

Related literature. In the generally preferred conformation the dihedral angle between the phenyl and γ -benzopyrone ring is expected to be small as shown in the case of the title compound where the value is $5.2(9)^\circ$. In related flavones, the reported increase in dihedral angle to 24.8 (Shoja, 1989) and 28° (Ting & Watson, 1972) has the effect of increasing the length of the C(1')—C(2) bond from $1.465(4)$ (Table 2), to $1.485(5)$ and $1.504(9)$ Å, respectively. Only intramolecular hydrogen bonding was found in the title compound in contrast to 3-hydroxyflavone which displayed both intra- and intermolecular hydrogen bonding (Etter, Urbanczyk-Lipkowska, Baer & Barbara, 1986).

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Structure of 3-Chloroflavanone

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Abstract. 3-Chloro-2-phenylbenzo- γ -pyrone, $C_{15}H_{11}ClO_2$, $M_r = 258.7$, monoclinic, $P2_1/n$, $a = 9.317(3)$, $b = 14.991(2)$, $c = 8.848(4)$ Å, $\beta = 94.45(3)^\circ$, $V = 1232.1$ Å³, $Z = 4$, $D_m = 1.37$, $D_x = 1.39$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 3.0$ cm⁻¹, $F(000) = 536$, $T = 295$ K, $R = 0.054$ for 2063 observed reflections ($|F_o| > 1\sigma|F_o|$). The pyran ring is puckered due to the saturation of the C(2)—C(3) bond. The puckering causes the pyran ring to be distorted into a C(2)-sofa conformation. Owing to the C(2)—C(3) saturation, there are two asymmetric centers present, one at C(2), the other at C(3). The exocyclic phenyl substituent is equatorially oriented at C(2) and the Cl(3) is axially oriented at C(3). The 2-phenyl substituent is twisted out of the benzo- γ -pyrone ring plane due to steric interactions with Cl(3) at C(3). The C(3)—C(2)—C(11)—C(12) torsion angle is $74.26(37)^\circ$.

Experimental. A white prism crystal of 3-chloroflavanone ($C_{15}H_{11}ClO_2$) was obtained by sublimation *in vacuo*. The crystal, with approximate dimensions $0.50 \times 0.25 \times 0.25$ mm, was mounted on a glass fiber. The density D_m was measured by flotation in a 38 wt% solution of calcium chloride. Preliminary Weissenberg film studies were performed on an Enraf-Nonius Diffractis 601 using Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å). The preliminary film work was used to facilitate space-group assignment through

systematic extinctions. The crystal was mounted on an Enraf-Nonius CAD-4 computer-controlled κ -axis diffractometer with the long axis of the crystal parallel to the φ axis of the goniometer. Preliminary examination and data collection were performed with Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) and a graphite-crystal incident-beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $5 < \theta < 12^\circ$ measured by the computer-controlled diagonal slit method of centering. The data were collected at a temperature of 296(1) K, using the θ - 2θ scan technique. The scan rate varied from 2 to 7° min⁻¹ in ω . The variable scan rate allows rapid data collection for intense reflections, where a fast scan rate is used, and ensures good counting statistics for weak reflections, where a slow scan rate is used. Three standard reflections ($3\bar{3}2$, $1\bar{2}4$, $3\bar{5}0$) were remeasured every 4 h; no significant loss of these intensities was observed throughout data collection. A crystal orientation check was also made after every 240 reflections. 4518 independent reflections were collected with 2θ up to 50.0° in $h - 11/11$, $k - 17/0$, $l - 10/10$. Corrections for Lorentz and polarization effects were applied to the intensity data, while no absorption correction was carried out. The structure was solved by direct methods. The non-hydrogen atoms were located from difference Fourier synthesis

