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Note

Crystal and molecular structure of α-D-ribopyranosylamine 1,3-(cyclic carbamate)

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Cyclic carbamates of glycosylamines are accessible by the reaction of aldoses with potassium cyanate in aqueous solution[1] and of glycosyl azides with triphenylphosphine and carbon dioxide[2,3]. Application of the latter method to β-D-gluco- and -D-xylo-pyranosyl azide gave the corresponding 1,2-(cyclic carbamates) in high yields. The analogous reaction of the corresponding α-glycosyl azides gave complex mixtures of products[3]. The ^{1}H and ^{13}C NMR data indicated that a main by-product in each of the reactions of the α-D-*gluco* and α-D-*xylo* azides was a 1,3-(cyclic carbamate) with the *allo* or *ribo* configuration, respectively[3]. As there was no precedent for this unexpected inversion of configuration at C-3, the title compound **1** (**19** in the preceding paper[3]) was subjected to X-ray analysis at 25°C in order to verify the structure.

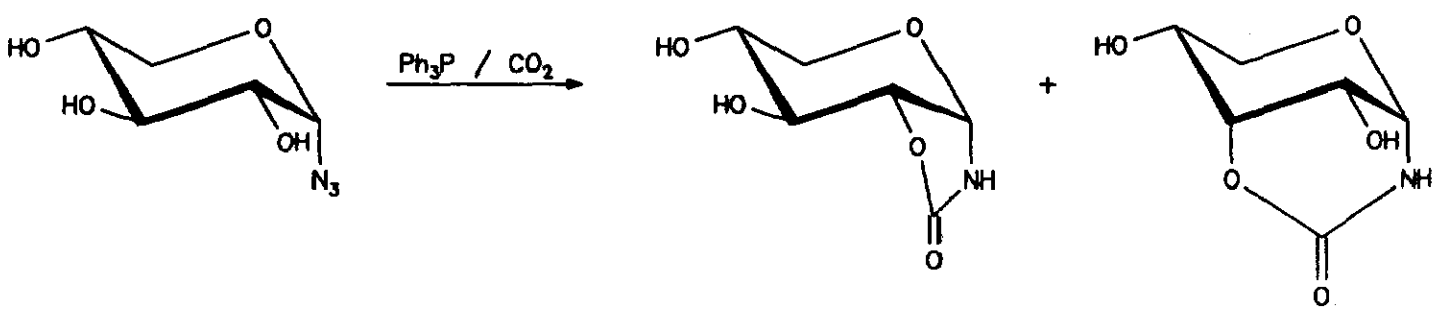

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TABLE I

Crystallographic data for **1** [a]

Formula	$C_6H_9NO_5$	Calculated density D_x ($g \times cm^{-3}$)	1.692
Mol wt	175.14	λ (Cu-K_{α_1})(pm)	154.051
Mp (°C)	194	μ (cm^{-1})	12.5
Crystal dimensions (mm)	$0.5 \times 0.4 \times 0.3$	2θ range (degrees)	4.5–153
Space group	$P2_1$	Symmetry independent reflections	
Cell parameters (pm, degrees)			763
a	633.3(1)	Reflections with $F_0 > 2\sigma(F_0)$	763
b	827.8(1)	Number of refined parameters	145
c	655.9(1)	Final residual factors	
β	90.66(1)	R	0.034
Volume V (pm)	$343.83(9) \times 10^6$	R_w	0.045
F (000)	184	Diffractometer	Enraf–Nonius
Z	2		CAD4

[a] Standard deviations in parentheses.

TABLE II

Fractional positional parameters ($\times 10^4$) and equivalent temperature factors U_{eq}[a] ($\times 10^3$) for C, N, and O atoms in **1** [b]

Atom	x	y	z	U_{eq}
O-1	4707(3)	4539 [c]	9669(3)	32(1)
O-2	7491(3)	6095(4)	5293(3)	37(1)
O-3	9355(3)	3361(4)	7427(3)	31(1)
O-4	9977(4)	3758(4)	11720(3)	40(1)
O-6	8188(4)	1215(4)	5811(3)	37(1)
N-1	5797(4)	3106(4)	6688(4)	29(1)
C-1	5269(4)	4659(5)	7550(4)	28(1)
C-2	7163(4)	5770(4)	7352(4)	27(1)
C-3	8973(4)	4911(4)	8424(4)	27(1)
C-4	8449(4)	4699(4)	10650(4)	29(1)
C-5	6325(5)	3854(5)	10897(4)	33(1)
C-6	7755(4)	2517(5)	6617(4)	28(1)

[a] $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$. [b] Standard deviations in parentheses. [c] This co-ordinate was fixed.

TABLE III

Hydrogen-bond pattern [a] in **1** (bond lengths in pm, angles in degrees) [b]

Distances D–H···A	Symmetry operation on A	Distance D···A	Angle D–H···A
O-2—$\overset{85(4)}{}$H–O2$\overset{201(4)}{\cdots\cdots}$O-6	$-x+2, 1/2+y, -z+1$	284.0(3)	167(5)
O-4—$\overset{95(5)}{}$H–O4$\overset{193(6)}{\cdots\cdots}$O-6	$-x+2, 1/2+y, -z+2$	284.0(4)	158(5)
N-1—$\overset{99(5)}{}$H–N1$\overset{200(5)}{\cdots\cdots}$O-2	$-x+1, 1/2+y-1, -z+1$	295.5(4)	160(3)

[a] A, Acceptor oxygen; D, donor oxygen or nitrogen. [b] Standard deviations in parentheses.

