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## Structure of Garcinone B\*

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**Abstract.** 5,9,11-Trihydroxy-3,3-dimethyl-10-(3-methyl-2-butenyl)-3*H*,12*H*-pyrano[3,2-*a*]xanthen-12-one monohydrate,  $C_{23}H_{22}O_6 \cdot H_2O$ ,  $M_r = 412.4$ , triclinic,  $P\bar{1}$ ,  $a = 8.306$  (1),  $b = 8.543$  (1),  $c = 14.695$  (1) Å,  $\alpha = 95.12$  (1),  $\beta = 101.44$  (1),  $\gamma = 86.91$  (1)°,  $V = 1017.2$  (2) Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.342$  (3) (floatation),  $D_x = 1.346$  Mg m<sup>-3</sup>, Cu *K*α radiation,  $\lambda = 1.5418$  Å,  $\mu = 0.787$  mm<sup>-1</sup>,  $F(000) = 436$ ,  $T = 294$  K, final  $R = 0.062$  for 2652 reflections [ $I > 3\sigma(I)$ ]. The xanthenone ring system is nearly planar. The dihedral angle between the xanthenone ring plane and the plane of the isoprenyl side chain is 111.5 (2)°. The molecules are linked by hydrogen bonds *via* a molecule of water.

**Introduction.** Several naturally occurring xanthenes isolated from plants have created considerable interest in terms of their biological importance and potential as drugs (Gopalakrishnan, Shankaranarayanan, Nazimudeen, Viswanathan & Kameswaran, 1980; Shankaranarayanan, Gopalakrishnan & Kameswaran, 1979). The title compound is one of the constituents of the mangosteen fruit hulls (*Garcinia mangostana*, Guttiferae), which have been in use as a folk medicine for the treatment of dysentery (Yates & Stout, 1958). The X-ray structural analysis of this compound was carried out in order to ascertain its conformation and molecular geometry.

**Experimental.** The fruit hulls after extraction with petroleum ether were further extracted with benzene. The benzene extract was chromatographed on silica gel (4:1 benzene/chloroform), further purified by prep. TLC to yield the title compound, which is identical in all respects, *viz* m.p., TLC and IR, to an authentic specimen. Recrystallization of the compound from methanol gave yellow needles. Crystal dimensions

0.11 × 0.07 × 0.10 mm. CAD-4 diffractometer, monochromated Cu *K*α radiation. Cell parameters from least-squares refinement of setting angles of 25 reflections ( $\theta$  range 25–35°). Intensity data for  $0 < \theta < 55^\circ$ ,  $\omega/2\theta$  scans, two check reflections for every 98 reflections did not vary significantly over the course of the data collection. Lp but no absorption correction, 3939 reflections ( $h\ 0 \rightarrow 9$ ,  $k\ -9 \rightarrow 9$ ,  $l\ -16 \rightarrow 16$ ) of which 2652 [ $I > 3\sigma(I)$ ] used in calculations. Direct methods with *MULTAN80* (Main, fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); an *E* map calculated from the set of phases with the highest figure of merit revealed the structure. Full-matrix least-squares refinement on *F*. Anisotropic temperature factors for C and O atoms, isotropic for H. H positions except those bound to the water molecule were revealed from a difference map.  $w = 1.032/\sigma^2(F_o) + 0.003F_o^2$ , final  $R = 0.062$ ,  $wR = 0.067$  for 2652 reflections.  $R = 0.072$  for all reflections.  $S = 1.51$ ; final  $\Delta F$  map featureless,  $(\Delta/\sigma)_{\max} = 0.51$ , final  $\Delta\rho$  excursions  $-0.23$ – $0.32$  e Å<sup>-3</sup>. No corrections for secondary extinction, scattering factors as in *SHELX* (Sheldrick, 1976). Calculations of geometrical data and crystal packing were computed by the program *PARST* (Nardelli, 1983). Calculations performed on an IBM 370 computer.

**Discussion.** Final positional parameters of the non-H atoms are given in Table 1.‡ Bond distances and angles are given in Fig. 1. A perspective view of the molecule is in Fig. 2. The values of the bond lengths and angles are similar to those observed in other comparable systems (Yoshida, Tanaka, Ashida, Kakudo, Fukuyama & Katsube, 1979; Soderholm, Sonnerstam, Norrestam & Palm, 1976).

