

for the *erythro* (0,0,0°), in terms of the pseudo-configurational angles.

The torsion angles of Table 7 give a conformation for molecule *A* with both Me groups almost staggered, and for molecule *B* with *R* at C(1) staggered with the Me group at C(3), the other substituents in configurations as described. The deviations from this theoretical reference conformation (Cano, Foces-Foces & García-Blanco, 1979) are  $\Delta\tau = 0.6^\circ$  at C(1)–C(2) and  $2.4^\circ$  at C(3)–O(2) for compound *A* and  $14.5$  and  $-2.6^\circ$  respectively for compound *B*, to give overall twists of  $3.0^\circ$  in *A* and  $11.9^\circ$  in *B*. This means that from the reference conformation with the chain R–C–O–C–R planar, the torsion angles are  $-119.4$ ,  $-117.6$  and  $14.5$ ,  $-122.6^\circ$ , respectively, as before, to give overall twists of  $123.0^\circ$  for compound *A* and  $-108.1^\circ$  for compound *B* around the C(1)···C(3) line.

There are some deformations (Cano *et al.*, 1979) in the substituents of C(1) and C(3) from the ideal  $sp^3$  geometry, which are given in Table 8.

The angles between rings are  $30.3$  and  $40.3^\circ$  respectively for each compound. These rings are about  $48^\circ$  on average from the O–C–C plane.

In compound *A* an approximate non-crystallographic twofold axis relates both halves of the molecule, passing, when adjusted by least squares through the mid-points of the related atoms, almost through O(2) and running almost parallel to the *x* axis.

Finally, no relevant intermolecular contacts have been detected in the packing.

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### Structure of 5-Acetyl-1-(3,5-*O*-isopropylidene- $\beta$ -D-xylofuranosyl)uracil

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#### Abstract

The structure of 5-acetyl-1-(3,5-*O*-isopropylidene- $\beta$ -D-xylofuranosyl)uracil ( $\beta$ -AXU), a nucleoside with a six-membered isopropylidene ring linked to a five-membered xylose ring, has been solved by direct methods and refined to a final residual *R* of 0.048 over 1684 reflections.  $C_{14}H_{18}N_2O_7$ ,  $M_r = 326$ , is orthorhombic,  $P2_12_12_1$ , with  $a = 6.135$  (1),  $b = 9.227$  (2),  $c = 26.11$  (1) Å,  $Z = 4$ ,  $V = 1478$  (1) Å<sup>3</sup>.

$D_m = 1.44$  (1),  $D_x = 1.46$  Mg m<sup>-3</sup>,  $\mu$ (Cu  $K\alpha$ ) = 1.05 mm<sup>-1</sup>. The slightly non-planar [maximum displacement of a ring atom is 0.03 (2) Å for the imido N(2)] uracil ring is  $\beta$ -linked to a 3'-endo, 4'-exo (<sup>3</sup>*T*<sub>4</sub> puckered) xylofuranose ring. Location of all 18 H atoms revealed a 2.715 (4) Å intermolecular hydrogen bond between OH(2') of the sugar and the acetyl O of the uracil.

#### Introduction

From its mode of preparation (Cusack, Robinson, Rugg, Shaw & Lofthouse, 1974), 5-acetyl-1-(3,5-

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*O*-isopropylidene- $\beta$ -D-xylofuranosyl)uracil ( $\beta$ -AXU) might be expected to possess a six-membered isopropylidene ring, rather than a five-membered one as when *cis*-hydroxyl groups of the sugar are bridged (de Kok, Romers, De Leeuw, Altona & van Boom, 1977). Juxtaposition of this with a furanosyl (rather than pyranosyl) xyloside in a nucleoside is uncommon (Jones, Rugg, Shaw & Sowden, 1975) and an X-ray analysis was undertaken to establish the conformation of the sugar ring and to confirm the anomeric assignment inferred from solution NMR spectroscopy. This is the first crystal structure determined for a group of nucleosides synthesized by a procedure applicable to sugars that can form a pyranosylamine with an isopropylidene cyclic acetal (Cusack, Hildick, Robinson, Rugg & Shaw, 1973).

