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Structure of 5′-*O*-Acetyl-2′,3′-*O*-isopropylideneuridine, $C_{14}H_{18}N_2O_7$

By T. P. Seshadri, N. Gautham and M. A. Viswamitra

Department of Physics and ICMR Centre on Genetics and Cell Biology, Indian Institute of Science, Bangalore 560 012, India

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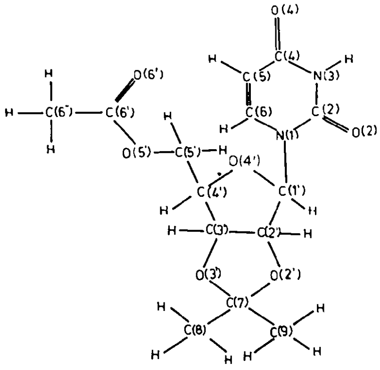
Abstract. $M_r = 326{\cdot}3$, monoclinic, $P2_1$, $a = 6{\cdot}510\ (2)$, $b = 8{\cdot}432\ (2)$, $c = 15{\cdot}114\ (2)$ Å, $\beta = 101{\cdot}42\ (3)°$, $Z = 2$, $V = 813{\cdot}15$ Å^3, $D_x = 1{\cdot}33$ Mg m^{-3}, $F(000) = 172$, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu(\mathrm{Cu}\ K\alpha) = 0{\cdot}906$ mm^{-1}, final $R = 6{\cdot}4\%$ for 1924 observed counter reflections. The conformation about the glycosidic bond is *syn* [torsion angle C(6)—N(1)—C(1′)—O(4′) = −103·9 (3)°]. The sugar pucker is C(2′)-*exo*,C(3′)-*endo* ($^3T_2$). The conformation about the C(4′)—C(5′) bond is *gauche–trans*. An uncommon intermolecular hydrogen bond involving the ribose-ring oxygen O(1′) and the base-nitrogen N(3) stabilizes the crystal structure.

Introduction. We report here the crystal structure of the title compound (I). The investigation was undertaken as part of our studies of isopropylidene derivatives of nucleosides (Katti, Seshadri & Viswamitra, 1981; Gautham, Ramakrishnan, Seshadri, Viswamitra, Salisbury & Brown, 1982; Gautham, Seshadri & Viswamitra, 1983; Gautham, Seshadri, Viswamitra & Salisbury, 1983).



(I)

Experimental. Large crystals by evaporation of an acetone solution of the compound (Sigma Chemical Co.); D_m not determined; crystals characterized by rotation and Weissenberg photographs; unit-cell parameters refined from 2θ values of 25 high-angle reflections measured on an Enraf–Nonius CAD-4 diffractometer; ω–2θ scans, $\theta \leq 60°$; 2000 unique reflections, 1924 $[|F_o| \geq 3\sigma(|F_o|)]$ considered observed after Lorentz and polarization corrections; no absorption correction; index range h 0 to 8, k 0 to 10, l −18 to 18; structure solved by direct methods with *MULTAN*80 (Main *et al.*, 1980); full-matrix least-squares refinement with anisotropic temperature factors using *SHELX* (Sheldrick, 1976) brought R to 10·32%. High temperature factors observed for atoms of the acetyl group [C(6′), C(6″) and O(6′)]. Successive difference Fourier maps at this stage revealed all the H atoms except those attached to C(5), C(4′), C(8) and one of the C(9) methyl group; these were fixed from geometrical considerations. Further block-diagonal least-squares refinement (Shiono, 1968) of the non-hydrogen atoms alone brought R to 6·4% ($R_w = 8{\cdot}1\%$); $w(|F_o| - |F_c|)^2$ minimized where $w = 1/(a|F_o|^2 + b|F_o| + c)$ with $a = 0{\cdot}282$, $b = 1{\cdot}0$ and $c = 0{\cdot}032$ (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961); maximum shift/error ratio = 0·21; residual electron density in final difference map

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±0·6 e Å^{-3}; atomic scattering factors for non-hydrogen atoms from Cromer & Waber (1965), for H from Stewart, Davidson & Simpson (1965); secondary-extinction correction was applied.