Table 1. Atomic coordinates and equivalent isotropic temperature factors (\AA^2) with e.s.d.'s in parentheses

| | x | y | z | $B_{eq}(\text{\AA}^2)^*$ |
|-------|-------------|-------------|------------|--------------------------|
| Cl(3) | 0.5354 (1) | 0.2044 (7) | 0.0753 (1) | 4.99 (2) |
| C(3) | 0.4775 (3) | 0.2038 (2) | 0.2642 (4) | 3.49 (7) |
| O(1) | 0.3314 (2) | 0.0712 (1) | 0.2209 (3) | 3.78 (5) |
| C(4) | 0.3418 (4) | 0.2614 (2) | 0.2581 (4) | 3.68 (8) |
| C(10) | 0.2071 (3) | 0.2128 (2) | 0.2253 (3) | 3.35 (7) |
| C(6) | -0.0480 (4) | 0.2124 (3) | 0.1658 (4) | 4.67 (9) |
| C(7) | -0.0458 (4) | 0.1212 (3) | 0.1400 (4) | 4.68 (9) |
| O(4) | 0.3503 (3) | 0.3411 (2) | 0.2774 (3) | 5.34 (7) |
| C(9) | 0.2083 (4) | 0.1208 (2) | 0.2019 (3) | 3.39 (8) |
| C(5) | 0.0753 (4) | 0.2574 (2) | 0.2067 (4) | 4.08 (8) |
| C(2) | 0.4472 (4) | 0.1100 (2) | 0.3154 (4) | 3.30 (8) |
| C(15) | 0.7096 (4) | -0.0716 (2) | 0.2226 (4) | 5.0 (1) |
| C(12) | 0.6816 (4) | 0.0577 (2) | 0.4383 (4) | 4.17 (9) |
| C(11) | 0.5751 (4) | 0.0476 (2) | 0.3213 (3) | 3.21 (7) |
| C(8) | 0.0818 (4) | 0.0747 (2) | 0.1584 (4) | 4.02 (8) |
| C(13) | 0.8007 (4) | 0.0032 (3) | 0.4460 (4) | 4.9 (1) |
| C(14) | 0.8152 (4) | -0.0609 (4) | 0.3396 (4) | 4.97 (9) |
| C(16) | 0.5895 (4) | -0.0167 (2) | 0.2141 (4) | 4.22 (9) |

* As defined by Johnson & Levy (*International Tables for X-ray Crystallography*, 1974).

Table 2. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

| | | | |
|------------|-----------|-------------|------------|
| Cl(3)—C(3) | 1.795 (3) | C(6)—C(5) | 1.357 (5) |
| C(3)—C(4) | 1.529 (5) | C(7)—C(8) | 1.377 (5) |
| C(3)—C(2) | 1.511 (5) | C(9)—C(8) | 1.394 (5)* |
| O(1)—C(9) | 1.366 (4) | C(2)—C(11) | 1.512 (5) |
| O(1)—C(2) | 1.436 (4) | C(15)—C(14) | 1.382 (6) |
| C(4)—C(10) | 1.461 (5) | C(15)—C(16) | 1.386 (6) |
| C(4)—O(4) | 1.209 (4) | C(12)—C(11) | 1.386 (4) |
| C(10)—C(9) | 1.394 (5) | C(12)—C(13) | 1.376 (5) |
| C(10)—C(5) | 1.397 (5) | C(11)—C(16) | 1.368 (5) |
| C(6)—C(7) | 1.387 (5) | C(13)—C(14) | 1.358 (5) |

