Xanthosine Dihydrate

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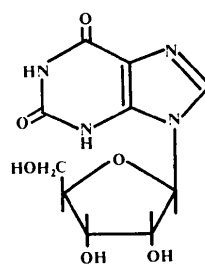
and Yoichi Iitaka

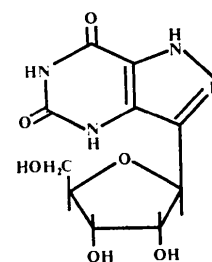*Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo 113, Japan*

Abstract. $C_{10}H_{12}O_6N_4 . 2H_2O$, F.W. 320·26, orthorhombic, $P2_12_12_1$, $a=11·805$ (5), $b=12·506$ (6), $c=8·801$ (4) Å, $U=1299·3$ Å^3, $Z=4$, $D_x=1·638$ g cm^{-3}. The final R value was 0·051 for 1478 reflexions including all the hydrogen atoms. The conformation of the glycosyl bond is *syn* with a χ angle of $-125·7°$. This conformation is stabilized by the intramolecular hydrogen bond $N(3)-H\cdots O(5')$. The ribofuranose group takes a C(2')-*endo* form and *gg* conformation about the $C(4')-C(5')$ bond.

Introduction. Having shown the conformation of oxoformycin B (OXOFMB), a *C*-glycosyl nucleoside analogue of xanthosine, to be *syn* (Koyama, Nakamura, Umezawa & Iitaka, 1976), the present study was undertaken in order to compare the conformation with the usual nucleoside.

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Xanthosine   Oxoformycin B (OXOFMB)

The crystals were grown from a mixed solution of ethyl acetate and water as transparent colourless thick plates. Lattice constants and intensity data were obtained by a Philips four-circle X-ray diffractometer with graphite monochromated Cu $K\alpha$ radiation using a crystal $0·15 \times 0·23 \times 0·3$ mm. Of the 1602 reflexions within $2\theta=156°$, 1478 were measured as $I \geq 2\sigma(I)$ and

Table 1. *Final atomic parameters with estimated standard deviations in parentheses*

The positional and thermal parameters for non-hydrogen atoms are multiplied by 10^4, and those for hydrogen atoms are $\times 10^3$ and $\times 1$, respectively. The temperature factors for non-hydrogen atoms are of the form:

$T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$, and those for hydrogen atoms: $T=\exp[-\beta_{11}(\sin\theta/\lambda)^2]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	7731 (3)	3172 (3)	−1287 (4)	26 (2)	47 (2)	47 (4)	4 (2)	5 (3)	−6 (3)
C(2)	6745 (3)	3737 (3)	−1538 (5)	26 (2)	32 (2)	55 (5)	−2 (2)	5 (3)	−2 (3)
N(3)	6213 (3)	4152 (3)	−272 (4)	26 (2)	40 (2)	33 (4)	6 (2)	0 (2)	−1 (3)
C(4)	6662 (3)	3934 (3)	1123 (4)	26 (2)	28 (2)	36 (5)	1 (2)	−1 (3)	0 (3)
C(5)	7653 (3)	3394 (3)	1354 (5)	31 (3)	31 (2)	47 (5)	4 (2)	−2 (3)	−6 (3)
C(6)	8265 (3)	2962 (3)	94 (5)	27 (2)	28 (2)	68 (6)	0 (2)	−1 (3)	−9 (3)
N(7)	7893 (3)	3321 (3)	2892 (4)	36 (2)	35 (2)	46 (4)	9 (2)	−6 (3)	3 (3)
C(8)	7054 (4)	3811 (3)	3559 (5)	35 (3)	29 (2)	52 (5)	1 (2)	−8 (3)	0 (3)
N(9)	6273 (3)	4224 (3)	2538 (4)	28 (2)	32 (2)	40 (4)	5 (2)	3 (3)	−4 (3)
O(2)	6375 (3)	3885 (3)	−2826 (3)	40 (2)	68 (2)	39 (4)	9 (2)	−2 (2)	2 (3)
O(6)	9169 (3)	2486 (3)	143 (4)	32 (2)	45 (2)	91 (5)	12 (2)	−9 (3)	−23 (3)
C(1')	5258 (3)	4819 (3)	2921 (5)	24 (2)	25 (2)	49 (5)	1 (2)	2 (3)	−3 (3)
C(2')	4140 (3)	4297 (3)	2427 (5)	31 (2)	23 (2)	48 (5)	−5 (2)	3 (3)	−2 (3)
C(3')	3363 (3)	5271 (3)	2365 (5)	25 (2)	38 (2)	36 (5)	0 (2)	0 (3)	−8 (3)
C(4')	4159 (3)	6147 (3)	1779 (5)	29 (2)	27 (2)	55 (5)	4 (2)	−4 (3)	−5 (3)
O(1')	5305 (2)	5790 (2)	2109 (4)	23 (2)	25 (2)	76 (4)	−2 (1)	−4 (2)	7 (2)
O(2')	3792 (3)	3435 (2)	3344 (4)	55 (2)	32 (2)	58 (4)	−14 (2)	3 (3)	3 (2)
O(3')	2977 (2)	5570 (3)	3852 (3)	28 (2)	59 (2)	49 (4)	−3 (2)	10 (2)	−16 (3)
C(5')	4085 (4)	6391 (3)	90 (5)	45 (3)	31 (2)	60 (5)	1 (2)	−6 (4)	7 (3)
O(5')	4210 (3)	5417 (3)	−762 (3)	46 (2)	40 (2)	46 (4)	3 (2)	−1 (3)	4 (2)
O*W*(1)	9060 (3)	1331 (3)	3633 (4)	46 (2)	51 (2)	84 (4)	6 (2)	4 (3)	20 (3)
O*W*(2)	808 (4)	3755 (3)	1454 (4)	70 (3)	82 (3)	73 (4)	−34 (3)	10 (3)	−15 (3)