‡ Lists of structure factors, anisotropic thermal parameters of the non-H atoms, hydrogen-bond distances and angles, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44048 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The bond length of C=O when involved in a hydrogen bond, as in the present structure [1.283 (6) Å] and in other related structures [1.253 (6) Å in epishamixanthone (Fukuyama, Hamada, Tsukihara & Katsube, 1978), 1.248 (15) Å in demethylsterigmatocystin (Yoshida *et al.*, 1979) and 1.27 Å in celebixanthone (Stout, Stout & Welsh, 1963)]

Table 1. Fractional positional parameters and equivalent isotropic thermal parameters

$$B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{eq} (\text{Å}^2)$
C(1)	0.6723 (6)	0.0013 (6)	0.7148 (4)	3.1 (2)
C(2)	0.7323 (6)	0.0537 (6)	0.6419 (4)	2.9 (2)
C(3)	0.6261 (6)	0.1451 (6)	0.5781 (4)	2.8 (2)
C(4)	0.6752 (6)	0.2199 (6)	0.5043 (4)	3.1 (2)
C(5)	0.5514 (6)	0.3013 (6)	0.4429 (4)	2.9 (2)
C(6)	0.5838 (6)	0.3752 (6)	0.3669 (4)	3.2 (2)
C(7)	0.4640 (6)	0.4513 (6)	0.3060 (4)	3.2 (2)
C(8)	0.3026 (6)	0.4599 (6)	0.3263 (4)	3.3 (2)
C(9)	0.2660 (6)	0.3928 (6)	0.4010 (4)	3.2 (2)
C(10)	0.3876 (6)	0.3140 (6)	0.4579 (4)	3.0 (2)
C(11)	0.4602 (6)	0.1663 (6)	0.5889 (4)	2.8 (2)
C(12)	0.4012 (6)	0.1061 (6)	0.6596 (4)	3.3 (2)
C(13)	0.5075 (6)	0.0237 (6)	0.7225 (4)	3.2 (2)
C(14)	0.4997 (6)	0.5204 (6)	0.2219 (4)	3.7 (2)
C(15)	0.5109 (6)	0.3958 (6)	0.1435 (4)	3.7 (2)
C(16)	0.4051 (6)	0.3711 (6)	0.0654 (4)	4.3 (2)
C(17)	0.2482 (6)	0.4698 (6)	0.0384 (4)	5.5 (2)
C(18)	0.4372 (6)	0.2362 (6)	-0.0064 (4)	6.3 (2)
C(19)	0.9030 (6)	0.0022 (6)	0.6341 (4)	3.6 (2)
C(20)	0.9993 (6)	-0.0524 (6)	0.7089 (4)	4.0 (2)
C(21)	0.9415 (6)	-0.0523 (6)	0.8001 (4)	4.2 (2)
C(22)	1.0231 (6)	-0.1866 (6)	0.8554 (4)	5.0 (2)
C(23)	0.9622 (6)	0.1075 (6)	0.8576 (4)	5.8 (2)
O(1)	0.3462 (4)	0.2491 (5)	0.5306 (3)	3.1 (1)
O(2)	0.4528 (4)	-0.0374 (5)	0.7932 (3)	4.4 (1)
O(3)	0.7677 (4)	-0.0840 (5)	0.7805 (3)	3.8 (1)
O(4)	0.8250 (4)	0.2166 (4)	0.4936 (3)	4.0 (1)
O(5)	0.7429 (4)	0.3696 (4)	0.3531 (3)	3.8 (1)
O(6)	0.1874 (4)	0.5388 (5)	0.2693 (3)	4.3 (1)
OW	0.0613 (4)	0.3648 (5)	0.6500 (3)	5.2 (2)

is greater than the bond length of the carbonyl not involved in hydrogen bonding [1.22 Å in lysolipin I (Dobler & Schierlein, 1977), 1.211 (13) Å in hexachloroxanthone (Soderholm *et al.*, 1976) and 1.226 (2) Å in 2-hydroxy-1,3,4,7-tetramethoxyxanthone (Stout, Shun Lin & Singh, 1969)]. A similar situation has also been observed in the crystal structures of benzoxazine derivatives (Kashino, Nakashima & Haisa, 1978) and also in deoxyuridine and its related structures (Rahman & Wilson, 1972).

The three rings *A*, *B* and *C* of the xanthone ring system are not significantly planar [ $\sum (\Delta/\sigma)^2 = 22.2$ , 49.6 and 62.4 respectively]. Rings *A* and *C* are inclined at an angle of 1.8 (2)°. Ring *D*, angularly fused and formed by the cyclization of an isoprenoid side chain, is in a half-chair conformation. The corresponding asymmetry parameter (Duax, Weeks & Rohrer, 1976)  $\Delta C_2[C(21)-O(3)] = 7.1 (8)^\circ$ .

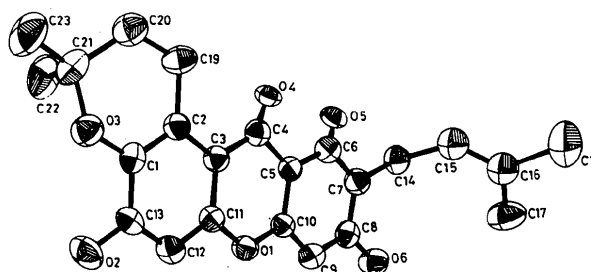


Fig. 2. ORTEP drawing (Johnson, 1976) of the title compound. Thermal ellipsoids are at the 55% probability level.

