

Redetermination of orotic acid monohydrate

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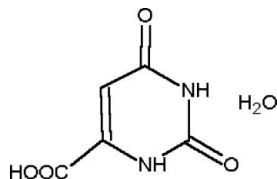
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.001$ Å; R factor = 0.044; wR factor = 0.134; data-to-parameter ratio = 17.6.

The crystal structure of the title compound, which is also known as vitamin B₁₃ (systematic name: 2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylic acid monohydrate), C₅H₄N₂O₄·H₂O, was reported for the first time by Takusagawa & Shimada [*Bull. Chem. Soc. Jpn* (1973), **46**, 2011–2019]. The present redetermination provides more precise values of the molecular geometry. The asymmetric unit comprises a planar diketo tautomer and a solvent water molecule. In the crystal structure, molecules are connected by O—H···O, N—H···O and C—H···O hydrogen bonds involving NH groups, two carbonyl O atoms and the solvent water molecule.

Related literature

For the previous structure determination, see: Takusagawa & Shimada (1973). For a general approach to the use of multiple hydrogen-bonding DNA/RNA nucleobases as potential supramolecular reagents, see: Portalone *et al.* (1999); Brunetti *et al.* (2000, 2002); Portalone & Colapietro (2007 and references therein). For the computation of ring patterns formed by hydrogen bonds in crystal structures, see: Etter *et al.* (1990); Bernstein *et al.* (1995); Motherwell *et al.* (1999).



Experimental

Crystal data

C₅H₄N₂O₄·H₂O

$M_r = 174.12$

Triclinic, $P\bar{1}$

$a = 5.89854$ (14) Å

$b = 6.92921$ (15) Å

$c = 9.59160$ (18) Å

$\alpha = 74.6778$ (12)°

$\beta = 72.3232$ (16)°

$\gamma = 68.447$ (2)°

$V = 342.21$ (1) Å³

$Z = 2$

Mo $K\alpha$ radiation

$\mu = 0.15$ mm⁻¹

$T = 298$ (2) K

0.20 × 0.15 × 0.15 mm

Data collection

Oxford Diffraction Xcalibur S CCD diffractometer

Absorption correction: multi-scan

(*CrysAlis RED*; Oxford

Diffraction, 2006)

$T_{\min} = 0.977$, $T_{\max} = 0.985$

64781 measured reflections

2340 independent reflections

2048 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.133$

$S = 1.08$

2340 reflections

133 parameters

All H-atom parameters refined

$\Delta\rho_{\text{max}} = 0.19$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.22$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4—H4···O5	0.89 (3)	1.65 (3)	2.5231 (11)	166 (2)
N1—H1···O1 ⁱ	0.85 (2)	2.03 (2)	2.8824 (11)	175.2 (19)
N3—H3···O2 ⁱⁱ	0.94 (2)	1.87 (2)	2.8112 (11)	174.6 (18)
O5—H51···O2 ⁱⁱⁱ	0.81 (3)	2.00 (3)	2.7786 (12)	161 (3)
O5—H52···O3 ^{iv}	0.82 (3)	1.98 (3)	2.7787 (12)	164 (2)
C5—H5···O4 ⁱⁱⁱ	0.879 (19)	2.740 (19)	3.5922 (13)	163.7 (15)

Symmetry codes: (i) $-x, -y, -z + 2$; (ii) $-x, -y + 1, -z + 1$; (iii) $-x + 2, -y, -z + 1$; (iv) $-x + 2, -y - 1, -z + 2$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2160).

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supplementary materials

Acta Cryst. (2008). E64, o656 [doi:10.1107/S160053680800562X]

