organic compounds

Mammeigin

Antônio C. Doriguetto,[a]* Javier Ellena,[b] Marcelo H. Dos Santos,[c] Maria E. C. Moreira[d] and Tanus J. Nagem[e]

[a]Departamento de Ciêcias Exatas, Universidade Federal de Alfenas – UNIFAL-MG, Rua Gabriel Monteiro da Silva 714, CEP 37130-000, Alfenas, MG, Brazil, [b]Instituto de Física de São Carlos – USP, Caixa Postal 369, CEP 13560-970, São Carlos, SP, Brazil, [c]Departamento de Farmácia, Universidade Federal de Alfenas – UNIFAL-MG, Rua Gabriel Monteiro da Silva 714, CEP 37130-000, Alfenas, MG, Brazil, [d]Universidade José Rosário Vellano – UNIFENAS, Laboratório de Fitofármacos, Rod. MG-179, Km-0, CEP 37130-000, Alfenas, MG, Brazil, and [e]Departamento de Química, Universidade Federal de Ouro Preto, CEP 35400-000, Ouro Preto, MG, Brazil

Correspondence e-mail: doriguetto@unifal-mg.edu.br

Single crystals of the phenylcoumarin named mammeigin (or mammea A/AA cycle D) [systematic name: 5-hydroxy-8,8-dimethyl-6-(3-methylbutanoyl)-4-phenyl-2H,8H-pyrano[2,3-f]-chromen-2-one], $C_{25}H_{24}O_5$, were obtained in the course of a chemotaxonomic study of the Guttiferae family. Mammeigin was extracted from the fruits of *Kilmeyera pumila*. The structure reveals an infinite three-dimensional network stabilized by non-classical intermolecular hydrogen bonds.

Comment

In the course of our chemical studies of plants belonging to the family Guttiferae, we have investigated the lipophilic extract of the fruits of *Kilmeyera pumila* Pohl and this led to the isolation of two phenylcoumarins, (I) and (II) (see scheme). The title compound, (I), named mammeigin [or mammea A/AA cycle D, or 5-hydroxy-8,8-dimethyl-6-(3-methylbutan-oyl)-4-phenyl-2H,8H-pyrano[2,3-f]chromen-2-one (9CI)], has already been isolated from Guttiferae species (Lopez-Perez *et al.*, 2005; Reutrakul *et al.*, 2003; Gramacho *et al.*, 1999; Dennis & Akshaya Kumar, 1998; Castellano *et al.*, 1988; Crombie *et al.*, 1987, 1967; Carpenter *et al.*, 1971; Chakraborty & Chatterji, 1969; Finnegan & Mueller, 1964), and its structure has been established based on spectroscopic evidence and chemical correlation (Finnegan & Mueller, 1965). The structure of (II), a phenylcoumarin from Guttiferae species, was proposed for a new natural product named isomammeigin from IR and NMR data (de Abreu e Silva, 1987). Later, its structure was unambiguously determined by X-ray diffraction by Castellano *et al.* (1988).

Some phenylcoumarins described previously have shown cytotoxic (Reutrakul *et al.*, 2003; Scio *et al.*, 2003) and anti-HIV (Ishikawa, 2000; Spino *et al.*, 1998) activities. Chemopreventive activity against cancer *in vitro* without cytotoxicity

has also been reported for some of these derivatives (Itoigawa *et al.*, 2001; Ito *et al.*, 2003).
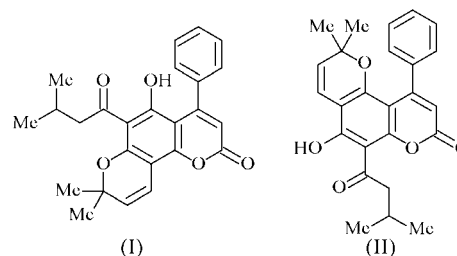
The crystal structure of (I), reported here, was part of a chemotaxonomic study of the Guttiferae family. X-ray analysis is important in this case, since from spectroscopic data alone, structures (I) and (II) are possible alternatives. In this way, we have identified (I) by spectroscopic methods (UV, EI–MS, and ^{1}H and ^{13}C NMR) and its structure was unambiguously confirmed by the X-ray data.