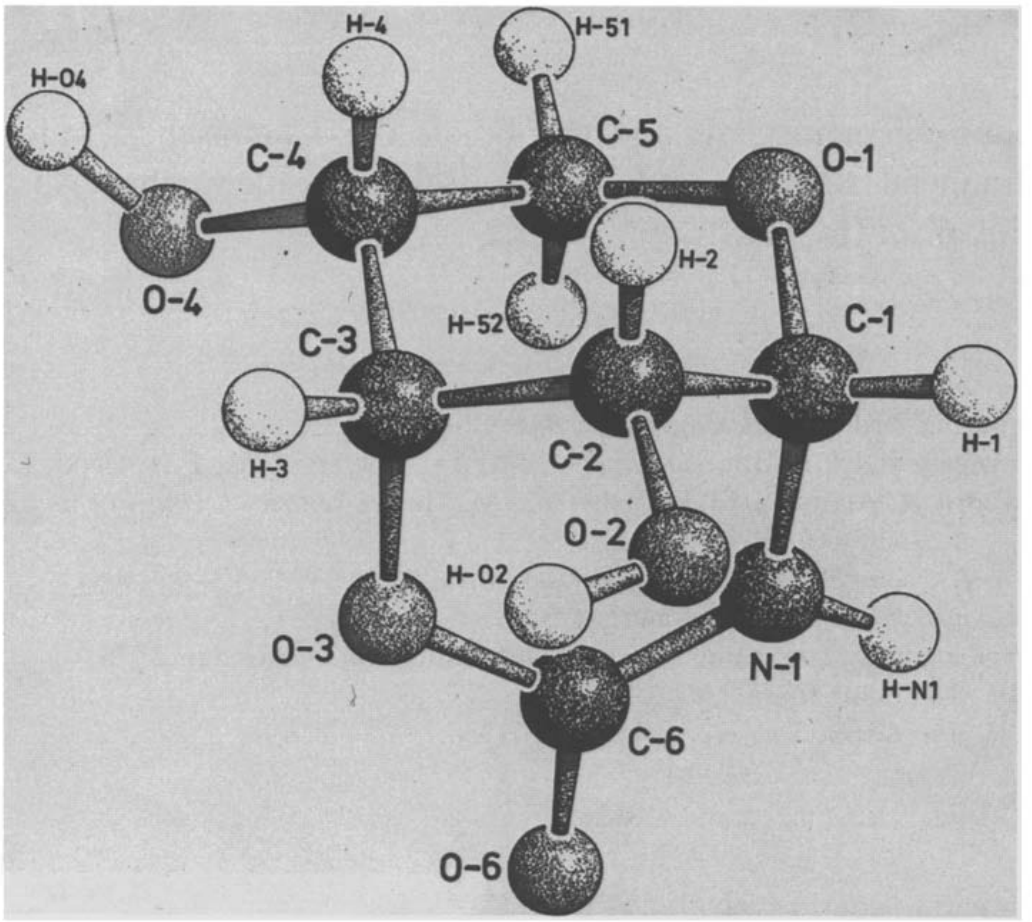

Fig. 1. A SCHAKAL-88[6] drawing of a molecule of α-D-ribopyranosylamine 1,3-(cyclic carbamate) (**1**), showing atom numbering.

The relevant crystallographic data for **1** are given in Table I. The structure was solved by direct methods in the usual way, with the help of the programs SHELXS-90[4] and SHELX-76[5].

All atoms were refined. The H atoms were introduced at the theoretical positions. The final co-ordinates of C, N, and O atoms are listed in Table II *. A perspective view (SCHAKAL-88[6] plot) of a molecule of **1** is presented in Fig. 1, which clearly shows that the structure is as given in the title.

The pyranose ring adopts a chair conformation with puckering parameters[7] $Q = 59.3(3)$ pm, $\theta = 12.0(3)°$, and $\phi = 109(1)°$. The carbamate ring has an almost ideal envelope conformation with C-2 out of the plane of the five other ring atoms [puckering parameters[7]: $Q = 53.7(3)$ pm, $\theta = 54.4(3)°$, and $\phi = 115.7(4)°$].

The molecules of **1** are interlinked in the crystal by hydrogen bonds, which involve O-2, O-4, and N-1 as donors, and O-2 and O-6 (twice) as acceptors. Details are given in Table III.

* Lists of observed and calculated structure amplitudes, fractional co-ordinates of all atoms, anisotropic and isotropic thermal parameters, tables of bond distances and angles, and further information have been deposited with, and can be obtained from, Elsevier Science Publishers B.V., BBA Data Deposition, P.O. Box 1527, Amsterdam, Netherlands. Reference should be made to No. BBA/DD/513/*Carbohydr. Res.*, 239 (1993) 245–248.

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