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Transformation of D-allose and L-gulose with potassium cyanate into cyclic carbamates

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Abstract

Treatment of D-allose and L-gulose with potassium cyanate in aqueous solutions, buffered with sodium dihydrogen phosphate, gave cyclic carbamates (*N,O*-carbonyl derivatives) of the derived glycosylamines. D-Allose gave the furanoid 1,2-*cis*-carbamate as a single product, but L-gulose yielded a complex mixture of the furanoid 1,2-*cis*-carbamate, the pyranoid 1,2- and 1,3-*cis*-carbamates, and the furanoid 1,2-*cis*-carbamate of β-L-*ido* configuration as a product of epimerization at C-2. The structures were derived from the NMR spectra of the free compounds and those of their acetates. The structure of the main product in the reaction of L-gulose, that of the pyranoid 1,2-*cis*-carbamate, was proved independently by X-ray structure determination of the tetra-acetate. The pyranoid ring was found to exist in the ${}_{O}T^{2}$(L) conformation.

1. Introduction

The reaction of free aldoses with potassium cyanate in water in the presence of weakly acidic buffers (NH_4Cl, NaH_2PO_4) yields 1,2-*cis*-(cyclic carbamates) (*N,O*-carbonyl derivatives) of glycosylamines [1]. We now report further examples of this reaction.

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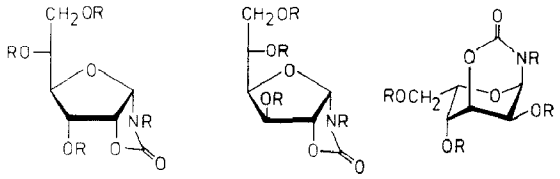
2. Results and discussion

Treatment of D-allose with potassium cyanate (1.5 mol) in aqueous solution buffered with sodium dihydrogen phosphate (2 mol) for 2.5 h at 60°C gave α-D-allofuranosylamine 1,2-(cyclic carbamate) (**1**) besides unreacted D-allose, which was present even after prolonged reaction.



1 R = H
2 R = Ac

3 R = H
4 R = Ac

5 R = H
6 R = Ac

Treatment of **1** with hot acetic anhydride and sodium acetate gave the *N*-acetyl-tri-*O*-acetyl derivative **2**. In agreement with the furanoid structure, acetylation caused a significant downfield shift (1.38 ppm) of the resonance for H-5, but only a small shift (0.37 ppm) of the resonance for H-4 (Tables 1 and 3). The $J_{3,4}$ values (9.15 and 8.9 Hz, respectively) of **1** and **2** accord with the *trans* arrangement of H-3,4, as was found [1–3] for analogous furanoid structures.

Unlike D-allose, transformation of L-gulose under the same conditions gave a complex mixture of four cyclic carbamates partially separated by column chromatography into three fractions: an isomeric mixture (15%) of 1-*N*,2-*O*-carbonyl-β-L-idofuranosylamine (**3**) and 1-*N*,3-*O*-carbonyl-α-L-gulopyranosylamine (**5**) in the

Table 1
^{1}H NMR data [a] for the cyclic carbamates

Compound	Chemical shifts (δ)						
	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b
1	5.681	5.007	4.232	3.768	3.943	3.651	3.568
3	5.813	4.951	4.305	3.859	3.950	3.658	3.542
5	4.947	4.194	4.598	4.073			
7	5.577	4.909	———	3.87	———	3.754	3.652
9	5.549	5.058	4.450	3.873	3.824	3.654	3.517
	Coupling constants (Hz)						
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$
1	5.35	5.55	9.15	3.25	3.8	7.2	−11.9
3	5.4	~0	~1.5	~8.0	3.1	5.2	−12.0
5	3.1	1.9	4.15	1.4			
7	6.5	2.65			3.0	7.7	−12.3
9	6.3	5.75	4.6	6.7	3.6	6.1	−11.7

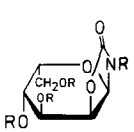
[a] Recorded at 300 MHz for solutions in D_2O.

