

A least-squares plane [$3.494x - 2.667y + 6.700z = 2.1565$] through the six atoms O(1), O(2), C(3), C(4), C(5) and O(3) reveals that the α,β -unsaturated carboxylic acid is essentially planar. Two features of this structure are somewhat curious: the C(7) methyl carbon is nearly in the plane (-0.0002 \AA) described above and also the double bond between C(2) and C(3) is *cis* to the shorter C—O carboxylic acid bond, *i.e.* C(1)—O(1).

The carboxyl end of this structure is close to a crystallographic inversion center so that a hydrogen-bonded dimer is a more accurate representation of the solid.

All C—C bond lengths are equivalent to one another within experimental error and these lengths agree well with what is expected (Kennard, 1962). From the final residual electron density map it is clear that there is some disorder in the crystal due to different rotamers of the trichloromethyl group. We believe that this fact accounts for the slightly high final wR and residual electron density.

A view of the packing is given in Fig. 2. Intermolecular hydrogen bonds holding two asymmetric units together are shown with dashed lines. No other unusual short intermolecular contacts were noted.

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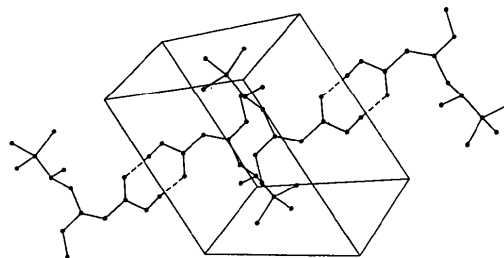


Fig. 2. A view of the packing.

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Structure of 5-Fluoroarabinosylcytosine

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Abstract. $C_9H_{12}FN_3O_5$, $M_r = 261.2$, orthorhombic, $P2_12_12_1$, $a = 5.927(2)$, $b = 7.882(1)$, $c = 23.069(4) \text{ \AA}$, $U = 1077.7 \text{ \AA}^3$, $Z = 4$, $D_x = 1.61 \text{ g cm}^{-3}$, Mo $K\alpha$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 1.35 \text{ cm}^{-1}$, $F(000) = 544$, $T = 296 \text{ K}$, $R = 0.030$ for 1077 unique observed reflections. The *N*-glycosidic torsion angle, χ ,

is $164.0(2)^\circ$, in the *anti* range; the sugar pucker is 2E , $P = 165.4(2)^\circ$, $\psi_m = 37.3(2)^\circ$; the C(4')—C(5') conformation is *ap* with $\gamma = 173.8(2)^\circ$. These are typical values for arabinosyl nucleosides. The *ap* conformation about the C(4')—C(5') bond precludes the formation of an intramolecular hydrogen bond between O(5') and

O(2') as is found in some other arabinosyl nucleosides. The absolute configuration of the title compound is not known.

Introduction. The arabinosyl nucleosides possess a wide range of antiviral and other biological properties (Saenger, 1984). One of the most potent of such compounds is arabinosylcytosine (ara-C). We report here the structure of the 5-fluoro derivative of ara-C, designated ara-FC. This determination is one of our series of nucleoside structure determinations.

Experimental. Needle-shaped crystals grown from aqueous solution. Accurate cell dimensions and crystal orientation matrix determined on a CAD-4 diffractometer by least-squares treatment of 25 reflections in the range $8^\circ < \theta < 12^\circ$. Crystal dimensions $0.08 \times 0.10 \times 0.20$ mm; intensities of reflections with indices h 0 to 7, k 0 to 10, l 0 to 29 with $2^\circ < 2\theta < 54^\circ$ measured; ω - 2θ scans; graphite-monochromatized MoK α radiation; intensities of three reflections chosen as standards monitored every 2 h and showed no evidence of crystal decay; 1460 reflections measured, 1383 unique; 1077 had $I > 3\sigma(I)$ and used in the structure solution and refinement; $R_{\text{int}} = 0.045$. Data corrected for Lorentz and polarization effects but not for absorption. Phase problem solved using direct methods. An E map revealed all non-hydrogen atoms; H atoms located and their positions and isotropic temperature factors refined; all other atoms refined anisotropically. The final cycle of refinement included 212 variable parameters, $R = 0.030$ and $wR = 0.038$, $w = 1/(\sigma^2 F_o + 0.05 F_o^2)$. Max. $\Delta/\sigma < 0.00$; max. difference-map peak $0.23 \text{ e } \text{\AA}^{-3}$, min. difference-map peak $-0.43 \text{ e } \text{\AA}^{-3}$. Anomalous-dispersion effects were included in F . Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a PDP11/73 computer using *SDP-Plus* (Frenz, 1978). Conformation parameters are described according to the IUPAC-IUB Joint Commission on Biochemical Nomenclature (1983).

