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X-ray Structure of 8α-Acetoxy-1,3,4,10-tetrahydro-1α,10α-epoxyachillin

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Abstract. (5αH,6βH,11αH)-8α-Acetoxy-1,5-dihydro-2-oxo-1α,10α-epoxyguaian-6,12-olide, $C_{17}H_{22}O_6$, $M_r = 322 \cdot 3$, orthorhombic $P2_12_12_1$, $a = 14 \cdot 964$ (6), $b = 17 \cdot 057$ (4), $c = 6 \cdot 218$ (4) Å, $V = 1587$ (1) Å^3, $Z = 4$, $D_m = 1 \cdot 349$ (5), $D_x = 1 \cdot 349$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0 \cdot 09$ mm^{-1}, $F(000) = 688$, room temperature, final $wR = 0 \cdot 068$ for 1899 observed reflexions. The conformations displayed by the cyclopentanone, γ-lactone and cycloheptane rings are near to a twist, an envelope and a chair form, respectively. The cyclopentanone–cycloheptane and γ-lactone–cycloheptane ring fusions are *cis* and *trans*, respectively. Packing in the crystal is due to weak C—H···O hydrogen-bond interactions giving chains of molecules parallel to [010] and [001].

Introduction. The title compound (I) (m.p. 469–471 K, M^+ m/z 322) was prepared, along with its stereoisomer at C(1) and C(10) (II), from 8α-hydroxyachillin (III), a natural product isolated from *Artemisia lanata* Willd (González, Bermejo, de la Rosa & Massanet, 1976).

(I)   (II)   (III)
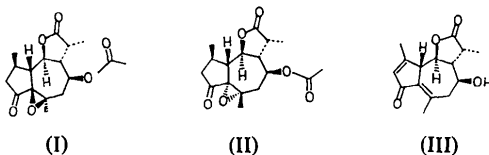
The detailed ^{1}H NMR analysis and the criteria based on the H(6) paramagnetic shift (Bates, Procházka & Cekan, 1963; Ando, Akahane & Takase, 1978), usually employed to establish the stereochemistry of the 1,10-epoxyguaianolides (Bhacca & Williams, 1964), seem to fail in this case (Massanet, 1986). An X-ray diffraction analysis was suggested to establish definitely the conformational details of (I).

Experimental. Single crystals in the form of colourless needles elongated along [001], prepared in the Organic Chemistry Department of the University of Cádiz. D_m by flotation. Crystal $0 \cdot 12 \times 0 \cdot 10 \times 0 \cdot 16$ mm. Unit-cell parameters from 25 reflexions, $5 < \theta < 15°$. Enraf–Nonius CAD-4 diffractometer, graphite monochromator, $2 \le \theta \le 30°$ ($0 \le h \le 21$, $0 \le k \le 24$, $0 \le l \le 8$), ω–2θ scan mode. Two standard reflexions ($\bar{4}10$, $4\bar{1}0$), variation in intensity < 3% of mean value. 2638 independent reflexions measured, 739 considered unobserved [$I < 2\sigma(I)$]. Lorentz and polarization correction, no correction for absorption or extinction. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). The chirality was assumed on the basis of chemical information. Full-matrix least-squares refinement; $\sum w(|F_o| - |F_c|)^2$ minimized with weighting scheme based on statistical-count criterion ($w = 1/\sigma_F^2$). Difference Fourier synthesis revealed the 22 H-atom positions; isotropic temperature factor $B = 4 \cdot 0$ Å^2 for H atoms; further least-squares refinement including positional parameters of H atoms. At final convergence $\Delta/\sigma < 0 \cdot 4$, $R = 0 \cdot 081$, $wR = 0 \cdot 068$, $S = 2 \cdot 7$ for 274 refined variables; number of reflexions/number of parameters = 7·87. Final accuracy of the refinement is limited by the poor quality of the crystals.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$)

