H atoms treated by a mixture of independent and constrained refinement

$\Delta\rho_{min} = -0.603$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

N1—C8	1.456 (5)	C16—C17	1.416 (8)
C8—C9	1.473 (7)	C17—C18	1.390 (11)
C14—C15	1.477 (5)	C18—C19	1.347 (10)
C15—C16	1.359 (7)	C19—C20	1.391 (7)
C15—C20	1.402 (7)		
C2—N1—C8	125.2 (3)	C15—C16—C17	120.7 (6)
N1—C8—C9	114.2 (3)	C18—C17—C16	118.0 (6)
O5—C9—C8	117.3 (5)	C19—C18—C17	121.6 (6)
O3—C14—C15	111.5 (3)	C18—C19—C20	120.5 (6)
C16—C15—C14	118.9 (4)	C19—C20—C15	119.3 (6)
C20—C15—C14	121.2 (4)		
C1—C2—N1—C8	−174.5 (3)	O3—C14—C15—C20	−10.7 (5)
C2—N1—C8—C9	84.6 (5)	C14—C15—C16—C17	−177.0 (4)
N1—C8—C9—O5	57.7 (7)	C16—C17—C18—C19	−1.2 (10)
C13—O3—C14—C15	−177.8 (3)	C18—C19—C20—C15	−0.4 (8)
O3—C14—C15—C16	167.8 (4)		

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1	0.82 (3)	2.01 (4)	2.689 (4)	140 (4)
N1—H1···O4^{i}	0.82 (3)	2.49 (4)	3.079 (5)	129 (3)
N2—H2A···O1^{ii}	0.83 (3)	2.30 (4)	3.004 (4)	143 (4)
N2—H2A···O4^{iii}	0.83 (3)	2.51 (4)	3.105 (5)	129 (4)
N2—H2B···O6^{iv}	0.83 (4)	2.20 (4)	3.006 (4)	162 (4)

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

A 1 mm collimator was used for both data collections. The structures were solved by direct methods, locating all non-H atoms, except those disordered in (I) which were located in difference Fourier maps. All atoms of the disordered group were refined with restrained bond distances, angles and displacement parameters to improve convergence. Occupancy of both positions of disordered groups was refined and converged to 0.5 within experimental error. The refinement was then concluded with this occupancy fixed at 0.5. The displacement parameters of furan ring atoms of (I) were restrained to reduce anisotropy to acceptable values. In compound (I), all H atoms, except those belonging to the disordered group and the furan ring, were located in difference Fourier maps and freely refined. The rest were calculated at geometrical positions and refined riding with $U_{iso} = 1.2U_{eq}$ of the parent atom. In compound (II), H atoms belonging to C3, C6, C8, C13, C16, C20, N1 and N2 were located in a difference Fourier map. Those belonging to C3, C6, C16, C20 and N1 were freely refined and the others were refined with restrained distances. Those belonging to C10, C11, C12, C17, C18 and C19 were placed at calculated positions and refined riding on the atom to which they are bonded. All H-atom isotropic displacement parameters were fixed at $U_{iso} = 1.2U_{eq}$ of the parent atom.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *MSC/AFC Diffractometer Control Software*; program(s) used to solve structures: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997*b*); molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1995); software used to prepare material for publication: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1070). Services for accessing these data are described at the back of the journal.

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Two new spiro lactam-lactones

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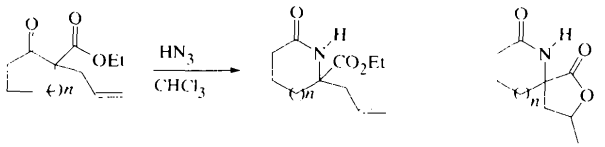
Abstract

In 3-methyl-2-oxa-6-azaspiro[4.5]decane-1,7-dione, (1) ($C_9H_{13}NO_3$), and 3-methyl-2-oxa-6-azaspiro[4.6]undecane-1,7-dione, (2) ($C_{10}H_{15}NO_3$), the lactone rings are in an envelope conformation. The lactam rings are in a distorted half-chair conformation in compound (1) and in a chair conformation in (2). Molecules are joined through hydrogen bonds in both compounds.