Discussion. Table 1[*] gives the final positional parameters, and Table 2 gives bond lengths and angles.

Uracil. The uracil base is planar. The maximum deviations are shown by the exocyclic atoms O(2) [0·027 (3) Å] and O(4)[−0·089 (3) Å].

The glycosidic torsion angle χ [C(6)—N(1)—C(1′)—O(4′)] is −103·9 (3)°. The orientation of the heterocyclic base about the C(1′)—N(1) bond is thus *syn* (Fig. 1), unlike the *anti* conformation more commonly observed for pyrimidine nucleosides. Other *syn* uracil nucleosides are 4-thiouridine ($\chi = -87{\cdot}1°$) (Saenger & Scheit, 1970), 2′-acetyluridine 3′,5′-cyclophosphate benzyl triester (−108·6°) (Depmeier, Engels & Klaska, 1977), 2′-deoxy-3′,5′-diacetyl-2′-fluorouridine (−108·3°) (Suck, Saenger, Main, Germain & Declercq, 1974) and 2′,3′-*O*-isopropylidene-5′-*O*-tosyluridine (116·0°) (Gautham, Seshadri, Viswamitra & Salisbury, 1983).

NMR solution studies on isopropylidene derivatives of pyrimidine nucleosides show a predominance of the *syn* conformation in water and DMSO (Hart & Davis, 1971). A similar study on the present compound performed in this laboratory has also indicated a *syn* conformation in solution (Gautham, Narasinga Rao, Anil Kumar & Viswamitra, unpublished results).

The furan–dioxolane moiety. The phase angle of pseudorotation P (Altona & Sundaralingam, 1972) for the ribose ring is 352·90 (1)° indicating a C(2′)-*exo*,C(3′)-*endo* ($^3T_2$) conformation. C(2′) and C(3′) are displaced by −0·199 (3) and 0·079 (4) Å respectively from the C(1′)—O(4′)—C(4) plane making the conformation predominantly C(2′)-*exo*. The maximum amplitude of pucker τ_m(max.) = 16·8 (2)°. The ribose is thus considerably flattened (Fig. 2) compared to normal nucleosides without constraints.

It is interesting to note that the other *syn* uracil nucleosides also have a sugar pucker close to that of the present structure (4-thiouridine, $P = 34{\cdot}6°$; 2′-deoxy-3′,5′-diacetyl-2′-fluorouridine, $P - 38{\cdot}5°$; 2′-acetyluridine 3′,5′-cyclophosphate benzyl triester, $P = 49{\cdot}6°$; 2′,3′-*O*-isopropylidene-5′-*O*-tosyluridine, $P = 16{\cdot}4°$). Energy calculations (Haschmeyer & Rich, 1967; Pullman & Saran, 1976; Lakshminarayanan & Sasisekharan, 1969; Wilson & Rahman, 1971) have indicated that it is energetically unfavourable for a C(3′)-*endo* sugar [which is close to C(2′)-*exo*] to coexist with a *syn* glycosidic orientation. The present results are not in agreement with these calculations, showing that in the crystal such a conformation can exist, although found to be unfavourable from theoretical considerations.

Table 1. *Positional parameters* (×10^4) *for non-hydrogen atoms and isotropic thermal parameters* (Å^2)

$$B_{\rm eq} = \tfrac{4}{3}\textstyle\sum_i\sum_j \mathbf{a}_i.\mathbf{a}_j\beta_{ij}.$$

