the equatorial hydroxy group on C-2 caused in this case the axial positions of the remaining OH groups.

^{1}H NMR spectrum of 6-amino-3,6-dideoxy-D-*ribo*-hexono-1,6-lactam (**1a**) at 300 and 340 K revealed the prevailing $^4C_{1,N}$ conformer in solution (Tables I–III). Low-temperature NMR experiments did not record any changes either in chemical shifts or in the values of coupling constants. The nuclear Overhauser effect between H-2 and H-6′, H-4, H-3′ (Fig. 2) confirmed the $^4C_{1,N}$ conformer with two equatorial and one axial hydroxy groups. NOE between H-3′ and H-5 supporting the less advantageous $^{1,N}C_4$ conformer was not observed.

^{1}H NMR spectrum of 6-amino-3,6-dideoxy-L-*lyxo*-hexono-1,6-lactam (**2a**) recorded in deuterium oxide at 300 K exhibited a quartet of H-3 at 1.82 ppm split with three coupling constants $J \approx 11$ Hz which correlates with geometry of the $^4C_{1,N}$ conformer (Tables I and III) with three equatorial OH groups. The low-temperature ^{1}H NMR spectrum of corresponding tri-*O*-acetyl derivative **2b** is similar to the spectrum recorded at normal tempera-

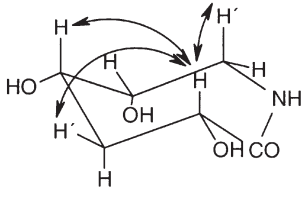


FIG. 2
NOE in 6-amino-3,6-dideoxy-D-*ribo*-hexono-1,6-lactam (**1a**)

TABLE I

^{1}H NMR (500 MHz) of lactams **1a**, **2a**, **3a** in CD_3SOCD_3 (A), CD_3OD (B), D_2O (C), and their tri-*O*-acetyl derivatives **1b**, **2b**, **3b** in $CDCl_3$ (D)

Parameter	**1a**			**1b**	**2a**	**2b**		**3a**			**3b**
	A[a] 300 K	B 200 K	B 300 K	D[b] 300 K	C 300 K	D[c] 300 K	D[d] 210 K	A[e] 300 K	B 300 K	B 190 K	D[f] 300 K
						Chemical shifts (δ-scale, ppm)					
H-2	4.00 (d)	4.29 (d)	4.19 (dd)	5.20 (dd)	4.51 (dd)	5.30 (dd)	5.20 (d)	4.40 (d)	4.69 (dd)	4.74 (d)	5.59 (dd)
H-3	1.68 (ddd)	2.00 (q)	1.98 (ddd)	2.33 (q)	1.82 (q)	2.15 (q)	2.17 (m[g])	1.64 (ddd)	1.89 (ddd)	2.01 (m[g])	2.28 (ddd)
H-3′	1.65 (dd)	1.85 (d)	1.83 (d)	2.05 (m[g])	2.16 (dd)	2.36 (ddd)	2.36 (d)	1.85 (ddd)	2.12 (ddd)	2.01 (m[g])	2.22 (ddd)
H-4	3.59 (ddd)	3.81 (d)	3.79 (ddd)	5.10 (ddd)	3.75 (ddd)	5.26 (ddd)	5.09 (bs)	3.83 (bs)	4.07 (d)	4.07 (bs)	5.49 (bs)
H-5	3.63 (dd)	3.84 (s)	3.84 (s)	5.18 (dd)	3.38 (ddd)	4.81 (ddd)	4.84 (bs)	3.28 (d)	3.52 (d)	3.51 (d)	4.83 (d)
H-6	3.03 (ddd)	3.24 (dd)	3.25 (dd)	3.56 (ddd)	3.18 (dd)	3.43 (dd)	3.55 (m[g])	2.63 (dd)	2.89 (d)	2.79 (d)	3.11 (dd)
H-6′	3.10 (dd)	3.31 (d)	3.30 (d)	3.47 (dd)	3.24 (dd)	3.33 (ddd)	3.55 (m[g])	3.43 (ddd)	3.67 (dd)	3.70 (dd)	3.88 (ddd)
NH	7.62 (s)	–	–	6.05 (t)	–	3.93 (bs)	7.28 (s)	7.85 (bs)	–	–	6.22 (bs)
						Coupling constants ^3J(H,H) in Hz					
J(2,3)	10.3	11.6	10.7	12.3	11.8	11.9	12.1	11.2	11.5	9.3	10.9
J(2,3′)	<0.5	<0.5	3.0	1.5	1.7	1.5	<0.5	1.9	2.2	<0.5	2.5
J(3,4)	10.4	11.6	11.6	12.3	11.7	11.3	[g]	1.8	2.1	[g]	2.4
J(3′,4)	4.2	<0.5	4.0	4.0	4.7	4.8	[g]	5.4	5.5	[g]	5.6
J(3,3′)	12.2	11.6	12.9	12.3	11.7	13.4	10.6	14.0	14.3	[g]	14.9
J(4,5)	2.5	[g]	3.0	2.7	9.0	9.5	[g]	<0.5	<0.5	<0.5	<0.5
J(5,6)	5.6	4.2	6.6	6.2	3.4	3.0	[g]	<0.5	<0.5	<0.5	<0.5
J(5,6′)	<0.5	<0.5	<0.5	<0.5	9.4	10.0	[g]	10.2	10.5	9.3	10.1
J(6,6)	15.1	11.5	15.6	16.0	15.0	15.5	[g]	14.0	14.3	11.1	13.0
J(6,NH)	7.3	–	–	7.6	–	10.3	[g]	6.3	–	–	7.0
J(6′,NH)	4.7	–	–	5.4	–	2.9	[g]	4.9	–	–	5.4

Other signals: [a] 4.70, 4.50, 4.27 (3 s, 3 H, 3 OH); [b] 2.16, 2.11, 2.03 (3 s, 9 H, 3 OAc); [c] 2.20, 2.09, 2.08 (3 s, 9 H, 3 OAc); [d] 2.17 (1 s, 9 H, 3 OAc); [e] 4.80, 4.73, 4.20 (3 s, 3 H, 3 OH); [f] 2.06, 2.18, 2.19 (3 s, 9 H, 3 OAc); [g] overlapping signals.