Comment

The Schmidt reaction of ethyl 1-allyl-2-oxocyclopentanecarboxylate (*a*) and of ethyl 1-allyl-2-oxocyclohexanecarboxylate (*b*) should give compounds (*c*) and (*d*); instead, an unexpected course of this reaction led to different compounds, namely (1) and (2). This means



(*a*) $n=1$ (*b*) $n=2$ Expected (*c*) $n=1$ (*d*) $n=2$ Obtained (1) $n=1$ (2) $n=2$

that in a one-step synthesis, two new spiro lactam-lactones were obtained. As compounds of this type can be potentially useful intermediates in organic synthesis (Guingant & Hammami, 1993; Degnan *et al.*, 1995), an unambiguous determination of the stereochemistry is required. We report here the crystal structure determination of both compounds.

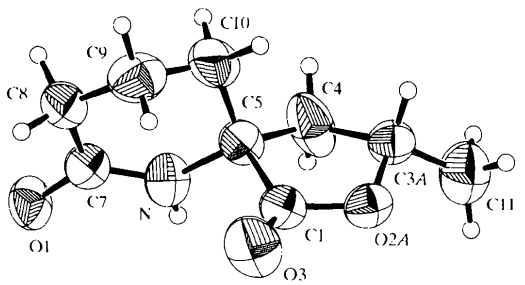


Fig. 1. The molecular structure of (1); for clarity, only the major conformer is shown. Displacement ellipsoids are drawn at the 50% probability level.

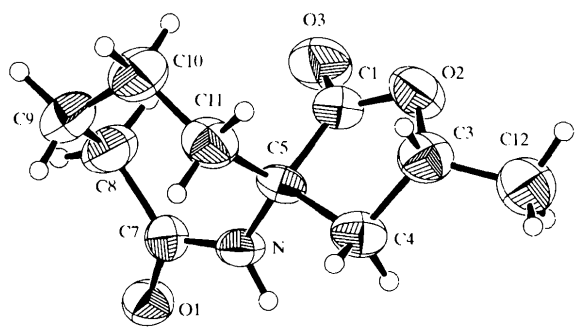


Fig. 2. The molecular structure of (2) showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level.

In compound (1), the five-membered lactone ring was found to be disordered. A difference map indicated, however, that the disorder could be satisfactorily described by a simple model postulating two different orientations (*A* and *B*); these were refined using the DELU and SIMU options in *SHELXL*97 (Sheldrick, 1997). In both structures, the lactone rings adopt an envelope conformation, as shown by the Cremer & Pople (1975) parameters [q_2 and φ_2 of 0.279 (8), 0.203 (8) and 0.334 (4) Å, and 142 (2), −20 (4) and 113.6 (7)°, for rings *A* and *B* of (1) and for (2), respectively]. Atom C4 occupies the flap position at a distance of 0.426 (7) and −0.335 (6) Å, respectively, for rings *A* and *B* in (1) and 0.518 (4) Å for (2) from the least-squares plane through the remaining four atoms in the ring. A very similar geometry for this moiety has been observed in various compounds containing this lactone ring (Lamotte *et al.*, 1978 and references therein).

The six-membered lactam ring in (1) is in a distorted half-chair (towards a half-boat) conformation, while the seven-membered lactam in (2) is in a chair conformation [puckering parameters for the six-membered rings: q_2 = 0.351 (5), 0.254 (4); q_3 = 0.294 (5), 0.614 (5); Q = 0.458 (6), 0.665 (5) Å; θ = 50.1 (6), 22.5 (4); φ_2 = −82.8 (9), −152 (1)° for (1) and (2), respectively, and φ_3 = 125.9 (4)° for the seven-membered ring of (2)]. The torsion angle about the N—C7 bond of 0.0 (8) in (1) and of −0.1 (6)° in (2) shows that the amide group is planar. In both cases the molecules are joined through N—H···O hydrogen bonds to form centrosymmetric dimers.

