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(2*R*,3*S*)-3-Hydroxy-*N*,*N*-dimethylproline monohydrate

Sarah F. Jenkinson,[a] Andrew Cowley,[b] Atsushi Kato,[c] Noriko Kato,[c] Jackie Hollinshead,[d] Robert J. Nash,[d] Kathrine V. Booth[a]* and George W. J. Fleet[a]

[a]Chemistry Research Laboratory, Department of Chemistry, Mansfield Road, University of Oxford, Oxford OX1 3TA, England, [b]Chemistry Research Laboratory, Department of Chemical Crystallography, Mansfield Road, University of Oxford, Oxford OX1 3TA, England, [c]Department of Pharmacy, Toyama University Hospital, University of Toyama, 2630 Sugitani, Toyama 930-0194, Japan, and [d]VASTox Chemical Genomics Limited, Plas Gogerddan, Aberystwyth SY23 3EB, Wales
Correspondence e-mail: victoria.booth@chem.ox.ac.uk

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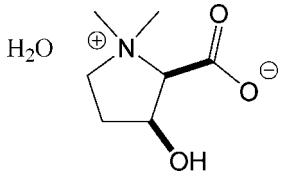
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.002 Å; R factor = 0.033; wR factor = 0.038; data-to-parameter ratio = 11.5.

The absolute stereochemistry of the title compound, $C_7H_{13}NO_3\cdot H_2O$, was firmly established by X-ray crystallography. The crystal structure exists as O—H···O hydrogen-bonded layers of molecules lying perpendicular to the *a* axis.

Related literature

For related literature, see: Cornforth & Henry (1952); Delaveau *et al.* (1973); Sakiyama *et al.* (1964); Nash *et al.* (1986).



Experimental

Crystal data

$C_7H_{13}NO_3\cdot H_2O$
M_r = 177.20
Monoclinic, $P2_1$
a = 6.0647 (2) Å
b = 7.1798 (2) Å
c = 10.1956 (2) Å
β = 109.195 (2)°
V = 419.27 (2) Å^3
Z = 2
Cu $K\alpha$ radiation
μ = 0.97 mm^{-1}
T = 150 K
0.30 × 0.30 × 0.24 mm

Data collection

Oxford Diffraction Gemini area-detector diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2005)
T_{min} = 0.75, T_{max} = 0.79
3114 measured reflections
1452 independent reflections
1407 reflections with $I > 3\sigma(I)$
R_{int} = 0.010

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.039
S = 1.08
1407 reflections
122 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Absolute structure: Flack (1983), 571 Friedel pairs
Flack parameter: 0.08 (18)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1···O2^{i}	0.82 (2)	1.91 (3)	2.712 (2)	168 (3)
O4—H3···O2^{ii}	0.83 (3)	1.95 (3)	2.777 (2)	172 (3)
O4—H2···O1	0.80 (3)	2.10 (3)	2.873 (2)	162 (3)

Symmetry codes: (i) $-x, y+\frac{1}{2}, -z$; (ii) $-x, y+\frac{1}{2}, -z+1$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2473).

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supplementary materials

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(2*R*,3*S*)-3-Hydroxy-*N*,*N*-dimethylproline monohydrate

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Comment

L-*N*,*N*-Dimethylproline (*L*-stachydrine) and the *L*-2*R*,3*S*-3-hydroxy compound have been reported from the plant family *Capparidaceae*. Cornforth & Henry (1952) first reported the *L*-2*R*,3*S* compound from *Capparis tomentosa* and then Delaveau *et al.* (1973) conducted a taxonomic survey suggesting these compounds were ubiquitous in this plant family. The structure of the *L*-2*R*,3*S* form was confirmed by synthesis by Sakiyama *et al.* (1964). This is the first report of the *L*-2*R,3*S form in the genus Baphia (*Leguminosae*).

