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6-Deoxyjacareubin

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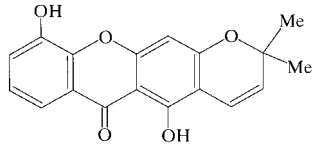
The natural compound 5,10-dihydroxy-2,2-dimethylpyrano-[3,2-*b*]xanthen-6(2*H*)-one (6-deoxyjacareubin), $C_{18}H_{14}O_5$, was isolated from leaves of *Vismia latifolia* (Guttiferae family). The compound has four six-membered rings. The molecule has two planar benzenoid and one planar pyranoid ring, plus a pyranoid ring in a distorted chair conformation. The crystal is stabilized by one intra- and one intermolecular hydrogen bond.

Comment

The title compound, (I), is a natural xanthone. Xanthones are heterocyclic ring systems with many pharmacological applications (Santos, Nagem, Silva & da Silva, 2000). It was isolated from *Vismia latifolia* Choisy (Syn. *Hypericum latifolium* Aubl.). This species belongs to the Guttiferae family, subfamily Hypericoideae and tribe *Vismieae* and is a tree commonly known in the Bahia state (Brazil) as pau-de-sangue. This plant is widely used in traditional medicine as a tonic and febrifugal agent (Corrêa, 1978). Previous works have reported the presence of several xanthones, terpenoids, benzophenones, flavonoids and anthranoids in *Vismia* species (Santos *et al.*, 1999; Santos, Nagem, da Silva & Silva, 2000; Nagem & De Oliveira, 1997; Peres & Nagem, 1997; Nagem & Alves, 1995; Nagem & Ferreira, 1993; Delle Monache *et al.*, 1983).

As part of a chemotaxonomic study of the Guttiferae family (*Vismia* genus), we have determined the structure of the compound known as 6-deoxyjacareubin, (I). We have identified (I) by spectroscopic methods (UV, EI–MS, and ^{1}H and ^{13}C NMR) and the presence of the γ-pyrone was confirmed by the X-ray data. This compound was first isolated from *Calophyllum inophyllum* by Jackson *et al.* (1969). It is described as an antifungal agent against *Postia placenta* (Reyes Chilpa *et al.*, 1997) and *Cladosporium cucumerinum* (Rocha *et al.*, 1994). For this reason, we have also tested its biological activity against fungi [*Cândida albicans*, *Aspergillus fumigatus*, *Aspergillus ochraceus* (*allutaceus*) and *Penicillium citrinum*] and bacteria (*Escherichia coli* and *Streptococcus muttans*). Our tests, however, did not show biological inhibition on these organisms.



(I)

Fig. 1 is an *ORTEP*-3 (Farrugia, 1997) view of the title compound. As expected, the molecule is almost flat. All atoms in the *A*, *B* and *C* rings lie within 0.149 (1) Å of the least-squares plane through the three-ring system. The *A*, *B* and *C* rings are also individually almost planar, including the O1, O2 and O3 atoms linked to them. The largest deviations from the individual least-squares planes are 0.006 (2), 0.037 (1) and 0.009 (1) Å for rings *A*, *B* and *C*, respectively. The least-squares planes of the *A* and *B* rings form an angle of 3.64 (8)°, those of the *B* and *C* rings form an angle of 3.69 (8)°, and those of the *A* and *C* rings form an angle of 7.31 (9)°. The planes of the *A* and *C* ring systems intersect on a line which is approximately through the middle of the *B* ring. A folding point along an imaginary line drawn between O5 and C6 defines an angle of 6.55 (6)° (least-squares planes of rings *A* and *C* calculated by including O5 and C6). Ring *D* is in a deformed chair conformation. The weighted average absolute torsion angle (Domenicano *et al.*, 1975) in the *D* ring is 27 (8)°. The main bond lengths and angles are given in Table 1. The mean value of the intramolecular C—C bond distances within the *A* and *C* benzenoid rings is 1.39 (1) Å, which agrees well with the normal aromatic value. In the same way, the mean bond angles in rings *A* and *C* are 120 (2)°. The average value of the two C—O5 bond lengths in pyranoid ring *B* is 1.373 (2) Å. The observed geometry of pyranoid ring *B* agrees well with similar pyranxanthone geometries (Ho *et al.*, 1987; Vijayalakshmi *et al.*, 1987; Ferguson *et al.*, 1985; Söderholm *et al.*, 1976).