Redetermination of orotic acid monohydrate

G. Portalone

Comment

Orotic acid monohydrate, the only effective precursor in the biosynthesis of pyrimidine nucleobases, was determined some 35 years ago (Takusagawa & Shimada, 1973). In this study, 1488 unique reflections were collected at an ambient temperature by photographic techniques using Cu $K\alpha$ radiation. 1344 of these, having values significantly above background, were estimated visually and no absorption correction was applied [$\mu(\text{Cu } K\alpha) = 15.4 \text{ cm}^{-1}$]. The final refinement led to $R = 0.058$ with standard deviations of 0.005 \AA in C—C bond lengths. As a part of a more general study of multiple hydrogen-bonded DNA/RNA-nucleobases as potential supramolecular reagents (Brunetti *et al.*, 2000, 2002; Portalone *et al.*, 1999; Portalone & Colapietro, 2007), this paper reports a redetermination of the crystal structure of the title compound, (I), with greater precision and accuracy. The asymmetric unit of (I) (Fig. 1) comprises a planar diketo tautomer and a crystal water molecule. The analysis of the crystal packing of (I) shows five N—H \cdots O and O—H \cdots O intermolecular hydrogen bonds (Table 1) which link the molecules into planar layers (Fig. 2). Two kinds of inversion-related N—H \cdots O hydrogen bonds with graph-set motifs $R^2_2(8)$ (Etter *et al.*, 1990; Bernstein *et al.*, 1995; Motherwell *et al.*, 1999) (Table 1) are formed between NH groups and two carbonyl O atoms (O1ⁱ and O2ⁱⁱ) [symmetry code: (i) $-x, -y, z + 2$; (ii) $-x, -y + 1, -z + 1$] to give a zigzag chain. Each chain is joined by three O—H \cdots O intermolecular hydrogen bonds to form rings of descriptor $R^4_4(12)$, $R^4_3(13)$ and $R^4_4(18)$ through a water molecule (O4—H4 \cdots O5, O5—H51 \cdots O2ⁱⁱⁱ and O5—H52 \cdots O2^{iv}; symmetry code: (iii) $-x + 2, -y, -z + 1$; (iv) $-x + 2, -y - 1, -z + 2$). The hydrogen-bonded two-dimensional array involves the C5—H5 \cdots O4ⁱⁱⁱ intermolecular interaction.

Experimental

The title compound (0.1 mmol, Sigma Aldrich of 98% purity) was dissolved in water (9 ml) and heated under reflux for 2 h. After cooling the solution to ambient temperature, crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation.

Refinement

All H atoms were found in a difference map and refined isotropically.

Figures

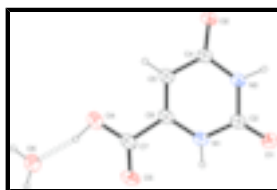


Fig. 1. The molecular structure of (I), showing the atom-labelling scheme. Displacements ellipsoids are at the 50% probability level. Hydrogen bonding is indicated by dashed lines.

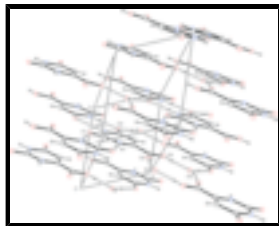


Fig. 2. Crystal packing diagram of (I). All atoms are shown as small spheres of arbitrary radii. Hydrogen bonding is indicated by dashed lines.

2,6-dioxo-1,2,3,6-tetrahydropyrimidine-4-carboxylic acid monohydrate

Crystal data

$C_5H_4N_2O_4 \cdot H_2O$	$Z = 2$
$M_r = 174.12$	$F_{000} = 180$
Triclinic, $P\bar{1}$	$D_x = 1.690 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation
$a = 5.89854 (14) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 6.92921 (15) \text{ \AA}$	Cell parameters from 64781 reflections
$c = 9.59160 (18) \text{ \AA}$	$\theta = 3.2\text{--}32.0^\circ$
$\alpha = 74.6778 (12)^\circ$	$\mu = 0.15 \text{ mm}^{-1}$
$\beta = 72.3232 (16)^\circ$	$T = 298 (2) \text{ K}$
$\gamma = 68.447 (2)^\circ$	Plate, colourless
$V = 342.207 (13) \text{ \AA}^3$	$0.20 \times 0.15 \times 0.15 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur S CCD diffractometer	2340 independent reflections
Radiation source: Enhance (Mo) X-ray source	2048 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.017$
Detector resolution: $16.0696 \text{ pixels mm}^{-1}$	$\theta_{\text{max}} = 32.0^\circ$
$T = 298(2) \text{ K}$	$\theta_{\text{min}} = 3.2^\circ$
ω and φ scans	$h = -8 \rightarrow 8$
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2006)	$k = -10 \rightarrow 10$
$T_{\text{min}} = 0.977$, $T_{\text{max}} = 0.985$	$l = -14 \rightarrow 14$
64781 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.044$	All H-atom parameters refined
$wR(F^2) = 0.133$	$w = 1/[\sigma^2(F_o^2) + (0.0846P)^2 + 0.0376P]$
$S = 1.08$	where $P = (F_o^2 + 2F_c^2)/3$
	$(\Delta/\sigma)_{\text{max}} < 0.001$