	x	y	z	$B_{\rm eq}$
N(1)	2110 (3)	4341 (3)	3812 (1)	1·73 (0·05)
C(2)	3632 (4)	4359 (4)	3293 (2)	1·93 (0·06)
O(2)	3397 (4)	5043 (4)	2569 (2)	2·80 (0·06)
N(3)	5449 (4)	3550 (4)	3654 (2)	2·17 (0·06)
C(4)	5923 (4)	2760 (4)	4475 (2)	2·35 (0·06)
O(4)	7634 (4)	2161 (4)	4726 (2)	3·39 (0·06)
C(5)	4187 (5)	2722 (5)	4943 (2)	2·54 (0·07)
C(6)	2415 (4)	3505 (4)	4615 (2)	2·10 (0·06)
C(1′)	126 (4)	5155 (3)	3493 (2)	1·61 (0·06)
C(2′)	287 (5)	6849 (4)	3167 (2)	1·92 (0·05)
O(2′)	−1331 (4)	7751 (3)	3445 (1)	2·64 (0·05)
C(3′)	−440 (5)	6813 (4)	2136 (2)	2·09 (0·06)
O(3′)	−1864 (5)	8111 (3)	1932 (1)	3·35 (0·07)
C(4′)	−1606 (4)	5226 (4)	1956 (2)	1·98 (0·06)
O(4′)	−1134 (3)	4304 (3)	2781 (1)	1·92 (0·05)
C(5′)	−996 (6)	4320 (5)	1192 (2)	2·89 (0·07)
O(5′)	−2380 (4)	2985 (4)	984 (2)	3·37 (0·06)
C(7)	−1998 (6)	8896 (4)	2754 (2)	2·95 (0·07)
C(8)	−4274 (8)	9301 (7)	2742 (3)	4·55 (0·12)
C(9)	−571 (9)	10311 (5)	2888 (3)	4·74 (0·12)
C(6′)	−2154 (9)	2123 (7)	279 (3)	5·02 (0·28)
O(6′)	−902 (11)	2458 (8)	−165 (4)	11·28 (0·13)
C(6″)	−3690 (12)	776 (9)	107 (4)	6·92 (0·20)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

N(1)—C(2)	1·380 (4)	C(3′)—O(3′)	1·428 (4)
C(2)—O(2)	1·220 (4)	C(3′)—C(4′)	1·536 (4)
C(2)—N(3)	1·381 (4)	C(4′)—O(4′)	1·450 (3)
N(3)—C(4)	1·388 (4)	C(4′)—C(5′)	1·502 (4)
C(4)—O(4)	1·213 (4)	C(5′)—O(5′)	1·437 (5)
C(4)—C(5)	1·448 (4)	O(5′)—C(6′)	1·322 (6)
C(5)—C(6)	1·336 (4)	C(6′)—O(6′)	1·188 (9)
C(6)—N(1)	1·384 (4)	C(6′)—C(6″)	1·501 (10)
N(1)—C(1′)	1·457 (4)	O(2′)—C(7)	1·426 (4)
C(1′)—C(2′)	1·522 (4)	O(3′)—C(7)	1·425 (4)
C(1′)—O(4′)	1·413 (3)	C(7)—C(8)	1·518 (6)
C(2′)—O(2′)	1·427 (4)	C(7)—C(9)	1·501 (6)
C(2′)—C(3′)	1·536 (4)		

