

## Structure of 5-Hydroxy-8,9-dimethoxy-2,2-dimethyl-7-(3-methyl-2-butenyl)-2H,6H-pyranol[3,2-b]xanthen-6-one\*

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**Abstract.**  $C_{25}H_{26}O_6$ ,  $M_r = 422.5$ , monoclinic,  $P2_1/c$ ,  $a = 19.228$  (3),  $b = 6.216$  (1),  $c = 20.016$  (3) Å,  $\beta = 121.05$  (2)°,  $V = 2049.6$  (7) Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.349$  (2) (floatation),  $D_x = 1.369$  Mg m<sup>-3</sup>, Mo  $K\alpha$  radiation,  $\lambda = 0.7107$  Å,  $\mu = 0.0909$  mm<sup>-1</sup>,  $F(000) = 896$ ,  $T = 294$  K, final  $R = 0.065$  for 1239 reflections [ $I > 1\sigma(I)$ ]. The xanthone ring system is nearly planar. The dihedral angle between the xanthone ring plane and the plane of the 3-methyl-2-butenyl side chain is 66.8 (3)°.

**Introduction.** The fruit hulls and the bark of the East Indian mangosteen tree (*Garcinia mangostana*, Guttiferae) have been of use in the treatment of dysentery (Yates & Stout, 1958). The xanthone mangostin (a major component – about 50% – in the mangosteen fruit hulls) and its derivatives were reported to inhibit prostaglandin synthetase, similar to non-steroidal anti-inflammatory compounds (Shankaranarayanan, Gopalakrishnan & Kameswaran, 1979). Further many xanthenes obtained from different plants but belonging to the Guttiferae family have been reported to possess anti-inflammatory and CNS depressant activities (Gopalakrishnan, Shankaranarayanan, Nazimudeen, Viswanathan & Kameswaran, 1980). The title compound is one of the constituents of the mangosteen fruit hulls, but there are no reports on the pharmacological properties of this compound itself so far. An 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 petrol 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 0.13 × 0.15 × 0.19 mm. Computer-controlled four-circle diffractometer (locally fabricated at BARC, India), monochromated Mo  $K\alpha$  radiation. Cell parameters from least-squares refinement of setting angles of 25 reflections ( $\theta$  range 8–15°), intensity data for  $0 < \theta < 26^\circ$ ,  $\omega/2\theta$  scans, three check reflections for every 97 data points did not vary significantly over the course of the data collection. Lp but no absorption correction, 1900 unique reflections ( $h$  0→19,  $k$  0→7,  $l$  -20→20) of which 1239 [ $I > 1\sigma(I)$ ], owing to the poor quality of the crystal] 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 from a difference map. Owing to the poor ratio of observations to the number of variables, final refinements were carried out in two blocks (non-hydrogens, 279 variables; hydrogens, 104 variables).  $w = 1.2160/[\sigma^2(F) + 0.0002|F_o|^2]$ , final  $R = 0.065$ ,  $wR = 0.073$  for 1239 reflections.  $R = 0.086$  for all reflections.  $S = 1.73$ ; final  $\Delta F$  map featureless,  $(\Delta/\sigma)_{\max} = 0.53$ , final  $\Delta\rho$  excursions  $-0.26 \rightarrow 0.30$  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 IBM 370 computer.

**Discussion.** Final positional parameters of the non-H atoms are given in Table 1.‡ Bond distances and angles are given in Table 2. A perspective view of the molecule

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‡ Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43464 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional positional parameters and equivalent isotropic thermal parameters

