

Acta Cryst. (1975). B31, 1202**6-Methyl-9-β-D-ribofuranosylpurine**

BY TATSUMICHI TAKEDA, YUJI OHASHI AND YOSHIO SASADA

Laboratory of Chemistry for Natural Products, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan

AND MASAO KAKUDO

Institute for Protein Research, Osaka University, Suita, Osaka 565, Japan

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Abstract. C₁₁H₁₄N₄O₄, orthorhombic, $P2_12_12_1$, $a = 10.588$ (2), $b = 20.381$ (3), $c = 5.550$ (1) Å, $Z = 4$. The structure was solved by a vector-set search method and refined by the block-diagonal least-squares method. The final R value was 0.057 for 1380 reflexions. The relative orientation of the purine and ribose groups is *anti*; $\chi_{CN} = +46.2^\circ$. The sugar puckering is C(2')-*endo* (2E), and the conformation about C(4')-C(5') is *gauche-gauche*. The intermolecular hydrogen bonds are between O(3') and O(2'), O(2') and N(1), and O(5') and N(7).

Introduction. In purines, the polar substituents at C(6) play an important role in hydrogen-bond formation, especially in base pairs of nucleic acids. It seems interesting as regards the stereochemistry of nucleosides to examine the effect of replacement by a non-polar methyl group which is sterically similar to the amino group.

Prismatic crystals of the title compound were obtained by evaporating a methanol solution at room temperature. The crystal data are given in Table 1. Three-dimensional intensity data up to $2\theta = 55^\circ$ were collected using a crystal, $0.14 \times 0.31 \times 0.24$ mm, on a

Rigaku four-circle automatic diffractometer with Mo $K\alpha$ radiation (0.71069 Å) monochromatized by graphite, an ω - 2θ scan with 1° (2θ) min^{-1} being employed. Lorentz and polarization correction was made as usual. Structure factors for 1618 reflexions were obtained, in which 232 with $|F_o| < 1.5\sigma(|F_o|)$ were considered as zero reflexions.

Table 1. *Crystal data for 6-methyl-9-β-D-ribofuranosylpurine*

C ₁₁ H ₁₄ N ₄ O ₄	Space group $P2_12_12_1$
M.W. 266.26	$Z = 4$
$a = 10.588$ (2) Å	$D_x = 1.47$ g cm ⁻³
$b = 20.381$ (3)	$D_m = 1.46$
$c = 5.550$ (1)	$\mu(\text{Mo } K\alpha) = 1.371$ cm ⁻¹
$U = 1197.7$ (4) Å ³	$F(000) = 560$

The vector-set search method was applied, using nine atoms of purine. By rotation and then translation search (Tanaka, Tanaka, Ashida & Kakudo, 1975), two alternative sets of atomic coordinates for the purine group were obtained. One of the electron-density maps derived from these gave a reasonable crystal structure for which the R value was 0.36.