Table 2
^{13}C NMR data [a] for the cyclic carbamates

Compound	Chemical shifts (δ)						
	C-1	C-2	C-3	C-4	C-5	C-6	NCOO
1	85.57	80.24	70.05	78.06	70.81	62.31	160.58
3	85.87 [b]	85.77 [b]	72.96	79.61	70.40	62.69	160.17
5	78.23	60.56	77.70	67.44	68.34	58.12	154.91
7	80.49	77.89	71.10 [b]	70.19 [b]	72.01 [b]	60.33	160.85
9	85.43	80.47	70.16 [b]	80.47	70.03 [b]	62.85	160.58

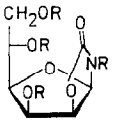
[a] Recorded at 75.5 MHz for solutions in D_2O. [b] Assignments may have to be interchanged.

ratio 7:3 (NMR data), 1-*N*,2-*O*-carbonyl-α-L-gulopyranosylamine (**7**, 25%), and its α-L-furanoid analogue **9** (9%).



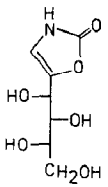
7 R = H

8 R = Ac



9 R = H

10 R = Ac



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Although compounds **3** and **5** could not be separated, their structures were determined by the ^1H and ^{13}C NMR spectra of a solution of the mixture in D_2O. The chemical shifts of the C=O resonances were found at δ 160.17 for the main component **3** and at δ 154.91 for **5** (Table 2), which are characteristic of the five-membered ring of the 1,2-(cyclic carbamate) and the six-membered ring of the 1,3-(cyclic carbamate), respectively, in accordance with our recent results [4]. The signal for C-1 in **3** appeared at significantly lower field (δ 85.87, furanoid system) than that for **5** (δ 78.23, pyranoid system) in agreement with the ^{13}C NMR data [5] of aldofuranoses and aldopyranoses. The β-L-idofuranose configuration of **3** was deduced from the $J_{2,3}$ value of 0 Hz, indicative of the *trans* arrangement of H-2,3 as shown for numerous analogous 1,2-*cis*-fused furanoid systems [1,6,7]. The structure of **5** was assigned on the basis of its small and medium $^3J_{H,H}$ values which accord well with the $^1C_4$ conformation of the pyranoid ring. Further proofs for the stereochemistry of **3** and **5** were provided by their tetra-*N*,*O*-acetyl derivatives **4** and **6**, respectively, the NMR spectra of which could be assigned completely (Tables 3 and 4). Both ^1H and ^{13}C NMR data of **3** and **4** are in good agreement with those of their α-D-glucofuranose analogues [1], while the data of **5** and **6** exhibit a close relationship to those of their α-D-allopyranose analogues [4].

The structures of **7** and **9** and the corresponding acetylated derivatives **8** and **10** were established by their ^1H and ^{13}C NMR data (Tables 1–4), which correspond well with those of the closely related β-D-lyxopyranose and β-D-lyxofuranose derivatives [1], respectively. The large $J_{1,2}$ values of the α-L-gulopyranose derivatives (6.5 and 6.4 Hz for the solutions of **7** and **8**, respectively) suggested a

Table 3
^{1}H NMR data [a] for the acetylated derivatives of cyclic carbamates

Compound	Chemical shifts (δ)								
	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b	NAc	OAc
2	6.242	5.206	5.038	4.134	5.327	4.366	4.098	2.546	2.162, 2.083, 2.061
4	6.312	4.856	5.422	4.372	5.324	4.381	4.009	2.551	2.167, 2.103, 2.060
6	6.188	5.371	4.768	5.288	4.027	4.203	4.129	2.690	2.173, 2.110, 2.033
8	6.168	4.881	5.270	5.443	4.167	4.247	4.091	2.568	2.143, 2.088, 2.016
10	6.206	5.107	5.381	4.652	5.263	4.281	4.061	2.576	2.137, 2.122, 2.028
	Coupling constants (Hz)								
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$		
2	5.5	5.45	8.9	4.6	4.3	6.35	−12.0		
4	5.5	0.95	3.8	6.9	3.75	5.6	−12.3		
6 [b]	3.7	1.8	4.7	2.1	7.05	6.0	−11.2		
8	6.4	3.1	6.75	4.75	6.65	4.6	−10.4		
10	6.0	6.5	8.4	3.1	4.7	7.25	−11.7		

[a] Recorded at 300 MHz for solutions in $CDCl_3$. [b] $J_{1,3}$ −2.4 Hz.

