Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Matrinium picrolonate 0.28-hydrate

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Key indicators

Single-crystal X-ray study
T = 273 K
Mean σ(C–C) = 0.006 Å
Disorder in main residue
R factor = 0.051
wR factor = 0.122
Data-to-parameter ratio = 6.4

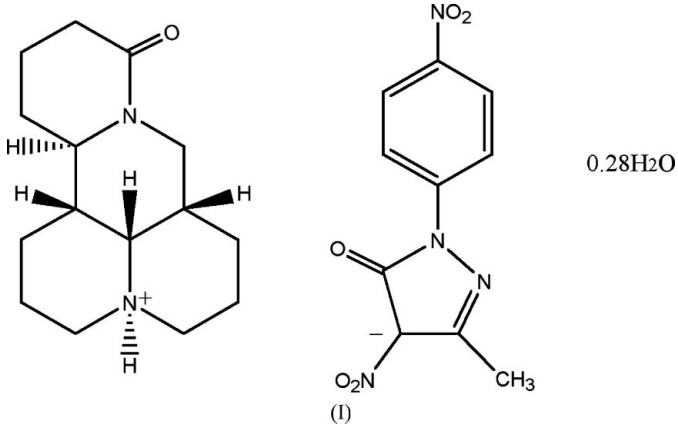
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 5 July 2006
Accepted 18 August 2006

The title compound [systematic name: (7a*S**,13a*R**,13b*R**,13c*S**)-10-oxo-dodecahydro-1*H*,5*H*,8*H*-dipyrido[2,1-*f*:3′,2′,1′-*ij*][1,6]naphthyridinium 3-methyl-4-nitro-1-(4-nitrophenyl)-5-oxo-2-pyrazolinate 0.28-hydrate], $C_{15}H_{25}N_2O^+\cdot C_{10}H_7N_4O_5^-\cdot 0.28H_2O$, consists of one matrinium cation [matrine is (7a*S*,13a*R*,13b*R*,13c*S*)-dodecahydro-1*H*,5*H*,8*H*-dipyrido[2,1-*f*:3′,2′,1′-*ij*][1,6]naphthyridin-10-one], one picrolonate anion and 0.28 water molecules, held together by N—H···O and O—H···O hydrogen bonds. Disordered C atoms in the ring bearing the carbonyl group of the matrinium cation cause the ring to appear in half-chair and half-boat conformations.

Comment

Matrine is an active key component isolated from the Chinese herb 'Ku Shen' (*Radix Sophorae Fiavescentis*). It shows various bio-activities, such as anti-inflammatory (Tan *et al.*, 1985), anti-arrhythmic (Zhang *et al.*, 1990), antiproligerous in cells (Zhang *et al.*, 2001), protective properties for lipopolysacchride-reduced liver injury (Lin *et al.*, 1997) *etc*. In our laboratory, matrinium tetracholoroferrate(III) has been synthesized and characterized previously (Jin *et al.*, 2005). Recently, in a continuation of this work, the title compound, (I), was prepared.



(I)

As shown in Fig. 1, compound (I) consists of one matrinium cation, one picrolonate anion and 0.28 water molecules. In (I), matrine is protonated at N1 and is linked to the picrolonate anion *via* an N1—H1···O4 hydrogen bond (Table 1). The water molecule acts as hydrogen-bond acceptor for matrinium cations and picrolonate anions in C8—H8*B*···O7^{i}, C19—H19···O7^{iii} and C23—H23···O7 hydrogen bonds (symmetry codes in Table 1), and may act as a hydrogen-bond donor in a

putative O7—H7*WA*···O1 hydrogen bond. Two disordered C atoms are observed in ring *D* (containing C15) of the matrinium cation, causing the ring to appear in half-chair (atoms C12 and C13) and half-boat conformations (atoms C12′ and C13′). The geometry of the picrolonate anion is similar to that observed in oxythiaminium dipicrolonate dihydrate (Hu *et al.*, 1999).

Experimental

Matrine and 3-methyl-4-nitro-1-(*p*-nitrophenyl)-2-pyrazolin-5-one (picrolonic acid) in a molar ratio of 1:1 were mixed and dissolved in sufficient water by heating to 365 K, giving a clear solution. Crystals of (I) were formed by gradual evaporation of excess water over a period of one week at 293 K. Analysis found (%): C 57.98, H 6.37, N 16.19; calculated (%): C 58.01, H 6.34, N 16.23.

