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(±)-(2,3,4,4a,5,6,7,8-Octahydro-2-oxonaphthalen-1-yl)acetic acid: hydrogen-bonding pattern of the monohydrate of an unsaturated bicyclic γ-keto acid

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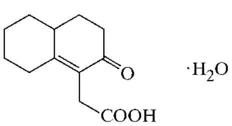
In the title compound, $C_{12}H_{16}O_3 \cdot H_2O$, the water of hydration accepts a hydrogen bond from the carboxyl group and donates hydrogen bonds to the carboxyl carbonyl and the ketone groups of two different neighbors, yielding a complex three-dimensional hydrogen-bonding array. There are two independent hydrated molecules in the asymmetric unit ($Z' = 2$) related by a pseudo-translation.

Comment

Five hydrogen-bonding modes are known for keto carboxylic acids, whose crystal structures are the basis of our continuing study. Besides the common dimeric and rare chain arrangements typical of simpler acids, the five modes also include two intermolecular acid-to-ketone patterns and an intramolecular hydrogen-bonding mode. Several examples of hydrated arrangements also exist, and we report here the structure and hydrogen-bonding pattern of (±)-(2,3,4,4a,5,6,7,8-octahydro-2-oxonaphthalen-1-yl)acetic acid monohydrate, (I).



(I)

The asymmetric unit of (I) contains two hydrated molecules, I and I′, which are nearly identical. Fig. 1 shows one of these molecules, half of the asymmetric unit, with the atom-numbering scheme. The molecule has little conformational flexibility and the only available rotations involve the bonds to atom C9 and the carboxyl group. The former is turned so that the C10—C9—C1—C8a torsion angle is −91.8 (3)° for molecule I and −90.3 (3)° for molecule I′, and the carboxyl group is turned so that its carbonyl is aimed back 'under' the conjugated ketone system, with O2—C10—C9—C1 torsion angles of 13.2 (4) and 7.6 (4)° for molecules I and I′, respectively. The resulting dihedral angle between the ketone and carboxyl planes is 88.0 (2)° for molecule I and 88.8 (2)° for molecule I′. Each carboxyl group donates a hydrogen bond to a water of hydration, which, in turn, donates hydrogen bonds

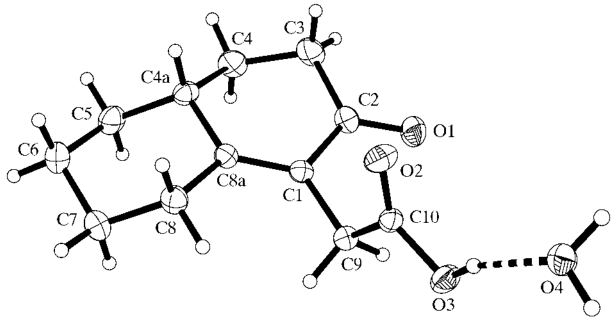


Figure 1
One-half of the asymmetric unit of (I), showing only molecule I, with the atom numbering; molecule I′ is essentially identical and related by a non-crystallographic translation (see *Comment*). The water of hydration is shown, arbitrarily, in its hydrogen-bonding relationship to the carboxyl OH group. Displacement ellipsoids are shown at the 20% probability level.