2340 reflections $\Delta\rho_{\max} = 0.19 \text{ e } \text{\AA}^{-3}$
 133 parameters $\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$
 Primary atom site location: structure-invariant direct methods Extinction correction: none

Special details

Experimental. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	-0.14403 (15)	0.19593 (14)	0.87497 (9)	0.0437 (2)
O2	0.33017 (14)	0.40869 (13)	0.43298 (8)	0.0402 (2)
O3	0.67729 (18)	-0.25757 (17)	0.92057 (11)	0.0575 (3)
O4	0.94015 (16)	-0.17721 (14)	0.70790 (10)	0.0430 (2)
H4	1.045 (5)	-0.276 (4)	0.759 (3)	0.072 (6)*
N1	0.27952 (15)	0.03091 (13)	0.83018 (9)	0.03108 (19)
H1	0.248 (4)	-0.038 (3)	0.918 (2)	0.052 (4)*
C2	0.06502 (18)	0.17428 (15)	0.79307 (10)	0.0302 (2)
N3	0.09988 (15)	0.29328 (13)	0.65310 (8)	0.03059 (19)
H3	-0.050 (4)	0.391 (3)	0.630 (2)	0.054 (5)*
C4	0.32531 (17)	0.28849 (14)	0.55477 (10)	0.0284 (2)
C5	0.54286 (17)	0.13666 (14)	0.60218 (10)	0.0295 (2)
H5	0.689 (3)	0.127 (3)	0.540 (2)	0.042 (4)*
C6	0.51057 (17)	0.01317 (13)	0.73716 (9)	0.02706 (19)
C7	0.72006 (19)	-0.15575 (15)	0.79814 (11)	0.0325 (2)
O5	1.28887 (17)	-0.45822 (16)	0.81521 (11)	0.0523 (3)
H51	1.421 (5)	-0.460 (4)	0.757 (3)	0.080 (7)*
H52	1.313 (5)	-0.528 (4)	0.896 (3)	0.082 (7)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0285 (4)	0.0499 (5)	0.0329 (4)	-0.0054 (3)	-0.0022 (3)	0.0094 (3)
O2	0.0291 (4)	0.0447 (4)	0.0298 (4)	-0.0065 (3)	-0.0079 (3)	0.0154 (3)
O3	0.0390 (5)	0.0612 (6)	0.0449 (5)	-0.0062 (4)	-0.0138 (4)	0.0266 (4)
O4	0.0302 (4)	0.0449 (4)	0.0385 (4)	-0.0003 (3)	-0.0112 (3)	0.0054 (3)
N1	0.0289 (4)	0.0311 (4)	0.0247 (3)	-0.0063 (3)	-0.0080 (3)	0.0067 (3)

supplementary materials

C2	0.0277 (4)	0.0308 (4)	0.0252 (4)	-0.0071 (3)	-0.0065 (3)	0.0037 (3)
N3	0.0245 (4)	0.0319 (4)	0.0258 (3)	-0.0047 (3)	-0.0077 (3)	0.0070 (3)
C4	0.0260 (4)	0.0289 (4)	0.0244 (4)	-0.0064 (3)	-0.0078 (3)	0.0041 (3)
C5	0.0243 (4)	0.0308 (4)	0.0258 (4)	-0.0045 (3)	-0.0072 (3)	0.0029 (3)
C6	0.0268 (4)	0.0251 (4)	0.0257 (4)	-0.0045 (3)	-0.0106 (3)	0.0014 (3)
C7	0.0306 (4)	0.0297 (4)	0.0322 (4)	-0.0049 (3)	-0.0137 (3)	0.0038 (3)
O5	0.0287 (4)	0.0598 (6)	0.0426 (5)	0.0010 (4)	-0.0082 (3)	0.0118 (4)

Geometric parameters (Å, °)