Crystal data

$C_{15}H_{25}N_2O^+\cdot C_{10}H_7N_4O_5^-\cdot 0.28H_2O$
M_r = 517.61
Monoclinic, $P2_1$
a = 8.3939 (7) Å
b = 14.9227 (13) Å
c = 10.0939 (9) Å
β = 92.166 (2)°
V = 1263.46 (19) Å^3
Z = 2
D_x = 1.360 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 273 (2) K
Block, colourless
0.37 × 0.35 × 0.32 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.955, T_{max} = 0.961
6696 measured reflections
2353 independent reflections
2173 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 25.2°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.122
S = 1.13
2353 reflections
368 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 0.2261P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
07—H7*WA*···O1	0.83 (2)	1.95 (2)	2.832 (5)	171 (4)
N1—H1···O4	0.89 (4)	1.95 (4)	2.832 (5)	171 (4)
C2—H2*B*···O5	0.97	2.42	3.209 (6)	139
C8—H8*B*···O7^{i}	0.97	2.47	3.088 (6)	121
C10—H10*A*···O5	0.97	2.55	3.317 (7)	136
C11—H11···O4	0.98	2.52	3.362 (5)	144
C13—H13*A*···N4^{ii}	0.97	2.50	3.404 (6)	156
C17—H17*B*···O4	0.97	2.56	3.401 (5)	145
C19—H19···O7^{iii}	0.93	2.35	3.237 (6)	158
C23—H23···O7	0.93	2.54	3.207 (5)	129

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

Two disordered C atoms in ring *D* of the matrinium cation were split into approximately equal components, with occupancies of 0.52 (2) for C12′ and C13′ and of 0.48 (2) for C12 and C13. Atom O7

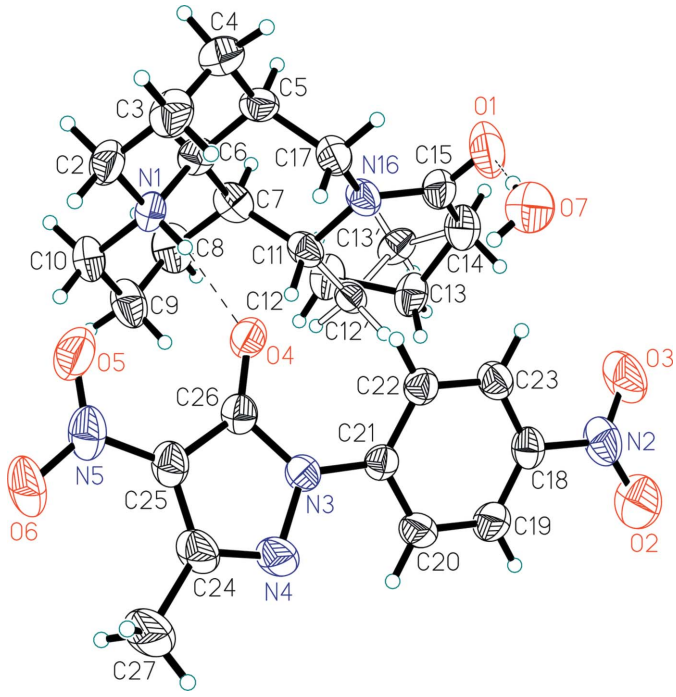


Figure 1
View of the asymmetric unit of (I) with atom labels, showing 40% probability displacement ellipsoids. The dashed line indicates a hydrogen bond.

was located in a difference electron-density map and refined isotropically; the occupancy, 0.28 (2), was established in the refinement, and the result is consistent with CHN elemental analysis. The H atom of NH was located in a difference electron-density map and was freely refined. The water H atoms were located tentatively in difference electron-density maps and were refined with the O—H and H···H distances restrained to 0.83 (2) and 1.39 (1) Å, respectively. Other H atoms were placed in calculated positions and allowed to ride on their parent atoms at distances of 0.93 (phenyl), 0.96 (methyl), 0.97 (methylene) and 0.98 Å (methine), with U_{iso}(H) values 1.2 times U_{eq} of the parent atoms. As the compound contains no heavy atoms, 2176 Friedel pairs were merged before the final refinement.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Bruker (2000). *SMART* (Version 5.618), *SADABS* (Version 2.05), *SAINT* (Version 6.02a) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Hu, N. H., Tokuno, T. & Aoki, K. (1999). *Inorg. Chim. Acta*, **295**, 71–83.

Jin, Z.-M., Li, Z.-G., Li, L., Li, M.-C. & Hu, M.-L. (2005). *Acta Cryst.* E**61**, m2466–m2468.

Lin, W., Zhang, J. P., Hu, Z. L. & Qian, D. H. (1997). *Acta Pharm. Sin.* **32**, 93–96.

Tan, H. R., Zhang, B. & Zhong, H. (1985). *J. Integr. Trad. Chin. West. Med.* **5**, 108–110.

Zhang, B. H., Wang, N. S., Li, X. J., Kong, X. J. & Cai, Y. L. (1990). *Acta Pharm. Sin.* **11**, 253–257.

Zhang, L. P., Jiang, J. K., Tam, J. W., Zhang, O. Y., Liu, X. S., Xu, X. R., Liu, B. Z. & He, Y. (2001). *J. Leuk. Res.* **25**, 793–800.