Refinement of the Flack enantiopole parameter gave a value of 0.08 (18), which for an *enantio*-pure material unambiguously shows the crystal to consist of the 2*R* enantiomer (*i.e* a derivative of a D amino acid).

The crystal structure of the title compound (Fig. 1) exists as hydrogen bonded layers of molecules lying perpendicular to the *a* axis (Fig. 2). One of the hydrogen bonds (involving atom O2) is bifurcated.

Experimental

2.9 g of 2*R, 3*S 3-hydroxy-*N, N*-dimethylproline was obtained from the 50% EtOH extract of 2 kg of leaves of the African medicinal tree *Baphia confusum* (Fabaceae). The compound was isolated by binding it to Amberlite IR-120 (H^+ form, 2*L*) and eluting with 2*M* NH_4OH. The eluate was concentrated to give a brown oil (30.8 g). This oil was applied to an Amberlite CG-50 column (3.6 *x* 48 cm, NH_4^+ form) and eluted with distilled water. The concentrated eluate was chromatographed over a Dowex 1-X8 column (2.2 *x* 42 cm, OH^-, form) with water. The eluate was concentrated to give a colorless oil (3.64 g). This oil was further chromatographed on a Amberlite CG-50 column (3.6 *x* 48 cm, NH_4^+ form) with water as an eluant to give 2*R, 3*S 3-hydroxy-*N,N*-dimethylproline·The compound was crystallized from 95% aq. EtOH by layering with acetone. The purification was followed using GC—MS of the trimethylsilyl-derivative (Nash *et al.*, 1986) scanning from 100–400 daltons which gave distinctive fragmentation with major ions at 196 (20%), 226 (100%), 270 (20%) and 285 (80%) amu. m.p. crystals decomposed above 495 K, without melting; $[\alpha]_D^{18}$ +17.2 (*c*, 0.21 in water).

Refinement

The use of Cu—Kα radiation enabled the absolute configuration to be determined from the anomalous differences of the Friedel Pairs.

The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98,*O*—H = 0.82 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

Figures

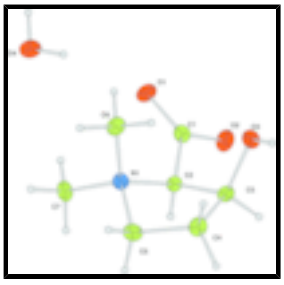

Fig. 1. The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

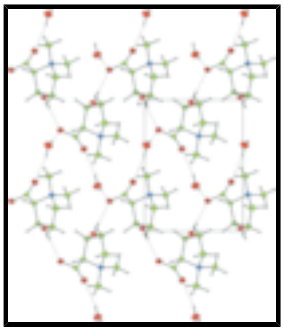

Fig. 2. Packing diagram showing the hydrogen bonded (dashed lines) layers lying perpendicular to the *a*-axis and the hydrogen bonds between each molecule and a molecule of water.

(2*R*,3*S*)-3-Hydroxy-*N*,*N*-dimethylproline monohydrate

Crystal data

$C_7H_{13}N_1O_3 \cdot H_2O$	$F_{000} = 192$
$M_r = 177.20$	$D_x = 1.404$ Mg m^{-3}
Monoclinic, $P2_1$	Cu $K\alpha$ radiation $\lambda = 1.5418$ Å
Hall symbol: P 2yb	Cell parameters from 2601 reflections
$a = 6.0647$ (2) Å	$\theta = 5$–70°
$b = 7.1798$ (2) Å	$\mu = 0.97$ mm^{-1}
$c = 10.1956$ (2) Å	$T = 150$ K
$\beta = 109.195$ (2)°	Fragment, colourless
$V = 419.27$ (2) Å^3	0.30 × 0.30 × 0.24 mm
$Z = 2$	