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* a_i.a_j(\cos a_i, a_j).$$

	x	y	z	U_{eq}
O(1)	0·6743 (2)	0·0376 (2)	0·1305 (5)	35 (1)
O(2)	0·6950 (2)	−0·0913 (2)	0·1379 (5)	46 (1)
O(3)	0·6375 (2)	0·3552 (2)	0·3343 (6)	56 (1)
O(4)	0·4871 (2)	0·2727 (1)	0·1455 (4)	34 (1)
O(5)	0·4031 (2)	0·0290 (2)	0·4900 (4)	30 (1)
O(6)	0·3865 (2)	0·0793 (2)	0·8204 (5)	59 (1)
C(1)	0·4711 (2)	0·0870 (2)	0·4425 (6)	25 (1)
C(2)	0·5320 (2)	0·0475 (2)	0·2818 (6)	26 (1)
C(3)	0·6172 (2)	0·0947 (2)	0·2371 (6)	24 (1)
C(4)	0·6056 (3)	0·1653 (2)	0·0901 (6)	28 (1)
C(5)	0·5672 (2)	0·2341 (2)	0·2199 (7)	28 (1)
C(6)	0·4838 (3)	0·2317 (2)	0·3492 (7)	31 (1)
C(7)	0·4254 (2)	0·1590 (2)	0·3445 (7)	33 (1)
C(8)	0·5709 (3)	−0·0325 (2)	0·3418 (8)	35 (1)
C(9)	0·6522 (3)	−0·0362 (3)	0·1950 (7)	36 (1)
C(10)	0·6976 (3)	0·1966 (2)	0·0101 (7)	32 (1)
C(11)	0·7289 (3)	0·2493 (2)	0·1941 (8)	39 (1)
C(12)	0·6444 (3)	0·2892 (2)	0·2657 (6)	36 (1)
C(13)	0·3667 (2)	0·0309 (2)	0·6902 (7)	34 (1)
C(14)	0·2993 (3)	−0·0319 (3)	0·7188 (8)	52 (2)
C(15)	0·5988 (3)	−0·0430 (3)	0·5785 (7)	48 (2)
C(16)	0·6861 (3)	0·2429 (3)	−0·1984 (7)	46 (2)
C(17)	0·4701 (3)	0·2835 (3)	0·5445 (7)	40 (1)
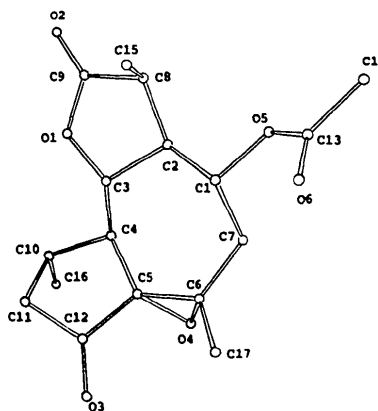
Fig. 1. A view of the molecule in the *xy* projection.

Max. and min. values in final difference density map 0·3 and −0·25 e Å^{-3}, respectively. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations carried out on a Univac 1100 computer. Crystallographic programs of *XRAY*70 system (Stewart, Kundell & Baldwin, 1970) used throughout.

Discussion. Fractional atomic coordinates and equivalent isotropic temperature factors (Hamilton, 1959) for non-H atoms are listed in Table 1.* The molecular conformation and atom labelling are shown in Fig. 1. Bond lengths and angles for non-H atoms are indicated in Fig. 2. C—H distances range from 0·88 (5) to 1·13 (5) Å [mean value 1·01 (5) Å].

Molecular geometry

The Newman projections of Fig. 3 show how the three rings are fused along the C(3)—C(2) and C(4)—C(5) bonds. The stereochemistry of the molecule (Fig. 1) is as follows: C(4)—βH is *cis* to C(15)—βO(4); C(2)—βH is *trans* to C(3)—αH; C(4)—βH is *cis* to C(10)—βCH₃ and to C(5)—C(6); C(2)—βH is *cis* to the C(1) acetoxy group. Thus the cyclopentanone–cycloheptane and the γ-lactone–cycloheptane ring junctions are *cis* and *trans*, respectively.

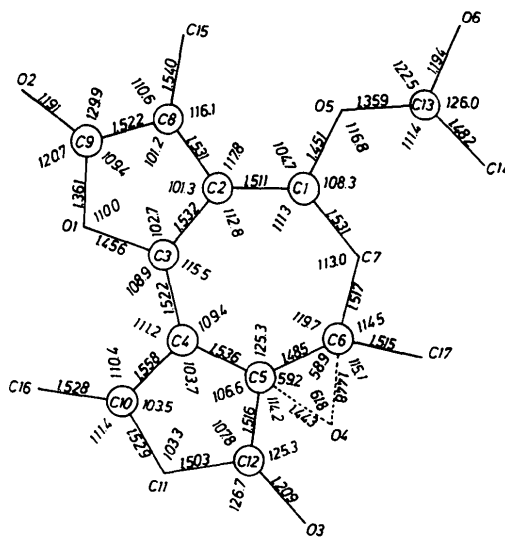Fig. 2. Bond distances (Å) and angles (°) in the molecule. Values of angles C(6)—C(5)—C(12), C(5)—C(6)—C(17), O(4)—C(5)—C(4) and O(4)—C(6)—C(7) are 123·8 (3), 122·1 (3), 119·4 (3) and 113·4 (3)°, respectively. Standard deviations are in the ranges 0·004–0·007 Å for distances and 0·3–0·4° for angles.
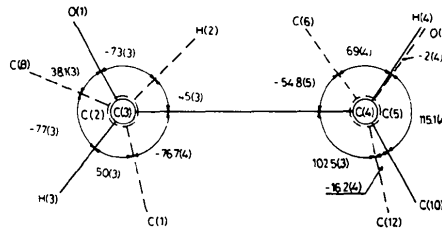

Fig. 3. Newman projections illustrating the coupling of the three fused rings in the molecule. Torsion angles are in °.