### Experimental

Colourless tabular crystals, elongated along **a**, were kindly provided by Professor G. Shaw and Dr P. W. Rugg. X-ray oscillation and Weissenberg photographs indicated unit-cell dimensions and symmetry in good agreement with subsequent diffractometer measurements (from 17 reflections).

Intensities were collected with Cu *K* $\alpha$  radiation from a 0.4  $\times$  0.1  $\times$  0.2 mm single crystal on an Enraf-Nonius CAD-4 diffractometer (Biophysics Department, Leeds University) [ $\theta$  range 0–70°; rate 22 reflections h<sup>-1</sup>; sweep width (0.75 + 0.5 tan  $\theta$ )°]. A standard reflection, recorded every 50 measurements, showed no significant intensity variation with time; of 1684 reflections explored, 71 were too weak to measure.

### Solution and refinement of the structure

Solution by direct methods with *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974) revealed all 23 non-hydrogen atoms, plus a small peak at the centre of the pyrimidine ring. With atomic scattering factors taken from *International Tables for X-ray Crystallography* (1962), the starting residual  $R = \sum |F_o| - |F_c| / \sum |F_o|$  was 0.205 over the 1613 non-zero reflections. Least-squares refinement with *XRAY* (Stewart, 1972), anisotropic for the non-hydrogen atoms and isotropic for the H atoms (all located in Fourier difference syntheses), converged to a residual  $R = 0.048$ .\* The final weighting scheme was  $w = [12 + |F_o| + 5 \times 10^{-3} |F_o|^2 + 2 \times 10^{-3} |F_o|^3]^{-1}$ . Final atomic coordinates are in Table 1 (C, N and O)

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36752 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ( $\times 10^4$ ) for non-hydrogen atoms and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}^*$
C(1)	9553 (5)	6360 (3)	404 (1)	3.1 (1)
C(2)	7532 (5)	4046 (3)	369 (1)	2.9 (1)
C(3)	9199 (6)	3433 (3)	698 (1)	3.0 (1)
C(4)	10874 (5)	4280 (3)	854 (1)	3.0 (1)
C(5)	9226 (7)	1889 (3)	862 (1)	3.9 (1)
C(6)	7429 (8)	903 (4)	719 (2)	3.6 (2)
C(7)	12839 (5)	6656 (3)	907 (1)	2.4 (1)
C(8)	12106 (5)	7683 (3)	1340 (1)	2.3 (1)
C(9)	13090 (5)	6959 (3)	1809 (1)	2.5 (1)
C(10)	15179 (5)	6324 (3)	1594 (1)	2.0 (1)
C(11)	16080 (5)	5096 (4)	1909 (1)	3.2 (1)
C(12)	12631 (6)	4826 (4)	2321 (1)	3.8 (1)
C(13)	10973 (7)	3646 (5)	2395 (2)	4.5 (2)
C(14)	13266 (7)	5561 (5)	2819 (1)	6.6 (2)
N(1)	11054 (4)	5705 (3)	722 (1)	2.6 (1)
N(2)	7918 (4)	5485 (3)	230 (1)	2.9 (1)
O(1)	9673 (4)	7651 (2)	292 (1)	3.4 (1)
O(2)	5878 (5)	3466 (3)	214 (1)	3.0 (1)
O(3)	10722 (6)	1455 (3)	1126 (1)	5.3 (2)
O(4)	14531 (3)	5790 (3)	1098 (1)	3.4 (1)
O(5)	13146 (5)	9031 (2)	1275 (1)	3.0 (1)
O(6)	11656 (3)	5835 (2)	1970 (1)	2.6 (1)
O(7)	14424 (4)	4141 (2)	2078 (1)	3.7 (1)

$$* B_{eq} = \frac{1}{3} \pi^2 (U_{11} + U_{22} + U_{33}).$$

Table 2. Fractional coordinates ( $\times 10^3$ ) for hydrogen atoms with e.s.d.'s in parentheses; isotropic temperature factor  $B = 4.0 \text{ \AA}^2$  for all H atoms

