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Structure of 1,2-Dideoxy-1-(3-pyridyl)-α-D-ribofuranose

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Abstract. $C_{10}H_{13}NO_3$, $M_r = 195{\cdot}22$, orthorhombic, $P2_12_12_1$, $a = 5{\cdot}370\ (1)$, $b = 9{\cdot}417\ (1)$, $c = 19{\cdot}475\ (2)$ Å, $V = 948{\cdot}9$ Å^3, $Z = 4$, $D_x = 1{\cdot}317$ g cm^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54178$ Å, $\mu = 7{\cdot}70$ cm^{-1}, $F(000) = 416$, $T = 293$ K, $R = 0{\cdot}031$ for 584 significant reflections. The molecule has an *anti* conformation about the glycosidic bond. The sugar-ring pucker is C2′-*exo*–C1′-*endo* ($^1T_2$), and the C4′—C5′ conformation is *gauche–trans*. The C1—C(pyridyl) distance of 1·510 (5) Å is significantly longer than the range commonly observed in true nucleosides.

Introduction. Previous studies from our laboratories on modified nucleosides incorporated into oligonucleotide sequences have shown that replacement of standard purines or pyrimidines by benzene acting as a pseudo-base results in marked destabilization of the oligonucleotide secondary structure (Gunning, Neidle, Millican, Eaton, Mock & Mann, 1985). The present study represents aspects of the extension of this work to heterocyclic pseudo-bases, rather than the non-polarized case of benzene. Theoretical studies have shown (Islam & Neidle, unpublished data) that polarizability is an important factor contributing to the stabilization of a planar aromatic group between nucleic acid bases.

The synthesis of a pyridyl nucleoside analogue (Eaton & Millican, 1987) resulted in the formation of both α and β anomers. We report here on the α form, thus confirming the configurational assignment. Conformational details are presented here in view of the continuing interest in modified nucleosides in terms of

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their antiviral and/or anticancer behaviour (Saenger, 1984).

Experimental. Recrystallization from aqueous solution produced colourless elongated prismatic crystals. Crystal 0·4 × 0·1 × 0·1 mm mounted on glass fibre, space group $P2_12_12_1$ (No. 19, orthorhombic) from systematic absences. Cell dimensions from 25 θ values measured on an Enraf–Nonius diffractometer; Ni-filtered Cu $K\alpha$ radiation. Intensity data collected with an $\omega - 2\theta$ scan technique and a maximum scan time of 120s per reflection, for $1{\cdot}5 \le \theta \le 60°$ and $0 \le h \le 6$, $0 \le k \le 10$, $0 \le l \le 21$. 868 unique reflections, of which 584 had $|F_o| > 3\sigma(F_o)$. Three intensity-standard reflections monitored every 250 reflections showed no statistically significant crystal decay during data collection. No absorption correction applied.

Structure solved by direct methods with *MULTAN*82 (Main *et al.*, 1982). H atoms located in difference Fourier synthesis, and their positional and isotropic thermal parameters refined by full-matrix least-squares methods on F, together with non-H atom parameters. Final R of 0·031 and wR of 0·036 with weights of $1/[\sigma^2(F) + 0{\cdot}04F^2]$. Max. Δ/σ of 0·01, $-0{\cdot}25 < \rho < 0{\cdot}2$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations were performed on a VAX 11/750 computer using the *SDP* system (Frenz, 1981).

Discussion. The molecular structure of the title compound is shown in Fig. 1. Absolute configuration was assigned on the basis of the known stereochemistry at C4′. Atomic parameters and bond distances and angles are given in Tables 1 and 2.* Bonding geometry for the ribose ring is in accord with that found in β- (Saenger, 1984) and α-nucleosides (for example, Cline & Hodgson, 1979). The C1′—C1*P* bond length of 1·510 (5) Å is significantly longer than the range commonly observed in true nucleosides (1·40–1·48 Å) (Saenger, 1984).

