Matschiner, H., Maschmeier, C.-P. & Hansen, J. (1992). In preparation.
McKenzie, T. C. (1975). *Acta Cryst.* B31, 1778–1780.
Sheldrick, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
Sheldrick, G. M. (1986). *SHELXS*86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
Stoe & Cie (1991*a*). *DIF*4. Version 7.08. Stoe four-circle diffractometer control program. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1991*b*). *REDU*4. Version 7.08. Stoe four-circle data reduction routine. Stoe & Cie, Darmstadt, Germany.

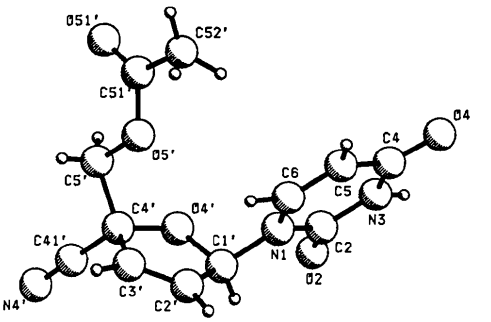

Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule.

Acta Cryst. (1992). C48, 2277–2278

Structure of a 4′-*C*-Branched 2′,3′-Didehydro-2′,3′-dideoxyuridine

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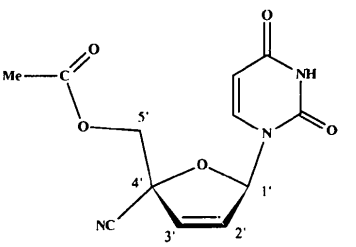
Abstract

The structure of a 4′-*C*-branched 2′,3′-unsaturated uracil nucleoside, 4′-cyano-2′,3′-didehydro-2′,3′-dideoxyuridine 5′-acetate, has been determined. The *N*-glycoside torsion angle χ has a value of $-82.7(3)°$ in the *anti* range. The C4′—C5′ side-chain conformation is *+sc* with $\gamma = 47.2(4)°$. The sugar ring is essentially planar. The conformational parameters are in accordance with the IUPAC–IUB Joint Commission on Biochemical Nomenclature [*Pure Appl. Chem.* (1983), **55**, 1273–1280] guidelines.

Comment

Despite the recent finding that 4′-cyanothymidine acts as a potent inhibitor of the replication of human immunodeficiency virus (O-Yang, Wu, Fraser-Smith & Walker, 1992), only two methods for introducing carbon substituents to the 4′-position of nucleosides have been available. These are 4′-hydroxymethylation of nucleoside 5′-aldehydes (Youssefyeh, Tegg, Verheyden, Jones & Moffatt, 1977) and a Claisen-type rearrangement of nucleoside 4′,5′-enamines (Secrist & Winter, 1978). A new approach to produce a series of 4′-*C*-branched 2′,3′-unsaturated uracil nucleosides has been disclosed quite recently (Haraguchi, Tanaka, Itoh, Saito & Miyasaka, 1992), wherein carbon nucleophiles generated from organosilicon reagents of various types can be transferred to a 3′,4′-unsaturated derivative through an allylic rearrangement. The use of trimethylsilyl cyanide in this reaction gave an epimeric mixture of two 4′-cyano derivatives from which the title compound (1) was isolated as the major product after deprotection followed by acetylation. This molecule shows an *anti* conformation with respect to the sugar ring: χ(C2—N1—C1′—O4′) = $-82.73(3)°$. The sugar ring is essentially planar. The maximum displacement from the least-squares plane is 0.023 Å (O4′). The C4′—C5′ side-chain conformation is *+sc* with the torsion angle γ(C3′—C4′—C5′—O5′) = 47.2(4)°. Two weak C—H—O intermolecular hydrogen bonds are observed: O2—C1′($1-x$, $1/2+y$, $2-z$) 3.174(4) Å and O4—C1′(x, y, $1+z$) 3.148 Å.