Experimental

To a cooled mixture of 2-allyl-2-carbethoxycyclopentanone for (1) and 2-allyl-2-carbethoxycyclohexanone for (2) and concentrated sulfuric acid (2.00 g 20.4 mmol) in 10 ml of chloroform, sodium azide was added (5.10 mmol), then stirred for 10 min at 288 K and for more than 1 h at room temperature. The reaction mixture was poured over a mixture of ice and water and the organic layer separated. The aqueous layer was extracted with chloroform (3 × 30 ml), then the organic layer was washed with a 5% sodium bicarbonate solution and dried over magnesium sulfate. Evaporation yielded colourless crystalline powders which were recrystallized from ethanol to obtain suitable crystals for X-ray studies. Compound (1): 65% yield, m.p. 477–478 K; elemental analysis: found C 58.90, H 7.08, N 7.69%; $C_9H_{13}NO_3$ requires C 59.2, H 7.10, N 7.65%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 and 1.47 (*dd*, 3H, CH_3), 1.72, 2.60 (*m*, 8H), 4.51, 4.61 and 4.85, 4.95 (*m*, 1H, $-CH_2-CH-CH_3$), 7.70 and 8.40 (*s*, 1H, N—H). Compound (2): 60% yield, m.p. 418–420 K; elemental analysis: found C 60.87, H 7.49, N 7.14%; $C_{10}H_{15}NO_3$ requires C 60.91, H 7.61, N 7.11%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.43 and 1.49 (*dd*, 3H, CH_3), 1.75, 2.91 (*m*, 10H), 4.48, 4.59 and 4.73, 4.79 (*m*, 1H, $-CH_2-CH-CH_3$), 6.50 and 6.90 (*s*, 1H, N—H).

Compound (1)

Crystal data

$C_9H_{13}NO_3$
M_r = 183.20
Mo $K\alpha$ radiation
λ = 0.71073 Å

Monoclinic
$P2_1/n$
a = 11.009 (2) Å
b = 5.949 (1) Å
c = 14.466 (3) Å
β = 105.66 (1)°
V = 912.25 (30) Å^3
Z = 4
D_x = 1.334 Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
θ = 9.24–17.16°
μ = 0.100 mm^{-1}
T = 293 K
Irregular
0.25 × 0.15 × 0.08 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
1658 measured reflections
1592 independent reflections
711 reflections with $F^2 > 2\sigma F^2$

R_{int} = 0.055
θ_{max} = 25°
$h = -13 \rightarrow 12$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 30 min
intensity decay: 0.8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.074
$wR(F^2)$ = 0.163
S = 1.026
1592 reflections
137 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2 + 1.5064P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.400 e Å^{-3}
$\Delta\rho_{min}$ = −0.358 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

N—C7	1.319 (6)	O1—C7	1.242 (6)
N—C5	1.464 (6)	O3—C1	1.178 (6)
C7—N—C5	127.9 (4)		

Table 2. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H···A	D—H	H···A	D···A	D—H···A
N—H1N···O^i	0.86	2.057	2.916 (6)	176

Symmetry code: (i) $1-x, -y, -z$.

Compound (2)

Crystal data

$C_{10}H_{15}NO_3$
M_r = 197.23
Monoclinic
$P2_1/n$
a = 9.991 (1) Å
b = 10.098 (1) Å
c = 10.576 (1) Å
β = 108.98 (1)°
V = 1008.99 (18) Å^3
Z = 4
D_x = 1.298 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 23 reflections
θ = 9.77–14.74°
μ = 0.096 mm^{-1}
T = 293 K
Irregular
0.20 × 0.15 × 0.08 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
1656 measured reflections
1558 independent reflections
742 reflections with $F^2 > 2\sigma F^2$

R_{int} = 0.033
θ_{max} = 24°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 11$
$l = -12 \rightarrow 11$
3 standard reflections
frequency: 30 min
intensity decay: 1.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.104
S = 0.970
1558 reflections
128 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0544P)^2 + 0.1276P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.177 e Å^{-3}
$\Delta\rho_{min}$ = −0.198 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (2)*

N—C7	1.345 (4)	O2—C3	1.465 (4)
N—C5	1.454 (4)	O1—C7	1.227 (4)
O2—C1	1.335 (4)		
C7—N—C5	132.2 (3)	C1—O2—C3	110.7 (3)

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···A	D—H	H···A	D···A	D—H···A
N—H1N···O^i	0.86	2.055	2.905 (3)	169

Symmetry code: (i) $2-x, -y, 2-z$.