TABLE II

^{13}C NMR (75 MHz) chemical shifts (δ-scale, ppm) of lactams **1a**, **2a** in D_2O (A) and **3a** in CD_3SOCD_3 (B), and their acetyl derivatives **1b**, **2b** and **3b** in $CDCl_3$ (C)

Parameter	**1a** (A)	**1b** (C)	**2a** (A)	**2b** (C)	**3a** (B)	**3b** (C)
C-1	176.1	171.9	177.8	172.2	177.8	173.0
C-2	65.2	68.2	64.9	67.3	61.9	68.6
C-3	35.8	29.7	38.7	33.5	35.5	30.4
C-4	71.6	72.1	52.6	72.7	66.7	68.5
C-5	67.9	68.4	55.0	73.3	68.7	72.1
C-6	41.4	40.4	42.3	41.5	37.8	39.7
	–	170.8	–	170.7	–	170.7
COCH$_3$		170.7		170.6		170.5
		170.5		170.6		170.3
CO**C**H$_3$	–	21.3	–	21.4	–	21.7
		21.3		21.3		21.4
		21.1		21.2		21.4

TABLE III

Calculated values of vicinal coupling constants ^3J(H,H) (in Hz) in the $^4C_{1,N}$ and $^{1,N}C_4$ conformers of 6-amino-3,6-dideoxyhexono-1,6-lactams **1a**, **2a**, and **3a**

Lactam	**1a**	**2a**	**3a**
J(2,3) $^4C_{1,N}$	11.5	11.6	11.6
J(2,3) $^{1,N}C_4$	6.3	6.7	6.9
J(2,3′) $^4C_{1,N}$	2.1	1.9	2.1
J(2,3′) $^{1,N}C_4$	1.1	1.2	1.1
J(3,4) $^4C_{1,N}$	11.3	11.3	1.8
J(3,4) $^{1,N}C_4$	4.5	4.3	4.4
J(3′,4) $^4C_{1,N}$	4.3	4.3	4.8
J(3′,4) $^{1,N}C_4$	2.2	2.2	11.2
J(4,5) $^4C_{1,N}$	2.1	8.9	2.3
J(4,5) $^{1,N}C_4$	2.2	2.7	2.2
J(5,6) $^4C_{1,N}$	5.9	2.9	2.8
J(5,6) $^{1,N}C_4$	10.8	0.9	0.9
J(5,6′) $^4C_{1,N}$	0.9	10.9	10.9
J(5,6′) $^{1,N}C_4$	2.8	5.9	5.9

ture. NOE observed between H-2, H-6′ and H-4 confirms their axial positions (Fig. 3) and supports the prevailing $^{4}C_{1,N}$ conformer. The directive influence of the equatorial hydroxy groups on C-2 is in this case in accordance with the influence of hydroxy groups on C-4 and C-5, so that the occurrence of the $^{1,N}C_{4}$ conformer is practically impossible.

Prevailing $^{4}C_{1,N}$ (L) conformation of 6-amino-3,6-dideoxy-L-*arabino*-hexono-1,6-lactam (**3a**) and of the corresponding tri-*O*-acetyl derivative **3b** is evident from comparison of ^{1}H NMR spectra (Table I) with the calculated values of the coupling constants (Table III). The expected more advantageous $^{4}C_{1,N}$ conformer was confirmed also by low-temperature ^{1}H NMR without important changes in chemical shifts and coupling constants and by NOE between H-3 and H-5, H-2 and H-6 (Fig. 4).

CD Measurement

The lactam rule[25–27], applicable to four- to seven-membered rings, describes the relationship between the conformation of a lactam ring and the sign of the Cotton effect. The quadrant (amide) rule[28–30] projects the molecule in quadrants. The sign of the Cotton effect is given as the sum of contributions of particular atoms including substituents. Japanese authors[22,23] stud-

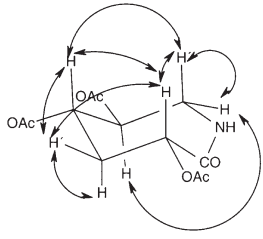


FIG. 3
NOE in 2,4,6-tri-*O*-acetyl-6-amino-3,6-dideoxy-L-*lyxo*-hexono-1,6-lactam (**2b**)

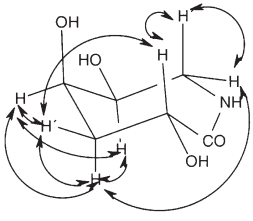


FIG. 4
NOE in 6-amino-3,6-dideoxy-L-*arabino*-hexono-1,6-lactam (**3a**)

ied circular dichroism of five- and six-membered lactams substituted in α-position to carbonyl by groups with a heteroatoms with lone electron pairs (OR, NR_2, SR). They revealed a crucial effect of the configuration on the atom neighboring to carbonyl on the sign of the Cotton effect. The existence of an inherently chiral chromophore arising by the interaction between π-electrons of the carbonyl and the lone electron pair of the substituent was suggested. These investigations lead to the following rule: compounds with *R* configuration on C-2 show a negative Cotton effect, whereas *S* configuration on C-2 gives rise to positive Cotton effect.

The study of chiroptic properties of bi- and tricyclic lactams[31,32] led to the formulation of the spiral rule for non-planar amides. Amides with a positive torsion angle O=C1–N–C6 exhibite a negative Cotton effect and *vice versa*. This means that a negative Cotton effect corresponds to a negative torsion angle[33] C2–C1–N–C6 (Fig. 5).

Circular dichroism was studied only in the case of free lactams **4a**, **1a**, **2a** and **3a** with a single chromophor -CONH. In all spectra, bands with a negative Cotton effect at 195 nm belonging to the π→π* transition were found but they are not convenient for stereochemical conclusions. Bands lying above 200 nm belonging to the n→π* transition were analyzed in this study. For conformational study of lactams of D- and L-configuration, we formally converted the obtained data to a single configurational series by multiplication of measured values Δε of lactams **2a** and **3a** by –1. Table IV shows CD bands recorded in CD spectra of four studied lactams.

The signs of extremes found in the range 208–215 nm correspond according to lactam[25–27] and amide[28–30] rules with the observed $^4C_{1,N}$ (D) or $^{1,N}C_4$ (D) conformation (Table V). The remaining rule[22,23] predicts the opposite sign of Cotton effect to the observed conformations. According to X-ray analysis[9], the amide segment in the crystalline lactam **4a** is not quite planar, with a torsion angle C6–N–C1–C2 Φ = +5°. On condition the unity of lactam conformations in solid state and in the solution this fact supports the validity of spiral rule[31,32], according to which the positive Cotton effect corresponds with the positive torsion angle of amide non-planarity.

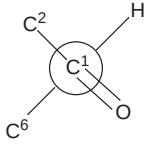


FIG. 5
Torsion angles in non-planar amide

TABLE IV
Circular dichroism of lactams **1a**, **2a**, **3a**, and **4a**

Lactam	Configuration on C-2	Conformation in solution (from ^{1}H NMR)	CD bands λ, nm; Δε, cm^2 mmol^{-1}	Sign of Cotton effect
1a	*R*	$^4C_{1,N}$ (D)	215, –0.15; 236, –0.2	+[a] –
2a (D)[b]	*S*	$^{1,N}C_4$ (D)	215, –0.07; 227, +0.13	– +
3a (D)[b]	*R*	$^{1,N}C_4$ (D)	208, –2.4	–
4a	*S*	$^4C_{1,N}$ (D)	212, +1.8	+

[a] Negative minimum corresponding to positive band. [b] The actually measured compound was of the L-configuration and its Δε band had the opposite sign than given in Table IV.