The title molecule exhibits a moderated intramolecular hydrogen bond, O3—H3′···O2, with an O···O distance of 2.561 (2) Å (Table 2). The intermolecular hydrogen bond

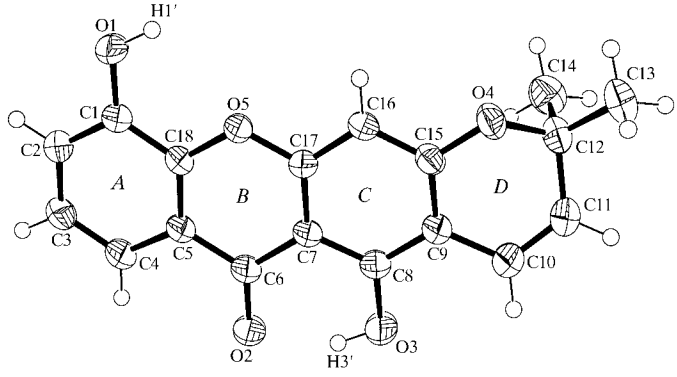


Figure 1
ORTEP-3 (Farrugia, 1997) view of 6-deroxyjacareubin, showing the atom and ring labelling and 50% probability ellipsoids.

between hydroxyl group O1—H1′ and adjacent carboxyl oxygen O2 at ($x+1$, y, z) [the O···O distance is 2.778 (2) Å] stabilizes the structure and gives rise to a chain parallel to the [100] direction (Fig. 2). The separation between the least-squares planes through the molecules at (x, y, z) and ($-x$, $-y$, $-z$) is 3.67 (2) Å.

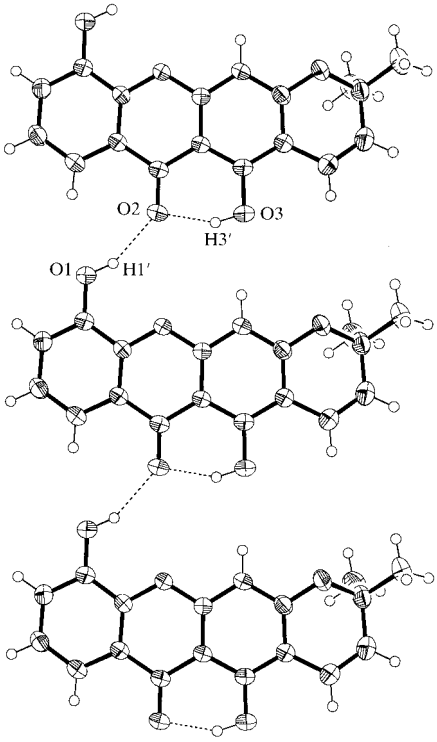


Figure 2
View of the chain of hydrogen bonds parallel to [100]. Symmetry codes from top to bottom are ($1+x$, y, z), (x, y, z) and ($1-x$, y, z).

Experimental

Dried and ground leaves (1502.0 g) of *Vismia latifolia* were extracted (at room temperature) with *n*-hexane (32.85 g) and EtOH (200.0 g) in succession. The ethanol extract was stirred with water for 24 h and filtered. The soluble portion was extracted with $CHCl_3$, EtOAc and *n*-butanol in succession. The solid obtained by evaporation (under vacuum) of the fraction soluble in $CHCl_3$ (30.0 g) was chromatographed on silica-gel (Merck, 352 g) column chromatography and eluted with CH_2Cl_2, EtOAc and EtOH. The 90 fractions obtained yielded nine groups (D1–D9). D3 (fractions 4–6, 658.0 mg) was washed with petrol ether giving an insoluble portion that was washed with methanol yielding 6-deoxyjacareubin (101.0 mg) as a yellow solid. The powder mass obtained was crystallized from methanol by slow evaporation at room temperature.

Crystal data

$C_{18}H_{14}O_5$
$M_r = 310.29$
Triclinic, $P\overline{1}$
$a = 7.4450$ (2) Å
$b = 9.5200$ (3) Å
$c = 10.9390$ (3) Å
$\alpha = 105.051$ (2)°
$\beta = 103.154$ (2)°
$\gamma = 93.083$ (2)°
$V = 723.80$ (4) Å^3
$Z = 2$
$D_x = 1.424$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3315 reflections
$\theta = 1.0$–27.5°
$\mu = 0.11$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.24 × 0.17 × 0.12 mm

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.354 (2)	C10—C11	1.327 (3)
O3—C8	1.346 (2)	C11—C12	1.504 (3)
O4—C15	1.360 (2)	C12—C13	1.517 (2)
O4—C12	1.470 (2)	C12—C14	1.522 (3)
C9—C10	1.458 (2)		
O4—C12—C11	109.3 (1)	O4—C12—C14	107.4 (2)
O4—C12—C13	104.5 (2)	C11—C12—C14	111.8 (2)
C11—C12—C13	112.2 (2)	C13—C12—C14	111.3 (2)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1′···O2^{i}	0.87 (3)	1.97 (3)	2.778 (2)	154 (3)
O3—H3′···O2	0.89 (3)	1.74 (3)	2.561 (2)	152 (4)

Symmetry code: (i) $1+x$, y, z.

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
6210 measured reflections
3319 independent reflections
2674 reflections with $I > 2\sigma(I)$
$R_{int} = 0.014$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R(F) = 0.051$
$wR(F^2) = 0.150$
$S = 1.02$
3319 reflections
218 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 0.4000P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.49$ e Å^{-3}

The H atoms of the phenyl and methyl groups were positioned stereochemically and were refined with fixed individual displacement parameters [U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}($C_{methoxy}$)] using a riding model with aromatic C—H = 0.93 Å and methyl C—H = 0.98 Å. The hydroxyl H atoms were located by difference Fourier synthesis and were set as isotropic.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1189). Services for accessing these data are described at the back of the journal.

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