Table 1 (cont.)

	x	y	z	B
H(N1)	802 (5)	276 (5)	−206 (7)	3 (1)
H(N3)	564 (5)	456 (5)	−29 (7)	3 (1)
H(C8)	701 (5)	406 (5)	468 (7)	5 (1)
H(C1′)	528 (4)	502 (4)	416 (6)	3 (1)
H(C2′)	420 (4)	404 (4)	130 (6)	2 (1)
H(C3′)	270 (4)	512 (4)	171 (6)	2 (1)
H(C4′)	403 (4)	684 (4)	239 (7)	2 (1)
H(O2′)	394 (5)	352 (5)	427 (7)	5 (1)
H(O3′)	241 (5)	533 (5)	399 (7)	5 (1)
H(C5′)	473 (5)	694 (4)	−7 (7)	3 (1)
H′(C5′)	327 (4)	677 (4)	−17 (5)	1 (1)
H(O5′)	419 (5)	558 (5)	−145 (7)	5 (1)
H(OW1)	886 (5)	188 (5)	327 (6)	4 (1)
H′(OW1)	966 (6)	116 (5)	331 (7)	4 (1)
H(OW2)	32 (5)	323 (5)	112 (7)	4 (1)
H′(OW2)	117 (5)	396 (5)	95 (6)	3 (1)

used for the subsequent analysis. Intensities were measured by the θ–2θ scan method with a scan speed of $\theta = 4°$ min^{-1}. Scans were repeated twice when the total counts during a scan were less than 10^3. The background was measured at each end of the scan for half the total scan time.

The structure was determined by the direct method using the *MULTAN* program of Main, Woolfson & Germain (1971).

Refinement by the full-matrix least-squares method using the *ORFLS* program (Busing, Martin & Levy, 1962) yielded the final R value of 0·051, in which the positional parameters and isotropic temperature factors of the whole hydrogen atoms were allowed to vary. The weighting system was: $\sqrt{w} = 1/(0·67 + 0·056|F_o|)$.