O1—C2	1.2241 (12)	N3—C4	1.3716 (12)
O2—C4	1.2418 (10)	N3—H3	0.94 (2)
O3—C7	1.2056 (13)	C4—C5	1.4387 (12)
O4—C7	1.3040 (13)	C5—C6	1.3525 (12)
O4—H4	0.89 (3)	C5—H5	0.879 (19)
N1—C6	1.3656 (12)	C6—C7	1.5012 (12)
N1—C2	1.3702 (12)	O5—H51	0.81 (3)
N1—H1	0.85 (2)	O5—H52	0.82 (3)
C2—N3	1.3772 (11)		
C7—O4—H4	104.3 (16)	N3—C4—C5	115.74 (8)
C6—N1—C2	122.36 (8)	C6—C5—C4	118.56 (8)
C6—N1—H1	126.4 (14)	C6—C5—H5	124.1 (11)
C2—N1—H1	111.2 (14)	C4—C5—H5	117.3 (11)
O1—C2—N1	123.81 (8)	C5—C6—N1	122.13 (8)
O1—C2—N3	121.35 (8)	C5—C6—C7	124.03 (9)
N1—C2—N3	114.83 (8)	N1—C6—C7	113.84 (8)
C4—N3—C2	126.29 (7)	O3—C7—O4	125.70 (9)
C4—N3—H3	120.3 (12)	O3—C7—C6	120.28 (10)
C2—N3—H3	113.3 (12)	O4—C7—C6	114.02 (8)
O2—C4—N3	119.61 (8)	H51—O5—H52	110 (2)
O2—C4—C5	124.64 (9)		
C6—N1—C2—O1	-178.86 (10)	C4—C5—C6—N1	-1.20 (15)
C6—N1—C2—N3	2.20 (15)	C4—C5—C6—C7	178.02 (9)
O1—C2—N3—C4	177.12 (10)	C2—N1—C6—C5	0.18 (16)
N1—C2—N3—C4	-3.91 (15)	C2—N1—C6—C7	-179.11 (9)
C2—N3—C4—O2	-178.17 (10)	C5—C6—C7—O3	178.85 (12)
C2—N3—C4—C5	2.97 (15)	N1—C6—C7—O3	-1.87 (15)
O2—C4—C5—C6	-179.05 (10)	C5—C6—C7—O4	-1.13 (15)
N3—C4—C5—C6	-0.26 (14)	N1—C6—C7—O4	178.15 (9)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O4—H4 \cdots O5	0.89 (3)	1.65 (3)	2.5231 (11)	166 (2)
N1—H1 \cdots O1 ⁱ	0.85 (2)	2.03 (2)	2.8824 (11)	175.2 (19)
N3—H3 \cdots O2 ⁱⁱ	0.94 (2)	1.87 (2)	2.8112 (11)	174.6 (18)
O5—H51 \cdots O2 ⁱⁱⁱ	0.81 (3)	2.00 (3)	2.7786 (12)	161 (3)
O5—H52 \cdots O3 ^{iv}	0.82 (3)	1.98 (3)	2.7787 (12)	164 (2)

C5—H5 \cdots O4ⁱⁱⁱ 0.879 (19) 2.740 (19) 3.5922 (13) 163.7 (15)
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Fig. 1

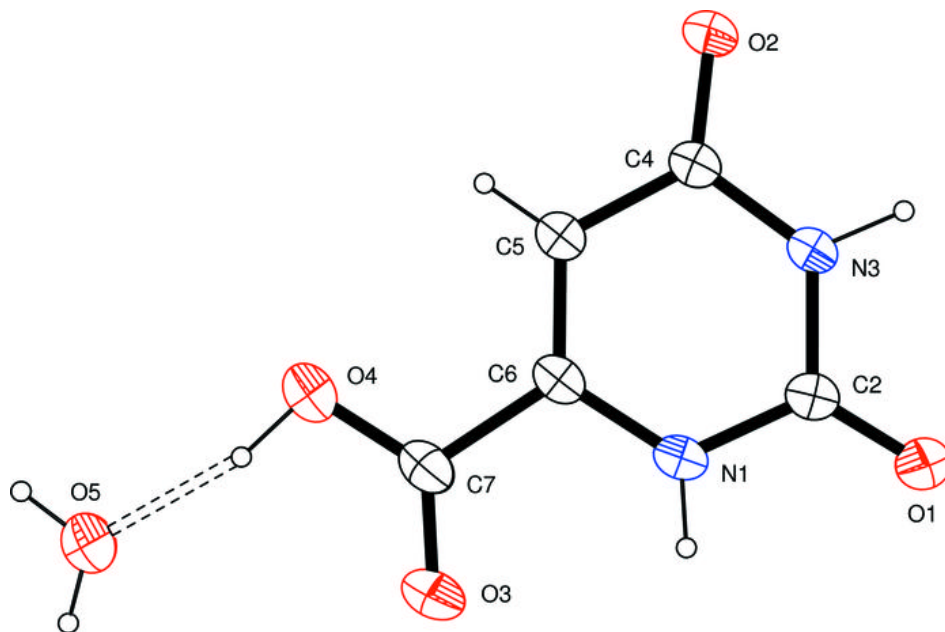


Fig. 2