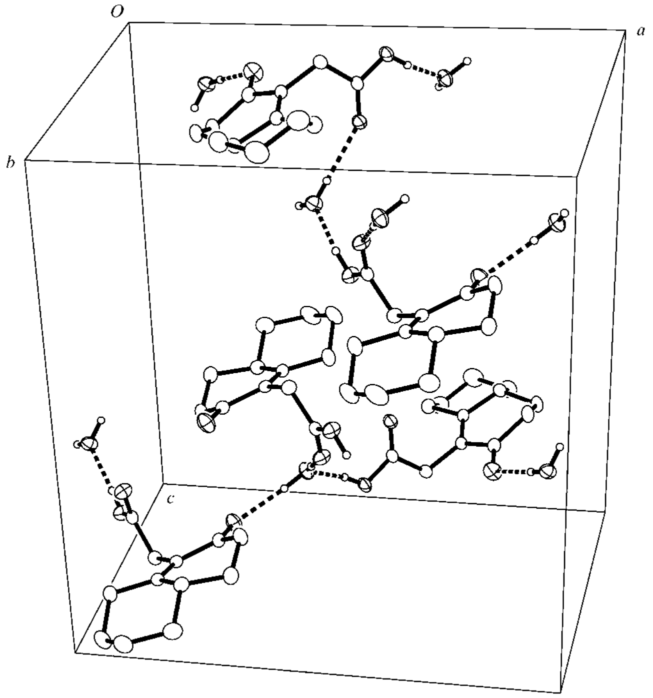


Figure 2
A partial packing diagram, showing the complex three-dimensional hydrogen-bonding arrangement. Illustrated are a water molecule with its three molecular connections (below), and two molecules (above), each of which has three water connections. The molecule at the lower left (molecule I) and that connected to the water at the upper right (molecule I′) constitute one asymmetric unit. All carbon-bound H atoms have been omitted for clarity, but some peripheral waters are shown. Displacement ellipsoids are shown at the 20% probability level.

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to two different C═O groups in separate neighboring molecules (see below); Fig. 1 shows this water molecule, arbitrarily, in its hydrogen-bonding relationship to the carboxyl OH group.

The two nearly identical halves of the asymmetric unit have a non-crystallographic translational relationship. They are found at positions which differ by essentially half a cell each in *a* and *c*, but whose difference in *b* is non-crystallographic, amounting to between one-seventh and one-eighth of the *b* cell dimension [$\Delta x_{\rm ave}$ = 0.5010 (3), $\Delta y_{\rm ave}$ = 0.1370 (4) and $\Delta z_{\rm ave}$ = 0.5009 (2)]. No additional symmetry beyond $P2_1/c$ ($Z = 8$) could be found.

Averaging of the C—O bond lengths and C—C—O angles by disorder is common in carboxyl dimers (Leiserowitz, 1976), but is not seen in hydrated hydrogen-bonding arrangements, whose geometries exclude the averaging mechanisms. Here, these C—O bond lengths (Table 1) are 1.213 (3)/1.322 (3) Å for molecule I and 1.211 (3)/1.320 (3) Å for molecule I′, with angles of 125.0 (3)/112.0 (2) and 125.0 (3)/111.3 (2)° for molecules I and I′, respectively. Our own survey of 56 keto acid structures which are not acid dimers gives average values of 1.200 (10)/1.32 (2) Å and 124.5 (14)/112.7 (17)° for these lengths and angles, in accord with typical values of 1.21/1.31 Å and 123/112° cited for highly ordered dimeric carboxyls (Borthwick, 1980).

Fig. 2 illustrates the packing arrangement with its hydrogen bonding (Table 2), which adheres to a recurrent pattern among hydrated keto acids (Thompson & Lalancette, 2001). In virtually identical arrangements for each half of the asymmetric unit, the carboxyl donates its hydrogen bond to a water molecule, which, in turn, donates hydrogen bonds to the carboxyl carbonyl group in a glide-related molecule and a ketone group in a molecule of opposite type (I *versus* I′). Thus, each water molecule participates in hydrogen bonds to three separate molecules, while each molecule participates in hydrogen bonds to three separate water molecules, producing a complex three-dimensional network.

We characterize the geometry of hydrogen bonding to carbonyls using a combination of the H···O═C angle and the H···O═C—*X* torsion angle. These describe the approach of the H atom to the O atom in terms of its deviation from, respectively, C═O axiality (ideal = 120°) and planarity with the carbonyl (ideal = 0°). Here, these criteria are applicable to two of the three hydrogen bonds present. Approach angles for the water-to-acid hydrogen bond are 138.0 (10) and 2.6 (15)° for molecule I, and 138.0 (10) and 9.0 (15)° for molecule I′. The analogous values for the water-to-ketone hydrogen bond are 123.9 (10) and −5.9 (12)° for molecule I, and 122.3 (10) and −3.5 (12)° for molecule I′. No C—H···O close contacts were found within the 2.7 Å range we usually employ for such non-bonded packing interactions (Steiner, 1997).

The solid-state (KBr) IR spectrum of (I) displays C═O absorptions at 1709 and 1637 cm^{-1} for hydrogen-bonded carboxyl and ketone groups, respectively, with an alkene peak at 1611 cm^{-1}. In $CHCl_3$ solution, bands appear at 1711, 1660 and 1629 cm^{-1}; a band at 1749 cm^{-1} is presumably due to monomeric acid.