TABLE V
Theoretical sense of CD bands according to semiempirical rules

Lactam	Sign of Cotton effect		
	lactam rule (refs[25–27])	amide rule (refs[28–30])	meguro (refs[22,23])
4a	+	+	–
1a	+	+	–
2a (D)[a]	–	–	+
3a (D)[a]	–	–	+

[a] The actually measured compound was of the L-configuration and its Δε band had the opposite sign than given in Table V.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. Optical rotations were measured with an Opton photoelectric polarimeter at 20 °C, $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. NMR spectra in $CDCl_3$, CD_3OD, CD_3SOCD_3 and D_2O were recorded with Bruker AM 400 instrument (^{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) instruments. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. Most of measurements were recorded at 300 K, low-temperature experiments at 190–210 K. Assignments of signals were proved by 2D homonuclear and heteronuclear correlated spectra (^{1}H-^{1}H COSY, ^{1}H-^{13}C HETCOR) or spectra based on APT experiments. NOE

experiments were made using the DPFGSE-NOE method[34]. IR spectra (wavenumbers in cm^{-1}) were measured with a Nicolet 750 FT IR instrument in chloroform solutions, KBr pellets or films. UV spectra were measured with an M 40 Carl Zeiss Jena instrument in water. CD spectra of lactams measured in the range 190–260 nm in water (concentrations *ca* $1 \cdot 10^{-3}$ mol l^{-1}) were obtained using a Jobin–Yvon dichrograph Mark V. The data are given as differences of molar absorption coefficients for the left and right polarized light, $\Delta\varepsilon = \varepsilon_\Lambda - \varepsilon_R$ (cm^2 $mmol^{-1}$).

The geometry of lactams was optimized using MM+ molecular mechanics[24]. 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) in petroleum ether–ethyl acetate 2 : 1 (A), toluene–acetone 9 : 1 (B), toluene–acetone 7 : 3 (C), petroleum ether–diethyl ether 3 : 1 (D) or petroleum ether–diethyl ether–ethyl acetate 6 : 1 : 1 (E) mixtures, and 1% solution of cerium(IV) sulfate in 10% sulfuric acid was used for detection. Solutions were evaporated on a rotatory vacuum evaporator at 40–50 °C.

3-Deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranose (**8**)

a) 3-Deoxy-3-iodo-1,2-*O*-isopropylidene-α-D-allofuranose (**9**; 2.4 g, 7.2 mmol) was reduced by 2 h hydrogenation in methanol (70 ml) with triethylamine (5 ml). After removing the catalyst, evaporation of the solvent and column chromatography of the crude product (system C) compound **8** (1.48 g, 100%) was isolated.

b) 3-Deoxy-3-iodo-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**6**; 4.0 g, 10.8 mmol) was dissolved in methanol (70 ml) and reduced with hydrogen in the presence of 5% Pd/C (1 g). After 12 h according to TLC (system C), the hydrolysis of an isopropylidene group in position 5,6 occurred to give 3-deoxy-3-iodo-1,2-*O*-isopropylidene-α-D-allofuranose (**9**). After addition of triethylamine (10 ml), reduction by means of hydrogen was continued and after 1 h TLC (C) showed quantitative transformation of the intermediate to the desired product **8**, which was isolated by the procedure identical to the procedure *a*) described above. Column chromatography in system C afforded the syrupy product **8** (1.5 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): 5.81 d, 1 H, $J(1,2) \approx 3.6$ (H-1); 4.76 t, 1 H, $J(2,3) < 0.5$, $J(2,3') \approx 4.1$ (H-2); 4.23 dt, 1 H, $J(4,3) \approx J(4,5) \approx 4.4$, $J(4,3') \approx 10.8$ (H-4); 3.94 ddd, 1 H, $J(5,6) \approx 4.0$, $J(5,6') \approx 7.6$ (H-5); 3.73 dd, 1 H, $J(6,6') \approx 11.4$ (H-6); 3.60 dd, 1 H (H-6′); 2.13 bs, 2 H (OH); 2.06 dd, 1 H, $J(3,3') \approx 13.5$ (H-3); 1.85 ddd, 1 H (H-3′); 1.5 s, 3 H (CH_3); 1.32 s, 3 H (CH_3). These data are comparable with those obtained[17] at 500 MHz in MeOH-d_4.

3-Deoxy-3-iodo-1,2-*O*-isopropylidene-α-D-allofuranose (**9**)

A solution containing 3-deoxy-3-iodo-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**6**; 8.0 g, 21.6 mmol) in methanol (150 ml) was reduced by means of hydrogen in the presence of 5% Pd/C (0.68 g). After 12 h, the reaction mixture was neutralized with triethylamine (8 ml), then the catalyst was filtered off and methanol evaporated. After column chromatography of the crude product in system C, the following products were isolated: the white crystalline compound **9** (2.4 g, 34%; R_F 0.38), m.p. 103–105 °C (ref.[35] gives 103–105 °C), starting material **6** (5 g; R_F 0.92), 3-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranose (**8**; 0.13 g, 3.2%; R_F 0.15). ^{1}H NMR (400 MHz, $CDCl_3$) of compound **9** was in accordance with ref.[36]

6-Azido-3,6-dideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranose (**11**)

According to general procedure[17] the syrupy azido derivative **11** (0.86 g, 87%) was obtained from 3-deoxy-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-*ribo*-hexofuranose (**10**; 1.56 g, 4.35 mmol), $[\alpha]_D^{20}$ –15 (*c* 0.6, chloroform). IR (chloroform): 3 588, 3 480 (OH); 2 107 (N_3); 1 375 ($C(CH_3)_2$). ^{1}H and ^{13}C NMR are in accordance with ref.[17]

6-Azido-3,6-dideoxy-D-*ribo*-hexono-1,4-lactone (**13**)

Azidohexose **12** (0.6 g, 3.17 mmol) dissolved in water (30 ml) was oxidized at 0 °C with bromine (0.6 ml) in the presence of barium carbonate (3.4 g) added to the solution. When TLC showed completion of 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 the freshly prepared silver carbonate (2 g) to remove bromide anions. After removing the salts and thorough washing with water, the solution was poured through a column of Dowex 50WX4 in H^+ cycle and water was evaporated. The yield of syrupy lactone **13** was 0.59 g (99%), $[\alpha]_D^{20}$ +14.8 (*c* 0.19, water), R_F 0.62 (EtOAc). IR (neat): 3 370, 3 207 (OH); 2 112 (N_3); 1 743 (CO). ^{1} H NMR (400 MHz, D_2O): 4.70 m, 2 H (H-2, H-4); 2.26 ddd, 1 H, *J*(3,2) ≈ 2.6, *J*(3,3′) ≈ 13.6, *J*(3,4) ≈ 8.9 (H-3); 2.63 ddd, 1 H, *J*(3′, 2) ≈ 8.7, *J*(3′,4) ≈ 2.6 (H-3′); 4.02 ddd, 1 H, *J*(5,4) ≈ 8.11, *J*(5,6) ≈ 3.9, *J*(5,6′) ≈ 4.1 (H-5); 3.45 dd, 1 H, *J*(6,6′) ≈ 13.1 (H-6); 3.39 dd (H-6′). ^{13}C NMR (100 MHz, D_2O): 180.43 (C-1); 79.94, 74.40 (C-2, C-4, interchangeable); 31.63 (C-3); 67.79 (C-5); 53.35 (C-6). For $C_6H_9N_3O_4$ (187.2) calculated: 38.50% C, 4.81% H; found: 38.14% C, 4.86% H.