Data collection

Oxford Diffraction Gemini area-detector diffractometer	1407 reflections with $I > 3\sigma(I)$
Monochromator: graphite	$R_{int} = 0.010$
$T = 150$ K	$\theta_{max} = 71.8^\circ$
ω scans	$\theta_{min} = 4.6^\circ$
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2005)	$h = -7 \rightarrow 7$
$T_{min} = 0.75$, $T_{max} = 0.79$	$k = -8 \rightarrow 8$
3114 measured reflections	$l = -12 \rightarrow 12$

1452 independent reflections

Refinement

Refinement on *F*	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.033$	Method, part 1, Chebychev polynomial [*P*rince (1982). Mathematical Techniques in Crystallography and Materials Science. Ne*w* York: Springer-Verlag; Watkin (1994). Acta Cryst. A50, 411–437] [*w*eight] = $1.0/[A_0*T_0(x) + A_1*T_1(x) \cdots + A_{n-1}]*T_{n-1}(x)$ where A_i are the Chebychev coefficients listed below and x = *F* /*F*max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 13.0 -4.75 9.02
$wR(F^2) = 0.039$	$(\Delta/\sigma)_{max} = 0.004$
S = 1.08	$\Delta\rho_{max} = 0.35$ e Å^{-3}
1407 reflections	$\Delta\rho_{min} = -0.29$ e Å^{-3}
122 parameters	Extinction correction: None
1 restraint	Absolute structure: Flack (1983), 571 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.08 (18)

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.1524 (3)	0.2948 (2)	0.27919 (14)	0.0152
C2	0.3289 (2)	0.3724 (2)	0.21421 (13)	0.0140
C3	0.2330 (2)	0.4103 (2)	0.05749 (15)	0.0152
C4	0.4060 (3)	0.5546 (2)	0.03266 (15)	0.0187
C5	0.5849 (3)	0.5926 (2)	0.17550 (16)	0.0188
N1	0.4544 (2)	0.5514 (2)	0.27595 (12)	0.0151
O1	0.11267 (19)	0.38049 (18)	0.37433 (11)	0.0209
O2	0.0669 (2)	0.14086 (17)	0.22910 (11)	0.0212
O3	0.00020 (18)	0.47790 (18)	0.02103 (11)	0.0184
C6	0.2944 (3)	0.7127 (2)	0.27524 (16)	0.0188
C7	0.6228 (3)	0.5226 (2)	0.41945 (15)	0.0203
O4	0.2618 (2)	0.5178 (2)	0.65461 (14)	0.0289
H1	−0.040 (4)	0.524 (3)	−0.056 (2)	0.019 (5)*
H2	0.197 (5)	0.497 (4)	0.574 (3)	0.043 (7)*
H3	0.153 (5)	0.553 (4)	0.682 (2)	0.030 (5)*
H21	0.4398	0.2648	0.2367	0.0168*
H31	0.2230	0.2974	−0.0016	0.0187*
H41	0.3220	0.6718	−0.0078	0.0229*
H42	0.4845	0.5024	−0.0315	0.0229*
H51	0.6375	0.7253	0.1834	0.0235*
H52	0.7233	0.5087	0.1931	0.0235*
H61	0.3898	0.8245	0.3173	0.0228*