Table 4
^{13}C NMR data [a] for the acetylated derivatives of cyclic carbamates

Compound	Chemical shifts (δ)							
	C-1	C-2	C-3	C-4	C-5	C-6	NCOO	Others
2	85.17	75.68	72.26	73.89	69.33	61.66	152.07	170.33, 169.65, 169.58, 169.38 (COO, CON), 23.59 (*Me*CON) 20.65, 20.57, 20.21 (*Me*COO)
4	85.26	80.06	76.99	74.61	68.95	62.22	151.73	170.35, 169.70, 169.48, 169.34 (COO, CON) 23.68 (*Me*CON), 20.93, 20.59(2) (*Me*COO)
6	75.41	61.20	72.99	67.59	65.22	60.62	148.60	172.31, 170.24, 169.23(2) (COO,CON), 27.11 (*Me*CON), 20.66(3) (*Me*COO)
8	79.77	71.53	70.16 [b]	68.45 [b]	68.21 [b]	60.74	152.27	170.19, 170.07, 169.72, 168.90 (COO, CON), 23.57 (*Me*CON), 20.64, 20.48(2) (*Me*COO)
10	85.48	78.03	71.18	73.96	67.81	62.73	152.14	170.43, 170.12, 169.70, 169.60 (COO, CON), 23.63 (*Me*CON) 20.59, 20.44, 20.08 (*Me*COO)

[a] Recorded at 75.5 MHz for solutions in $CDCl_3$. [b] Assignments may have to be interchanged.

significant flattening of the pyranoid ring. Generally, compounds in which a five-membered ring is fused α-1,2-*cis* to a pyranoid ring adopt conformations deviating from the usual chairs in solution as well as in the solid state [8], in contrast to the related β-*cis*- and β-*trans*-fused analogues [9]. X-ray diffraction studies (compare Fig. 1, Tables 5 and 6, and data in the Experimental section) of **8** substantiated this assumption. The pyranoid ring of **8** is highly distorted as can be seen from Fig. 1 and the selected torsion angles of Table 7. The puckering amplitude according to Cremer and Pople [10] has the extreme value of 74.5(4) pm. The theta and phi angles [10] of 92.6(3)° and 154.5(3)°, respectively, are almost ideally in accord with the twist-boat conformation ${}_{O}T^{2}_{(L)}$ of the pyranoid ring in **8**. Whereas, in related cases [8], mostly skew-boat ("*S*") conformations have been discussed, which differ in the theta angle by only 22.5°, this investigation indicates that *T* conformations might be considered for related compounds as well.

The observed high distortion of the pyranoid ring in **7** imposes a thermodynamic barrier to the formation of such compounds, which is not obvious from simple molecular models. Previous erroneous claims [11] to have synthesized the related 1,2-*cis*-carbamate of α-D-glucopyranosylamine are therefore understandable. This compound was described [4] only recently. and was shown from the NMR data to possess a highly distorted conformation of the pyranoid ring.

Inversion of configuration at C-2, resulting for instance in the formation of compounds like **3**, was observed in several cases during the reaction of aldoses with potassium cyanate [1] and Meldrum's acid [6,12], and in the Wittig [6] and Knoevenagel–Doebner reactions [13], in which unsaturated intermediates, analogues of **11**, were encountered [6,7,13,14]. The epimerization at C-2 might occur through the unsaturated intermediate **11** which can be formed from the intermedi-