The atomic scattering factors for C, N and O atoms were taken from *International Tables for X-ray Crystallography* (1962) and those for H were from Stewart, Davidson & Simpson (1965). The final atomic parameters are listed in Table 1.*

Discussion. The bond lengths and angles of the molecule and the conformational angles of the sugar moiety are shown in Tables 2 and 3, respectively, and can be compared with those listed in Tables 4, 5 and 6 of the paper by Koyama, Nakamura, Umezawa & Iitaka (1976). Comparison of the values shows that:

(1) Some significant differences in the bond lengths and angles are observed in the imidazole ring, which can be well accounted for by the difference in the chemical structures, that is by the difference in the state of resonance in the conjugated system and by the difference in the protonation site.

(2) The length of the glycosyl N–C bond is usual and is about 0·05 Å shorter than the glycosyl C–C bond observed in OXOFMB.

Table 2. Bond lengths (Å) and angles (°)

Pyrimidine group

N(1)–C(2)	1·380 (5)	C(2)–N(1)–C(6)	128·1 (4)
C(2)–N(3)	1·380 (5)	N(1)–C(2)–N(3)	116·5 (4)
N(3)–C(4)	1·364 (5)	N(1)–C(2)–O(2)	121·6 (4)
C(4)–C(5)	1·367 (6)	O(2)–C(2)–N(3)	121·8 (4)
C(5)–C(6)	1·429 (6)	C(2)–N(3)–C(4)	118·3 (3)
C(6)–N(1)	1·394 (6)	N(3)–C(4)–C(5)	124·4 (4)
C(6)–O(6)	1·223 (5)	C(4)–C(5)–C(6)	120·3 (4)
C(2)–O(2)	1·229 (5)	C(5)–C(6)–N(1)	112·1 (4)
		C(5)–C(6)–O(6)	126·7 (4)
		O(6)–C(6)–N(1)	121·1 (4)

Imidazole group

C(5)–N(7)	1·386 (6)	C(5)–C(4)–N(9)	106·3 (3)
N(7)–C(8)	1·304 (6)	N(3)–C(4)–N(9)	129·2 (4)
C(8)–N(9)	1·387 (5)	C(4)–C(5)–N(7)	110·6 (4)
N(9)–C(4)	1·376 (5)	C(6)–C(5)–N(7)	129·0 (4)
N(9)–C(1′)	1·450 (5)	C(5)–N(7)–C(8)	104·7 (3)
		N(7)–C(8)–N(9)	112·8 (4)
		C(8)–N(9)–C(4)	105·5 (3)
		C(8)–N(9)–C(1′)	126·2 (3)
		C(4)–N(9)–C(1′)	128·4 (3)

Ribofuranose group

C(1′)–C(2′)	1·535 (5)	C(1′)–O(1′)–C(4′)	109·2 (3)
C(1′)–O(1′)	1·410 (5)	C(2′)–C(1′)–N(9)	115·3 (3)
C(2′)–C(3′)	1·525 (6)	C(2′)–C(1′)–O(1′)	104·9 (3)
C(2′)–O(2′)	1·409 (5)	N(9)–C(1′)–O(1′)	106·9 (3)
C(3′)–C(4′)	1·533 (6)	C(3′)–C(2′)–C(1′)	100·8 (3)
C(3′)–O(3′)	1·436 (5)	C(3′)–C(2′)–O(2′)	117·1 (3)
C(4′)–O(1′)	1·455 (5)	C(1′)–C(2′)–O(2′)	114·5 (3)
C(4′)–C(5′)	1·520 (6)	C(4′)–C(3′)–C(2′)	102·4 (3)
C(5′)–O(5′)	1·438 (5)	C(4′)–C(3′)–O(3′)	108·3 (3)
		C(2′)–C(3′)–O(3′)	111·5 (3)
		O(1′)–C(4′)–C(3′)	106·4 (3)
		O(1′)–C(4′)–C(5′)	108·1 (3)
		C(3′)–C(4′)–C(5′)	116·0 (3)
		O(5′)–C(5′)–C(4′)	109·5 (3)

Table 3. Torsion angles (°) and the displacement (Å) of atoms in the furanose ring

