

many edible plants and are therefore part of the human diet (Cody, Middleton & Harborne, 1986). Many flavonoid compounds have recognized therapeutic properties. (e.g. anticarcinogenic, anti-inflammatory). Flavonoids are also important for normal plant growth, development, and defense against infection and injury. Our structural information will contribute to the growing structural data becoming available to those characterizing structure/activity relationships.

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The Structure of a Tetracyclic Enone Containing the 5–7–6 Ring System of the Tiglianes

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Abstract. [3*R*-(3 α ,3 β ,6 α ,6 α ,10 β)]-1,2,3,6*a*,7,8,9,10*b*-Octahydro-9-oxo-3,6-epoxy-3*aH*,6*H*-benz[*e*]azulene, C₁₄H₁₆O₂, *M_r* = 216.28, monoclinic, *P*2₁/*n*, *a* = 5.7314 (7), *b* = 15.577 (2), *c* = 12.334 (2) Å, β = 90.11 (1)°, *V* = 1101.1 (2) Å³, *Z* = 4, *D_x* = 1.304 g cm⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 0.92 cm⁻¹, *F*(000) = 464, *T* = 298 (2) K, *R* = 0.044 and *wR* = 0.025 for 1550 unique observed reflections. The molecule consists of five-, seven- and six-membered fused rings with an ether bridge between the *A* and *B* rings, creating a 5–7–6 ring system. The cyclopentane ring is in a half-chair conformation with $\Delta C_2 = 3.2^\circ$ for the twofold axis passing through C1. The six-membered dihydropyran ring is in a near-ideal boat conformation with $\Delta C_{s,s,2} = 1.0^\circ$ for the two mirrors and a twofold axis. The cycloheptene ring is a distorted boat ($\Delta C_s = 10.2^\circ$) and the cyclohexenone ring is a distorted half-chair ($\Delta C_2 = 11.8^\circ$) or a distorted sofa ($\Delta C_s = 11.1^\circ$). There is a quasi-*trans* junction between the cyclohexenone ring and the cycloheptene ring. The cyclopentane ring and cyclohexenone ring are fused in a *trans* relationship across the cycloheptene ring. The H atom on one

bridgehead of the benzazulene system is in an axial orientation.

Experimental. The title compound was prepared as part of a strategy towards the total synthesis of the tumor-promoting tigliane diterpene phorbol. The *A/B/C* ring system of the tiglianes (5–7–6) has been constructed *via* Robinson annulation of a four-C-atom fragment onto a stereochemically biased hydroazulenic building block.

Colorless square rods, 0.28 × 0.28 × 0.52 mm; Nicolet R3 diffractometer, monochromated Mo *K* α ; $\theta/2\theta$ scans; $2.5 \leq 2\theta \leq 50^\circ$; lattice parameters from 25 high-angle reflections ($2\theta > 20^\circ$); constrained monoclinic; no absorption corrections or extinction corrections applied; $0 \leq h \leq 7$, $0 \leq k \leq 19$, $-15 \leq l \leq 15$; three standard reflections fluctuated 4%; 2307 total reflections, 1930 unique, 1550 observed with $I_o \geq 2.0\sigma(I)$. Direct methods; full-matrix refinement *via* SHELX76 (Sheldrick, 1976) on *F*'s minimizing $\sum w(|F_o| - |F_c|)^2$; $I = P - (B/r)$, where *P* = scan counts, *r* = background/scan ratio, *B* = sum background counts; $\sigma(I)^2 = P + (B/r^2)$; all C atoms anisotropic; H atoms were placed in observed positions and refined with all *U*(H) tied to a single variable

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Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
O1	0.6544 (3)	0.50893 (9)	0.2319 (1)	0.0704 (7)
O2	0.1314 (2)	0.81081 (8)	-0.0443 (1)	0.0539 (5)
C1	0.5273 (4)	0.5606 (1)	0.1864 (2)	0.0494 (8)
C2	0.2828 (5)	0.5387 (1)	0.1543 (2)	0.062 (1)
C3	0.2147 (4)	0.5848 (1)	0.0504 (2)	0.0580 (9)
C4	0.2458 (4)	0.6822 (1)	0.0583 (2)	0.0407 (7)
C5	0.4792 (3)	0.7058 (1)	0.1064 (1)	0.0341 (6)
C6	0.6033 (4)	0.6488 (1)	0.1627 (2)	0.0414 (7)
C7	0.5648 (4)	0.7967 (1)	0.0952 (2)	0.0382 (7)
C8	0.5525 (4)	0.8330 (1)	-0.0226 (2)	0.0401 (7)
C9	0.3105 (4)	0.8739 (1)	-0.0277 (2)	0.0448 (8)
C10	0.2036 (4)	0.7224 (1)	-0.0543 (2)	0.0455 (8)
C11	0.4121 (4)	0.7138 (1)	-0.1262 (2)	0.0483 (8)
C12	0.5846 (4)	0.7679 (1)	-0.1103 (2)	0.0461 (8)
C13	0.4184 (5)	0.8607 (1)	0.1621 (2)	0.0553 (9)
C14	0.2801 (4)	0.9155 (2)	0.0822 (2)	0.0600 (9)