C(6)—N(1)—C(2)	120·6 (2)	C(2′)—C(3′)—O(3′)	105·1 (2)
C(6)—N(1)—C(1′)	119·6 (2)	C(2′)—C(3′)—C(4′)	103·9 (2)
C(2)—N(1)—C(1′)	119·8 (2)	O(3′)—C(3′)—C(4′)	110·6 (2)
N(1)—C(2)—O(2)	122·6 (3)	C(3′)—O(3′)—C(7)	108·5 (3)
N(1)—C(2)—N(3)	115·2 (2)	C(3′)—C(4′)—O(4′)	107·5 (2)
O(2)—C(2)—N(3)	122·2 (3)	C(3′)—C(4′)—C(5′)	112·5 (3)
C(2)—N(3)—C(4)	127·7 (3)	O(4′)—C(4′)—C(5′)	110·2 (2)
N(3)—C(4)—O(4)	120·4 (3)	C(4′)—C(5′)—O(5′)	108·5 (3)
N(3)—C(4)—C(5)	113·0 (3)	C(5′)—O(5′)—C(6′)	116·2 (3)
O(4)—C(4)—C(5)	126·5 (3)	O(5′)—C(6′)—O(6′)	121·5 (5)
C(4)—C(5)—C(6)	120·5 (3)	O(5′)—C(6′)—C(6″)	112·3 (5)
C(5)—C(6)—N(1)	122·7 (3)	O(6′)—C(6′)—C(6″)	126·2 (6)
N(1)—C(1′)—O(4′)	110·8 (2)	O(2′)—C(7)—C(8)	108·4 (3)
N(1)—C(1′)—C(2′)	115·9 (2)	O(2′)—C(7)—C(9)	110·4 (3)
O(4′)—C(1′)—C(2′)	107·3 (2)	O(3′)—C(7)—C(8)	108·8 (3)
C(1′)—C(2′)—O(2′)	107·7 (2)	O(3′)—C(7)—C(9)	110·2 (3)
C(1′)—C(2′)—C(3′)	106·4 (2)	O(2′)—C(7)—O(3′)	105·1 (3)
O(2′)—C(2′)—C(3′)	102·2 (2)	C(8)—C(7)—C(9)	113·5 (4)
C(2′)—O(2′)—C(7)	106·3 (2)		

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[*] Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38797 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

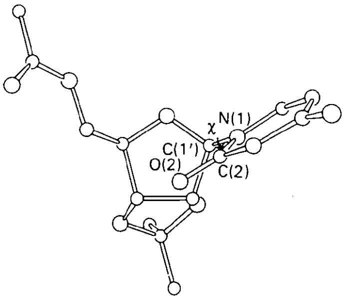

Fig. 1. View of the molecule (I) illustrating the glycosidic *syn* conformation.

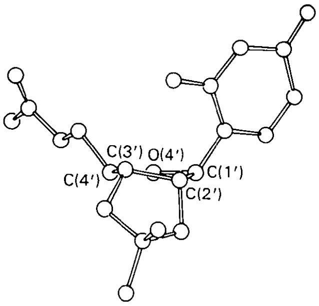

Fig. 2. View of (I) showing the flattened C(2′)-*exo*,C(3′)-*endo* ($^3T_2$) conformation of the ribose ring.

The dioxolane ring is puckered O(2′)-*exo* [$P = 56{\cdot}78\,(6)°$]. The maximum amplitude of pucker is 37·7 (2)° indicating a considerable deviation from planarity; O(2′) deviates by 0·495 (3) Å from the mean plane of the other four atoms in the ring.

The 5′-O-*acetyl moiety.* The torsion angles θ_{OO} and θ_{OC} about C(4′)—C(5′) are 68·6 (3) and −171·4 (3)° respectively. Thus the C(5′)—O(5′) bond is *gauche–trans* with respect to the C(4′)—O(4′) and C(4′)—C(3′) bonds of the ribose. This conformation serves to relieve the short contacts that would occur if the conformation were *gauche–gauche* and *syn*. The present geometry is very similar to that of the 5′-*O*-tosyl analogue (Gautham, Seshadri, Viswamitra & Salisbury, 1983).

The torsion angles C(5′)—O(5′)—C(6′)—O(6′) and C(5′)—O(5′)—C(6′)—C(6″) are −1·4 (7) and −179·0 (4)° respectively. Thus C(6′)—O(6′) is *cis* and C(6′)—C(6″) *trans* to the C(5′)—O(5′) bond.

Crystal packing. The crystal structure is stabilized by an intermolecular N—H···O hydrogen bond involving the ribose ring O(4′) and the base N(3) of molecules related by $1+x$, y, z [N(3)···O(4′) 2·870 (3), O(4′)···H 1·936 Å, N(3)—H···O(4′) 169·3°]. The angle between the plane of C(1′), O(4′), C(4′) and the hydrogen-bonded uracil base is 87·0 (5)°. Although hydrogen bonds involving O(4′) and an N atom of the base are not common, the bond parameters in the present case are as unequivocal as in 6-azauridine (Schwalbe & Saenger, 1973), where such a bond has been reported.

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