Fig. 1 is an *ORTEP-3* (Farrugia, 1997) view of the title compound. The main geometrical parameters are given in Table 1. The intramolecular conformation was analyzed using *MOGUL* (Bruno *et al.*, 2004). This study showed that all bond lengths and angles are in agreement with the expected values. As expected, aromatic ring A is planar and shows nearly equal C—C distances and C—C—C angles. The molecular moiety, considering only the atoms of rings B, C and D, is also almost planar. All atoms in rings B, C and D, except for atom C18, which is a Csp^3 C atom, lie within ±0.152 (3) Å of the least-squares plane through the three-ring system. Ring D presents an envelope conformation, with atom C18, which deviates by 0.488 (4) Å from the least-squares plane through the three-ring system, at the flip point. The weighted average absolute torsion angle (Domenicano *et al.*, 1975) in ring D is 24.2 (1)°. Rings B and C are also individually almost planar, including the first-neighbour atoms linked to them. The largest deviations from the individual least-squares planes are 0.059 (2)
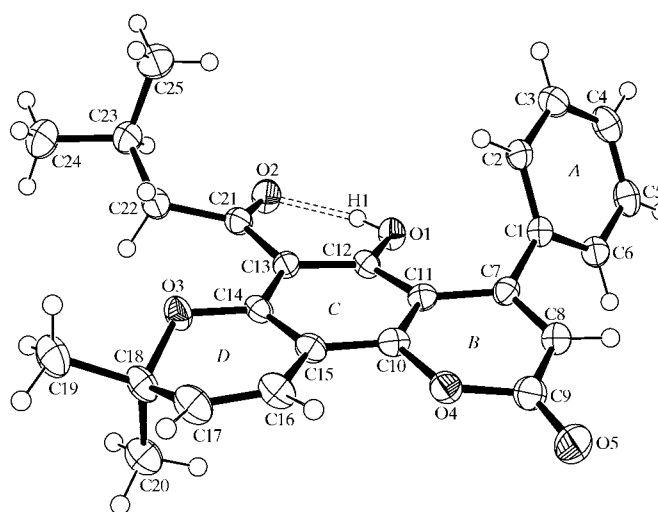

Figure 1
A view of (I), showing the labelling of the rings and atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

(C9) and 0.033 (2) Å (C12) for rings *B* and *C*, respectively. The least-squares planes of rings *B* and *C* form an angle of 5.5 (1)° and those of rings *C* and *D* form an angle of 1.9 (2)°. Phenyl ring *A* and the least-squares plane through ring *B* form an angle of 51.9 (1)°. This appreciable deviation from 90° can be viewed as a co-operative consequence of the non-classical intermolecular hydrogen-bond interactions [C4—H4···O5^i and C20—H20*A*···*Cg*^{iii}, where *Cg* is the centroid of ring *A*; symmetry code as in Table 2] (Figs. 2 and 3, and Table 2).

Compound (I) exhibits a strong classical intramolecular hydrogen bond, O1—H1···O2 (Fig. 1 and Table 2). An interesting structural feature is that the crystal packing of (I) is formed by an infinite three-dimensional network involving non-classical hydrogen bonds. The intermolecular hydrogen bond between phenyl ring *A* and the adjacent carboxyl atom O5 (C4—H4···O5) gives rise to a chain, in a zigzag molecular fashion, parallel to the [10$\bar{1}$] direction (Fig. 2). Networks parallel to the [10$\bar{1}$] direction are themselves hydrogen
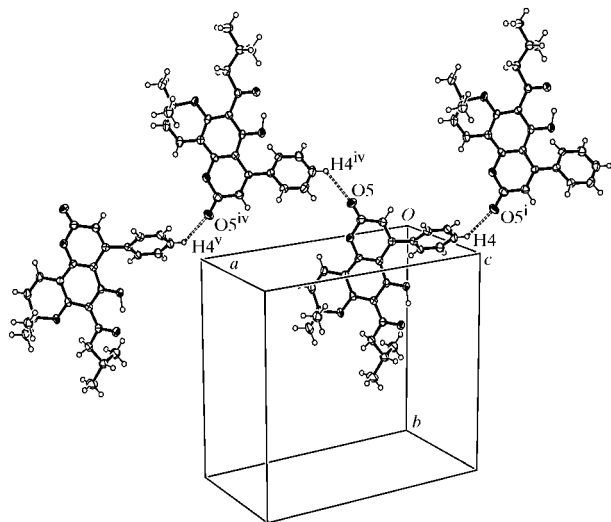
bonded *via* two other non-classical associations, forming infinite chains along the [001] and [101] directions. The chain along [001] is stabilized by C19—H19*B*···O5 interactions, whereas that along [101] is stabilized by intermolecular bonds of the type H···π-aryl (Fig. 3). The result is an extended three-dimensional supramolecular assembly mediated by non-classical C—H···O/π bonding. Details of all hydrogen-bond contacts involved in these networks are given in Table 2.