Table 2. *Fractional atomic coordinates and thermal parameters*

The coordinates and thermal parameters of non-hydrogen atoms have been multiplied by 10^4 . Hydrogen-atom coordinates are $\times 10^3$. The form of the anisotropic temperature factor is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - \beta_{12}hk - \beta_{13}hl - \beta_{23}kl)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	369 (3)	640 (2)	2699 (8)	54 (3)	18 (1)	289 (15)	-9 (3)	37 (12)	-11 (7)
C(2)	1080 (5)	375 (2)	949 (9)	66 (4)	20 (1)	276 (16)	-17 (4)	1 (16)	-34 (8)
N(3)	2274 (3)	522 (2)	358 (7)	53 (3)	18 (1)	212 (11)	-11 (3)	7 (11)	-32 (6)
C(4)	2747 (4)	979 (2)	1824 (8)	48 (3)	12 (1)	212 (14)	3 (3)	11 (12)	5 (6)
C(5)	2123 (4)	1285 (2)	3729 (7)	50 (3)	12 (1)	186 (12)	3 (3)	36 (13)	1 (6)
C(6)	870 (4)	1113 (2)	4102 (9)	50 (3)	15 (1)	264 (16)	9 (3)	41 (14)	7 (7)
N(7)	2924 (3)	1730 (2)	4866 (7)	56 (3)	17 (1)	247 (13)	-3 (3)	39 (12)	-28 (6)
C(8)	3989 (4)	1687 (2)	3658 (8)	50 (3)	15 (1)	242 (15)	-6 (3)	-8 (14)	-26 (7)
N(9)	3942 (3)	1241 (2)	1799 (6)	42 (3)	14 (1)	203 (11)	4 (3)	-6 (10)	-19 (5)
C(10)	64 (5)	1433 (2)	5985 (11)	68 (4)	22 (1)	387 (21)	-4 (4)	162 (18)	-15 (9)
C(1')	4920 (3)	1127 (2)	13 (7)	38 (3)	12 (1)	158 (12)	2 (3)	-2 (11)	3 (6)
O(1')	5322 (3)	1744 (1)	-870 (6)	61 (3)	14 (1)	270 (11)	6 (2)	27 (10)	34 (5)
C(2')	6105 (3)	794 (2)	1005 (7)	38 (3)	10 (1)	161 (11)	0 (3)	-21 (11)	-2 (5)
O(2')	5970 (3)	111 (1)	1226 (6)	62 (3)	11 (1)	263 (11)	5 (2)	-14 (11)	8 (5)
C(3')	7087 (4)	1021 (2)	-801 (8)	41 (3)	15 (1)	184 (13)	-2 (3)	12 (12)	-16 (6)
O(3')	6935 (3)	653 (2)	-2956 (6)	63 (3)	23 (1)	222 (10)	16 (3)	40 (10)	-57 (5)
C(4')	6687 (4)	1724 (2)	-1314 (7)	56 (3)	16 (1)	139 (12)	-11 (3)	49 (12)	16 (6)
C(5')	7324 (5)	2259 (2)	143 (9)	102 (5)	17 (1)	236 (15)	-32 (4)	92 (17)	-15 (8)
O(5')	7169 (4)	2129 (2)	2639 (6)	134 (4)	18 (1)	202 (10)	-36 (3)	-9 (13)	-10 (5)

Table 2 (cont.)

	x	y	z	B (Å ²)
H(C2)	76 (5)	2 (2)	-4 (10)	2.1 (12)
H(C8)	471 (5)	195 (2)	406 (9)	1.2 (11)
H(C101)	-54 (6)	159 (3)	511 (13)	4.5 (17)
H(C102)	-10 (7)	117 (3)	712 (14)	4.9 (17)
H(C103)	52 (7)	187 (4)	664 (16)	6.8 (22)
H(C1')	449 (4)	82 (2)	-127 (9)	1.2 (10)
H(C2')	626 (4)	98 (2)	253 (8)	0.3 (9)
H(O2')	575 (5)	-4 (3)	7 (11)	2.3 (12)
H(C3')	802 (5)	104 (2)	3 (10)	1.3 (11)
H(O3')	754 (5)	40 (3)	-302 (12)	3.0 (14)
H(C4')	687 (5)	179 (2)	-295 (10)	1.6 (11)
H(C5'1)	693 (4)	271 (2)	-26 (9)	0.8 (10)
H(C5'2)	821 (6)	225 (3)	-30 (12)	3.4 (15)
H(O5')	743 (6)	258 (3)	346 (12)	4.6 (17)

Several cycles of block-diagonal least-squares refinement decreased R to 0.10. At this stage, all of the hydrogen atoms were found on a difference map. Anisotropic temperature factors were applied to the non-hydrogen atoms. The thermal parameters of the hydrogen atoms were taken as being equal to the reduced isotropic temperature factors of the atoms bonded to them. Six strongest reflexions were excluded, because they seemed to suffer from secondary extinction. The weighting scheme was $w=0.1$ if $|F_o| < 2.22$, $w=1$ if $2.22 \leq |F_o| \leq 22.17$, $w=22.17/|F_o|$ if $|F_o| > 22.17$. The final R value was 0.057. Atomic scattering factors were taken from *International Tables for X-ray Crystallography*

(1962). Atomic coordinates and thermal parameters are given in Table 2.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30845 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