	<i>x</i>	<i>y</i>	<i>z</i>
H(2)	690 (9)	594 (7)	0 (2)
H(4)	1218 (6)	395 (4)	108 (1)
H(5)	1204 (10)	974 (9)	118 (2)
H(7)	1334 (6)	712 (4)	61 (1)
H(8)	1054 (6)	773 (4)	136 (1)
H(9)	1327 (8)	772 (5)	208 (2)
H(10)	1631 (8)	712 (5)	155 (2)
H(61)	591 (14)	119 (9)	83 (3)
H(62)	718 (14)	77 (9)	39 (3)
H(63)	756 (14)	-3 (9)	91 (3)
H(111)	1701 (8)	556 (5)	219 (2)
H(112)	1714 (8)	466 (5)	167 (2)
H(131)	955 (9)	412 (6)	258 (2)
H(132)	1057 (9)	327 (5)	202 (2)
H(133)	1152 (12)	285 (8)	267 (3)
H(141)	1175 (10)	592 (6)	301 (2)
H(142)	1398 (10)	485 (6)	303 (2)
H(143)	1414 (16)	639 (9)	276 (3)

and Table 2 (H). E.s.d.'s of coordinates are about 0.003  $\text{\AA}$  and  $\sigma(U_{ii}) = 0.001\text{--}0.002 \text{ \AA}^2$ ; no correlation coefficients exceeded 0.25.

### Description and discussion of the structure

Bond lengths and the atomic numbering scheme are shown in Fig. 1, and Fig. 2 illustrates the overall

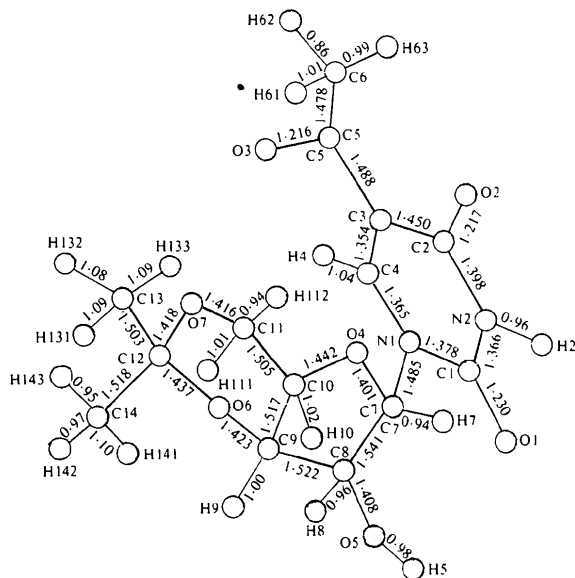


Fig. 1. Numbering of atoms and bond lengths in Å (e.s.d.'s 0.004 Å for heavy-atom bonds, 0.06 Å for C-H bonds).

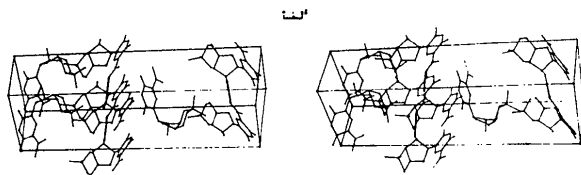


Fig. 2. Stereoscopic drawing (ORTEP II, Johnson, 1976) of the molecular packing. H atoms have been omitted.

packing in the unit cell. Bond angles not involving H atoms are in Table 3. Bond lengths and angles in the 5-acetyluracil moiety in  $\beta$ -AXU agree well with those in uracil (Stewart & Jensen, 1967), 5-nitouracil (Craven, 1967) and 5-bromouracil (Iball, Morgan & Wilson, 1966). At the carbonyl C(2), the acetyl substituent at C(3) causes C(3)-C(2)-O(2) = 127.9 (3)° to be significantly greater than N(2)-C(2)-O(2) = 118.2 (3)°, while the internal ring angle C(1)-N(2)-C(2) increases (Iball *et al.*, 1966) from 116 (3)° (without a hydrogen on the nitrogen) to 126.8 (3)° in  $\beta$ -AXU. Table 4 shows the small deviations [less than usual for C(7)] of atoms from the plane defined by the pyrimidine-ring atoms.