Experimental

The title compound has not been reported previously. The pyrrolidine enamine of cyclohexanone was treated with methyl vinyl ketone to generate the expected mixture of octalone enamines, which was isolated and purified by distillation (Stork *et al.*, 1963; House *et al.*, 1965). This was alkylated with ethyl bromoacetate, and the resulting product was isolated by distillation and saponified. Material suitable for X-ray analysis (m.p. *ca* 368 K, with loss of water) was obtained from cyclohexane/benzene or cyclohexane/ethyl acetate. Attempts to obtain usable crystals of the anhydrous form were unsuccessful.

Crystal data

$C_{12}H_{16}O_3 \cdot H_2O$
$M_r = 226.26$
Monoclinic, $P2_1/c$
$a = 15.153$ (6) Å
$b = 9.386$ (3) Å
$c = 17.122$ (6) Å
$\beta = 93.629$ (14)°
$V = 2430.2$ (15) Å^3
$Z = 8$
$D_x = 1.237$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 37 reflections
$\theta = 2.0$–10.0°
$\mu = 0.09$ mm^{-1}
$T = 293$ (2) K
Pyramid frustum, colorless
0.44 × 0.30 × 0.24 mm

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1997)
$T_{\rm min} = 0.94$, $T_{\rm max} = 0.96$
5434 measured reflections
4273 independent reflections
2276 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\rm max} = 25.0°$
$h = -18 \rightarrow 1$
$k = -1 \rightarrow 11$
$l = -20 \rightarrow 20$
3 standard reflections every 97 reflections intensity variation: <1.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.140$
$S = 1.01$
4273 reflections
308 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 0.7730P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL*97 in *SHELXTL*
Extinction coefficient: 0.0011 (3)

Table 1
Selected geometric parameters (Å, °).

O2—C10	1.213 (3)	O2′—C10′	1.211 (3)
O3—C10	1.322 (3)	O3′—C10′	1.320 (3)
O2—C10—C9	125.0 (3)	O2′—C10′—C9′	125.0 (3)
O3—C10—C9	112.0 (2)	O3′—C10′—C9′	111.3 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O4	0.80 (3)	1.86 (3)	2.637 (3)	165 (4)
O3′—H3′···O4′	0.89 (3)	1.77 (3)	2.644 (3)	169 (3)
O4—H4*A*···O1′$^{\rm i}$	0.86 (3)	1.96 (3)	2.819 (3)	178 (3)
O4′—H4′*A*···O1″$^{\rm ii}$	0.89 (3)	1.93 (3)	2.825 (3)	175 (3)
O4—H4*B*···O2′$^{\rm iii}$	0.86 (3)	2.02 (3)	2.875 (3)	174 (3)
O4′—H4′*B*···O2″$^{\rm iv}$	0.81 (3)	2.11 (3)	2.917 (3)	177 (3)

Symmetry codes: (i) $x-1, \frac{5}{2}-y, z-\frac{1}{2}$; (ii) $x, \frac{5}{2}-y, \frac{1}{2}+z$; (iii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$.

All the H atoms of molecules I and I′ were found in electron-density difference maps but were placed in calculated positions (with C—H distances of 0.98 Å for the methine and 0.97 Å for the methylene H atoms) and allowed to refine as riding models on their respective C atoms. The isotropic displacement parameters were fixed at 120% of the equivalent isotropic displacement parameters of their respective C atoms. The positional parameters of the carboxyl H atom and the water H atoms of molecules I and I′ were allowed to refine, but their displacement parameters were fixed at 0.08 Å^2.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 in *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 in *SHELXTL*; molecular graphics: *SHELXP*97 in *SHELXTL*; software used to prepare material for publication: *SHELXL*97 in *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1380). Services for accessing these data are described at the back of the journal.

References

Borthwick, P. W. (1980). *Acta Cryst.* B**36**, 628–632.

House, H. O., Trost, B. M., Magin, R. W., Carlson, R. G., Franck, R. W. & Rasmusson, G. H. (1965). *J. Org. Chem.* **30**, 2513–2519.

Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.

Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *XSCANS*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Steiner, T. (1997). *Chem. Commun.* pp. 727–734.

Stork, G., Brizzolara, A., Landesman, H., Szmuszkovicz, J. & Terrell, R. (1963). *J. Am. Chem. Soc.* **85**, 207–222.

Thompson, H. W. & Lalancette, R. A. (2001). *Acta Cryst.* C**57**, 841–843.