Discussion. The atomic numbering used is shown in the perspective drawing (Fig. 1); atomic parameters, bond distances and bond angles are listed in Tables 1 and 2.* The bond parameters in ara-FC show no unusual features, with, as expected, the C(1')-O(4') distance [1.418 (3) Å] shorter than the C(4')-O(4') distance [1.451 (3) Å]. The smallest ring angle in the sugar is at

* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving H, and details of hydrogen bonding have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42709 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

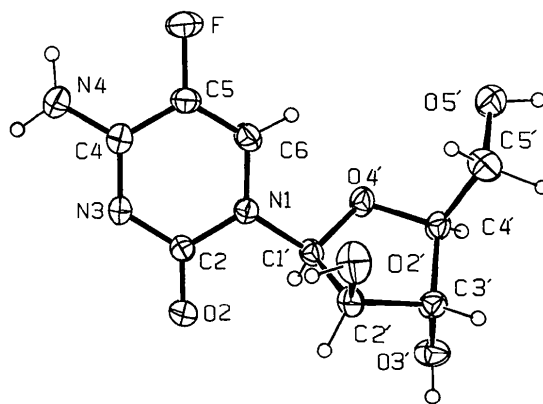


Fig. 1. An ORTEP drawing (Johnson, 1965) of the ara-FC molecule with 50% thermal ellipsoids, showing the atomic numbering.

Table 1. Positional parameters and equivalent isotropic temperature factors (\AA^2) with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j B_{ij} a_i^* a_j^* a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{eq}}(\text{\AA}^2)$
F	-0.1824 (3)	0.5202 (2)	0.74378 (7)	3.87 (3)
N(1)	0.1508 (3)	0.3555 (2)	0.86023 (8)	1.81 (4)
C(2)	0.0328 (4)	0.2083 (3)	0.87370 (9)	1.98 (4)
N(3)	-0.1557 (3)	0.1696 (3)	0.84234 (8)	2.09 (4)
C(4)	-0.2245 (4)	0.2689 (3)	0.7993 (1)	1.93 (4)
C(5)	-0.1047 (4)	0.4192 (3)	0.7868 (1)	2.23 (5)
C(6)	0.0787 (4)	0.4607 (3)	0.8169 (1)	2.21 (4)
O(2)	0.1018 (3)	0.1166 (2)	0.91298 (8)	3.14 (4)
N(4)	-0.4061 (4)	0.2252 (3)	0.76866 (9)	2.60 (4)
C(1')	0.3597 (4)	0.3927 (3)	0.8929 (1)	1.81 (4)
O(4')	0.4803 (3)	0.5184 (2)	0.86178 (7)	2.12 (3)
C(4')	0.5899 (4)	0.6343 (3)	0.90171 (9)	1.87 (4)
C(3')	0.5378 (4)	0.5660 (3)	0.96261 (9)	1.86 (4)
C(2')	0.3184 (4)	0.4663 (3)	0.95352 (9)	1.77 (4)
O(3')	0.7163 (3)	0.4531 (2)	0.97792 (7)	2.56 (3)
C(5')	0.5094 (6)	0.8143 (3)	0.8910 (1)	3.05 (6)
O(5')	0.5869 (4)	0.8717 (2)	0.83587 (8)	3.63 (4)
O(2')	0.1377 (3)	0.5828 (2)	0.95349 (8)	2.55 (3)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) with *e.s.d.*'s in parentheses