| | | | |
|-----------------|-----------|-------------------|-----------|
| Cl(3)—C(3)—C(4) | 105.8 (3) | C(10)—C(9)—C(8) | 121.0 (3) |
| Cl(3)—C(3)—C(2) | 111.1 (2) | C(10)—C(5)—C(6) | 120.8 (3) |
| C(4)—C(3)—C(2) | 111.3 (3) | C(3)—C(2)—O(1) | 110.6 (2) |
| C(9)—O(1)—C(2) | 116.0 (2) | C(3)—C(2)—C(11) | 114.9 (3) |
| C(3)—C(4)—C(10) | 114.9 (3) | O(1)—C(2)—C(11) | 108.9 (2) |
| C(3)—C(4)—O(4) | 120.5 (3) | C(14)—C(15)—C(16) | 119.7 (3) |
| C(10)—C(4)—O(4) | 124.6 (3) | C(11)—C(12)—C(13) | 120.0 (3) |
| C(4)—C(10)—C(9) | 120.4 (3) | C(2)—C(11)—C(12) | 118.4 (3) |
| C(4)—C(10)—C(5) | 121.2 (3) | C(2)—C(11)—C(16) | 122.2 (3) |
| C(9)—C(10)—C(5) | 118.3 (3) | C(12)—C(11)—C(16) | 119.4 (3) |
| C(7)—C(6)—C(5) | 120.7 (3) | C(7)—C(8)—C(9) | 119.0 (3) |
| C(6)—C(7)—C(8) | 120.2 (3) | C(12)—C(13)—C(14) | 120.7 (3) |
| O(1)—C(9)—C(10) | 122.4 (3) | C(15)—C(14)—C(13) | 119.9 (3) |
| O(1)—C(9)—C(8) | 116.6 (3) | C(15)—C(16)—C(11) | 120.3 (3) |

and were refined anisotropically. H atoms were also located from difference Fourier synthesis and their positions and isotropic thermal parameters were refined. The structure was refined in full-matrix least squares, where the function minimized was $\sum w(|F_o| - |F_c|)^2$ and the weight w is defined as $4F_o^2/(\sigma F_o)^2$. Only the 2063 reflections having $|F_o| > 1\sigma|F_o|$ were used in the refinements. The final cycle of refinement included 208 variable parameters and converged (largest parameter shift was 0.01 times its e.s.d.) with unweighted and weighted R values of 0.054 and 0.050 respectively. No significant peaks

were observed in the final difference Fourier map; highest peak $0.32(8) \text{ e \AA}^{-3}$. All calculations were performed on a DEC VAX 8250 minicomputer using *SDP/VAX* (Frenz, 1978). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

The final non-hydrogen atomic coordinates and equivalent isotropic temperature factors (\AA^2) with e.s.d.'s are listed in Table 1. Non-hydrogen bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s are listed in Table 2. The molecular structure with atomic numbering sequence is given in Fig. 1 (Johnson, 1976). The crystal packing diagram showing the four molecules per unit cell is depicted in Fig. 2.*

Related literature. We have been interested in elucidating the structures of various 2-phenylbenzo- γ -pyrone derivatives, or flavonoids. Flavonoids are widely distributed, being responsible for much of the coloring in nature. These compounds are found in

* 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 52294 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

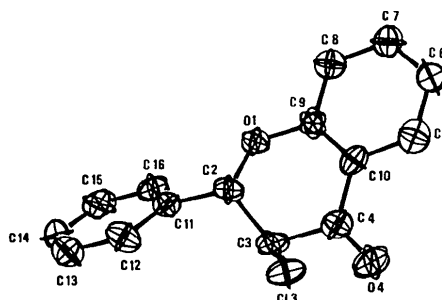


Fig. 1. Molecular structure with atomic numbering scheme.

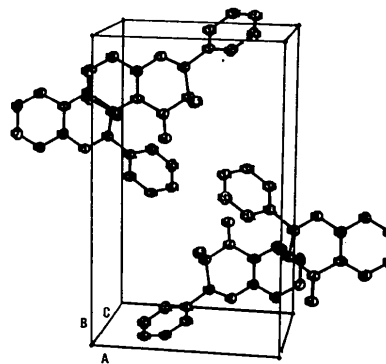


Fig. 2. Crystal packing diagram.

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)]-1,2,3,6a,7,8,9,10b-Octahydro-9-oxo-3,6-epoxy-3a*H*,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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