H62	0.1911	0.6792	0.3305	0.0228*
H63	0.1963	0.7414	0.1775	0.0228*
H71	0.7012	0.6433	0.4561	0.0233*
H72	0.5366	0.4766	0.4815	0.0233*
H73	0.7429	0.4287	0.4166	0.0233*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0156 (6)	0.0168 (6)	0.0121 (6)	0.0012 (5)	0.0031 (5)	0.0039 (5)
C2	0.0141 (6)	0.0141 (6)	0.0140 (7)	0.0000 (5)	0.0048 (5)	−0.0012 (5)
C3	0.0168 (6)	0.0163 (6)	0.0137 (6)	−0.0002 (5)	0.0068 (5)	0.0000 (5)
C4	0.0210 (7)	0.0204 (7)	0.0159 (7)	−0.0030 (6)	0.0076 (6)	0.0010 (5)
C5	0.0169 (6)	0.0231 (8)	0.0188 (7)	−0.0026 (5)	0.0093 (6)	0.0020 (6)
N1	0.0151 (5)	0.0169 (6)	0.0133 (6)	−0.0006 (4)	0.0047 (5)	0.0006 (4)
O1	0.0249 (5)	0.0226 (5)	0.0189 (5)	−0.0012 (4)	0.0124 (4)	−0.0024 (4)
O2	0.0270 (6)	0.0215 (5)	0.0170 (5)	−0.0080 (5)	0.0096 (4)	−0.0020 (4)
O3	0.0164 (5)	0.0239 (5)	0.0134 (5)	0.0015 (4)	0.0029 (4)	0.0037 (4)
C6	0.0219 (7)	0.0149 (6)	0.0202 (7)	0.0007 (6)	0.0075 (6)	−0.0018 (5)
C7	0.0174 (7)	0.0266 (8)	0.0142 (7)	−0.0034 (6)	0.0015 (6)	−0.0007 (6)
O4	0.0226 (5)	0.0382 (8)	0.0255 (7)	0.0088 (5)	0.0074 (5)	−0.0059 (5)

Geometric parameters (Å, °)

C1—C2	1.5366 (18)	C5—H51	1.000
C1—O1	1.237 (2)	C5—H52	1.000
C1—O2	1.256 (2)	N1—C6	1.5098 (19)
C2—C3	1.5346 (19)	N1—C7	1.4979 (18)
C2—N1	1.5207 (19)	O3—H1	0.82 (2)
C2—H21	1.000	C6—H61	1.000
C3—C4	1.553 (2)	C6—H62	1.000
C3—O3	1.4217 (18)	C6—H63	1.000
C3—H31	1.000	C7—H71	1.000
C4—C5	1.528 (2)	C7—H72	1.000
C4—H41	1.000	C7—H73	1.000
C4—H42	1.000	O4—H2	0.80 (3)
C5—N1	1.5152 (18)	O4—H3	0.83 (3)
C2—C1—O1	120.05 (13)	C4—C5—H52	110.8
C2—C1—O2	113.37 (12)	N1—C5—H52	110.8
O1—C1—O2	126.54 (14)	H51—C5—H52	109.5
C1—C2—C3	115.71 (11)	C2—N1—C5	100.76 (11)
C1—C2—N1	116.91 (11)	C2—N1—C6	114.40 (11)
C3—C2—N1	104.34 (11)	C5—N1—C6	108.96 (12)
C1—C2—H21	97.6	C2—N1—C7	112.05 (11)
C3—C2—H21	111.9	C5—N1—C7	110.32 (11)
N1—C2—H21	110.5	C6—N1—C7	109.94 (12)
C2—C3—C4	104.06 (12)	C3—O3—H1	110.3 (14)
C2—C3—O3	109.69 (11)	N1—C6—H61	109.5

C4—C3—O3	113.31 (12)	N1—C6—H62	109.5
C2—C3—H31	114.2	H61—C6—H62	109.5
C4—C3—H31	110.7	N1—C6—H63	109.5
O3—C3—H31	105.1	H61—C6—H63	109.5
C3—C4—C5	105.65 (12)	H62—C6—H63	109.5
C3—C4—H41	110.4	N1—C7—H71	109.5
C5—C4—H41	110.4	N1—C7—H72	109.5
C3—C4—H42	110.4	H71—C7—H72	109.5
C5—C4—H42	110.4	N1—C7—H73	109.5
H41—C4—H42	109.5	H71—C7—H73	109.5
C4—C5—N1	104.15 (11)	H72—C7—H73	109.5
C4—C5—H51	110.8	H2—O4—H3	103 (3)
N1—C5—H51	110.8		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H1···O2^{i}	0.82 (2)	1.91 (3)	2.712 (2)	168 (3)
O4—H3···O2^{ii}	0.83 (3)	1.95 (3)	2.777 (2)	172 (3)
O4—H2···O1	0.80 (3)	2.10 (3)	2.873 (2)	162 (3)

Symmetry codes: (i) −*x*, *y*+1/2, −*z*; (ii) −*x*, *y*+1/2, −*z*+1.