2,5-Di-*O*-acetyl-6-azido-3,6-dideoxy-D-*ribo*-hexono-1,4-lactone (**14**)

Lactone **13** (0.1 g, 0.53 mmol) was treated with acetic anhydride (1 ml) in pyridine (14 ml). The reaction mixture was worked up by a usual procedure and acetate **14** (0.14 g, 98%) was obtained as a colorless syrup, $[\alpha]_D^{20}$ +24 (*c* 1.0, chloroform). ^{1}H NMR (400 MHz, $CDCl_3$): 5.41 dd, 1 H, *J*(2,3) ≈ 8.9, *J*(2,3′) ≈ 7.4 (H-2); 2.36 ddd, 1 H, *J*(3,3′) ≈ 13.0, *J*(3,4) ≈ 8.3 (H-3); 2.67 ddd, 1 H, *J*(3′,4) ≈ 3.9 (H-3′); 4.81 ddd, 1 H, *J*(4,5) ≈ 5.4 (H-4); 5.11 q, 1 H, *J*(5,6) ≈ 5.0, *J*(5,6′) ≈ 5.0 (H-5); 3.59 dd, 1 H, *J*(6,6′) ≈ 13.3 (H-6); 3.54 dd (H-6′); 2.13 s, 3 H ($COCH_3$); 2.15 s, 3 H ($COCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): 172.36 (C-1); 76.13, 72.68, 67.99 (C-2, C-4, C-5, interchangeable); 30.55 (C-3); 50.82 (C-6); 170.34, 170.26 ($COCH_3$); 21.43, 21.20 ($COCH_3$). For $C_{10}H_{13}N_3O_6$ (271.1) calculated: 44.30% C, 4.79% H, 15.49% N; found: 44.36% C, 4.92% H, 15.49% N.

6-Amino-3,6-dideoxy-D-*ribo*-hexonolactam (**1a**)

Azidolactone **13** (0.5 g, 2.67 mmol) was reduced in methanol (25 ml) by means of hydrogen using 5% Pd/C (50 mg) for 5 h. The catalyst was removed, methanol was evaporated, and the lactam was obtained as a syrup, $[\alpha]_D^{20}$ –28 (*c* 0.5, water). IR (KBr): 3 342 (OH, NH); 1 640 (CONH). UV: λ_{max} 194 nm. For NMR, see Tables I and II. For $C_6H_{11}NO_4$ (161.1) calculated: 44.74% C, 6.83% H, 8.69% N; found: 44.86% C, 6.57% H, 8.41% N.

2,4,5-Tri-*O*-acetyl-6-amino-3,6-dideoxy-D-*ribo*-hexonolactam (**1b**)

Lactam **1a** (0.1 g, 0.62 mmol) was treated with acetic anhydride (2 ml) in pyridine (3 ml) for 24 h. The reaction mixture was poured into water with ice and the product was extracted

with chloroform. Combined organic layers were dried and thickened. The syrupy product **1b** was purified by column chromatography in system C (0.13 g, 69%) to give a white crystalline material, m.p. 155–165 °C (ethanol), $[\alpha]_D^{20}$ –83 (*c* 0.7, chloroform). For NMR, see Tables I and II. For $C_{12}H_{17}NO_7$ (287.1) calculated: 50.21% C, 5.92% H, 4.88% N; found: 49.96% C, 6.01% H, 4.62% N.

5,6-Anhydro-3-deoxy-1,2-*O*-isopropylidene-β-L-*lyxo*-hexofuranose (**17**)
and 3-Deoxy-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-*ribo*-hexofuranose (**19**)

6-*O*-Benzoyl-3-deoxy-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-*ribo*-hexofuranose (**16**; 2.2 g, 4.7 mmol) dissolved in chloroform (100 ml) was treated with a methanolic sodium methoxide (100 ml, 0.055 M solution). After 12 h, the reaction mixture contained anhydro derivative **17** (TLC B, R_F 0.5) and tosylate **19** (R_F 0.17) which after heating at 50 °C disappeared in 15 min. The reaction mixture was washed with 20 ml of water. The organic layer containing product **17** and methyl benzoate was dried over anhydrous magnesium sulfate. The solvent was evaporated to give 1.5 g of the crude product which, after column chromatography on silica gel (40 g, system B), yielded syrupy anhydro derivative **17** (0.6 g, 68%), $[\alpha]_D^{20}$ –31 (*c* 2, chloroform); ref.[37] gives –21.9, ref.[38] gives –27.6 (*c* 1.1, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): 5.78 d, 1 H, *J*(1,2) ≈ 3.5 (H-1); 4.72 t, 1 H, *J*(2,3) < 0.5, *J*(2,3′) ≈ 4.1 (H-2); 2.13 dd, 1 H, *J*(3,3′) ≈ 13.3, *J*(3,4) ≈ 4.5 (H-3); 1.82 ddd, 1 H, *J*(3′,4) ≈ 10.3 (H-3′); 4.14 ddd, 1 H, *J*(4,5) ≈ 4.5 (H-4); 3.01 ddd, 1 H, *J*(5,6) ≈ 3.9, *J*(5,6′) ≈ 3.9 (H-5); 2.78 m, 2 H (H-6, H-6′); 1.48 s, 3 H, 1.29 s, 3 H ($C(CH_3)_2$). ^{13}C NMR (100 MHz): 106.39 (C-1); 80.98 (C-2); 36.32 (C-3); 77.68 (C-4); 53.00 (C-5); 44.98 (C-6); 27.48, 26.89 ($C(\mathbf{C}H_3)_2$); 112.09 ($\mathbf{C}(CH_3)_2$). Intermediate **19** (0.2 g, 12%) was also isolated, $[\alpha]_D^{20}$ –6.3 (*c* 0.66, chloroform). IR (chloroform): 3 601, 3 537 (OH); 1 374 ($C(CH_3)_2$); 1 175 (OSO_2). ^{1}H NMR (500 MHz, $CDCl_3$): 5.56 d, 1 H, *J*(1,2) ≈ 3.5 (H-1); 4.66 m, 2 H (H-2, H-5); 2.12 dd, 1 H, *J*(3,2) < 0.5, *J*(3,3′) ≈ 13.5, *J*(3,4) ≈ 4.5 (H-3); 1.71 ddd, 1 H, *J*(3′,2) ≈ 4.7, *J*(3′,4) ≈ 10.7 (H-3′); 4.29 ddd, 1 H, *J*(4,5) ≈ 5.0 (H-4); 3.86 dd, 1 H, *J*(6,5) ≈ 3.6, *J*(6,6′) ≈ 12.7 (H-6); 3.76 dd, 1 H, *J*(6′,5) ≈ 5.3 (H-6′); 1.50 s, 3 H, 1.28 s, 3 H ($C(CH_3)_2$); 2.45 s ($ArCH_3$); 7.81, 2 H, 7.35, 2 H (Ar). ^{13}C NMR (100 MHz): 106.03 (C-1); 83.57, 80.86 (C-2, C-5, interchangeable); 35.73 (C-3); 77.23 (C-4); 63.30 (C-6); 27.48, 26.82 ($C(\mathbf{C}H_3)_2$); 112.35 ($\mathbf{C}(CH_3)_2$); 22.37 ($ArCH_3$); 130.49, 128.72 (Ar).