F-C(5)	1.353 (3)	C(1')-O(4')	1.418 (3)
N(1)-C(2)	1.390 (3)	C(1')-C(2')	1.533 (3)
N(1)-C(6)	1.366 (3)	O(4')-C(4')	1.451 (3)
N(1)-C(1')	1.479 (3)	C(4')-C(3')	1.536 (3)
C(2)-N(3)	1.366 (3)	C(4')-C(5')	1.518 (4)
C(2)-O(2)	1.229 (3)	C(3')-C(2')	1.534 (3)
N(3)-C(4)	1.328 (3)	C(3')-O(3')	1.427 (3)
C(4)-C(5)	1.411 (3)	C(2')-O(2')	1.411 (3)
C(4)-N(4)	1.333 (3)	C(5')-O(5')	1.425 (4)
C(5)-C(6)	1.331 (4)		
C(2)-N(1)-C(6)	120.8 (2)	N(1)-C(1')-O(4')	107.6 (2)
C(2)-N(1)-C(1')	118.2 (2)	N(1)-C(1')-C(2')	114.0 (2)
C(6)-N(1)-C(1')	121.0 (2)	O(4')-C(1')-C(2')	106.2 (2)
N(1)-C(2)-N(3)	118.7 (2)	C(1')-O(4')-C(4')	110.1 (2)
N(1)-C(2)-O(2)	119.2 (2)	O(4')-C(4')-C(3')	105.7 (2)
N(3)-C(2)-O(2)	122.1 (2)	O(4')-C(4')-C(5')	110.2 (2)
C(2)-N(3)-C(4)	121.0 (2)	C(3')-C(4')-C(5')	114.5 (2)
N(3)-C(4)-C(5)	119.6 (2)	C(4')-C(3')-C(2')	103.0 (2)
N(3)-C(4)-N(4)	119.5 (2)	C(4')-C(3')-O(3')	107.2 (2)
C(5)-C(4)-N(4)	121.0 (3)	C(2')-C(3')-O(3')	110.1 (2)
F-C(5)-C(4)	118.2 (2)	C(1')-C(2')-C(3')	100.5 (2)
F-C(5)-C(6)	121.1 (2)	C(1')-C(2')-O(2')	111.5 (2)
C(4)-C(5)-C(6)	120.7 (2)	C(3')-C(2')-O(2')	108.1 (2)
N(1)-C(6)-C(5)	119.2 (3)	C(4')-C(5')-O(5')	109.9 (3)

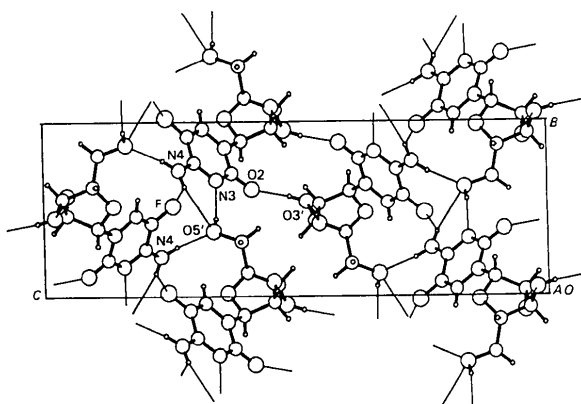


Fig. 2. The arrangement of molecules in the unit cell, viewed along *a*, showing hydrogen bonding.

$C(2')$ [$C(1')-C(2')-C(3')$ $100.5(2)^\circ$]. This agrees with the observation made by Sundaralingam (1975), to the effect that 'in the arabinosides the puckered atoms always assume the smallest ring valency angle'. The *N*-glycosidic torsion angle χ [$C(2)-N(1)-C(1')-O(4')$] is $164.0(2)^\circ$, in the usual *anti* range. The sugar pucker, as defined by the pseudorotational phase angles $P = 165.4(2)^\circ$, $\psi_m = 37.3(2)^\circ$, is 2E , $C(2')$ -*endo*, which is in the same conformational region as all arabinosides studied to date.

The conformation about $C(4')-C(5')$ as defined by the angle γ [$C(3')-C(4')-C(5')-O(5')$ $173.8(2)^\circ$], is *ap*. In the structures of arabinosyl nucleosides an intramolecular hydrogen bond is sometimes formed between $C(2')$ and $O(5')$. Formation of this intramolecular hydrogen bond in *ara*-FC is precluded by the *ap* conformation of the $C(4')-C(5')$ bond.

The possible intermolecular hydrogen-bond contacts are given in Table 3 (deposited). All possible donor H atoms are involved in these contacts. There is one bifurcated (three-centred) contact involving H(N4) and F and O(5') (Fig. 2).

As has been noted in previous halogenated nucleosides (Wilson, Low & Young, 1983), the halogen atom stacks above a symmetry-related base. The perpendicular distance of the F atom above the mean plane of the base ring atoms is $3.015(4)$ Å.

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Structure of 5-Methylthio-1,3,4-thiadiazole-2-thione*

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Abstract. $C_3H_4N_2S_3$, $M_r = 164.3$, monoclinic, $P2_1/n$, $a = 4.126(1)$, $b = 9.507(1)$, $c = 16.701(2)$ Å, $\beta =$

$92.12(1)^\circ$, $V = 654.7$ Å³, $Z = 4$, $D_m = 1.68$, $D_x = 1.67$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.98$ mm⁻¹, $F(000) = 336.0$, $T = 293$ K, $R = 0.037$ for 900 observed reflections. The thiadiazole ring is planar with S-C(2) and C(2)-N(3) partial double bonds. The

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