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Structure of 2′,3′-*O*-Cyclohexylidene-4′-*C*-(2-methyl-2-propenyl)uridine, $C_{19}H_{26}N_2O_6$

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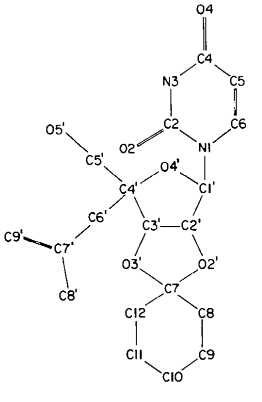
Abstract. $M_r = 378{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 16{\cdot}785\ (10)$, $b = 15{\cdot}922\ (5)$, $c = 7{\cdot}115\ (2)$ Å, $V = 1901\ (2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}32$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\bar{\alpha}) = 1{\cdot}5418$ Å, $\mu = 8{\cdot}29$ cm^{-1}, $F(000) = 808$, $T = 295$ K, final $R = 0{\cdot}098$ for 1107 observed reflections. The base is in the *syn* orientation, and there is an intramolecular hydrogen bond between O(5′) of the ribose and O(2) of the base. The ribose assumes an unusual conformation, O(4′)-*endo*, C(1′)-*exo* (${}^{0}_{1}T$) with the phase angle of pseudorotation $P = 107\ (1)°$.

Introduction. Synthetic methods for incorporation of allyl substituents at C(4′) of nucleosides have been described (Secrist & Winter, 1978). The synthesis involves the N-alkylation of a nucleoside 4′,5′-enamine with allylic halides, followed by thermal rearrangement of the allylic group to C(4′). A mixture of the two isomers at C(4′) is obtained. One of the key intermediates in the synthetic pathway is the title compound (I). Since the uridine molecule used in the synthesis has the β-D conformation, the absolute configurations about C(1′), C(2′), and C(3′) are known. However, the absolute configuration about C(4′) in this compound has been in doubt. This structural study was undertaken to answer this question.



(I)

Experimental. Colorless, needle-like crystals from methylene chloride; crystal 0·7 × 0·05 × 0·05 mm; Picker FACS-1 diffractometer; cell constants determined by least squares using 12 medium-angle reflections; intensities were assigned variances, $\sigma^2(I)$, according to the statistics of the scan and background counts plus a correction term $(0{\cdot}035S)^2$, S being the scan count; Lorentz and polarization correction, no absorption correction; 1107 independent reflections with $2\theta < 100°$ and $I > 0{\cdot}0$; direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); anisotropic full-matrix refinement based on F; H positions (calculated) not refined; R values based on all reflections; $R = 0{\cdot}098$, $wR = 0{\cdot}095$, $S = 2{\cdot}51$, $w = 1/\sigma^2$; LS $\Delta/\sigma = 0{\cdot}05$, final difference Fourier peaks $< |0{\cdot}43|$ e Å^{-3}; scattering factors from *International Tables for X-ray Crystallography* (1974); programs used were the Enraf–Nonius *SDP* (Frenz, 1978).*

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1; bond lengths and angles are given in Table 2. The conformation of the molecule is shown in Fig. 1.

The uracil base is essentially planar; the maximum deviation from the least-squares plane is 0·04 (1) Å,

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, torsion angles and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39125 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Positional* (×10⁴) *and thermal* (×10³) *parameters and their estimated standard deviations*