$$B_{eq} = \frac{1}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	B <sub>eq</sub> (Å <sup>2</sup> )
C(1)	0.3256 (6)	0.8338 (9)	0.6426 (6)	4.0 (4)
C(2)	0.3189 (6)	0.7144 (9)	0.5816 (6)	3.8 (4)
C(3)	0.2733 (6)	0.5192 (9)	0.5631 (6)	3.7 (3)
C(4)	0.2563 (6)	0.3842 (9)	0.4972 (6)	3.8 (3)
C(5)	0.2029 (6)	0.2059 (9)	0.4828 (6)	3.6 (4)
C(6)	0.1792 (6)	0.0650 (9)	0.4203 (6)	4.3 (3)
C(7)	0.1303 (6)	-0.1057 (9)	0.4063 (6)	3.8 (4)
C(8)	0.1005 (6)	-0.1432 (9)	0.4572 (6)	3.7 (4)
C(9)	0.1219 (6)	-0.0146 (9)	0.5199 (6)	4.3 (5)
C(10)	0.1725 (6)	0.1568 (9)	0.5304 (6)	4.5 (4)
C(11)	0.2395 (6)	0.4588 (9)	0.6075 (6)	3.5 (4)
C(12)	0.2531 (6)	0.5791 (9)	0.6730 (6)	4.1 (4)
C(13)	0.2943 (6)	0.7672 (9)	0.6876 (6)	4.6 (4)
C(14)	0.2650 (6)	0.8519 (9)	0.7861 (6)	7.4 (5)
C(15)	0.4339 (6)	1.0813 (9)	0.7292 (6)	6.6 (5)
C(16)	0.3514 (6)	0.8057 (9)	0.5340 (6)	3.3 (4)
C(17)	0.4352 (6)	0.7241 (9)	0.5614 (6)	4.8 (4)
C(18)	0.5015 (6)	0.8468 (9)	0.5863 (6)	4.6 (4)
C(19)	0.5798 (6)	0.7433 (9)	0.6079 (6)	5.7 (5)
C(20)	0.5055 (6)	1.0845 (9)	0.5963 (6)	6.0 (5)
C(21)	0.1096 (6)	-0.2692 (9)	0.3476 (6)	4.7 (4)
C(22)	0.0488 (6)	-0.4109 (9)	0.3305 (6)	4.5 (4)
C(23)	0.0016 (6)	0.3947 (9)	0.3677 (6)	4.4 (3)
C(24)	-0.0683 (6)	-0.2334 (9)	0.3248 (6)	5.4 (5)
C(25)	-0.0258 (6)	-0.6141 (9)	0.3810 (6)	5.7 (4)
O(1)	0.1942 (3)	0.2822 (5)	0.5936 (3)	4.3 (3)
O(2)	0.3053 (3)	0.9011 (5)	0.7454 (3)	5.9 (3)
O(3)	0.3615 (3)	1.0339 (5)	0.6565 (3)	5.3 (4)
O(4)	0.2874 (3)	0.4104 (5)	0.4567 (3)	5.3 (3)
O(5)	0.2083 (3)	0.0985 (5)	0.3731 (3)	4.3 (3)
O(6)	0.0515 (3)	-0.3107 (5)	0.4467 (3)	4.9 (3)