Torsion angle	
χ[C(8)–N(9)–C(1′)–O(1′)]	−125·7
Conformation about the glycosyl bond	*syn*
τ_0[O(1′)–C(1′)]	−27·4
τ_1[C(1′)–C(2′)]	39·8
τ_2[C(2′)–C(3′)]	−36·0
τ_3[C(3′)–C(4′)]	21·3
τ_4[C(4′)–O(1′)]	3·8
Puckering of the furanose ring	C(2′)-*endo*
φ_{oo}[O(1′)–C(4′)–C(5′)–O(5′)]	−66·6
φ_{oc}[C(3′)–C(4′)–C(5′)–O(5′)]	52·7
Conformation about the C(4′)–C(5′) bond	*gg*

Displacement of atoms from the least-squares plane

C(1′)	−0·014	C(4′)	−0·020
C(2′)	0·607*	O(1′)	0·022
C(3′)	0·012		

* This atom is not included in the least-squares calculations.

(3) The glycosyl bond takes the *syn* conformation as in OXOFMB, but in the present case, the conformation of the furanose ring is C(2′)-*endo* (Table 3) and the plane of the purine base nearly bisects the angle O(1′)–C(1′)–C(2′). The xanthosine molecule takes one

of the stable conformations of the purine nucleosides as calculated by Haschemeyer & Rich (1967). In Fig. 1, the conformation of the molecule and the close intramolecular contacts between the atoms in the base and in the sugar group are shown.

(4) In OXOFMB, a marked difference in the two bond angles, C(4)–C(9)–C(1') and N(8)–C(9)–C(1') (131·1° and 119·6° respectively), widening of the bond angle N(3)–C(4)–C(9) (133·5°) and lengthening of the C(1')–O(1') bond (1·455 Å) were observed but in the present compound, no such abnormal features were found: C(4)–N(9)–C(1') = 128·4°, C(8)–N(9)–C(1') = 126·2°, N(3)–C(4)–N(9) = 129·2° and C(1')–O(1') = 1·410 Å. This may indicate that although the present compound takes the *syn* conformation, it is not in an unacceptable form as described in (3), and is in a less distorted state than that in OXOFMB.

(5) The *syn* conformation is stabilized by the intramolecular hydrogen bond N(3)–H···O(5') as in

OXOFMB. It seems that the protonation at N(3) favours the formation of an intramolecular hydrogen bond and plays an important role in taking the *syn* conformation.

(6) The conformation about the C(4')–C(5') bond is *gauche–gauche* as in OXOFMB.

The projection of the crystal structure along the *b* axis is shown in Fig. 2. The molecules are held together mainly by hydrogen bonds as shown in Table 4 and Fig. 2. Those linking the nucleoside molecules are

Table 4. *Hydrogen bond lengths* (Å) *and angles* (°)

Symmetry operations are: (i) x,y,z; (ii) $\frac{1}{2}+x,\frac{1}{2}-y,-z$; (iii) $x,y,1+z$; (iv) $-\frac{1}{2}+x,\frac{1}{2}-y,1-z$; (v) $1+x,y,z$; (vi) $1-x,\frac{1}{2}+y,\frac{1}{2}-z$; (vii) $\frac{1}{2}-x,1-y,-\frac{1}{2}+z$; (viii) $1\frac{1}{2}-x,1-y,-\frac{1}{2}+z$. Operation code (i) is omitted from the superscript.

			Distances		Angle
Atom 1	Atom 2	Atom 3	1–3	2–3	3–1–2
N(1)——H(N1)······O(2'ⁱⁱ)			2·980 (5)	2·08 (6)	10 (4)
*N(3)——H(N3)······O(5')			2·878 (5)	2·04 (6)	8 (4)
O*W*(1)–H'(O*W*1)···O(2ⁱⁱ)			2·836 (5)	2·07 (7)	12 (5)
O*W*(1)–H(O*W*1)···N(7)			2·919 (5)	2·15 (6)	14 (4)
O(2')——H(O2')·····O*W*(1ⁱᵛ)			2·696 (5)	1·86 (6)	6 (4)
O(5')——H(O5')·····O*W*(2'ᵛⁱⁱ)			2·660 (5)	2·03 (6)	5 (6)
O*W*(2)–H'(O*W*2)···O(3''ᵛⁱⁱ)			2·831 (5)	2·18 (6)	13 (5)
O*W*(2ᵛ)-H(O*W*2ᵛ)···O(6)			2·756 (5)	1·86 (6)	11 (4)
O(3''ᵛⁱⁱ)–H(O3''ᵛⁱⁱ)···O(5')			2·881 (4)	2·14 (6)	3 (5)

* Intramolecular hydrogen bond.