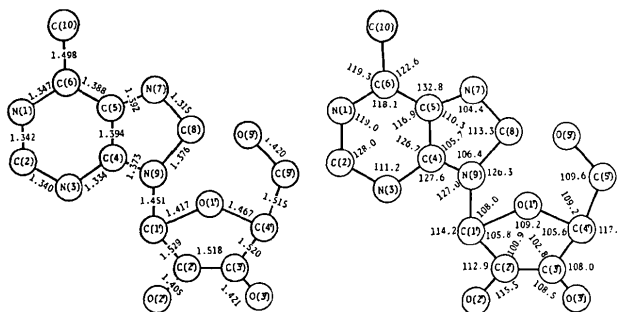


Fig. 2. Bond lengths (Å) and bond angles (°). The estimated standard deviations are 0.005–0.008 Å in distances and 0.3–0.5° in angles. The bond lengths involving hydrogen atoms are C(2)–H(C2) 0.96 (6), C(8)–H(C8) 0.96 (5), C(10)–H(C101) 0.87 (8), C(10)–H(C102) 0.84 (8), C(10)–H(C103) 1.08 (9), C(1')–H(C1') 1.05 (5), C(2')–H(C2') 0.95 (5), O(2')–H(O2') 0.75 (6), C(3')–H(C3') 1.09 (5), O(3')–H(O3') 0.82 (6), C(4')–H(C4') 0.94 (6), C(5')–H(C5'1) 1.03 (5), C(5')–H(C5'2) 0.97 (7) and O(5')–H(O5') 1.06 (7) Å.

Table 3. Hydrogen-bond lengths (Å) and angles (°)

Donor atom	Acceptor atom	Position of acceptor atom	Distance		Angle
			$D \cdots A$	$H \cdots A$	
O(2')	N(1)	$\frac{1}{2}-x, -y, -\frac{1}{2}+z$	2.861 (5)	2.15 (6)	O(2')–H(O2')–N(1) 158 (6)
O(3')	O(2')	$\frac{3}{2}-x, -y, -\frac{1}{2}+z$	2.747 (5)	1.94 (6)	O(3')–H(O3')–O(2') 168 (6)
O(5')	N(7)	$\frac{1}{2}+x, \frac{1}{2}-y, 1-z$	2.824 (6)	1.77 (7)	O(5')–H(O5')–N(7) 173 (6)

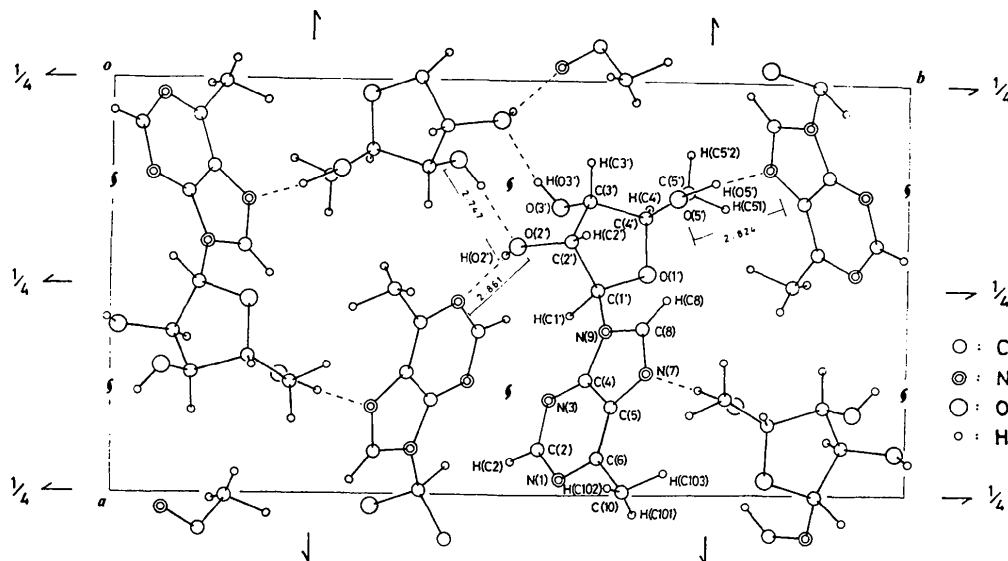


Fig. 1. The crystal structure viewed along the c axis. The hydrogen bonds are represented by broken lines.