At the glycosidic linkage, the external angles at N [C(1)-N(1)-C(7) = 115.4 (2)°; C(4)-N(1)-C(7) = 123.1 (2)°] diverge more than is usual (117, 121°) in pyrimidine derivatives (Sundaralingam & Jensen, 1965), but the dihedral angle of 73 (1)° between the least-squares planes of the pyrimidine and sugar rings is normal (Iball *et al.*, 1966). The dihedral angle (Sundaralingam, 1969) between O(4)-C(7) and N(1)-C(4) [measured along the C(7)-N(1) bond], describing the

Table 3. Bond angles (°) not involving H atoms with e.s.d.'s in parentheses

N(1)-C(1)-N(2)	115.6 (3)	C(8)-O(9)-C(10)	101.9 (2)
N(1)-C(1)-O(1)	121.9 (3)	C(8)-C(9)-O(6)	108.2 (2)
N(2)-C(1)-O(1)	122.5 (3)	C(10)-C(9)-O(6)	110.5 (2)
C(3)-C(2)-N(2)	113.9 (3)	C(9)-C(10)-C(11)	113.5 (2)
C(3)-C(2)-O(2)	127.9 (3)	C(0)-C(10)-O(4)	103.4 (2)
N(2)-C(2)-O(2)	118.2 (3)	C(11)-C(10)-O(4)	109.5 (3)
C(2)-C(3)-C(4)	119.3 (3)	C(10)-C(11)-O(7)	112.1 (3)
C(2)-C(3)-C(5)	123.5 (3)	C(13)-C(12)-C(14)	112.8 (3)
C(4)-C(3)-C(5)	117.2 (3)	C(1)-N(1)-C(4)	121.4 (3)
C(3)-C(4)-N(1)	122.8 (3)	C(1)-N(1)-C(7)	115.4 (2)
C(3)-C(5)-C(6)	120.5 (3)	C(4)-N(1)-C(7)	123.1 (2)
C(3)-C(5)-O(3)	119.2 (3)	C(1)-N(2)-C(2)	126.8 (3)
C(6)-C(5)-O(3)	120.3 (3)	C(7)-O(4)-C(10)	109.2 (2)
C(8)-C(7)-N(1)	112.8 (2)	C(9)-O(6)-C(12)	113.8 (2)
C(8)-C(7)-O(4)	107.9 (2)	C(11)-O(7)-C(12)	114.7 (2)
N(1)-C(7)-O(4)	108.9 (2)	C(14)-C(12)-O(6)	111.3 (3)
C(7)-C(8)-C(9)	101.8 (2)	C(14)-C(12)-O(7)	112.5 (3)
C(7)-C(8)-O(5)	108.8 (2)	C(13)-C(12)-O(6)	105.7 (3)
C(9)-C(8)-O(5)	107.8 (2)	C(13)-C(12)-O(7)	105.0 (3)
		O(6)-C(12)-O(7)	109.1 (2)

Table 4. Deviations of atoms (Å) from best plane through the six ring atoms in the pyrimidine fragment (e.s.d.'s 0.02 Å)