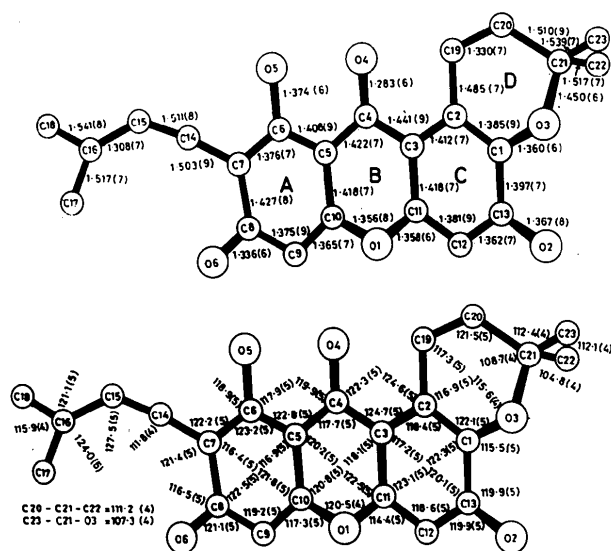


Fig. 1. Numbering scheme, bond distances (Å) and angles (°).

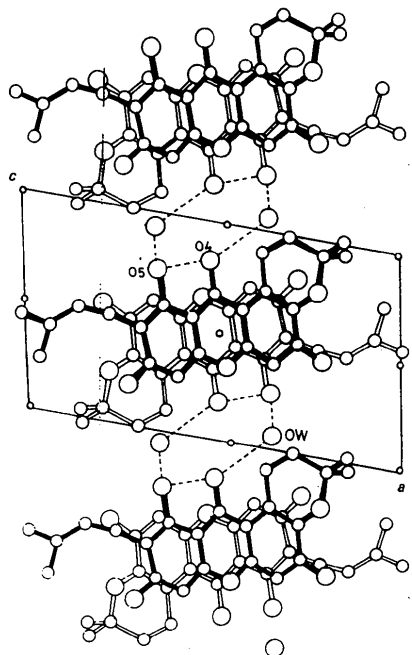


Fig. 3. Molecular packing of the title compound projected along the *bc* plane.

The mean plane of the isoprenyl side chain attached to ring *A* makes an angle of  $111.5 (1)^\circ$  with the mean plane of the xanthone ring system. The corresponding angle in other xanthenes is  $95.4^\circ$  in epishamixanthone and  $102^\circ$  in morellin (Kartha & Ambady, 1982).

The molecular arrangement projected along the *bc* plane is shown in Fig. 3. The xanthone rings are stacked on one another. Packing of the molecules in the crystal is essentially by hydrogen bonds between the water molecule and the carbonyl hydroxyl groups. The carbonyl and the adjacent hydroxyl are also involved in an intramolecular hydrogen bond.\* The O...O (donor→acceptor) hydrogen-bond distances vary from 2.503 (6) to 2.949 (5) Å.

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\* See deposition footnote.

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## Structure of a Dioxabicyclic Fluoro Octane Derivative

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**Abstract.** 2,2,3,3,4,4-Hexafluoro-1,7-dihydroxy-7-phenyl-6,8-dioxabicyclo[3.2.1]oct-5-yl phenyl ketone,  $C_{19}H_{12}F_6O_5$ ,  $M_r = 434.3$ , monoclinic,  $P2_1/n$ ,  $a = 6.789 (1)$ ,  $b = 23.554 (3)$ ,  $c = 11.486 (2) \text{ \AA}$ ,  $\beta = 99.03^\circ (1)$ ,  $V = 1813.98 \text{ \AA}^3$ ,  $Z = 4$ ,  $D_x = 1.590 \text{ g cm}^{-3}$ ,  $\lambda(\text{Mo } K\alpha_1) = 0.70926 \text{ \AA}$  (cell constants),  $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$  (intensity data),  $\mu = 1.46 \text{ cm}^{-1}$ ,  $F(000) = 880$ ,  $T = 293 \text{ K}$ ,  $R = 0.074$  for all 5325 independent reflections. Full-matrix least-squares refinement included isotropic H atoms and gave bond distances and angles with e.s.d.'s of  $0.002 \text{ \AA}$  and  $0.1^\circ$  respectively. Comparison with published *exo*-7-phenyl-

5,7-dimethyl-6,8-dioxabicyclo[3.2.1]octane parameters shows that the conformation of the bicyclic framework is similar, but in the six-membered heterocycle the C–C bonds are longer and the C–O bonds shorter in the hexafluoro derivative.

**Introduction.** Perfluoroalkylpolyketones, unlike simple monoketones, react in the presence of electron-donor molecules such as water, ethanol, tetrahydrofuran and pyridine to form heterocyclic compounds containing a fluorinated 6,8-dioxabicyclo[3.2.1]octane framework. The stability of the heterocycle is dependent on the