Fig. 2. A projection of the crystal structure along the *b* axis. Hydrogen bonds are shown by broken lines. Symmetry codes are defined in Table 4.
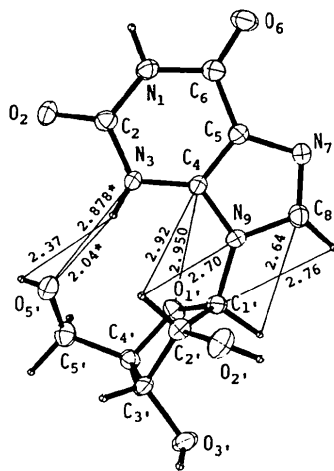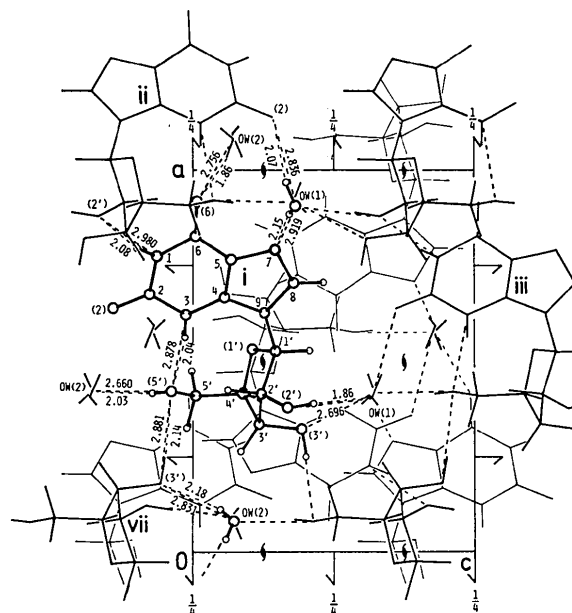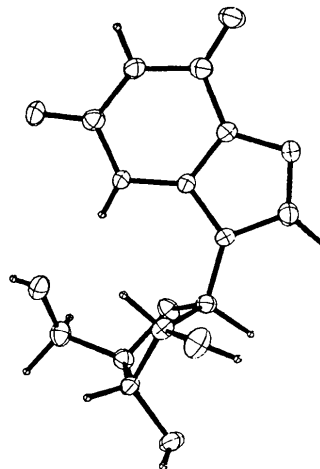

Fig. 1. An *ORTEP* (Johnson, 1965) drawing of the molecule showing the conformation and the closest intramolecular distances. An asterisk indicates an intramolecular hydrogen bond. Non-hydrogen atoms are drawn by ellipsoids of 50 % probability and hydrogen atoms by spheres of arbitrary scale.

N(1)–H$\cdots$O(2') and O(3')–H$\cdots$O(5') and the others link the molecules *via* water molecules. In Table 5 are listed the intermolecular contacts shorter than 3·5 Å.

Table 5. *Intermolecular distances* (Å) *less than* 3·5 Å

Hydrogen atoms are not included. Symmetry operations are listed in Table 4.

N(1)$\cdots$OW(2^{ii})	3·315 (6)	O(1')$\cdots$O(2'^{vi})	3·498 (4)
N(1)$\cdots$O(1'^{viii})	3·009 (5)	O(1')$\cdots$C(6^{viii})	3·492 (5)
C(2)$\cdots$OW(2^{ii})	3·308 (6)	O(1')$\cdots$O(6^{viii})	3·488 (5)
C(2)$\cdots$C(8^{viii})	3·379 (6)	C(3')$\cdots$OW(1^{vi})	3·273 (5)
N(3)$\cdots$C(8^{viii})	3·425 (5)	O(3')$\cdots$OW(1^{iv})	3·492 (5)
C(6)$\cdots$OW(2^{v})	3·381 (6)	O(3')$\cdots$C(6^{vi})	3·457 (5)
O(6)$\cdots$N(3^{ii})	3·167 (5)	O(3')$\cdots$OW(1^{vi})	3·386 (5)
O(6)$\cdots$C(2^{ii})	3·176 (5)	C(5')$\cdots$OW(2^{vii})	3·208 (6)
O(6)$\cdots$O(2'^{ii})	3·307 (5)	OW(1)$\cdots$O(5'^{ii})	3·346 (5)
C(8)$\cdots$O(2'^{iii})	3·282 (5)	OW(2)$\cdots$OW(1^{vi})	3·226 (6)