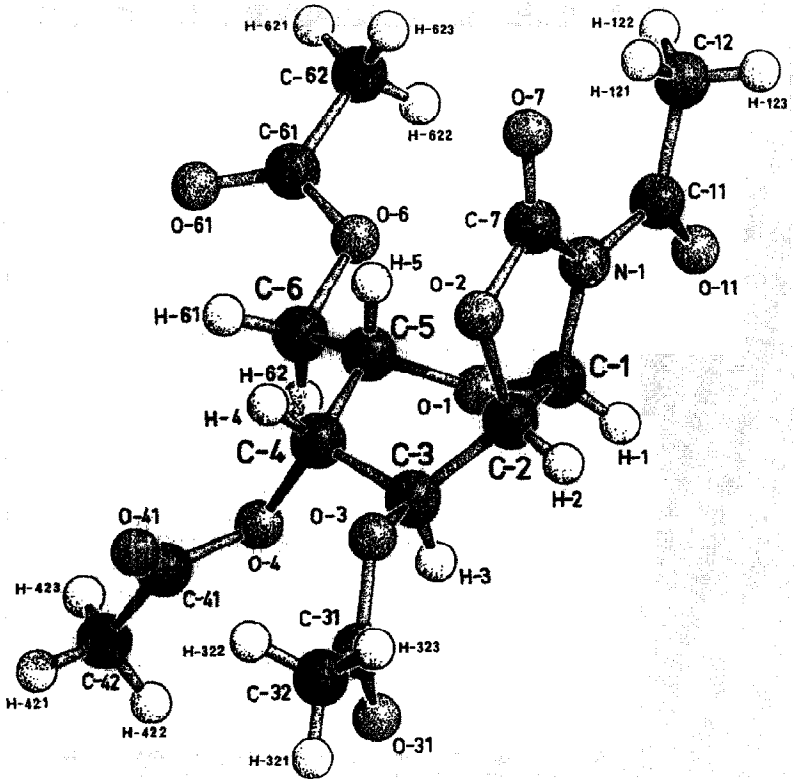

Fig. 1. A SCHAKAL-88 [18] drawing of a molecule of **8**, showing atom numbering.

ates with an open-chain sugar moiety during the formation of 1,2-(cyclic carbamates), but this proposal is not supported by experimental evidence. The formation of the 1,3-(cyclic carbamate) **5** might be a consequence of a 1,2- → 1,3-(cyclic carbamate) rearrangement as was found [4] recently.

Table 5
Crystallographic data for **8** [a]

Formula	$C_{15}H_{19}NO_{10}$	Density (calcd.)($g \times cm^{-3}$)	1.397
Mol wt	373.32	λ (Mo K_α)(pm)	70.9261
Mp (degrees)	164–165	μ (cm^{-1})	1.1
Crystal size (mm)	$0.4 \times 0.3 \times 0.2$	$2\Theta_{max}$ (degrees)	60
Space group	$P2_12_12_1$	Reflections measured	4982
Cell parameters (pm, degrees)		Symmetry independent reflections	4268
a	842.8(2)	Symmetry independent	
b	909.7(2)	reflections with $F_O > 3\,\sigma\,(F_O)$	2720
c	2314.8(5)	Number of refined parameters	236
Volume (pm^3)	$1774.7(7) \times 10^6$	Final residual factors	
Z	4	*R*	0.059
F (000)	784	R_W	0.055
		Diffractometer	Syntex $P2_1$

[a] Standard deviations in parentheses.

Table 6
Fractional positional parameters of C, N, and O atoms ($\times 10^4$) [a] and the temperature factors U_{eq} [b] for **8**

Atom	x	y	z	U_{eq}^b
O-1	−9057(3)	−10993(3)	53(1)	39(1)
O-2	−6150(3)	−8743(3)	−60(1)	42(1)
O-3	−6886(3)	−8931(3)	−1284(1)	52(1)
O-4	−8084(3)	−12210(3)	−1157(1)	51(1)
O-6	−8039(4)	−13582(3)	533(1)	55(1)
O-7	−5086(4)	−8790(3)	825(1)	56(1)
O-11	−9828(5)	−9698(4)	1263(2)	80(1)
O-31	−8904(5)	−9053(5)	−1906(2)	93(2)
O-41	−6168(5)	−11955(4)	−1821(1)	78(2)
O-61	−7179(4)	−15891(3)	447(1)	68(1)
N-1	−7778(4)	−9268(3)	669(1)	41(1)
C-1	−8762(5)	−9482(4)	166(2)	41(1)
C-2	−7746(5)	−8768(4)	−305(2)	42(1)
C-3	−7822(5)	−9649(4)	−850(2)	42(1)
C-4	−7258(4)	−11242(4)	−766(2)	39(1)
C-5	−7646(4)	−11734(4)	−150(2)	36(1)
C-6	−7922(5)	−13366(4)	−85(2)	41(1)
C-7	−6234(5)	−8905(4)	522(2)	42(1)
C-11	−8436(6)	−9396(5)	1226(2)	56(2)
C-12	−7365(8)	−9157(7)	1732(2)	86(2)
C-31	−7586(7)	−8665(5)	−1799(2)	61(2)
C-32	−6503(8)	−7892(7)	−2194(2)	91(2)
C-41	−7359(7)	−12541(5)	−1665(2)	62(2)
C-42	−8239(9)	−13684(7)	−1984(2)	98(3)
C-61	−7608(5)	−14907(5)	743(2)	49(1)
C-62	−7729(7)	-14943(6)	1382(2)	80(2)

[a] Standard deviations in parentheses. [b] $U_{eq} = 1/3\ \Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j \times 10^3$.

