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4β,15-Dihydro-3-dehydrosolstitialin A†

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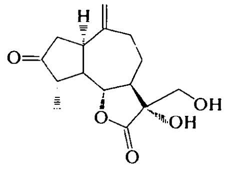
(*Received 24 May 1999; accepted 5 July 1999*)

Abstract

The sesquiterpene lactone 4β,15-dihydro-3-dehydrosolstitialin A, $C_{15}H_{20}O_5$, was isolated from *Centaurea musimomum*, a composite collected in the Souk-Ahra area in the east of Algeria. The fused-ring system contains a seven-membered ring in a twisted-boat and two five-membered rings with envelope conformations. The crystal structure is stabilized by intermolecular hydrogen bonds, with O···O separations of 2.709 (3) and 3.007 (2) Å.

Comment

In connection with a systematic investigation of the genus *Centaurea*, this paper presents the results of a structural study of 4β,15-dihydro-3-dehydrosolstitialin A, (I), a sesquiterpene lactone isolated from aerial parts of *Centaurea musimomum* (Bermejo, 1998), which could only be isolated as the diacetate from *C. behen* and *C. solstitialin* (Rustaiyan *et al.*, 1981; Öksüz *et al.*, 1993). Compound (I), m.p. 427–428 K, was obtained as colourless crystals by repeated silicic acid chromatography; IR bands at ν 3400, 1770, 1730 and 1640 cm^{-1} indicated the presence, respectively, of a hydroxy, a γ-lactone, a cyclopentanone and a double bond function. The spectroscopic properties (IR and ^{1}H and ^{13}C NMR) of this lactone are closely related to those of solstitialin A, the absolute configuration of which was established by Thiessen & Hope (1970). This structural information suggests that (I) is a guayanolide-type sesquiterpene containing two hydroxy groups, a γ-lactone, a cyclopentanone and a methylene double bond.



(I)

The structure and stereochemistry of (I) were established by our analysis; the absolute configuration was not determined by this X-ray analysis and that shown was chosen to be the same as that for solstitialin A The ground state of molecule (I) is non-planar. Bond lengths and angles are generally as expected. The molecule (Fig. 1) involves a seven-membered ring in a twisted-boat conformation. Deviations of atoms in this ring from the Cremer & Pople (1975) plane were less than 0.1 Å for atoms C5, C8 and C9 and more than 0.4 Å for the remaining atoms of the ring. Using the same definition for the two five-membered rings, the lactone is present in an

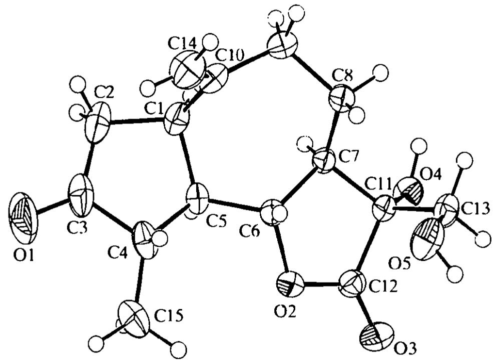


Fig. 1. A perspective view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

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† Alternative nomenclature: 11α-acetoxy-13-hydroxy-4α-methyl-3-oxo-1α*H*,5α*H*,6β*H*,7α*H*-guai-10(14)-en-6,12-olide or 3-hydroxy-3-hydroxymethyl-9-methyl-6-methyleneperhydroazuleno[4,5-*b*]furan-2,8-dione.

envelope conformation, with C7 in the flap position and a maximum deviation of 0.133 (2) Å for C7. The C6—O2—C12—C11 and O2—C6—C7—C8 torsion angles are −0.4 (2)° and −146.8 (1)°, respectively. The other five-membered ring also adopts an envelope conformation, with C5 0.211 (2) Å out of the plane. The C2—C1—C5—C6 torsion angle is −160.0 (2)°. The molecule can thus be described in terms of three 'planes': a seven-membered ring *A* and two fused five-membered rings, *B* (lactone) and *C*, forming the core of the molecule. The angles of the least-squares best planes between *A*^*B*, *A*^*C* and *B*^*C* are 26.36 (8), 35.82 (10) and 24.37 (10)°, respectively.