6-*O*-Benzoyl-3-deoxy-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-*ribo*-hexofuranose (**16**)

a) 6-*O*-Benzoyl derivative[7] (**15**; 2 g, 6.5 mmol), dissolved in pyridine (20 ml) was treated with tosyl chloride (3.7 g, 19.5 mmol) and the reaction mixture was poured into water after 60 h, whereupon product **16** crystallized (3 g, 100%).

b) 3-Deoxy-1,2-*O*-isopropylidene-5,6-di-*O*-tosyl-α-D-*ribo*-hexofuranose (**18**; 3.57 g, 6.98 mmol) was dissolved in dimethylformamide (30 ml) and the solution was stirred at 80 °C with sodium benzoate (1.09 g, 7.56 mmol). After 6 h, dimethylformamide was evaporated and the residue partitioned between water and chloroform. The organic layer was dried and evaporated, the crystalline material **16** (2.9 g, 90%; R_F 0.27 in system E) was obtained, m.p. 120–121 °C (ether), $[\alpha]_D^{20}$ +16.1 (*c* 2, chloroform); ref.[18] gives 121–122 °C, $[\alpha]_D^{20}$ +16 (*c* 1, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): 7.96 d, 2 H, 7.56 t, 1 H, 7.42 dd, 2 H (Bz); 7.76 d, 2 H, 7.21 d, 2 H (Ts); 5.56 d, 1 H, *J*(1,2) ≈ 3.4 (H-1); 5.01 dt, 1 H, *J*(5,6) ≈ *J*(5,6′) ≈ 3,4, *J*(5,4) ≈ 7.8 (H-5); 4.69 dd, 1 H, *J*(2,3).5, *J*(2,3′) ≈ 4.0 (H-2); 4.54 dd, 1 H, *J*(6,6′) ≈ 12.5 (H-6); 4.39 m, 2 H (H-6′, H-4); 2.35 s, 3 H (CH_3-Ar); 2.18 dd, 1 H, *J*(3,3′) ≈ 13.5, *J*(3,4) ≈ 4.7 (H-3); 1.87 ddd, 1 H,

$J(3',4) \approx 10.7$ (H-3′); 1.45 s, 3 H (CH_3); 1.29 s, 3 H (CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): 166.64 (CO); 133.93, 130.50, 130.37, 129.07, 128.51 (Ar); 112.41 ($C(CH_3)_2$); 106.11 (C-1); 80.92 (C-2); 80.37 (H-5); 77.14 (H-4); 64.50 (H-6); 35.50 (H-3); 27.51; 26.87 ($C(CH_3)_2$); 22.31 (CH_3-Ar).

6-Azido-3,6-dideoxy-1,2-*O*-isopropylidene-β-L-*lyxo*-hexofuranose (**20**)

To a solution of anhydro derivative **17** (0.6 g, 3.22 mmol) in 2-methoxyethan-1-ol (10 ml) water (0.8 ml), sodium azide (0.76 g, 11.6 mmol) and ammonium chloride (0.4 g, 7.5 mmol) were added and the reaction mixture was heated to 140 °C. After 15 min, the solvents were evaporated and the brown residue was purified using chromatography on silica gel (17 g; system B, R_F 0.31) yielding azido derivative **20** (0.66 g, 90%) as a colorless syrup, $[\alpha]_D^{20}$ –4.62 (*c* 0.7, chloroform). IR (chloroform): 3 560, 3 469 (OH); 2 106 (N_3); 1 375 ($C(CH_3)_2$). ^1H NMR (500 MHz, $CDCl_3$): 5.79 d, 1 H, $J(1,2) \approx 3.6$ (H-1); 4.72 t, 1 H, $J(2,3) < 0.5$, $J(2,3') \approx 4.7$ (H-2); 2.02 dd, 1 H, $J(3,3') \approx 13.4$, $J(3,4) \approx 4.5$ (H-3); 1.83 ddd, 1 H, $J(3',4) \approx 10.8$ (H-3′); 4.21 ddd, 1 H, $J(4,5) \approx 4.2$ (H-4); 3.68 ddd, 1 H, $J(5,6) \approx 4.2$, $J(5,6') \approx 7.6$ (H-5); 3.32 dd, 1 H, $J(6,6') \approx 12.8$ (H-6); 3.10 dd, 1 H (H-6′); 1.48 s, 3 H, 1.29 s, 3 H ($C(CH_3)_2$); 2.60 s (OH). ^{13}C NMR (100 MHz, $CDCl_3$): 106.20 (C-1); 81.25 (C-2); 35.20 (C-3); 79.14 (C-4); 72.18 (C-5); 54.83 (C-6); 27.45, 26.84 ($C(CH_3)_2$); 112.28 ($C(CH_3)_2$). For $C_9H_{15}N_3O_4$ (229.2) calculated: 47.16% C, 6.60% H; found: 47.16% C, 6.74% H.

6-Azido-3,6-dideoxy-L-*lyxo*-hexose (**21**)

Azidohexose **20** (0.5 g, 2.64 mmol) dissolved in water (5 ml) was stirred with Dowex 50WX4 in H^+ form (2.5 ml) at 60 °C. After 0.5 h, the ion exchanger was removed and the filtrate was evaporated yielding the syrupy product **21** (0.4 g, 99%), $[\alpha]_D^{20}$ –7.9 (10 h; *c* 0.7, water), R_F 0.5 (EtOAc). IR (neat): 3 371 (OH); 2 106 (N_3). For $C_6H_{11}N_3O_4$ (189.2) calculated: 38.09% C, 5.86% H; found: 38.35% C, 5.58% H.

6-Azido-3,6-dideoxy-L-*lyxo*-hexonic Acid (**22**)

Oxidation of azidohexose **21** (0.6 g, 3.17 mmol) with bromine in water was performed similarly to the other oxidations of azidohexoses described above. According to TLC (EtOAc), hydrolysis of the formed 6-azido-3,6-dideoxy-L-*lyxo*-hexonolactone (R_F 0.58) occurred giving rise to the corresponding azido acid. After 10 h, the reaction mixture contained only compound **22** (R_F 0.0). Azido acid **22** (0.4 g, 67%) was isolated as the white foam. IR (neat): 3 438, 3 295, 3 334, 3 205 (OH); 2 106 (N_3); 1 730, 1 636, 1 403 (COO^-). The crude material was used in the next step without purification.

6-Amino-3,6-dideoxy-L-*lyxo*-hexonic Acid (**23**)

Azido acid **22** (0.4 g, 2.14 mmol) was reduced by means of hydrogen in water on 5% Pd/C (0.05 g). After 24 h, the catalyst was removed and water was evaporated. The syrupy amino acid **23** (0.38 g, 99%) was obtained. IR (neat): 3 171, 3 036 (CH, OH, NH); 1 765, 1 720, 1 615, 1 405 (COO^-).