Remarkably, D-allose, like D-ribose, gave only one furanoid product, but L-gulose yielded several and analogous cyclic carbamates (beside the minor product **5**), as did D-lyxose [1]. Comparing these results with our earlier observations [1] for other aldoses, we can state that the reaction with potassium cyanate affords either only one cyclic carbamate of 1,2-*cis* furanoid structure, or a mixture of isomeric cyclic carbamates. The outcome of the reaction is apparently controlled by the relative

Table 7
Selected torsion angles (°) in **8** [a]

Angles in the pyranoid ring		Angles between vicinal hydrogens	
O-1–C-1–C-2–C-3	−99.9(3)	H-1–C-1–C-2–H-2	22.2(5)
C-1–C-2–C-3–C-4	−58.6(4)	H-2–C-2–C-3–H-3	−65.1(4)
C-2–C-3–C-4–C-5	31.2(4)	H-3–C-3–C-4–H-4	151.4(3)
C-3–C-4–C-5–O-1	30.5(4)	H-4–C-4–C-5–H-5	30.0(4)
C-4–C-5–O-1–C-1	−71.7(4)	H-5–C-5–C-6–H-61	−65.3(4)
C-5–O-1–C-1–C-2	42.7(4)	H-5–C-5–C-6–H-62	173.4(3)

[a] Standard deviations in parentheses.

configuration of C-2 and C-4 of the starting sugar. In order to prove this assumption, further studies are in progress.

3. Experimental

General.—TLC was performed on Silica Gel F_{254} (Merck) with *A*, 7:2:1 EtOAc–EtOH–H_2O; and *B*, 9:1 $CHCl_3$–acetone; and detection by charring with H_2SO_4. Silica gel (230–400 mesh) was used for column chromatography. Melting points were determined on a Leitz SM Lux microscope. Optical rotations were measured with a Perkin–Elmer 241 MC polarimeter and IR spectra with a Nicolet 205 FT spectrometer. A Bruker AM-300 spectrometer was used to obtain ^1H NMR (solutions in D_2O, internal HOD δ 4.78; solutions in $CDCl_3$, internal Me_4Si) and ^{13}C NMR spectra (solutions in D_2O, internal acetone δ 30.5; solutions in $CDCl_3$, internal Me_4Si). The δ and J values for ^1H resonances were calculated as first-order spectra at 300 MHz. The chemical shifts for the resonances of ring carbons were assigned by comparison with the ^{13}C NMR data [5] for aldoses, methyl aldosides, and their acetylated derivatives. CI (isobutane)-mass spectra were obtained with a Finnegan-MAT 212 instrument and an SS 200 data system.

Acetylation of the cyclic carbamates.—A mixture of the cyclic carbamate (1 mmol) and anhyd NaOAc (0.25 g, 3 mmol) in Ac_2O (3 mL) was boiled under reflux for 1 h, then poured into ice–water and extracted with $CHCl_3$. The extract was dried and concentrated, and a solution of the residue in EtOH was clarified with charcoal, then concentrated and dried in vacuo.

1-N,2-O-Carbonyl-α-D-allofuranosylamine (**1**).—To a solution of D-allose (1.26 g, 7 mmol) in water (7 mL) were added potassium cyanate (0.84 g, 10.5 mmol) and $NaH_2PO_4 \cdot H_2O$ (1.96 g, 14 mmol), and the mixture was heated at 60°C for 2.5 h (pH 5.5 → 7). TLC (solvent *A*) revealed one main product (R_f 0.4) and unreacted D-allose (R_f 0.2). The yellow solution was then concentrated together with silica gel (4 g), and dried by the evaporation of toluene. Dry-column flash chromatography [15] (solvent *A*) of the residue gave, first, **1** (437 mg, 30%) as a syrup; R_f 0.4 (solvent *A*); $[\alpha]_D$ + 62° (*c* 1.9, H_2O); ν_{max}^{MeOH} 1761 cm^{-1} (C=O). Mass spectrum: *m/z* 206 $(M + 1)^+$. Anal. Calcd for $C_7H_{11}NO_6$: C, 40.98; H, 5.40; N, 6.83. Found: C, 40.61; H, 5.29; N, 6.51.

Eluted second was D-allose (235 mg, 19%) identified by ^{13}C NMR spectroscopy [5].