$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}(Å^2)
O(2)	4094 (1)	8527 (4)	6753 (9)	61 (3)
O(4)	2392 (4)	9894 (5)	2905 (9)	63 (3)
O(4′)	4701 (3)	7059 (4)	4947 (10)	46 (2)
O(2′)	6177 (4)	8414 (4)	3215 (11)	64 (3)
O(3′)	6728 (4)	7255 (4)	4431 (12)	77 (3)
O(5′)	4959 (5)	7298 (4)	8741 (9)	69 (3)
N(1)	4207 (4)	8292 (4)	3548 (11)	39 (3)
N(3)	3262 (4)	9194 (5)	4761 (11)	43 (3)
C(2)	3856 (6)	8678 (6)	5079 (15)	47 (4)
C(4)	2964 (6)	9407 (6)	2969 (16)	54 (4)
C(5)	3294 (6)	8961 (7)	1488 (13)	47 (4)
C(6)	3878 (6)	8429 (7)	1876 (15)	55 (4)
C(1′)	4872 (6)	7770 (6)	3757 (14)	46 (4)
C(2′)	5666 (6)	8133 (6)	4540 (15)	49 (4)
C(3′)	6034 (6)	7412 (7)	5610 (14)	49 (4)
C(4′)	5436 (6)	6706 (6)	5707 (14)	45 (4)
C(5′)	5204 (7)	6538 (7)	7780 (16)	69 (4)
C(6′)	5645 (7)	5916 (7)	4666 (16)	68 (4)
C(7′)	4998 (6)	5324 (6)	4234 (16)	54 (4)
C(8′)	4596 (8)	5443 (8)	2522 (19)	111 (6)
C(9′)	4819 (7)	4705 (7)	5337 (20)	87 (5)
C(7)	6944 (6)	7955 (6)	3310 (16)	47 (4)
C(8)	7209 (6)	7607 (8)	1376 (19)	86 (5)
C(9)	7439 (8)	8335 (10)	107 (18)	121 (7)
C(10)	8081 (8)	8875 (9)	1012 (22)	121 (6)
C(11)	7836 (9)	9140 (8)	2869 (21)	107 (6)
C(12)	7566 (7)	8443 (8)	4145 (17)	79 (5)

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

N(1)—C(2)	1·382 (9)	C(4′)—C(5′)	1·548 (11)
N(1)—C(6)	1·329 (10)	C(4′)—C(6′)	1·500 (10)
N(1)—C(1′)	1·400 (8)	C(4′)—O(4′)	1·460 (8)
C(2)—N(3)	1·311 (8)	C(5′)—O(5′)	1·450 (9)
C(2)—O(2)	1·280 (9)	C(6′)—C(7′)	1·471 (11)
N(3)—C(4)	1·411 (10)	C(7′)—C(8′)	1·406 (11)
C(4)—C(5)	1·387 (10)	C(7′)—C(9′)	1·295 (11)
C(4)—O(4)	1·235 (8)	C(7)—O(2′)	1·482 (8)
C(5)—C(6)	1·326 (10)	C(7)—O(3′)	1·418 (9)
C(1′)—C(2′)	1·557 (10)	C(7)—C(8)	1·549 (12)
C(1′)—O(4′)	1·442 (8)	C(7)—C(12)	1·431 (10)
C(2′)—C(3′)	1·510 (9)	C(8)—C(9)	1·520 (13)
C(2′)—O(2′)	1·351 (9)	C(9)—C(10)	1·521 (15)
C(3′)—C(4′)	1·509 (10)	C(10)—C(11)	1·447 (16)
C(3′)—O(3′)	1·456 (8)	C(11)—C(12)	1·503 (13)
C(6)—N(1)—C(2)	117·1 (6)	C(3′)—C(4′)—C(6′)	116·5 (7)
C(6)—N(1)—C(1′)	121·5 (7)	O(4′)—C(4′)—C(5′)	101·9 (6)
C(2)—N(1)—C(1′)	121·3 (6)	O(1′)—C(4′)—C(6′)	109·7 (6)
N(1)—C(2)—N(3)	117·8 (7)	C(5′)—C(4′)—C(6′)	112·6 (7)
N(1)—C(2)—O(2)	121·1 (7)	C(4′)—O(4′)—C(1′)	110·6 (5)
N(3)—C(2)—O(2)	121·1 (7)	C(4′)—C(5′)—O(5′)	112·1 (7)
C(2)—N(3)—C(4)	125·2 (7)	C(4′)—C(6′)—C(7′)	117·9 (7)
N(3)—C(4)—C(5)	114·9 (6)	C(6′)—C(7′)—C(8′)	116·8 (9)
N(3)—C(4)—O(4)	117·4 (8)	C(6′)—C(7′)—C(9′)	122·2 (9)
C(5)—C(4)—O(4)	127·1 (8)	C(8′)—C(7′)—C(9′)	121·0 (9)
C(4)—C(5)—C(6)	117·7 (7)	C(2′)—O(2′)—C(7)	110·9 (6)
C(5)—C(6)—N(1)	126·8 (8)	C(3′)—O(3′)—C(7)	113·2 (6)
N(1)—C(1′)—O(4′)	111·7 (6)	O(2′)—C(7)—O(3′)	101·0 (6)
N(1)—C(1′)—C(2′)	120·0 (6)	O(2′)—C(7)—C(8)	112·6 (7)
O(4′)—C(1′)—C(2′)	104·6 (6)	O(2′)—C(7)—C(12)	112·6 (7)
C(1′)—C(2′)—C(3′)	104·4 (6)	O(3′)—C(7)—C(8)	107·0 (7)
C(1′)—C(2′)—O(2′)	114·6 (6)	O(3′)—C(7)—C(12)	112·4 (7)
C(3′)—C(2′)—O(2′)	110·1 (6)	C(12)—C(7)—C(8)	110·8 (7)
C(2′)—C(3′)—C(4′)	108·5 (6)	C(7)—C(8)—C(9)	109·1 (8)
C(2′)—C(3′)—O(3′)	99·6 (6)	C(8)—C(9)—C(10)	111·1 (9)
C(4′)—C(3′)—O(3′)	115·4 (6)	C(9)—C(10)—C(11)	110·5 (10)
C(3′)—C(4′)—O(4′)	105·0 (5)	C(10)—C(11)—C(12)	114·9 (10)
C(3′)—C(4′)—C(5′)	109·8 (7)	C(11)—C(12)—C(7)	111·7 (8)