Fig. 1

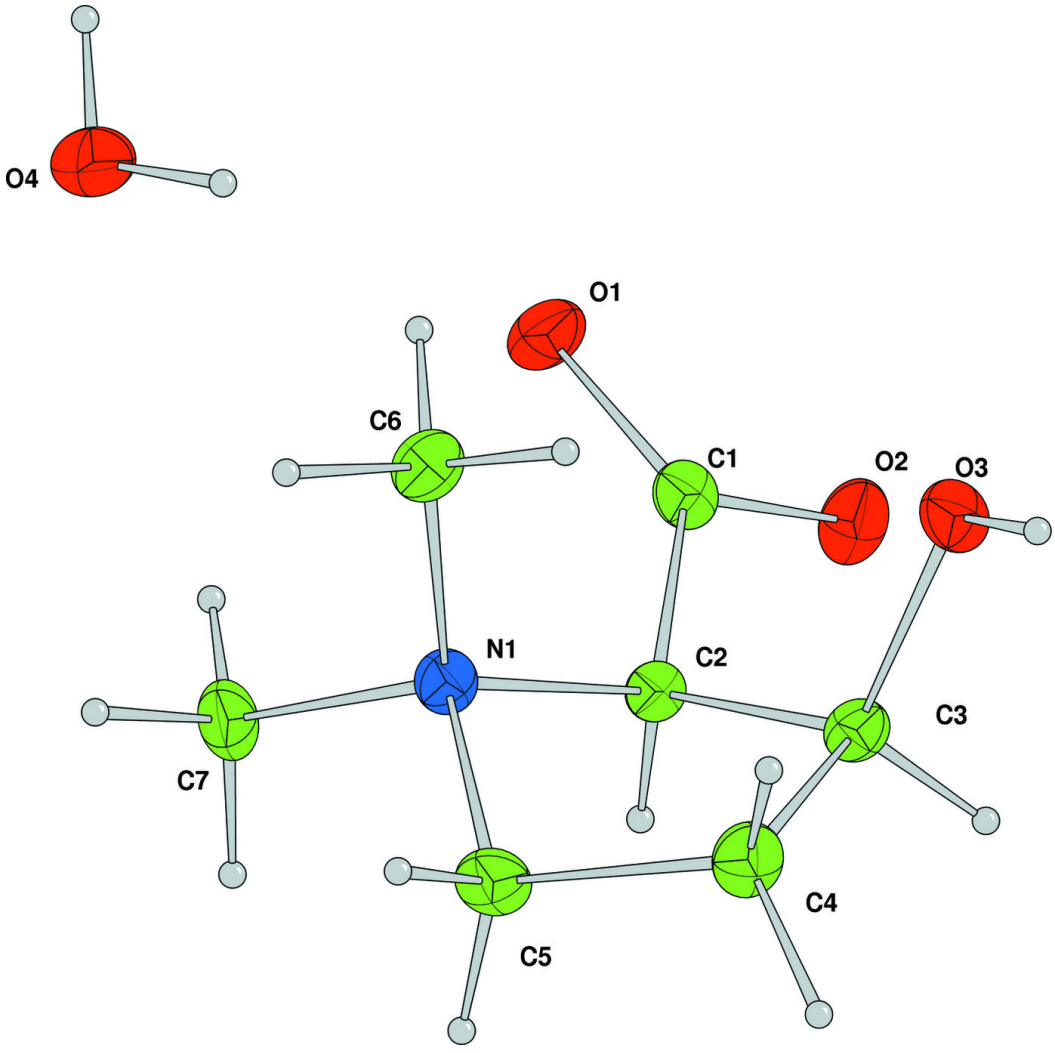

Fig. 2