6-Amino-3,6-dideoxy-L-*lyxo*-hexono-1,6-lactam (**2a**)

Acid **23** (0.38 g, 2.1 mmol) was dissolved in methanol (35 ml) with addition of methanolic HCl (10 ml of 5% solution) and the solution was refluxed for 5 h. Methanol was evaporated and the formed methyl ester hydrochloride **24** was alkalized with sodium methanolate (2.1 mmol) in methanol without purification. After evaporation of methanol, 6-amino-3,6-dideoxy-L-*lyxo*-hexono-1,6-lactam (**2a**) in a mixture with salts was treated with acetic anhydride (3 ml) in pyridine (5 ml) for 24 h. 2,4,5-Tri-*O*-acetyl-6-amino-3,6-dideoxy-L-*lyxo*-hexono-1,6-lactam (**2b**; 0.06 g, 10%) was isolated in a usual manner and purified on a column of silica gel in system B. The product melted at 96–98 °C (ethanol), $[\alpha]_D^{20}$ +4 (*c* 1, chloroform). For NMR, see Tables I and II. For $C_{12}H_{17}NO_7$ (287.1) calculated: 50.21% C, 5.92% H, 4.88% N; found: 50.30% C, 6.11% H, 4.74% N.

Transacetylation of compound **2b** (0.03 g, 0.18 mmol) by the action of sodium methoxide (0.3 ml 0.055 M solution) in 12 h, subsequent neutralization using Dowex 50WX4 in H^+ form and evaporation gave the required syrupy lactam **2a** (0.015 g, 89%). IR (KBr): 3 333, 3 309 (OH, NH); 1 656 (CONH). UV: λ_{max} 193 nm. For NMR, see Tables I and II. For $C_6H_{11}NO_4$ (161.1) calculated: 44.74% C, 6.83% H, 8.69% N; found: 44.96% C, 6.69% H, 8.52% N.

5,6-Anhydro-3-deoxy-1,2-*O*-isopropylidene-β-L-*arabino*-hexofuranose (**25**)

To a solution of 6-*O*-benzoyl-3-deoxy-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-*xylo*-hexofuranose (**27**; 1.9 g, 3.9 mmol) in chloroform (100 ml), a methanolic sodium methoxide solution (from 0.28 g of sodium and 10 ml of methanol) was added. After 12 h at room temperature, the reaction mixture was washed three times with water (20 ml) and the chloroform layer was dried with anhydrous magnesium sulfate. After evaporation, the product was purified on a column of silica gel in system B (R_F 0.42) yielding anhydro derivative **25** (0.53 g, 74%), $[\alpha]_D^{20}$ –32 (*c* 0.5, chloroform). ^{1}H NMR (500 MHz, $CDCl_3$): 5.85 d, 1 H, *J*(1,2) ≈ 3.6 (H-1); 4.80 dd, 1 H, *J*(2,3) ≈ 1.7, *J*(2,3′) ≈ 8.7 (H-2); 2.37 d, 1 H, *J*(3,3′) ≈ 14.3, *J*(3,4) ≈ 1.1 (H-3); 2.27 ddd, 1 H, *J*(3′,4) ≈ 8.2, 3.79 ddd, 1 H, *J*(4,5) ≈ 8.2 (H-4); 3.33 ddd, 1 H, *J*(5,6) ≈ 3.8, *J*(5,6′) ≈ 2.2 (H-5); 2.90 dd, 1 H, *J*(6,6′) ≈ 5.0 (H-6); 2.69 dd, 1 H (H-6′); 1.60 s, 3 H, 1.37 s, 3 H ($C(CH_3)_2$). ^{13}C NMR (100 MHz): 107.50 (C-1); 81.40 (C-2); 35.44 (C-3); 83.04 (C-4); 53.78 (C-5); 48.04 (C-6); 27.81, 26.55 ($C(CH_3)_2$); 113.00 ($C(CH_3)_2$). For $C_9H_{14}O_4$ (186.2) calculated: 58.05% C, 7.58% H; found: 57.81% C, 7.55% H.

After column chromatography, 3-deoxy-1,2-*O*-isopropylidene-5-*O*-tosyl-α-D-*xylo*-hexofuranose (**32**; 0.14 g, 10%; R_F 0.16, system B) was isolated, $[\alpha]_D^{20}$ –36 (*c* 0.8, chloroform). IR (chloroform): 3 588, 3 524 (OH); 1 175 (OSO_2); 1 375 ($C(CH_3)_2$). ^{1}H NMR (300 MHz, $CDCl_3$): 5.67 d, 1 H, *J*(1,2) ≈ 3.8 (H-1); 4.69 ddd, 1 H, *J*(2,3) ≈ 1.8, *J*(2,3′) ≈ 7.1 (H-2); 2.15 m, 2 H (H-3, H-3′); 4.30 ddd, 1 H, *J*(4,3) ≈ 4.9, *J*(4,3′) ≈ 8.3, *J*(4,5) ≈ 8.3 (H-4); 4.86 ddd, 1 H, *J*(5,6) ≈ 3.8, *J*(5,6′) ≈ 3.8 (H-5); 3.96 dd, 1 H, *J*(6,6′) ≈ 12.0 (H-6); 3.80 dd, 1 H (H-6′); 1.46 s, 3 H, 1.29 s, 3 H ($C(CH_3)_2$); 2.50 s, 1 H (OH); 2.42 s, 3 H ($ArCH_3$); 7.86, 2 H, 7.32, 2 H (Ar). ^{13}C NMR (75 MHz, $CDCl_3$): 106.9 (C-1); 79.04, 71.09, 84.36 (C-2, C-4, C-5, interchangeable); 33.69 (C-3); 63.10 (C-6); 27.54, 26.84 ($C(CH_3)_2$); 112.35 ($C(CH_3)_2$); 130.58, 130.29, 128.74 (Ar).

6-*O*-Benzoyl-3-deoxy-1,2-di-*O*-isopropylidene-5-*O*-tosyl-α-D-*xylo*-hexofuranose (**27**)