shown by N(1). The glycosidic torsion angle about the C(1′)—N(1) bond is −118 (1)°, corresponding to the *syn* conformation. This conformation is stabilized by an unusual intramolecular hydrogen bond between O(5′) of the ribose and O(2) of the pyrimidine base. The hydrogen-bond distance is 2·817 (7) Å. The *syn* conformation has been reported in 2′,3′-*O*-isopropylidene pyrimidine nucleoside derivatives (Yamagata, Kobayashi, Okabe, Tomita, Sano, Inoue & Ueda, 1983; Gautham, Seshadri, Viswamitra & Salisbury, 1983), although the intramolecular hydrogen bond has not.

The ribose assumes an unusual conformation, O(4′)-*endo*, C(1′)-*exo*, corresponding to ${}^{0}_{1}T$ symmetrical twist conformation. The phase angle P of pseudorotation is 107 (1)° (Altona & Sundaralingam, 1972). The deviations of O(4′) and C(1′) from the C(2′)—C(3′)—C(4′) three-atom plane are 0·191 (7) and 0·214 (10) Å, respectively. The maximum amplitude of pucker, τ_m, is 27 (1)°, showing that the ribose ring is somewhat flattened, compared to most pyrimidine nucleosides. The conformation about the C(4′)—C(5′) bond is the commonly observed *gauche–gauche* (Shefter & Trueblood, 1965), with the torsion angles ψ_{OO} [O(5′)—C(5′)—C(4′)—O(4′)] equal to −59 (1)° and ψ_{OC} [O(5′)—C(5′)—C(4′)—C(3′)] equal to 52 (1)°.

The molecular packing viewed along the c axis is shown in Fig. 2. The structure is stabilized by one

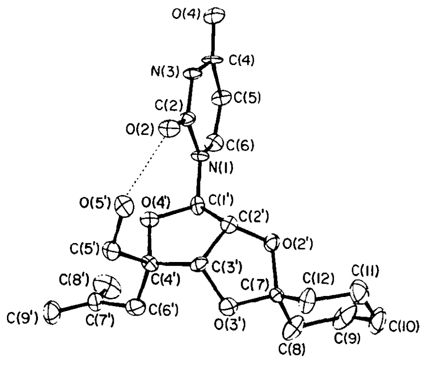

Fig. 1. Conformation of the title compound.