The tetra-acetyl derivative (**2**, 59%) of **1** was a syrup; R_f 0.4 (solvent *B*); $[\alpha]_D$ + 194° (*c* 2, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 1801 (carbamate C=O), 1750 cm^{-1} (Ac). Anal. Calcd for $C_{15}H_{19}NO_{10}$: C, 48.26; H, 5.13; N, 3.75. Found: C, 48.41; H, 5.23; N, 3.59.

Reaction of L-gulose with potassium cyanate.—Reaction of L-gulose (0.75 g, 4.17 mmol) for 6 h by the procedure described for **1** gave (TLC) a complex mixture that contained products with R_f 0.5, 0.4, and 0.3 together with L-gulose, R_f 0.15 (solvent *A*). Concentration of the solution followed by column chromatography (solvent *A*) gave, first, an inseparable mixture (125 mg, 15%) of 1-*N*,2-*O*-carbonyl-β-L-idofuranosylamine (**3**) and 1-*N*,3-*O*-carbonyl-α-L-gulopyranosylamine (**5**) in the ratio 7:3 (NMR); R_f 0.5 (solvent *A*); ν_{max}^{MeOH} 1760, 1714 cm^{-1} (C=O).

Eluted second was 1-*N*,2-*O*-carbonyl-α-L-gulopyranosylamine (**7**) as a syrup (217 mg, 25%); R_f 0.4 (solvent *A*); $[\alpha]_D$ −37° (*c* 5, H_2O); ν_{max}^{MeOH} 1760 cm^{-1} (C=O). Anal. Calcd for $C_7H_{11}NO_6$: C, 40.98; H, 5.40; N, 6.83. Found: C, 40.71; H, 5.53; N, 6.69.

Eluted third was 1-*N*,2-*O*-carbonyl-α-L-gulofuranosylamine (**9**; 79 mg, 9%); R_f 0.3 (solvent *A*); mp 159–161°C (from EtOH); $[\alpha]_D$ −55° (*c* 1.7, H_2O); ν_{max}^{KBr} 1715 cm^{-1} (C=O). Mass spectrum: *m/z* 206 $(M + 1)^+$. Anal. Found: C, 41.04; H, 5.45; N, 6.70.

Acetylation of the first fraction (a mixture of **3** and **5**) afforded a mixture of the corresponding tetra-acetyl derivatives **4** and **6**, R_f 0.35 and 0.6, respectively (solvent *B*). Column chromatography (solvent *B*) gave, first, **6** as a syrup (22%); R_f 0.6 (solvent *B*); $[\alpha]_D$ +18° (*c* 0.7, $CHCl_3$): Mass spectrum: *m/z* 374 $(M + 1)^+$. Anal. Calcd for $C_{15}H_{19}NO_{10}$: C, 48.26; H, 5.13; N, 3.75. Found: C, 48.09; H, 5.00; N, 3.63.

Eluted second was **4** (39%); syrup; R_f 0.35; $[\alpha]_D$ +45° (*c* 1, $CHCl_3$). Mass spectrum: *m/z* 374 $(M + 1)^+$. Anal. Found: C, 48.15; H, 4.97; N, 3.48.

The tetra-acetyl derivative (**8**, 84%) of **7** had R_f 0.4 (solvent *B*); mp 164–165°C (from MeOH); $[\alpha]_D$ −134° (*c* 1, $CHCl_3$); ν_{max}^{KBr} 1780 (carbamate C=O), 1730 (OAc), 1710 cm^{-1} (NAc). Anal. Found: C, 48.18; H, 5.21; N, 3.67.

X-ray structure determination of **8**: The relevant crystallographic data of **8** are given in Table 5. The structure was solved by direct methods in the usual way, with the help of the programs SHELXS-90 [16] and SHELX-76 [17]. All non-H atoms were refined. Hydrogens were introduced at theoretical positions. The final co-ordinates of C, N, and O atoms with equivalent isotropic thermal parameters are listed in Table 6 *. Selected torsion angles are given in Table 7, and a perspective view (SCHAKAL-88 [18] plot) of **8** is presented in Fig. 1.

The tetra-acetyl derivative (**10**, 59%) of **9** was obtained, after column chromatographic purification (solvent *B*), as a syrup; R_f 0.25 (solvent *B*); $[\alpha]_D$ −138° (*c* 2, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 1801 (carbamate C=O), 1748 cm^{-1} (Ac). Anal. Found: C, 48.07; H, 5.02; N, 3.59.

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* Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre. The coordinates may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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