Table 2. *Hydrogen-bonding and C—H···O contact geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O1^{i}	0.89 (4)	1.83 (4)	2.711 (3)	170 (3)
C8—H8*B*···O2^{ii}	0.96	2.68	3.64	175
C3—H3*A*···O3^{iii}	0.98	2.69	3.52	143

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

All H atoms were found in electron-density difference maps but were replaced in calculated positions and allowed to refine as riding models, except for the hydroxyl H3 atom whose coordinates and isotropic displacement parameter were allowed to refine individually. Isotropic displacement parameters for the methine, methylene and each of the three methyl-H-atom sets were refined as individual groups, yielding values of 0.064 (5), 0.081 (6), 0.083 (5), 0.097 (6) and 0.129 (9) Å^2, respectively.

Data collection: *XSCANS* (Siemens, 1996). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1053). Services for accessing these data are described at the back of the journal.

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(+)-3-Oxoglycyrrhetinic acid: catemeric hydrogen bonding in a non-racemic triterpenoid diketo acid

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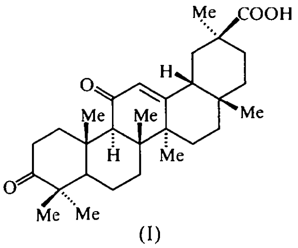
Abstract

The crystal structure of the title compound, (+)-10,13-dioxo-2α,4aβ,6aα,6bβ,9,9,12aβ-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8aα,9,10,11,12,12a,12bα,13,14bβ-icosahydropicene-2β-carboxylic acid, $C_{30}H_{44}O_4$, involves carboxyl-to-ketone hydrogen-bonding catemers. Distorted hydrogen bonds progress from the carboxyl H atom of one molecule to the remote-ring ketone O atom of a screw-related neighbor [O···O = 2.975 (5) Å], yielding helical hydrogen-bonding chains which proceed in the *b* direction. Two C—H···O close contacts were found, connecting the unsaturated ketone (2.71 Å) and the acid carbonyl (2.55 Å) to separate screw-related neighbors.

Comment

The carbonyl basicities of carboxylic acids and ketones are sufficiently similar that the two may compete as hydrogen-bond acceptors. As a result, keto acids display several solid-state hydrogen-bonding modes beyond those seen in functionally unelaborated acids and occupy a cusp of behavioral territory where these patterns may be markedly changed by minor structural differences. Our continuing interest in the crystallography of keto acids lies in mapping the molecular characteristics that control the five known hydrogen-bonding modes. The most common of these is acid dimerization without ketone involvement (Lalancette *et al.*, 1996), but carboxyl-to-ketone chains (catemers) constitute a sizable minority of cases (Brunskill *et al.*, 1997). The remaining types, *i.e.* intramolecular hydrogen bonds (Thompson *et al.*, 1996), acid-to-acid catemers (Lalancette *et al.*, 1998) and carboxyl-to-ketone dimers (Kosela *et al.*, 1995), are all comparatively rare. Several cases also exist of hydrates with more complex hydrogen-bonding patterns (Lalancette *et al.*, 1990, 1997, 1998).

As we have suggested previously (Brunskill *et al.*, 1999), conformational restrictions and the presence of a single enantiomer both appear to discourage carboxyl dimerization, while the presence of multiple ketone receptors for the hydrogen bond should favor carboxyl-to-ketone hydrogen-bonding patterns (Brunskill *et al.*, 1999). The title diketo acid, (I), is a pentacyclic ζ,λ-diketo acid, present as a single enantiomer, and we report here that it adopts the carboxyl-to-ketone catemeric hydrogen-bonding mode in the solid state. Compound (I) is a picenoid triterpene derived from the aglycone portion of glycyrrhizic acid, isolated from licorice (*Glycyrrhiza glabra* L.)