a) To a solution of of 3-deoxy-1,2-*O*-isopropylidene-5,6-di-*O*-tosyl-α-D-*xylo*-hexofuranose (**31**; 2.2 g, 4.3 mmol) in DMF (20 ml), sodium benzoate (0.72 g, 4.6 mmol) was added. The suspension was stirred at 80 °C. After 6 h TLC (system E, for **31** R_F 0.18, for **27** R_F 0.28) showed the proceeding reaction. Dimethylformamide was evaporated at 60 °C, the residue was diluted with water and the product was extracted with chloroform. The organic layer, after drying with anhydrous magnesium sulfate, was evaporated. The product after recrystallization from ether (1.8 g, 90%), m.p. 90–91 °C, $[\alpha]_D^{20}$ –20 (*c* 0.91, chloroform). IR (chloroform): 1 723 (CO); 1 273 (OSO_2); 1 376 ($C(CH_3)_2$). ^{1}H NMR (500 MHz, $CDCl_3$): 5.75 d, 1 H, *J*(1,2) ≈ 3.8 (H-1); 4.77 ddd, 1 H, *J*(2,3) ≈ 1.6, *J*(2,3′) ≈ 5.9 (H-2); 2.21 ddd, 1 H, *J*(3,3′) ≈ 14.5, *J*(3,4) ≈ 4.7 (H-3); 2.26 ddd, 1 H, *J*(3′,4) ≈ 8.2 (H-3′); 4.37 ddd, 1 H, *J*(4,5) ≈ 8.0 (H-4); 5.24 ddd, 1 H, *J*(5,6) ≈ 3.2, *J*(5,6′) ≈ 6.1 (H-5); 4.65 dd, 1 H, *J*(6,6′) ≈ 12.6 (H-6); 4.54 dd, 1 H (H-6′); 1.59 s, 3 H, 1.35 s, 3 H ($C(CH_3)_2$); 2.40 s, _ H ($ArCH_3$); 7.28, 2 H, 7.88, 2 H (Ar, Ts); 8.03, 2 H, 7.16, 2 H, 7.6, 1 H (Ar, Bz). ^{13}C NMR (100 MHz, $CDCl_3$): 107.05 (C-1); 81.14, 81.05 (C-2, C-5, interchangeable); 33.78 (C-3); 78.93 (C-4); 64.47 (C-6); 27.66, 26.91 ($C(CH_3)_2$); 114.03 ($C(CH_3)_2$); 145.24 (CO); 22.36 ($ArCH_3$); 133.98, 130.57, 130.24, 129.12, 128.80 (Ar). For $C_{23}H_{26}O_8S$ (462.5) calculated: 59.79% C, 5.67% H, 6.93% S; found: 59.77% C, 5.57% H, 6.55% S.

b) A solution of of 6-*O*-benzoyl-3-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (**28**; 0.34 g, 1.1 mmol) in pyridine (3 ml) was reacted with tosyl chloride (0.4 g, 2.2 mmol) at room temperature for 12 h (R_F of product 0.69, system B). The reaction mixture was poured into water, the crude crystalline product recrystallized from ether (0.48 g, 94%). Physical constants were identical with those of the product obtained by the method *a*).

6-*O*-Benzoyl-3-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (**28**)

To an ice cool solution of 3-deoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexofuranose (**26**; 0.69 g, 3.3 mmol) in pyridine (5 ml), benzoyl chloride (0.34 ml, 3.6 mmol) in chloroform (1 ml) was added dropwise. The reaction mixture was stirred at room temperature for 12 h. Then the reaction mixture was poured into water with ice and, after 1 h, extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate and the solvent was evaporated. After column chromatography in system C (R_F 0.66), 6-*O*-benzoyl derivative **28** (0.47 g, 46%) was isolated, $[\alpha]_D^{20}$ –11 (*c* 2, chloroform). IR (chloroform): 3 563 (OH); 1 719 (CO); 1 383 (CH_3). ^{1}H NMR (500 MHz, $CDCl_3$): 5.85 d, 1 H, *J*(1,2) ≈ 3.9 (H-1); 4.79 ddd, 1 H, *J*(2,3) ≈ 1.2, *J*(2,3′) ≈ 5.7 (H-2); 2.19 dd, 1 H, *J*(3,3′) ≈ 14.3, *J*(3,4) ≈ 3.3 (H-3); 2.29 ddd, 1 H, *J*(3′,4) ≈ 8.4 (H-3′); 4.30 ddd, 1 H, *J*(4,5) ≈ 8.3 (H-4); 4.16 ddd, 1 H, *J*(5,6) ≈ 5.3, *J*(5,6′) ≈ 4.3 (H-5); 4.40 dd, 1 H, *J*(6,6′) ≈ 11.3 (H-6); 4.43 dd, 1 H (H-6′); 1.49 s, 3 H, 1.23 s, 3 H ($C(CH_3)_2$); 8.07, 2 H, 7.57, 1 H, 7.44, 2 H (Ar); 3.40 s, 1 H (OH). ^{13}C NMR (100 MHz, $CDCl_3$): 106.97 (C-1); 81.36 (C-2); 34.21 (C-3); 81.99 (C-4); 71.68 (C-5); 66.41 (C-6); 27.70, 26.64 ($C(CH_3)_2$); 113.37 ($C(CH_3)_2$); 167.16 (CO); 133.81, 129.09, 130.42 (Ar). For $C_{16}H_{20}O_6$ (308.3) calculated: 62.33% C, 6.54% H; found: 62.39% C, 6.54% H.

Small amounts of other products were isolated after column chromatography:

*5-O-Benzoyl-3-deoxy-1,2-O-isopropylidene-*α*-D-xylo-hexofuranose* (**29**; 0.08 g, 8%; R_F 0.58, C). IR (chloroform): 3 608, 3 494 (OH); 1 715 (CO); 1 375 (CH_3). ^{1}H NMR (500 MHz, $CDCl_3$): 5.73 d, 1 H, *J*(1,2) ≈ 3.7 (H-1); 4.73 d, 1 H, *J*(2,3) < 0.5, *J*(2,3′) ≈ 7.6 (H-2); 2.17 dd, 1 H,

$J(3,3')$ ≈ 14.1, $J(3,4)$ ≈ 4.5 (H-3); 2.23 ddd, 1 H, $J(3',4)$ ≈ 7.6 (H-3′); 4.46 ddd, 1 H, $J(4,5)$ ≈ 7.7 (H-4); 5.36 ddd, 1 H, $J(5,6)$ ≈ 3.6, $J(5,6')$ ≈ 4.3 (H-5); 3.93 dd, 1 H, $J(6,6')$ ≈ 12.4 (H-6); 3.84 dd, 1 H (H-6′); 1.59 s, 3 H, 1.30 s, 3 H ($C(CH_3)_2$); 2.85 s, 1 H (OH); 8.8, 2 H, 7.54, 1 H, 7.41, 2 H (Ar). ^{13}C NMR (100 MHz, $CDCl_3$): 106.87 (C-1); 81.26 (C-2); 33.91 (C-3); 79.17 (C-4); 76.55 (C-5); 63.27 (C-6); 27.90, 26.99 ($C(CH_3)_2$); 113.90 ($C(CH_3)_2$); 167.24 (CO); 133.81, 130.62, 129.01 (Ar).

5,6-Di-O-benzoyl-3-deoxy-1,2-O-isopropylidene-α-D-xylo-hexofuranose (**30**; 0.05 g, 4%; R_F 0.8, C). IR (chloroform): 1 721 (CO); 1 376 ($C(CH_3)_2$). ^1H NMR (400 MHz, $CDCl_3$): 5.80 d, 1 H, $J(1,2)$ ≈ 3.7 (H-1); 4.80 ddd, 1 H, $J(2,3)$ ≈ 1.4, $J(2,3')$ ≈ 5.5 (H-2); 2.23 dd, 1 H, $J(3,3')$ ≈ 14.3, $J(3,4)$ ≈ 4.2 (H-3); 2.32 ddd, 1 H, $J(3',4)$ ≈ 8.1 (H-3′); 4.54 ddd, 1 H, $J(4,5)$ ≈ 8.0 (H-4); 7.77 ddd, 1 H, $J(5,6)$ ≈ 3.6, $J(5,6')$ ≈ 5.6 (H-5); 4.68 dd, 1 H, $J(6,6')$ ≈ 12.3 (H-6); 4.85 dd, 1 H (H-6′); 1.32 s, 3 H, 1.06 s, 3 H ($C(CH_3)_2$); 8.10, 2 H, 8.00, 2 H, 7.55, 2 H, 7.42, 4 H (Ar); 2.57 s, 1 H (OH). ^{13}C NMR (75 MHz, $CDCl_3$): 107.02 (C-1); 81.19, 79.02, 73.59 (C-2, C-4, C-5, interchangeable); 34.14 (C-3); 64.69 (C-6); 27.83, 26.96 ($C(CH_3)_2$); 113.97 ($C(CH_3)_2$); 166.85, 166.70 (CO); 133.88, 133.77, 130.76, 130.46, 129.14, 129.02 (Ar).