Table 2. Bond lengths (Å) and angles (°)

O1—C1	1.221 (3)	C5—C7	1.506 (3)
O2—C9	1.436 (2)	C7—C8	1.561 (3)
O2—C10	1.443 (2)	C7—C13	1.543 (3)
C1—C2	1.495 (4)	C8—C9	1.528 (3)
C1—C6	1.471 (3)	C8—C12	1.494 (3)
C2—C3	1.520 (4)	C9—C14	1.513 (3)
C3—C4	1.530 (3)	C10—C11	1.496 (3)
C4—C5	1.507 (3)	C11—C12	1.314 (3)
C4—C10	1.543 (3)	C13—C14	1.525 (3)
C5—C6	1.332 (3)		
O1—C1—C2	122.0 (2)	C5—C4—C10	113.1 (2)
O1—C1—C6	122.0 (2)	C5—C7—C8	114.3 (2)
O2—C9—C8	111.7 (2)	O2—C9—C13	112.4 (2)
O2—C9—C14	109.7 (2)	C6—C5—C7	120.1 (2)
O2—C10—C4	110.8 (2)	C7—C8—C9	103.2 (2)
O2—C10—C11	111.5 (2)	C7—C8—C12	115.0 (2)
C1—C2—C3	110.8 (2)	C7—C13—C14	107.4 (2)
C1—C6—C5	124.6 (2)	C8—C7—C13	103.9 (2)
C2—C1—C6	116.0 (2)	C8—C9—C14	104.4 (2)
C2—C3—C4	112.7 (2)	C8—C12—C11	116.7 (2)
C3—C4—C5	111.7 (2)	C9—O2—C10	117.4 (1)
C3—C4—C10	109.1 (2)	C9—C8—C12	111.5 (2)
C4—C5—C6	121.0 (2)	C9—C14—C13	106.2 (2)
C4—C5—C7	118.8 (2)	C10—C11—C12	117.1 (2)
C4—C10—C11	111.9 (2)		

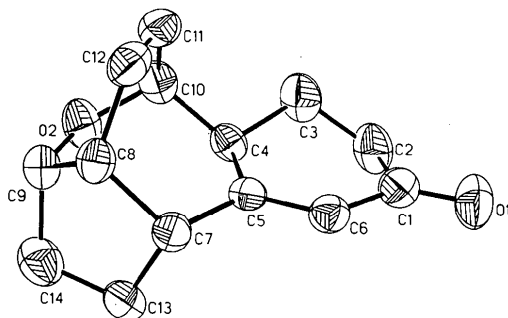
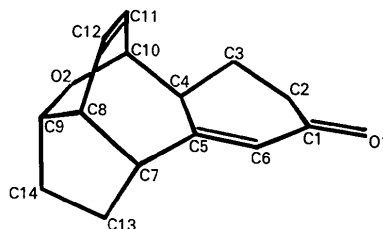


Fig. 1. ORTEP (Johnson, 1965) drawing (at 50% probability) of 1,2,3,6a,7,8,9,10b-octahydro-9-oxo-3,6-epoxy-3aH,6H-benz[e]azulene showing the adopted labeling.

which refined to 0.063 \AA^2 . Number of parameters varied was 194. For observed reflections $R = 0.044$, $wR = 0.025$, $S = 4.1$, $w = (\sigma_F)^{-2}$. For all (including weak) reflections: $R = 0.056$, $wR = 0.026$. In a final cycle: $(\Delta/\sigma)_{\max} < 0.02$, $(\Delta\rho)_{\max} = 0.17$, $(\Delta\rho)_{\min} = -0.15 \text{ e \AA}^{-3}$. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Table 1* gives the atomic coordinates and Table 2 lists bond distances and angles. Fig. 1 illustrates the geometry and labeling scheme. A diagram of the molecule is shown below.



Related literature. The preparation of this compound is described in a thesis (Kierkus, 1989). The structure of the natural product phorbol is available (Brandl, Rohrl, Zechmeister & Hoppe, 1971). Other synthetic work on phorbol systems has been published (Rigby & Kierkus, 1989; Wender, Keenan & Lee, 1987). Ring conformations have been discussed by Toromanoff (1980) and asymmetry parameters (ΔC_1 and ΔC_2) are described by Ladd & Palmer (1985).

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52331 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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