(I)

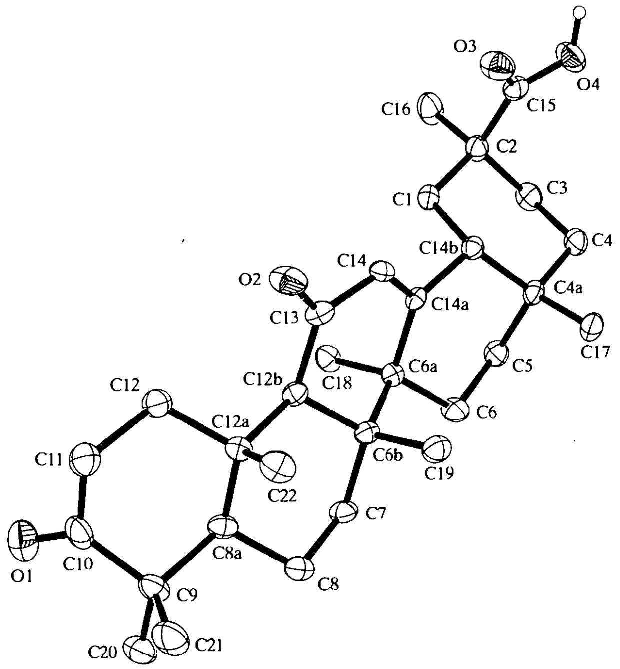


Fig. 1. The asymmetric unit of (I) with the atom-numbering scheme. For clarity, all carbon-bound H atoms have been omitted. Displacement ellipsoids are set at the 30% probability level.

The asymmetric unit for (I) with the atom-numbering scheme is shown in Fig. 1. All the rings adopt chair conformations, except the enone ring, which is flattened to a half-chair. The sole *cis* ring juncture, between the carboxyl-bearing ring and its neighbor, confers little skeletal flexibility because two of the remaining ring junctures are *trans* and the third involves an alkene. The chair conformation adopted by the carboxyl ring places its methyl groups equatorial and its carboxyl axial. The carboxyl group is turned as shown in Fig. 1, so that the C1—C2—C15—O3 torsion angle is −19.3 (5)°.

Averaging of C—O bond lengths and C—C—O angles by disorder is common in carboxyl dimers (Leiserowitz, 1976) but is not observed in catemers, whose geometry cannot support the mechanisms responsible for the averaging. In (I), these C—O bond lengths are 1.198 (5) and 1.345 (4) Å, with angles of 125.4 (3) and 112.8 (4)°. Our own survey of 56 keto acid structures which are not acid dimers gives average values of 1.20 (1) and 1.32 (2) Å, and 124.5 (14) and 112.7 (17)° for these lengths and angles, respectively, in accord with typical values of 1.21 and 1.31 Å, and 123 and 112° cited for highly ordered dimeric carboxyls (Borthwick, 1980). The methyl groups display no observable disordering.

The packing arrangement in (I) is shown in Fig. 2. Carboxyl-to-ketone catemers having an O···O distance of 2.975 (5) Å are formed by hydrogen bonds that progress among molecules screw-related in the *b* direction. The O—H···O angle is 168° [167° after O—H distance 'neutron-determined' normalization to 1.02 Å]. Because (I) is relatively flat and the hydrogen bonding extends between molecules stacked in the direction of the helical axis, the 'pitch' of the hydrogen-bonding helix in (I) is extraordinarily shallow. As we have defined previously (Coté *et al.*, 1997), the angle between the helical axis and the 'hydrogen-bonding axis' of each molecule (an intramolecular acid-H-to-ketone-O connector) constitutes the 'pitch' of the helix. In (I), this pitch is found to be 74 (1)° (90° = normal to the helical axis). We also characterize the hydrogen-bonding geometry of catemers, using a combination of the H···O═C angle [126.6°, neutron-normalized to 127.0°] and the H···O═C—C torsion angle [−52.3°, neutron-normalized to −53.5°]. These describe the approach of the acid H atom to the ketone O atom in terms of its deviation from, respectively, C═O axiality (ideal = 120°) and planarity with the ketone (ideal = 0°), and show, in this case, that the catemeric hydrogen bond is quite distorted as to coplanarity. Any loss in hydrogen-bonding stabilization for (I) is evidently more than compensated for by a resulting high efficiency in its packing. As a measure of this efficiency, we utilize the 'packing coefficient' (Kitaigorodsky, 1973), calculated as 'percent filled space' using the *PLATON* program (Spek, 1998). The value of 72.7% found for (I) lies within the top 8% of the packing-coefficient values we have calculated for 144 keto acids, which fall into the range 65.1–75.4% and depend on such factors as shape, chirality, rigidity *etc.* For this calculation, the C—H and O—H distances were neutron normalized to 1.08 and 1.02 Å, respectively.