6-Azido-3,6-dideoxy-1,2-*O*-isopropylidene-β-L-*arabino*-hexofuranose (**33**)

To a solution of anhydro derivative **25** (0.9 g, 4.8 mmol) in 2-methoxyethan-1-ol (15 ml) and water (1.2 ml), ammonium chloride (0.61g, 11.5 mmol) and sodium azide (1 g, 15.3 mmol) were added and the reaction mixture was refluxed for 0.5 h. After cooling and repeated evaporation with water, the obtained brown syrup was partitioned between water and chloroform. The organic layer was purified on a column of silica gel using system B (R_F 0.37) giving 0.85 g (78%) of the white crystalline material melting at 58–60 °C (chloroform–ether), $[\alpha]_D^{20}$ –26 (*c* 0.23, chloroform). IR (chloroform): 3 565, 3 485 (OH); 2 108 (N_3); 1 377 ($C(CH_3)_2$). ^1H NMR (400 MHz, $CDCl_3$): 5.79 d, 1 H, $J(1,2)$ ≈ 3.8 (H-1); 4.75 ddd, 1 H, $J(2,3)$ ≈ 0.6, $J(2,3')$ ≈ 6.1 (H-2); 2.35 d, 1 H, $J(3,3')$ ≈ 14.5, $J(3,4)$ < 0.5 (H-3); 4.05 m, 2 H (H-4, H-5); 3.60 dd, 1 H, $J(6,5)$ ≈ 2.4, $J(6,6')$ ≈ 12.5 (H-6); 3.42 dd, 1 H, $J(6',5)$ ≈ 6.2 (H-6′); 1.52 s, 3 H, 1.31 s, 3 H ($C(CH_3)_2$); 2.55 s, 1 H (OH). ^{13}C NMR (100 MHz, $CDCl_3$): 107.27 (C-1); 81.32 (C-2); 33.52 (C-3); 72.55, 82.02 (C-4, C-5, interchangeable); 55.04 (C-6); 27.74, 26.46 ($C(CH_3)_2$); 113.05 ($C(CH_3)_2$). For $C_9H_{15}N_3O_4$ (229.2) calculated: 47.16% C, 6.60% H, 18.33% N; found: 47.40% C, 6.47% H, 18.05% N.

6-Azido-3,6-dideoxy-β-L-*arabino*-hexose (**34**)

6-Azido-3,6-dideoxy-1,2-*O*-isopropylidene-L-*arabino*-hexofuranose (**33**; 0.8 g, 3.5 mmol) was hydrolyzed at 70 °C for 10 min with water (20 ml) in the presence of Dowex 50WX4 in H^+ cycle (4 ml). After removing the ion exchanger, water was evaporated and the rest dried in vacuum. This procedure afforded 0.67 g (100%) of pure (TLC) syrupy azidohexose **34**, $[\alpha]_D^{20}$ –34 (*c* 0.66, water). IR (neat): 3 373 (OH). For $C_6H_{11}N_3O_4$ (189.2) calculated: 38.09% C, 5.86% H, 22.21% N; found: 38.00% C, 5.64% H, 22.32% N.

6-Azido-3,6-dideoxy-L-*arabino*-hexono-1,4-lactone (**35**)

Azidohexose **34** (0.6 g, 3.2 mmol) dissolved in water (50 ml) was oxidized at 0 °C with bromine (0.6 ml) in the presence of barium carbonate (5 g). When TLC showed completion the reaction (R_F 0.64, ethyl acetate), 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 a column of Dowex 50WX4 in H^+ cycle and water was evaporated. The syrupy lactone **35** (0.5 g, 88%) was dried at 40 °C for 12 h in vacuum, $[\alpha]_D^{20}$ –17 (*c* 0.4, water). IR (neat): 3 376 (OH); 2 108 (N_3); 1 776 (CO). ^{1}H NMR (400 MHz, D_2O): 4.75 dd, 1 H, *J*(2,3) ≈ 10.9, *J*(2,3′) ≈ 8.8 (H-2); 2.11 q, 1 H, *J*(3,3′) ≈ 10.9, *J*(3,4) ≈ 10.9 (H-3); 2.71 ddd, 1 H, *J*(3′,4) ≈ 5.6 (H-3′); 4.57 ddd, 1 H, *J*(4,5) ≈ 5.0 (H-4); 4.11 ddd, 1 H, *J*(5,6) ≈ 3.8, *J*(5,6′) ≈ 7.3 (H-5); 3.40 dd, 1 H, *J*(6,6′) ≈ 13.2 (H-6); 3.52 dd, 1 H (H-6′). ^{13}C NMR (100 MHz, D_2O): 180.09 (C-1); 68.88 (C-2); 32.63 (C-3); 78.31 (C-4); 71.22 (C-5); 53.14 (C-6). For $C_6H_9N_3O_4$ (187.2) calculated: 38.50% C, 4.81% H, 22.44% N; found: 38.12% C, 4.90% H, 22.33% N.

6-Amino-3,6-dideoxy-D-*arabino*-hexono-1,6-lactam (**3a**)

Azidolactone **35** (0.42 g, 2.2 mmol) was reduced in methanol (20 ml) by means of hydrogen using 5% Pd/C (40 mg) as a catalyst for 7 h. The catalyst was removed, methanol was evaporated and the lactam **3a** was obtained as a syrupy form, $[\alpha]_D^{20}$ –15 (*c* 0.15, water). IR (KBr): 3 475 (OH); 3 241 (NH); 1 666 (CONH). UV: λ_{max} 195 nm. For NMR, see Tables I and II. For $C_6H_{11}NO_4$ (161.1) calculated: 44.74% C, 6.83% H, 8.69% N; found: 45.01% C, 6.81% H, 8.50% N.

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

Lactam **3a** (0.07 g, 0.43 mmol) was treated with acetic anhydride (1 ml) in pyridine (2 ml) for 48 h. The reaction mixture was poured into water with ice, the product was extracted with chloroform. The combined organic layers were dried and thickened. The syrupy product **3b** was purified by column chromatography in system C (0.1 g, 80%), $[\alpha]_D^{20}$ –18 (*c* 2.3, chloroform). For NMR, see Tables I and II. For $C_{12}H_{17}NO_7$ (287.1) calculated: 50.20% C, 5.92% H, 4.88% N; found: 50.48% C, 6.08% H, 4.59% N.

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