The ribose ring has a C2′-*exo*–C1′-*endo* pucker with a pseudorotation parameter $P = 324{\cdot}5$ (5)° and a maximum degree of sugar pucker $\psi_m = 38{\cdot}6$ (5)°. The ring valence angle at C2′ of 102·4 (4)° is the smallest in the ring, in accord with the prediction made by Sundaralingam (1973) (this is strictly for arabinosyl nucleosides). The C2′-*exo* sugar pucker is rare in the normal nucleoside series, but has been commonly observed in this series (Cline & Hodgson, 1979, and references therein). The glycosidic torsion angle (O4′—C1′—C1*P*—C6*P*) is 126·2 (5)°, which is in the normal *anti* range. The exocyclic torsion angle O5′—C5′—C4′—C3′ is 177·2 (5)°; this *trans* conformation is one of the less commonly observed ones for nucleosides, and is rare in nucleotides and nucleic acids (Berman, 1981; Saenger, 1984). The O5′—C5′—C4′—O4′ torsion angle is 62·8 (5)°, in the +*gauche* (+ synclinal) range. This orientation of *gauche–trans* about C5′—C4′ is equally observed in both α- and β-nucleosides, although

Table 1. *Fractional atomic coordinates and temperature factors for non-*H *atoms and their e.s.d.'s in parentheses*

	x	y	z	B*(Å^2)
O4′	0·9469 (5)	0·8104 (3)	0·8627 (1)	4·50 (6)
O3′	0·5925 (5)	0·8307 (3)	0·7097 (1)	4·45 (6)
O5′	1·1495 (5)	1·0897 (2)	0·8358 (1)	3·73 (5)
N5*P*	0·8042 (7)	0·4756 (3)	1·0311 (2)	4·41 (7)
C1*P*	0·8100 (7)	0·6090 (4)	0·9263 (2)	3·14 (7)
C1′	0·7272 (7)	0·7392 (4)	0·8872 (2)	3·69 (8)
C2*P*	0·9767 (8)	0·5151 (4)	0·8995 (2)	4·64 (9)
C2′	0·5768 (7)	0·7117 (4)	0·8229 (2)	4·24 (9)
C3′	0·6203 (7)	0·8467 (4)	0·7814 (2)	3·32 (8)
C3*P*	1·0574 (9)	0·3999 (4)	0·9384 (2)	5·4 (1)
C4′	0·8828 (7)	0·8919 (3)	0·8032 (2)	**2·97 (7)**
C4*P*	0·9678 (8)	0·3880 (4)	1·0034 (2)	**4·5 (1)**
C5′	0·9037 (8)	1·0485 (3)	0·8189 (2)	**3·68 (8)**
C6*P*	0·7324 (8)	0·5853 (4)	0·9919 (2)	**4·19 (9)**

* $B = \langle 8\pi^2(U_{11}U_{22}U_{33})^{1/3}\rangle$.

Table 2. *Bond distances* (Å) *and angles* (°)

Numbers in parentheses are e.s.d.'s in the least-significant digits.

O4′	C1′	1·439 (5)	C1*P*	C6*P*	1·362 (5)	
O4′	C4′	1·432 (4)	C1′	C2′	1·513 (6)	
O3′	C3′	1·412 (5)	C2*P*	C3*P*	1·393 (6)	
O5′	C5′	1·414 (5)	C2′	C3′	1·525 (6)	
N5*P*	C4*P*	1·321 (6)	C3′	C4′	1·532 (5)	
N5*P*	C6*P*	1·341 (5)	C3*P*	C4*P*	1·359 (6)	
C1*P*	C1′	1·510 (5)	C4′	C5′	1·511 (5)	
C1*P*	C2*P*					
C1′	O4′ C4′	108·7 (3)	O3′	C3′ C2′	114·8 (4)	
C1′	C1*P* C2*P*	121·8 (4)	O3′	C3′ C4′	113·6 (3)	
C1′	C1*P* C6*P*	121·0 (4)	C2′	C3′ C4′	103·0 (3)	
C2*P*	C1*P* C6*P*	117·0 (4)	C2*P*	C3*P* C4*P*	117·5 (5)	
O4′	C1′ C1*P*	107·7 (3)	O4′	C4′ C3′	107·3 (3)	
O4′	C1′ C2′	104·1 (3)	C3*P*	C4*P* N5*P*	124·3 (4)	
C1*P*	C1′ C2′	115·8 (4)	C4*P*	N5*P* C6*P*	116·1 (4)	
C1*P*	C2*P* C3*P*	120·1 (4)	N5*P*	C6*P* C1*P*	124·9 (4)	
C1′	C2′ C3′	102·4 (4)	C4′	C5′ O5′	112·6 (4)	