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

C(1)–C(2)	1.38 (2)	C(9)–C(10)	1.38 (1)
C(1)–C(13)	1.38 (2)	C(10)–O(1)	1.35 (1)
C(1)–O(3)	1.38 (1)	C(11)–C(12)	1.41 (1)
C(2)–C(3)	1.43 (1)	C(11)–O(1)	1.34 (1)
C(2)–C(16)	1.49 (2)	C(12)–C(13)	1.36 (1)
C(3)–C(4)	1.45 (2)	C(13)–O(2)	1.35 (1)
C(3)–C(11)	1.40 (2)	C(14)–O(2)	1.42 (1)
C(4)–C(5)	1.44 (1)	C(15)–O(3)	1.43 (1)
C(4)–O(4)	1.24 (2)	C(16)–C(17)	1.50 (1)
C(5)–C(6)	1.40 (1)	C(17)–C(18)	1.34 (1)
C(5)–C(10)	1.38 (2)	C(18)–C(19)	1.48 (1)
C(6)–C(7)	1.35 (1)	C(18)–C(20)	1.49 (1)
C(6)–O(5)	1.34 (2)	C(21)–C(22)	1.36 (1)
C(7)–C(8)	1.42 (2)	C(22)–C(23)	1.44 (2)
C(7)–C(21)	1.44 (1)	C(23)–C(24)	1.54 (1)
C(8)–C(9)	1.36 (1)	C(23)–C(25)	1.53 (1)
C(8)–O(6)	1.35 (1)	C(23)–O(6)	1.46 (1)
C(13)–C(1)–O(3)	118.7 (8)	C(9)–C(10)–O(1)	116.0 (8)
C(2)–C(1)–O(3)	118.2 (9)	C(5)–C(10)–O(1)	118.6 (7)
C(2)–C(1)–C(13)	123.0 (6)	C(3)–C(11)–O(1)	123.7 (8)
C(1)–C(2)–C(16)	118.8 (6)	C(3)–C(11)–C(12)	121.6 (7)
C(1)–C(2)–C(3)	116.8 (9)	C(12)–C(11)–O(1)	114.6 (8)
C(3)–C(2)–C(16)	124.0 (7)	C(11)–C(12)–C(13)	117.7 (9)
C(2)–C(3)–C(11)	119.2 (7)	C(1)–C(13)–C(12)	121.4 (9)
C(2)–C(3)–C(4)	123.1 (8)	C(12)–C(13)–O(2)	122.1 (8)
C(4)–C(3)–C(11)	117.5 (6)	C(1)–C(13)–O(2)	116.5 (6)
C(3)–C(4)–O(4)	124.0 (6)	C(2)–C(16)–C(17)	111.3 (7)
C(3)–C(4)–C(5)	115.6 (9)	C(16)–C(17)–C(18)	125.5 (6)
C(5)–C(4)–O(4)	120.4 (6)	C(17)–C(18)–C(20)	126.0 (10)
C(4)–C(5)–C(10)	123.0 (7)	C(17)–C(18)–C(19)	119.3 (6)
C(4)–C(5)–C(6)	122.2 (9)	C(19)–C(18)–C(20)	114.7 (9)
C(6)–C(5)–C(10)	114.8 (6)	C(7)–C(21)–C(22)	120.1 (9)
C(5)–C(6)–O(5)	118.2 (6)	C(21)–C(22)–C(23)	120.8 (7)
C(5)–C(6)–C(7)	123.4 (10)	C(22)–C(23)–O(6)	110.3 (9)
C(7)–C(6)–O(5)	118.4 (7)	C(22)–C(23)–C(24)	111.0 (8)
C(6)–C(7)–C(21)	126.3 (9)	C(22)–C(23)–C(25)	113.0 (7)
C(6)–C(7)–C(8)	118.4 (7)	C(25)–C(23)–O(6)	102.9 (6)
C(8)–C(7)–C(21)	115.0 (7)	C(24)–C(23)–O(6)	105.6 (5)
C(7)–C(8)–O(6)	121.5 (8)	C(24)–C(23)–C(25)	113.4 (8)
C(7)–C(8)–C(9)	121.5 (7)	C(10)–O(1)–C(11)	121.3 (7)
C(9)–C(8)–O(6)	116.9 (8)	C(13)–O(2)–C(14)	118.0 (5)
C(8)–C(9)–C(10)	116.5 (9)	C(1)–O(3)–C(15)	120.9 (5)
C(5)–C(10)–C(9)	125.3 (8)	C(8)–O(6)–C(23)	117.5 (6)

is given in Fig. 1. The values of bond lengths and angles are similar to those observed in other comparable systems (Yoshida, Tanaka, Ashida, Kakudo, Fukuyama & Katsube, 1979; Söderholm, Sonnerstam, Norrestam & Palm, 1976).

One of the methoxy groups, C(15)–O(3), is rotated so that C(15) is well out of the plane of ring *A* [deviation of C(15) = 0.85 (1) Å; rotation about C(1)–O(3) = 64 (1)°]. Similar rotations of the methoxy group have been observed in celebixanthone, 72.8° (Stout, Stout & Welsh, 1963) and in 2-hydroxy-1,3,4,7-tetramethoxyxanthone, 72.0, 58.1, 83.0° (Stout, Shun Lin & Singh, 1969), where the methoxy group is similarly hindered by adjacent alkyl and hydroxyl groups. However, the other methoxy group C(14)–O(2) is nearly coplanar with ring *A* [deviation of C(14) = 0.05 (1) Å; rotation about C(13)–O(2) = -6.6 (13)°], allowing maximum conjugation of the unshared oxygen electrons with the aromatic π cloud. The close approach of C(14)···C(12) [2.74 (1) Å] that arises is presumably relieved by the opening of the O(2)–C(13)–C(12) angle [122.1 (8)°].