(1)

Experimental

Crystal data

$C_{12}H_{11}N_3O_5$
$M_r = 277.24$
Monoclinic
$P2_1$
$a = 14.870$ (1) Å
$b = 5.411$ (1) Å
$c = 8.150$ (1) Å
$\beta = 95.71$ (2)°
$V = 652.5$ (1) Å^3
$Z = 2$
$D_x = 1.411$ Mg m^{-3}
Cu $K\alpha_1$ radiation
$\lambda = 1.5405$ Å
Cell parameters from 20 reflections
$\theta = 29.0$–$30.5°$
$\mu = 0.913$ mm^{-1}
$T = 297$ K
Plate
0.55 × 0.50 × 0.08 mm
Clear

0108-2701/92/122277-02$06.00

Data collection

Rigaku AFC-5 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1196 measured reflections
1165 independent reflections
1056 observed reflections [$F>3\sigma(F)$]

$R_{int} = 0.014$
$\theta_{max} = 60°$
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 6$
$l = 0 \rightarrow 9$
3 standard reflections monitored every 150 reflections
intensity variation: <3%

Refinement

Refinement on F^2
Final $R = 0.047$
$wR = 0.046$
$S = 3.04$
1056 reflections
225 parameters
All H-atom parameters refined
Calculated weights $w=1/[\sigma^2(F)+0.065F^2]$

$(\Delta/\sigma)_{max} = 0.164$
$\Delta\rho_{max} = 0.228$ e Å^{-3}
$\Delta\rho_{min} = -0.315$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
N1	0.6336 (1)	0.2698	1.1042 (2)	0.036 (1)
C2	0.5788 (1)	0.0789 (8)	1.1509 (3)	0.035 (1)
O2	0.5522 (1)	−0.0867 (7)	1.0594 (2)	0.045 (1)
N3	0.5579 (1)	0.0943 (8)	1.3112 (3)	0.045 (1)
C4	0.5877 (2)	0.2666 (10)	1.4267 (3)	0.048 (2)
O4	0.5639 (1)	0.2516 (9)	1.5669 (2)	0.065 (1)
C5	0.6460 (2)	0.4532 (10)	1.3699 (4)	0.052 (2)
C6	0.6663 (2)	0.4484 (9)	1.2136 (3)	0.043 (2)
C1′	0.6539 (1)	0.2643 (8)	0.9332 (3)	0.035 (1)
C2′	0.6847 (2)	0.5056 (8)	0.8707 (3)	0.042 (1)
C3′	0.7648 (2)	0.4824 (9)	0.8187 (4)	0.046 (1)
C4′	0.7970 (2)	0.2202 (8)	0.8419 (4)	0.044 (1)
C41′	0.8046 (2)	0.0991 (9)	0.6798 (4)	0.052 (1)
N4′	0.8110 (2)	0.0056 (10)	0.5563 (4)	0.075 (2)
O4′	0.7275 (1)	0.0984 (7)	0.9185 (2)	0.044 (1)
C5′	0.8864 (2)	0.1901 (10)	0.9483 (5)	0.058 (1)
O5′	0.8797 (1)	0.3374 (8)	1.0909 (3)	0.064 (1)
C51′	0.9422 (2)	0.3024 (10)	1.2185 (5)	0.060 (2)
O51′	1.0015 (2)	0.1574 (11)	1.2134 (5)	0.104 (1)
C52′	0.9287 (3)	0.4722 (14)	1.3569 (6)	0.073 (1)

Table 2. *Geometric parameters* (Å, °)