The conformation of the cyclopentanone ring as indicated by the endocyclic torsion angles is a twist form. In terms of puckering coordinates (Cremer & Pople, 1975) the amplitude and phase values are $q = 0.381$ (4) Å and $\varphi = 82.76$ (6)° for the sequence C(5)—C(4)—C(10)—C(11)—C(12). The asymmetry parameter (Nardelli, 1983a) $\Delta C_2[C(5)] = 0.026$ (2) shows an approximate twofold symmetry in the ring. For the γ-lactone ring the resulting conformation is an envelope form. In terms of puckering coordinates (Cremer & Pople, 1975) the amplitude and phase values are $q = 0.385$ (4) Å and $\varphi = 67.1$ (5)° for the sequence O(1)—C(3)—C(2)—C(8)—C(9) and the asymmetry parameter $\Delta C_s[C(2)] = 0.029$ (2) indicates an approximate mirror-plane symmetry in the ring. The cycloheptane ring displays an approximate chair conformation with a mirror pseudo-symmetry from C(2) to the midpoint of the C(5)—C(6) bond $\{\Delta C_s[C(2)] = 0.024\ (2)\}$. Values of the torsion angles C(4)—C(5)—C(6)—C(7) = -5.1 (6), C(5)—C(6)—C(7)—C(1) = 65.5 (5), C(2)—C(1)—C(7)—C(6) = -82.5 (4) and C(7)—C(1)—C(2)—C(3) = 72.2 (4)° are in agreement with those (0, 66, 84, 64°) proposed by Hendrickson (1967) for a cycloheptane molecule with equal bond lengths in a perfect chair conformation. For the ideal cycloheptane molecule the average bond angle is 116° and values range from 114 to 118°. In this case the mean value is 115.3 (3)° but a larger dispersion, from 109 to 125°, is observed. In terms of puckering coordinates the amplitude and phase values are $q_2 = 0.340$ (4), $q_3 = 0.710$ (4) Å and $\varphi_2 = 71.8$ (7), $\varphi_3 = -156.7$ (4)°   [$Q = 0.787$ (4) Å and $\theta_2 = 25.6$ (3)°] for the sequence C(1)—C(2)—C(3)—C(4)—C(5)—C(6)—C(7).

The epoxide bridge between C(5) and C(6) produces a high strain around the C(5)—C(6) bond. There are some features supporting this idea: the short C(5)—C(6) distance of 1.485 (6) Å, the tendency to have a planar distribution of the bonds around C(5) and C(6) as revealed by the torsion angles C(4)—C(5)—C(6)—C(7) = -5.1 (6), C(12)—C(5)—C(6)—C(7) = -158.8 (4) and C(17)—C(6)—C(5)—C(4) = 151.9 (4)° and the dihedral angle between the least-squares planes through the C(4)—C(5)—C(6)—C(7) group and the epoxide bridge of 76.6 (1)°. This is the usual geometrical deformation found around the epoxide bridge (Foces-Foces, Cano & García-Blanco, 1977).

Crystal packing

In the crystal cohesion, some intermolecular interactions may be considered as hydrogen bonds: C(8)—H(8)···O(4)($-x+1$, $y-\frac{1}{2}$, $-z+\frac{1}{2}$) and C(17)—H(172)···O(2)($-x+1$, $y+\frac{1}{2}$, $-z+\frac{1}{2}$), linking molecules related by a screw axis parallel to [010], and C(10)—H(10)···O(2)($-x+\frac{3}{2}$, $-y$, $z-\frac{1}{2}$), linking molecules related by a screw axis parallel to [001]. Details of the geometry of these contacts are: C(8)—H(8) = 0.99 (4),

C(8)···O(4) = 3.435 (5),   H(8)···O(4) = 2.61 (4) Å, C(8)—H(8)···O(4) = 140 (3)°;   C(17)—H(172) = 1.09 (5), C(17)···O(2) = 3.458 (5), H(172)···O(2) = 2.54 (5) Å,   C(17)—H(172)···O(2) = 141 (4)°; C(10)—H(10) = 1.09 (5),   C(10)···O(2) = 3.341 (5), H(10)···O(2) = 2.59 (5) Å,   C(10)—H(10)···O(2) = 125 (3)°. As observed, the H···O distances of these contacts are close to the sum of the van der Waals radii of H and O (1.20 and 1.50 Å) and the C—H···O angles have values lower than the mean value (152.7°) reported for intermolecular C—H···O hydrogen bonds with H···O = 2.40 Å (Taylor & Kennard, 1982). Therefore, values found for the C—H···O angles are appreciably higher than the generally accepted low limit of 90° for the donor—proton···acceptor angle in a hydrogen bond and so they should be considered as weak hydrogen bonds. No other contacts significantly shorter than the sum of the van der Waals radii have been detected. The molecular geometry and crystal packing were computed by *PARST* (Nardelli, 1983b).

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