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Borreiches Borarsenid

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Abstract. $B_{12}(As_{1.77}B_{0.23})$, rhombohedral, $R\bar{3}m$, $a = 5·3370$ (3) Å, $\alpha = 70·216$ (3)° (hexagonal setting: $a = 6·139$, $c = 11·970$ Å), $D_m = 3·38–3·52$, $D_c = 3·40$ g cm^{-3}. Crystals were produced by chemical vapour deposition by the method of Amberger & Rauh [*Acta Cryst.* (1974), B**30**, 2549–2553].

Einleitung. Die durch H_2-Reduktion von BCl_3 und $AsCl_3$ bei 1350–1500°C dargestellten, relativ frei liegenden, isolierbaren Kristalle waren ausnahmslos verzwillingt. Daher wurden zur Strukturuntersuchung kleine, einkristalline Bereiche aus dem grobkristallinen Untergrund der Abscheidung verwendet. $D_m = 3,38–3,52$, chemische Analyse: B 87,4–88,2 Atom-%, As 11,8–12,6 Atom-%.

Kristallsymmetrie und Raumgruppe wurden mit Weissenbergaufnahmen nach der Filmmethode bestimmt. Das reziproke Gitter ist dem der borreichen Bor–Phosphor-Phase (Amberger & Rauh, 1974) sehr ähnlich; Im Gang der Reflexintensitäten treten deutliche Parallelen auf. Den endgültigen Datensatz von

$B_{12}(As_{1.77}B_{0.23})$ lieferten Messungen am automatischen 3-Kreisdiffraktometer der Firma Siemens. Mit Mo $K\alpha$-Strahlung wurden die relativen Intensitäten aller Reflexe einer Viertelkugel des reziproken Gitters bis zur Obergrenze sin $\theta/\lambda = 0,70$ Å^{-1} vermessen. Die in $R\bar{3}m$ unabhängigen Reflexe wurden dabei mehrfach erfasst. Von den 482 Messdaten wurden 49 aussortiert, deren Verhältnis Untergrund/Intensität grösser als 0,8 war. Von den symmetrieverbundenen übrigen Reflexen wurden Mittelwerte der Intensitäten gebildet. Insgesamt wurden 137 unabhängige Messdaten erhalten.

Polarisations- und Lorentzkorrektur wurden wie üblich durchgeführt. Auf eine Absorptionskorrektur wurde verzichtet, da das verwendete Bruchstück extrem klein war (geschätzte Kantenlänge 0,01 mm). Die Verfeinerung der Struktur wurde mit allen 137 Reflexen auf der Basis der Raumgruppe $R\bar{3}m$ durchgeführt. Nach dem Verfahren der kleinsten Fehlerquadrate wurden die Lagekoordinaten aller Atome, die isotropen Temperaturfaktoren, der Skalenfaktor und die Lagebesetzungszahl der Arsenlage verfeinert. Der

Tabelle 1. *Punktlagen, Lagebesetzungszahlen, Koordinaten und isotrope thermische Parameter*

Grundlagen: rhomboedrische Raumgruppe $R\bar{3}m$, Temperaturfaktor = exp $(-B \sin^2 \theta/\lambda^2)$.

	Punktlage	Lagebesetzung	x	y	z	B (Å^2)
As	2(*c*)	0,904	3,9999 (1)	0,3999 (1)	0,3999 (1)	0,36 (3)
B	6(*h*)	1,0	0,8208 (1)	0,8208 (11)	0,2755 (19)	0,89 (13)
B	6(*h*)	1,0	0,9826 (11)	0,9826 (11)	0,6755 (91)	0,88 (12)