Discussion. In the crystal structure, as shown in Fig. 1, a three-dimensional network is formed by hydrogen bonds whose lengths and angles are given in Table 3. The hydrogen bond between sugar moieties is $O(3') \cdots O(2')$, which joins the molecules related by a screw axis. This hydrogen-bond scheme is similar to that in adenosine (Lai & Marsh, 1972) and inosine (Munns & Tollin, 1970). The N(3) atom does not participate in hydrogen bonding. Supposing that $O(3') \cdots O(2')$ is replaced by $O(5') \cdots O(2')$, the resulting hydrogen-bond scheme would become identical with that in nebularine (Takeda, Ohashi & Sasada, 1974). Distances between non-bonded atoms are not significantly shorter than the van der Waals contacts.

Table 4. *Deviations of the atoms from the least-squares planes* (Å)

Coordinates X, Y, Z are in Å referred to a, b and c .			
Ribose plane	I: $-0.1988X - 0.2701Y - 0.9421Z + 1.6480 = 0$		
	II: $-0.1683X - 0.3077Y - 0.9365Z + 1.5901 = 0$		
Purine plane	III: $-0.3097X + 0.7148Y - 0.6271Z + 0.1184 = 0$		
	Plane I	Plane II	Plane III
C(1')	-0.014*	0.000*	N(1) -0.009*
O(1')	0.023*	0.000*	C(2) -0.020*
C(2')	-0.599	-0.518	N(3) 0.009*
C(3')	0.013*	0.103	C(4) 0.009*
C(4')	-0.022*	0.000*	C(5) -0.004*
C(5')	-1.211	-1.206	C(6) 0.027*
			N(7) -0.014*
			C(8) -0.005*
			N(9) 0.007*
			C(10) 0.101
			C(1') 0.142

* Atoms defining the least-squares plane. The dihedral angle between the plane I and III is 62.7° .

The bond lengths and angles are shown in Fig. 2. Owing to the lack of the possible double-bond character between C(6) and the substitutional atom, the

bond alternation $C(2)=N(3)-C(4)=C(5)$ is not seen, as in nebularine. The purine ring is planar within 0.025 \AA , as shown in Table 4. Closer examination shows, however, that the purine base has a tendency to bend. The dihedral angle between the five- and six-membered rings is 1.0° . C(2), C(6) and C(10) atoms are significantly deviated from the plane owing to the interaction between molecules. In the sugar ring there is a significantly large difference (0.050 \AA) between the $C(4')-O(1')$ and $C(1')-O(1')$ lengths owing to the anomeric effect. The ring C-C bond distances and the $C(4')-C(5')$ bond distance are not different from those in other nucleosides. $C(2')-O(2')$ is shorter than $C(3')-O(3')$ and $C(5')-O(5')$, as observed in other nucleosides. The sugar puckering is $C(2')$ -endo referring to the least-squares plane of C(1'), C(3'), C(4') and O(1'), or $C(2')$ -endo-C(3')-exo referring to the plane of C(1'), O(1') and C(4'). The glycosidic torsional angle χ_{CN} [$C(8)-N(9)-C(1')-O(1')$] (Sundaralingam, 1969) is $+46.2^\circ$ and the conformation is *anti*. The torsional angles φ_{CO} [$C(3')-C(4')-C(5')-O(5')$] and φ_{OO} [$O(1')-C(4')-C(5')-O(5')$] are 55.3° and -64.6° , respectively, so that conformation about $C(4')-C(5')$ is *gauche-gauche* (Shefter & Trueblood, 1965).

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Crotocol, a Sesquiterpenoid Alcohol

BY MÁTYÁS CZUGLER AND ALAJOS KÁLMÁN

Central Research Institute for Chemistry of the Hungarian Academy of Sciences,
H-1525-Budapest, POB 17, Hungary

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Abstract. $C_{15}H_{20}O_4$, M.W. 264, orthorhombic, space group $P2_12_12_1$, $a=6.915$ (2), $b=22.174$ (8), $c=8.477$ (2) Å (from Weissenberg and precession photographs), $Z=4$, $D_c=1.349$, $D_x=1.36$ g cm $^{-3}$ (by flotation). Crotocol is a diepoxide alcohol isolated from an antibiotic crotocin [Gyimesi, J. *Acta Chim. Acad. Sci.*

Hung. (1965). **45**, 323-328]. Proximity of the epoxide rings confirmed by X-ray analysis seems to explain the behaviour of crotocol in various chemical reactions.

Introduction. Intensities were measured by photometer on integrated equi-inclination Weissenberg photo-