The three rings, *A*, *B* and *C*, of the xanthone ring system are nearly in a planar conformation [ $\sum(\Delta/\sigma)^2 = 22.0, 32.7$  and  $1.6$  respectively]. The rings *A* and *C* are inclined at an angle of 5.3 (3)°. The ring *D*, linearly fused, evolved by the cyclization of an isoprenoid side chain is in a half-chair conformation. The corresponding asymmetry parameter (Duax, Weeks & Rohrer, 1976)  $\Delta C_2[C(7)–C(21)] = 6.8^\circ$ .

The mean plane of the 3-methyl-2-butenyl side chain attached to ring *A* makes an angle of 66.8 (3)° with the mean plane of the xanthone ring system. The corresponding angle in other xanthenes is 95.4° in epishamixanthone (Fukuyama, Hamada, Tsukihara & Katsube, 1978) and 102° in morellin (Kartha & Ambady, 1982).

There is an intramolecular hydrogen bond O(5)···O(4), 2.500 (5), O(5)–HO(5), 0.95 (3), O(4)···HO(5), 1.82 (3) Å; angle O(5)–HO(5)···O(4), 126 (3)°. The molecular packing projected along the *ac* plane is shown in Fig. 2.

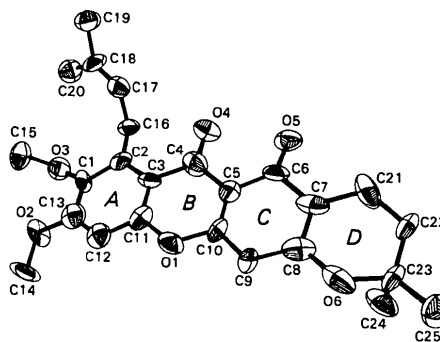


Fig. 1. ORTEP drawing (Johnson, 1976) of the title compound. Thermal ellipsoids are at the 50% probability level.

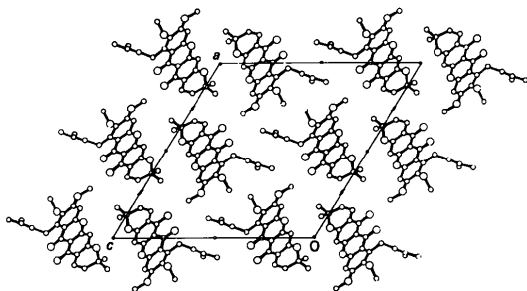


Fig. 2. Molecular packing of the title compound viewed along the *b* axis.

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## Structure of *ent*-(12*R*)-Methyl-15,16-epoxy-9,10-friedolabda-5(10),13(16),14-trien-19-oate 20,12-Lactone (Penduliflaworosin)

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**Abstract.** Systematic name: 5-(3-furanyl)-3',4,4',5,5',-6',7',8'-octahydro-2',5'-dimethyl-2-oxospiro[furan-3(2*H*),1'(2'*H*)-naphthalene]-5'-carboxylic acid methyl ester,  $C_{21}H_{26}O_5$ ,  $M_r = 358.4$ , orthorhombic,  $P2_12_12_1$ ,  $a = 6.2780$  (5),  $b = 12.3069$  (10),  $c = 25.1047$  (22) Å,  $V = 1939.66$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.227$  Mg m<sup>-3</sup>. Cu  $K\alpha$  radiation (graphite-crystal monochromator,  $\lambda = 1.54178$  Å),  $\mu(\text{Cu } K\alpha) = 0.67$  mm<sup>-1</sup>,  $F(000) = 768$ ,  $T = 290$  K. Final  $R = 0.044$ ,  $wR = 0.045$  for 1914 'observed' reflections and 313 variables. The two six-membered rings *A* and *B* adopt half-chair and intermediate half-chair/envelope conformations, respec-

tively, while the lactone ring is close to a half-chair (*C*<sub>2</sub> form). Methyl groups C(18) and C(17) are pseudo-axial and bisectonal respectively. The conformation of the methoxycarbonyl group is synperiplanar.

**Introduction.** The title compound, isolated from *Croton penduliflorus* Hutch (Euphorbiaceae), an important medicinal plant used by the Yorubas of Nigeria as a remedy for stomach complaints, was reported to have the structure (I) (Adesogan, 1981). In the structure (I), proposed on spectroscopic (NMR, IR, UV) and chemical evidence, the stereochemistry was inferred on biogenetic grounds. Penduliflaworosin is of interest in view of the current emphasis and importance which the Nigerian government places on local medicinal plants

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