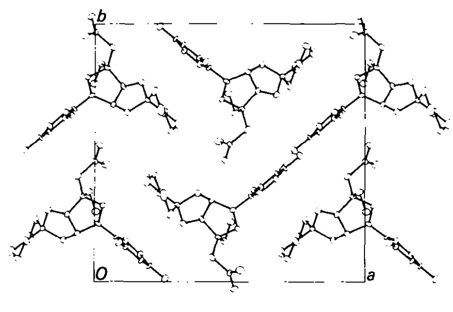

Fig. 2. Molecular packing viewed along the c axis. The intermolecular hydrogen bond between N(3) and O(4) is represented by a thin line.

intermolecular hydrogen bond. The bond [2·884 (7) Å] is formed between N(3) of one molecule and O(4) of another related by the symmetry operation ($\frac{1}{2}-x$, $2-y$, $\frac{1}{2}+z$). There is no base-pairing of the uracil bases.

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Structure of Methyl 3,3-Dimethyl-7-phenylsulfinyl-1,5-dioxaspiro[5.5]undecane-9-carboxylate, $C_{19}H_{26}O_5S$*

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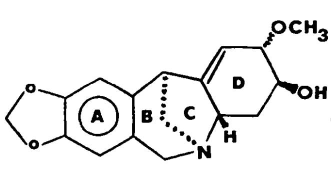
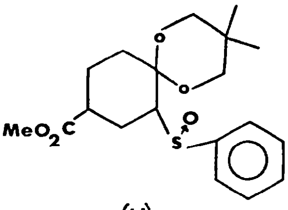
Abstract. $M_r = 366{\cdot}5$, monoclinic, $P2_1/a$, $a = 11{\cdot}094\,(1)$, $b = 11{\cdot}324\,(2)$, $c = 15{\cdot}298\,(2)$ Å, $\beta = 96{\cdot}22\,(1)^\circ$, $V = 1911\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}27$ Mg m^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 1{\cdot}62$ mm^{-1}, $F(000) = 784$, $T = 293$ K. Final $R = 0{\cdot}075$ for 1496 observed reflections. Both the cyclohexane and 1,3-dioxane rings are in chair conformations. The angle between the mean planes of the methoxycarbonyl group and the 1,3-dioxane ring is 93·8 (5)° so that the molecule forms a spiral-like structure. The packing in the crystal is entirely due to van der Waals forces.

Introduction. As part of our studies (Sánchez, López, Flores & Larraza, 1983) regarding the total synthesis of natural products, we became interested in designing a new synthetic entry into the 5,11-methano-morfanthridine-like Amaryllidaceae alkaloids (Wildman, 1970), as shown by montanine (I). Careful analysis of the structural features characteristic of such alkaloids suggested the utilization of (II) (GG-O) as a versatile synthon for the oxygenated *D* ring (Garcia, Larraza & Sánchez, 1983). We now report the crystal and molecular structure of (II).



(I)



(II)

Experimental. Prismatic crystal 0·12 × 0·20 × 0·20 mm, Nicolet *R*3 four-circle diffractometer, graphite-monochromated Cu *Kα*, lattice parameters from 20 machine-centered reflections with $9{\cdot}7 < 2\theta < 24{\cdot}3^\circ$; 2392 reflections with $3 < 2\theta < 115^\circ$ for two octants, 1496 independent with $I > 2{\cdot}5\sigma(I)$, index range $h \pm 11$, k 0/12, l 0/15, ω-scan mode, variable scan speed, scan width 1·0° (θ), two standard reflections monitored every 50 measurements, Lp correction, absorption ignored; structure solved by direct methods using *SHELXTL* (Sheldrick, 1981); least-squares refinement of all non-H atoms treated anisotropically, H atoms riding on the bonded C with a fixed isotropic temperature factor $U = 0{\cdot}06$ Å^2, function minimized $\sum w(\Delta F)^2$, $w = [\sigma^2(F_o) + 0{\cdot}00009(F_o)^2]^{-1}$, $(\Delta/\sigma)_{\max} < 0{\cdot}04$; residual electron density within $\pm 0{\cdot}4$ e Å^{-3}, isotropic extinction parameter $X = 0{\cdot}00179$;

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