H atoms were located on stereochemical grounds and refined with fixed geometry, each riding on a carrier atom, with an isotropic displacement parameter amounting to 1.5 (for methyl-H atoms) or 1.2 (for the other H atoms) times the value of the equivalent isotropic displacement parameter of the atom to which they are attached. The C3*A*—C4, C3*A*—C11, C3*B*—C4 and C3*B*—C11 distances of the minor conformer of compound (1) were set to 1.500 (5) Å, so using the dimensions from the same part of compound (2). Data collection of compound (2) was restricted to θ = 24.0° owing to the rather poor diffracting quality of the crystal.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1995); software used to prepare material for publication: *SHELXL97* and *PARST95* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1506). Services for accessing these data are described at the back of the journal.

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(+)-3-Oxo-5α-cholan-24-oic acid: catemeric hydrogen bonding in a steroidal keto acid

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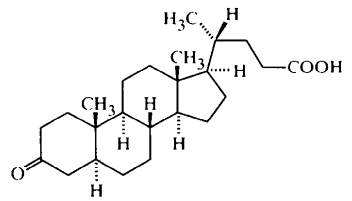
Abstract

The title keto acid ($C_{24}H_{38}O_3$) forms translational carboxyl-to-ketone hydrogen-bonding catemers, which follow no crystallographic axis [O···O = 2.712 (3) Å]. The cell contains two screw-related molecules having opposite end-to-end orientation, each of which participates in a separate hydrogen-bonding chain.

Comment

In the crystal structures of keto carboxylic acids, the commonest of the five known solid-state motifs is acid dimerization, in which the ketone is not involved (Coté *et al.*, 1996). In order of diminishing prevalence, the others are carboxyl-to-ketone chains (catemers) (Barcon *et al.*, 1998), intramolecular hydrogen bonds (Thompson *et al.*, 1996), carboxyl-to-ketone dimers (four cases known) (Kosela *et al.*, 1995), and acid-to-acid catemers (three cases known) (Lalancette *et al.*, 1998); several cases exist of hydrates with more complex hydrogen-bonding patterns (Lalancette *et al.*, 1997, 1998).

We have investigated the hydrogen-bonding motif of the steroidal keto acid (I), present as a single enantiomer. Fig. 1 shows the asymmetric unit with its steroid numbering. The significant conformational options all lie in the branched chain attached at C17. Here, the substituents at C20 (which has the *R* configuration) are staggered with respect to those at C17, with the methyl C24 *anti* to C16 [torsion angle C16—C17—C20—C24 = 176.6 (2)°]. The remainder of this chain (C20, C21, C22, C23, O2, O3) extends away from the ring system, as shown. The carboxyl group is oriented so that the carboxyl plane coincides approximately with the C21—C22 bond and its carbonyl group is nearly eclipsed with C21 [torsion angle O2—C23—C22—C21 = −5.4 (4)°].



(I)

While complete or partial averaging of carboxyl C—O bond lengths and C—C—O angles by disorder is frequent in dimers (Leiserowitz, 1976), the geometry of catemers precludes disordering processes. Acids engaged in catemeric hydrogen bonding are highly

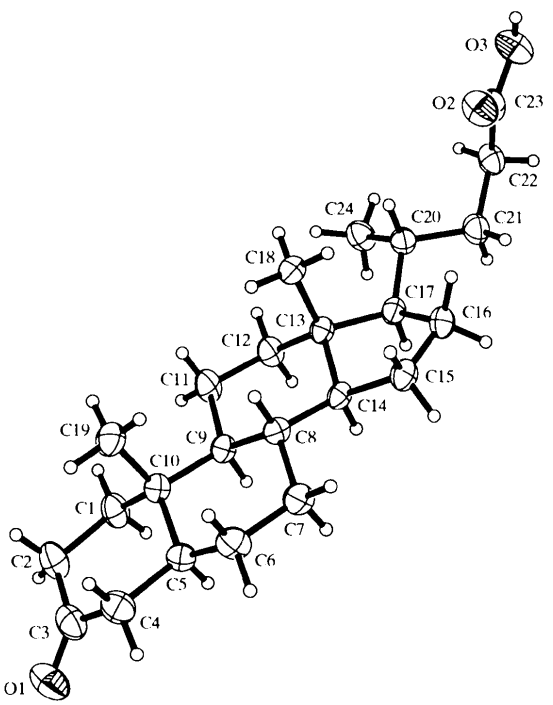


Fig. 1. *ORTEP*II (Johnson, 1976) plot of (I) with its steroidal numbering. Ellipsoids are set at the 30% probability level.