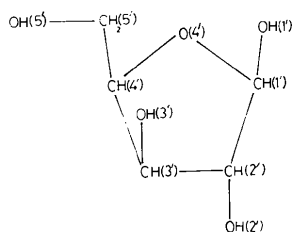
Equation of plane through N(1), C(1), N(2), C(2), C(3), C(4):

$$-3.309x + 2.534y + 20.786z = 0.723$$

C(1)	0.013	C(5)	-0.059
C(2)	0.023	C(6)	-0.013
C(3)	-0.000	C(7)	0.047
C(4)	-0.016	O(1)	0.067
N(1)	0.010	O(2)	0.100
N(2)	0.030	O(3)	-0.115

sugar/base orientation, is 16.9 (4)° in  $\beta$ -AXU [16.8 and 23.8° in  $\beta$ -uridine (Green, Shiono, Rosenstein & Abraham, 1971); 31.4° in 1- $\beta$ -D-arabinofuranosyluracil (Tollin, Wilson & Young, 1973)].

In the furanose sugar ring, with C(9) (Table 5) on the same side as C(11), and C(10) on the opposite side, the major puckering is C(3')-endo, with C(4')-exo minor puckering (in conventional sugar numbering; *cf.* Fig. 3). Torsion angles  $\varphi_{OO}$  and  $\varphi_{OC}$  (Shefter & Trueblood, 1965; Sundaralingam, 1969), O(7)-C(11)-C(10)-O(4) = -73 (1)° and O(7)-C(11)-C(10)-C(9) = +42 (1)°, agree well with those in analogues, but the isopropylidene ring in  $\beta$ -AXU causes C(12)-O(7)-C(11)-C(10) to be as high as -50.6 (1.0)°. The torsion angle H(9)-C(9)-C(10)-C(11) of +84.9 (4)° is in the preferred range for C(3')-endo sugars. Torsion angles (Table 6) about the ring bonds (Brown & Levy, 1963; Sundaralingam, 1969) are smallest opposite atoms deviating most from the ring plane (Table 5). In pseudorotation terms (Altona & Sundaralingam, 1972, 1973), the five torsion angles are appropriate for the C(3')-endo, C(4')-exo

Fig. 3. Conventional (sugar) atom numbering for  $\beta$ -D-xylose.

configuration of  $\beta$ -AXU [rather than C(3')-endo, C(2')-exo]; the maximum angle of pucker,  $\theta_m$  is  $40^\circ$ . Of the C—O bond lengths, C(9)—O(6) is rather long for a C(3')—O(3') and C(8)—O(5) surprisingly short for a furanose C(2')—O(2') bond. Torsion angles for the isopropylidene ring are given in Table 6.

A 2.715 (4) Å intermolecular hydrogen bond between the acetyl O(3) and the xylose hydroxyl O(5)—H(5) on C(8) [C(2') in the sugar nomenclature] has O(3)···H(5) 1.78 (2) Å.

Table 5. Best-plane calculations for furanose ring

Equation of best five-atom plane (I):

$$3.758x + 7.014y - 5.653z = 9.019$$

Equation of best four-atom plane [C(9) excluded] (II):

$$-3.805x - 6.286y + 10.167z = -8.100$$

Dihedral angle between planes I and II: 10.9 (1)°

Deviations of atoms from planes (Å)

Plane	C(7)	C(8)	C(9)	C(10)	O(4)
I	-0.03	0.16	-0.24	0.22	-0.11
II	-0.05	0.03	0.58	-0.03	0.05

Table 6. Torsion angles (°) across bonds in the furanose and isopropylidene rings

Xylofuranose ring		Isopropylidene ring	
Atoms labelled as in Fig. 3		Atoms labelled as in Fig. 1	
O(4')—C(1')	-9 (1)	C(10)—C(11)—O(7)—C(12)	-51 (1)
C(1')—C(2')	-17 (1)	C(11)—O(7)—C(12)—O(6)	+59 (1)
C(2')—C(3')	+34 (1)	O(7)—C(12)—O(6)—C(9)	-61 (1)
C(3')—C(4')	-40 (1)	C(12)—O(6)—C(9)—C(10)	+54 (1)
C(4')—O(4')	+31 (1)	O(6)—C(9)—C(10)—C(11)	-44 (3)
		C(9)—C(10)—C(11)—O(7)	+42 (3)

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