The crystal lattice is held together by hydrogen-bonding interactions (Table 2). The molecules are linked by O4—H4*W*···O1 hydrogen bonds to form infinite chains parallel to the *c* axis. The other hydrogen bonds (O5—H5*W*···O4) connect these chains (Fig. 2).

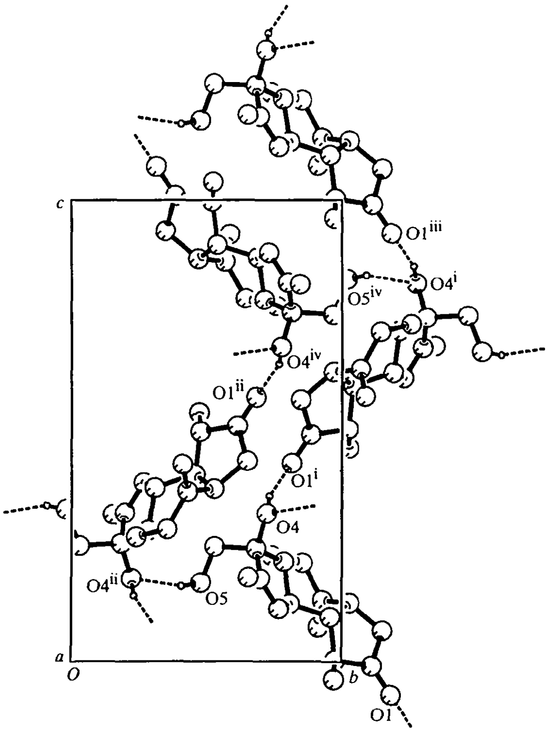

Fig. 2. A view of the hydrogen-bonding network along the *a* direction. Dashed lines indicate hydrogen bonds [symmetry codes: (i) $\frac{1}{2}-x, 2-y, \frac{1}{2}+z$; (ii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $x, y, z+1$; (iv) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$].

Experimental

Compound (I) was isolated from *Centaurea musimomum*. Single crystals were grown by slow evaporation of an EtOAc–hexane solution.

Crystal data

$C_{15}H_{20}O_5$
$M_r = 280.31$
Orthorhombic
$P2_12_12_1$
$a = 8.762 (1)$ Å
$b = 9.596 (2)$ Å
$c = 16.363 (3)$ Å
$V = 1375.8 (4)$ Å^3
$Z = 4$
$D_x = 1.353$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 11.97\text{–}18.41°$
$\mu = 0.101$ mm^{-1}
$T = 293 (2)$ K
Prism
0.45 × 0.20 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
2334 measured reflections
2289 independent reflections
2017 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.011$
$\theta_{\rm max} = 29.96°$
$h = -12 \rightarrow 0$
$k = -3 \rightarrow 13$
$l = -22 \rightarrow 6$
3 standard reflections
frequency: 120 min
intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.034$
$wR(F^2) = 0.098$
$S = 1.031$
2289 reflections
261 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0651P)^2 + 0.0897P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C3	1.219 (2)	O3—C12	1.199 (2)
O2—C12	1.340 (2)	O4—C11	1.429 (2)
O2—C6	1.466 (2)	O5—C13	1.417 (2)
C12—O2—C6	111.3 (1)	O4—C11—C12	106.9 (1)
O1—C3—C2	126.0 (2)	O4—C11—C7	113.1 (1)
O1—C3—C4	123.7 (2)	O3—C12—O2	122.4 (2)
O2—C6—C5	108.1 (1)	O3—C12—C11	126.5 (2)
O2—C6—C7	105.9 (1)	O2—C12—C11	111.0 (1)
O4—C11—C13	108.4 (1)	O5—C13—C11	110.3 (1)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4*W*···O1$^{\rm i}$	0.90 (3)	1.84 (3)	2.709 (3)	160 (3)
O5—H5*W*···O4$^{\rm ii}$	0.85 (3)	2.18 (3)	3.007 (2)	164 (3)

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

The H atoms were taken from a difference Fourier map and their atomic coordinates and isotropic displacement parameters were refined [O—H 0.85 (3)–0.90 (3) Å and C—H 0.92 (2)–1.07 (4) Å]. Successful refinement of the Flack (1983) parameter was not possible because the anomalous scattering was not observable. Friedel opposites were therefore merged before refinement.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*4 (Harms, 1997). Program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1998). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PLATON*.