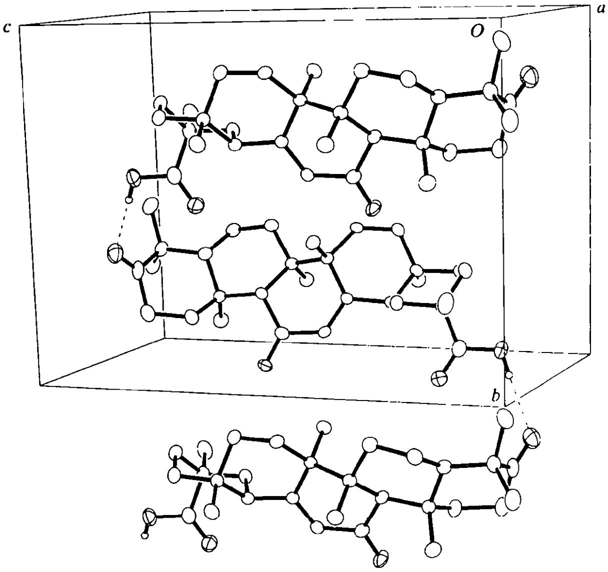


Fig. 2. A packing diagram for (I), with an extracellular molecule included to illustrate the catemeric carboxyl-to-ketone hydrogen-bonding. For clarity, all carbon-bound H atoms have been omitted. Displacement ellipsoids are set at the 30% probability level.

Two C—H···O close contacts were found, connecting separate screw-related neighbors to the unsaturated ketone (C18—H18*A*···O2 = 2.71 Å) and to the acid carbonyl (C8a—H8a*A*···O3 = 2.55 Å). Such contacts probably represent polar attractions contributing materially to the packing forces (Jönsson, 1972; Leiserowitz, 1976; Berkovitch-Yellin & Leiserowitz, 1982).

The solid-state (KBr) IR spectrum of (I) has C═O absorptions at 1727 and 1682 cm^{-1}, conforming to shifts seen typically in catemers and due, respectively, to removal of hydrogen bonding from carboxyl C═O and addition of hydrogen bonding to the ketone. In $CHCl_3$ solution, these coalesce to a single peak centered at 1700 cm^{-1}, with a typical carboxyl-dilution shoulder at *ca* 1740 cm^{-1}, consistent with a dimerically hydrogen-bonded carboxyl. Additional peaks assignable to the unsaturated ketone system are at 1643 and 1617 cm^{-1} in KBr, and 1654 and 1618 cm^{-1} in $CHCl_3$.

Experimental

Commercial 18β-glycyrrhetinic acid of known absolute configuration (Klyne & Buckingham, 1978) was obtained from ICN Pharmaceuticals, Costa Mesa, California, USA. Jones oxidation yielded (I) of known positive rotation (Logemann *et al.*, 1957), which was crystallized from CH_2Cl_2 (m.p. 568 K).