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44100 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

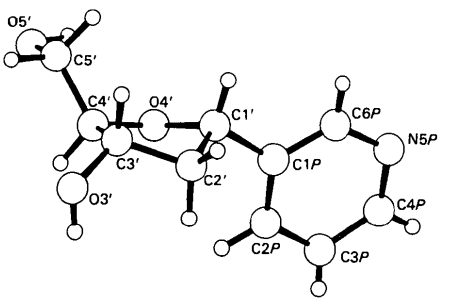

Fig. 1. Computer-drawn view of the molecular structure, perpendicular to the plane defined by atoms C4′, O4′ and C1′.

it is not the commonest conformation in either (Sundaralingam, 1971). The torsion angle about the C1′—C1*P* bond defined by the end atoms O4′ and C6*P* is 126·2 (5)°.

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2,2,5,5-Tetramethyl-3-oxocyclohexyl *p*-Toluenesulfonate

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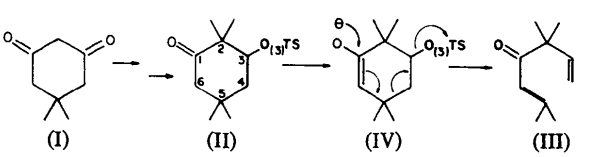
Abstract. $C_{17}H_{24}O_4S$, $M_r = 324{\cdot}4$, monoclinic, $P2_1/c$, $a = 9{\cdot}375$ (1), $b = 21{\cdot}334$ (4), $c = 9{\cdot}733$ (4) Å, $\beta = 113{\cdot}38$ (2)°, $V = 1786{\cdot}8$ (9) Å^3, $Z = 4$, $D_x = 1{\cdot}21$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}155$ mm^{-1}, $F(000) = 696$, $T = 296$ K, $R = 0{\cdot}054$ for 1964 reflections. The cyclohexane ring is in an almost ideal chair conformation and the relationship between the C(3)—O(Ts) and C(4)—C(5)$(CH_3)_2$ bonds is antiperiplanar, as required stereoelectronically for a successful occurrence of a fragmentation reaction. There are no unusual bond distances or angles.

Introduction. Commercially available dimedone (5,5-dimethyl-1,3-cyclohexanedione) (I) can be readily transformed into 2,2,5,5-tetramethyl-3-oxocyclohexyl *p*-toluenesulfonate (II) by standard methodology (Gaoni & Wenkert, 1966). The title compound (II) is the key intermediate in a synthetic sequence leading to Artemisia's ketone (III) (Simonsen & Owen, 1953) by fragmentation of the derived enolate (IV), as depicted in the scheme below. The success of such a fragmentation reaction (Brocksom, LaScala Teixeira, Kanawaga & Brocksom, 1987) is highly dependent upon the angular relationship that exists between the bonding electron pairs, and ideally should be antiperiplanar for the bonds C(3)—O(3) and C(4)—C(5) (II) (Marshall, 1969; Cookson, Edwards, Hudec & Kingsland, 1965). Therefore it became of interest to study the preferred conformation of the title compound (II), which has led to the present crystal structure determination.



Experimental. Prismatic colourless crystals 0·30 × 0·40 × 0·25 mm; Nonius CAD-4 diffractometer; graphite-monochromated Mo $K\alpha$; cell parameters by

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