This work was partly subsidized by grant No. PETRY 95.0178.OP (CICYT). JBB is indebted to Industrial Farmacéutica Cantabria, Madrid (Spain).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1363). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 1839–1841

11-Carboxylatomethyl-15-carboxymethyl-11,15-diazonia-3,23-dioxa-28-thiatetracyclo[23.2.1.0^{4,9}.0^{17,22}]octacosa-4,6,8,17,19,21,25,27-octaene bromide

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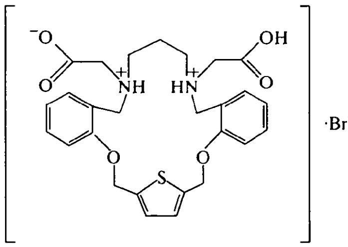
(Received 25 June 1999; accepted 2 July 1999)

Abstract

The title compound, $C_{27}H_{31}N_2O_6S^+\cdot Br^-$, has crystallographic mirror symmetry. The C—S distance of the thiophene ring is 1.702 (3) Å. The C—H···π interaction influences the crystal packing in addition to N—H···O, O—H···O and C—H···O interactions.

Comment

Selective complexation of macrocyclic ligands with specific metal ions is an important and rapidly expanding area of research (Van Veggel *et al.*, 1994). Zhang *et al.* (1998) and Adam *et al.* (1988) have investigated the complexing properties of macrocyclic ligands with N substituted by acetic acid. The title molecule, (I), is one such macrocyclic ligand and its structure is presented here.



(I)

The mirror-symmetric title compound has half a molecule in the asymmetric unit and the other half related by a mirror plane passing through atoms Br, C14 and S1 with no cavity inside. The results of the room temperature structure determination agree with the values reported for similar compounds. The C—S distance of the thiophene ring [1.702 (3) Å] is comparable with 1.723 (3) Å (Shanmuga Sundara Raj *et al.*, 1999) and slightly longer than 1.69 (1) (Morgant *et al.*, 1996) and 1.694 (4) Å (Youping *et al.*, 1995). The C—O distances of the carbonyl group [C12—O2 = 1.209 (4) and C12—O3 = 1.272 (4) Å] show that it is partially double-bonded and ionized. It is interesting to note that the ligand is zwitterionic, rather than in the 2+ state implied by protonation of N1.

The C2—C3—O1—C4 torsion angle [−170.6 (3)°] shows that the orientation of the phenyl ring is anti-periplanar with respect to the thiophene moiety. In the N—C—C—C—N chain the conformation is *anti–gauche–anti–anti*. The thiophene moiety deviates slightly from the mean plane of the whole molecule [dihedral angle 7.6 (3)°], while the phenyl ring makes a dihedral angle of 26.4 (2)° with the macrocycle. The methyl acetate group is nearly perpendicular to the macrocycle [interplanar angle 82.1 (3)°] and is in a synclinal orientation with respect to the phenyl ring. The thiophene moiety is highly disordered and exists in a planar conformation, with the two conformers in crossed positions. The value of the dihedral angle [61.5 (2)°] between the planar phenyl ring and the methyl acetate group indicates a large folding of the ligand. Analysis of the structure using *PLATON* (Spek, 1990) showed there are no solvent-accessible voids in the structure. The calculation of the least-squares plane shows that the methyl acetate group is planar, with a maximum deviation of −0.015 (3) Å for C11. Atom O1 is coplanar with the phenyl ring [deviation 0.017 (3) Å], but C10 deviates from planarity by −0.139 (3) Å.