N1—C6	1.370 (4)	C2′—C3′	1.309 (4)
N1—C2	1.392 (4)	C3′—C4′	1.504 (6)
N1—C1′	1.455 (3)	C4′—O4′	1.422 (4)
C2—O2	1.206 (4)	C4′—C41′	1.489 (5)
C2—N3	1.375 (3)	C4′—C5′	1.521 (5)
N3—C4	1.367 (5)	N4′—C41′	1.139 (5)
C4—O4	1.232 (4)	C5′—O5′	1.420 (6)
C4—C5	1.437 (6)	O5′—C51′	1.338 (4)
C5—C6	1.338 (4)	C51′—O51′	1.184 (6)
C1′—O4′	1.431 (4)	C51′—C52′	1.483 (8)
C1′—C2′	1.491 (6)		
C6—N1—C2	121.7 (2)	C3′—C2′—C1′	110.3 (3)
C6—N1—C1′	122.9 (2)	C2′—C3′—C4′	109.8 (3)
C2—N1—C1′	115.4 (2)	O4′—C4′—C41′	108.0 (3)
O2—C2—N3	122.7 (3)	O4′—C4′—C3′	104.8 (3)
O2—C2—N1	123.2 (2)	O4′—C4′—C5′	109.4 (3)
N3—C2—N1	114.1 (3)	C41′—C4′—C3′	110.8 (3)
C4—N3—C2	127.4 (3)	C41′—C4′—C5′	108.6 (3)
O4—C4—N3	119.4 (4)	C3′—C4′—C5′	115.0 (3)
O4—C4—C5	125.7 (4)	N4′—C41′—C4′	179.5 (5)
N3—C4—C5	114.9 (3)	C4′—O4′—C1′	110.0 (3)
C6—C5—C4	119.6 (4)	O5′—C5′—C4′	106.2 (3)
C5—C6—N1	122.2 (3)	C51′—O5′—C5′	117.2 (3)
O4′—C1′—N1	109.0 (2)	O51′—C51′—O5′	121.9 (4)
O4′—C1′—C2′	104.9 (2)	O51′—C51′—C52′	126.5 (4)
N1—C1′—C2′	114.2 (2)	O5′—C51′—C52′	111.6 (4)

Data collection and cell refinement: *AFD* (Rigaku Corporation, 1985*a*). Data reduction and structure refinement: *RCRYSTAN* (Rigaku Corporation, 1985*b*). Program used to solve structure: *SAPI*85 (Yao, Zheng, Qian, Han, Gu & Fan, 1985). Molecular graphics: *ACV* (Stardent Computer Inc, 1990). Software used for publication material: *XPACK* (Yamaguchi, 1987). The ω-scan width was $(1.3 + 0.14\tan\theta)°$ and the scan speed was 32° min^{-1}. Refinement was by full-matrix least-squares methods.

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55476 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS1021]

References

Haraguchi, K., Tanaka, H., Itoh, Y., Saito, S. & Miyasaka, T. (1992). *Tetrahedron Lett.* **33**, 2841–2844.

IUPAC-IUB Joint Commission on Biochemical Nomenclature (1983). *Pure Appl. Chem.* **55**, 1273–1280.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

O-Yang, C., Wu, H. Y., Fraser-Smith, E. B. & Walker, K. A. M. (1992). *Tetrahedron Lett.* **33**, 37–40.

Rigaku Corporation (1985*a*). *AFD*. Diffractometer control program system. Rigaku Corporation, Tokyo, Japan.

Rigaku Corporation (1985*b*). *RCRYSTAN*. X-ray analysis program system. Rigaku Corporation, Tokyo, Japan.

Secrist, J. A. III & Winter, W. J. Jr (1978). *J. Am. Chem. Soc.* **100**, 2554–2555.

Stardent Computer Inc. (1990). *ACV*. Application chemistry viewer. Stardent Computer Inc., Mewton, Massachusetts, USA.

Yamaguchi, K. (1987). *XPACK*. Programs for X-ray parameters report. Showa Univ., Tokyo, Japan.

Yao, J.-X., Zheng, C.-D., Qian., J.-Z., Han, F.-S., Gu, Y.-X. & Fan, H.-F. (1985). *SAPI* 85. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Institute of Physics, Chinese Academy of Sciences, Beijing, People's Republic of China.

Youssefyeh, R., Tegg, D., Verheyden, J. P. H., Jones, G. H. & Moffatt, J. G. (1977). *Tetrahedron Lett.* pp. 435–438.