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An unexpected oxidation product of α-santonin

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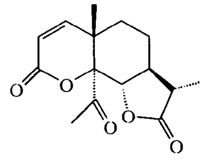
Abstract

The structure proposed previously for this unexpected oxidation product of α-santonin was verified by X-ray diffraction to be [3*S*-(3a,3aα,5aβ,9aα,9bβ)]-9a-acetyl-3a,4,5,5a,9a,9b-hexahydro-3,5a-dimethyl-2*H*-furo[3,2-*h*]-[1]benzopyran-2,8(3*H*)-dione, $C_{15}H_{18}O_5$.

Comment

α-Santonin, an anthelmintic sesquiterpene isolated from many *Artemisia* species on oxidation with permanganate or lead tetraacetate, was expected to give a $C_{15}H_{18}O_5$ triketone (Paknikar *et al.*, 1994). A product with this molecular formula was obtained, but from its NMR spectra it was postulated to have the ketolactone structure (I) instead. The X-ray study reported herein verifies the proposed structure except for the absolute configuration, which is defined by its synthesis from natural α-santonin, whose absolute configuration is well established (Cocker & McMurry, 1960).



(I)

An interesting feature of the NMR spectrum was the unusually far downfield location of the absorption for H-5α at δ 2.77, suggesting deshielding by the ketone carbonyl group. The X-ray study shows that in the solid phase, H-5α is indeed in a position to be strongly deshielded by the ketone carbonyl group. In fact, the asymmetric unit contains two molecules (1 and 2) which share this conformation, making it likely that this conformation is an energy minimum which would predominate in solution as well, as suggested by the above NMR evidence.

There are no unusually short intermolecular distances. The molecules stack along the *a* axis with lactone interactions involving γ-lactones with γ-lactones, γ-lactones with δ-lactones, and δ-lactones with δ-lactones. Both 2-bromo-α-santonin (Asher & Sim, 1965) and 2-bromo-β-santonin (Coggon & Sim, 1969) stack somewhat similarly in their crystals, but with α,β-unsaturated ketone units rather than lactones apparently interacting along the shortest axes in their unit cells.

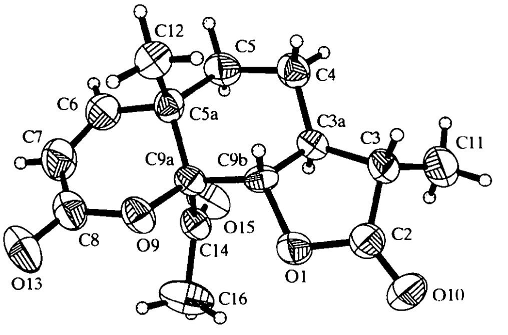


Fig. 1. The structure and atom-numbering scheme of molecule 1 of (I), drawn with 50% probability displacement ellipsoids.

Experimental

Compound (I) was prepared by $KMnO_4$ oxidation of α-santonin as described by Paknikar *et al.* (1994). Crystals were obtained by recrystallization from an ether–benzene (1:1) solution.

Crystal data

$C_{15}H_{18}O_5$
$M_r = 278.29$
Orthorhombic
$P2_12_12_1$
$a = 6.4840 (11)$ Å
$b = 15.2080 (11)$ Å
$c = 28.047 (3)$ Å
$V = 2765.7 (6)$ Å^3
$Z = 8$
$D_x = 1.337$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 20–26°$
$\mu = 0.100$ mm^{-1}
$T = 293 (2)$ K
Rod
0.25 × 0.13 × 0.10 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: none
5606 measured reflections
4856 independent reflections
2727 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.028$
$\theta_{\rm max} = 25°$
$h = -7 \rightarrow 7$
$k = -18 \rightarrow 18$
$l = -33 \rightarrow 33$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.118$
$S = 1.004$
4856 reflections
362 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.18$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Two Friedel-related octants of reflection data were collected to $\theta = 25°$, resulting in 2500 Friedel pairs with $I > 3\sigma(I)$. Refinement of the Flack parameter (Flack, 1983) was unsuccessful; the absolute configuration was then based on that known for α-santonin (Cocker & McMurry, 1960).

Data collection: *CAD*-4 *Manual* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *Manual*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992–1997). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *XP* in *SHELXTL* (Bruker, 1998). Software used to prepare material for publication: *SHELXL*97.

The title structure was determined by KJM as part of a course in Structural Chemistry taught in the Molecular Structure Laboratory, Department of Chemistry, University of Arizona, Tucson, AZ 85721, USA.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1090). Services for accessing these data are described at the back of the journal.

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DL-Cysteine at 298 K

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Abstract

In the room-temperature structure of DL-cysteine, $C_3H_7NO_2S$, the L-enantiomer has the −*gauche* confor-