Crystal data

$C_{30}H_{44}O_4$
$M_r = 468.65$
Monoclinic
$P2_1$
$a = 7.385$ (1) Å
$b = 11.491$ (2) Å
$c = 15.202$ (2) Å
$\beta = 101.94$ (1)°
$V = 1262.1$ (3) Å^3
$Z = 2$
$D_x = 1.233$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 4.55$–15.66°
$\mu = 0.080$ mm^{-1}
$T = 293$ (2) K
Plate
0.6 × 0.4 × 0.1 mm
Colorless

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: none
5030 measured reflections
4439 independent reflections
3316 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$

$\theta_{\rm max} = 25°$
$h = -8 \rightarrow 8$
$k = -13 \rightarrow 13$
$l = -18 \rightarrow 18$
3 standard reflections every 97 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.095$
$S = 1.03$
2340 reflections
319 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0399P)^2 + 0.1056P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.13$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O3—C15	1.198 (5)	O4—C15	1.345 (4)
O3—C15—C2	125.4 (3)	O4—C15—C2	112.8 (4)

Table 2. *Hydrogen-bonding and C—H···O contact geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O1$^{\rm i}$	0.82	2.17	2.975 (5)	168
C18—H18*A*···O2$^{\rm ii}$	0.96	2.71	3.581 (4)	151
C8a—H8a*A*···O3$^{\rm ii}$	0.97	2.55	3.515 (4)	169

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

Data collection: *XSCANS* (Siemens, 1996). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1571). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1905-1908

(±)-3-Benzoylbicyclo[2.2.1]heptane-2-carboxylic acid: structures and hydrogen-bonding patterns of the di-*endo* and the 2-*endo*-3-*exo* isomers

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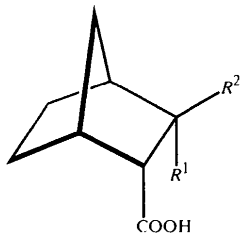
Abstract

Both the di-*endo*, (I), and the 2-*endo*-3-*exo*, (II), diastereomers of the title keto acid ($C_{15}H_{16}O_3$) crystallize as centrosymmetric carboxyl dimers, whose hydrogen bonding does not involve the ketone function [(I) O···O = 2.635 (3), (II) O···O = 2.675 (2) Å]. Conformational differences between (I) and (II) include significant rotations of the carboxyl group and of the benzoyl moiety relative to the bicycloheptane skeleton, plus a slight rotation of the phenyl ring relative to the ketone. Steric interactions involving the di-*endo* substituents in (I) produce significant twisting of the bridged bicyclic structure, which is essentially absent in (II). A C—H···O close contact at 2.58 Å was found for (I), involving the ketone, and at 2.49 Å for (II), also involving the ketone.

Comment

Compared with unelaborated carboxylic acids, the keto acids on which our crystallographic studies focus have an expanded repertoire of five solid-state hydrogen-bonding motifs. The commonest of these is acid dimerization without ketone involvement (Lalancette *et al.*, 1996), but carboxyl-to-ketone chains (catemers) constitute a sizable minority of cases (Brunskill *et al.*, 1997). The remaining modes, intramolecular hydrogen bonds (Thompson *et al.*, 1996), acid-to-acid catemers (Lalancette *et al.*, 1998) and carboxyl-to-ketone dimers (Kosela *et al.*, 1995), are all comparatively rare. We have previously referenced numerous examples and discussed factors that appear to govern the choice of hydrogen-bonding mode (Brunskill *et al.*, 1999; Lalancette *et al.*, 1999).

We report here the structure and hydrogen-bonding behavior of the title γ-keto acid, in both its di-*endo* (I) and 2-*endo*-3-*exo* (II) forms. The category of γ-keto acids is particularly diverse in hydrogen-bonding types, embracing internal hydrogen bonds, hydrated and anhydrous dimers, and catemers of both the heterochiral (glide-related) and homochiral types (screw-related or translational), plus other more complex hydrated patterns.



(I) : R^1 = CO-C_6H_5, R^2 = H
(II) : R^1 = H, R^2 = CO-C_6H_5

Fig. 1 shows the asymmetric unit for (I) with its atom numbering scheme. Full rotation of skeletal bonds is possible only for C2—C8, C3—C9 and C9—C10. The benzoyl group, whose component parts are only approximately coplanar [torsion angle O1—C9—C10—C15 = 11.2 (4)°], is oriented so that the ketone C=O is aimed toward C2 [torsion angle O1—C9—C3—C2 = −20.9 (4)°]. The carboxyl group is turned, with