Experimental

The title compound was extracted from the fruit of *Kilmeyera pumila* Pohl (family Guttiferae) using conventional methods of extraction and chromatography on silica gel, eluting with mixtures (increasing polarity) of hexane, diethyl ether and ethanol (de Abreu e Silva, 1987). The purified powder of compound (I) obtained was recrystallized from a solution in acetone by slow evaporation at room temperature.

Crystal data

$C_{25}H_{24}O_5$	$Z = 4$
$M_r = 404.44$	$D_x = 1.302$ Mg m^{-3}
Monoclinic, Cc	Mo $K\alpha$ radiation
$a = 16.727$ (1) Å	$\mu = 0.09$ mm^{-1}
$b = 14.152$ (1) Å	$T = 150$ (2) K
$c = 8.718$ (1) Å	Prism, pale yellow
$\beta = 90.79$ (1)°	$0.35 \times 0.12 \times 0.10$ mm
$V = 2063.5$ (3) Å^3	

Data collection

Nonius KappaCCD area-detector diffractometer	9028 measured reflections
	2350 independent reflections
φ scans, and ω scans with κ offsets	1799 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Blessing, 1995)	$R_{int} = 0.065$
	$\theta_{max} = 27.4°$
$T_{min} = 0.950$, $T_{max} = 0.985$	

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.0542P)^2]$
$wR(F^2) = 0.105$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
2350 reflections	$\Delta\rho_{max} = 0.22$ e Å^{-3}
271 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Figure 2
The packing of (I), showing the infinite network along the [10$\bar{1}$] direction. [Symmetry codes: (i) $x - \frac{1}{2}$, $-y - \frac{1}{2}$, $z + \frac{1}{2}$; (iv) $x + \frac{1}{2}$, $-y - \frac{1}{2}$, $z - \frac{1}{2}$; (v) $x + 1$, y, $z - 1$.]
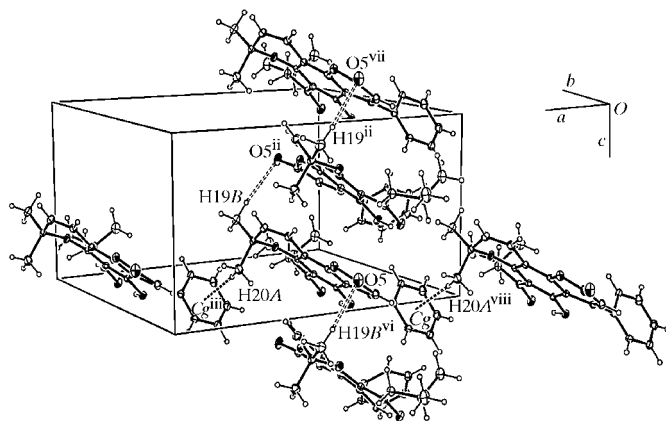

Figure 3
The packing of (I), showing the infinite networks along the [001] and [101] directions. [Symmetry codes: (ii) x, $-y$, $z - \frac{1}{2}$; (iii) $x + \frac{1}{2}$, $y + \frac{1}{2}$, z; (vi) x, $-y$, $z + \frac{1}{2}$; (vii) x, y, $z - 1$; (viii) $x - \frac{1}{2}$, $y - \frac{1}{2}$, z.]

Table 1
Selected geometric parameters (Å, °).

C9—O5	1.207 (4)	C15—C16	1.453 (4)
C9—O4	1.393 (4)	C16—C17	1.329 (4)
C10—O4	1.368 (3)	C17—C18	1.499 (5)
C12—O1	1.338 (3)	C18—O3	1.475 (3)
C14—O3	1.356 (3)	C21—O2	1.247 (3)
C14—O3—C18	118.4 (2)	C10—O4—C9	121.6 (2)

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

Cg is the centroid of ring *A* (atoms C1–C6).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2	0.82	1.73	2.467 (3)	149
C4—H4···O5^i	0.93	2.58	3.234 (4)	128
C19—H19*B*···O5^{ii}	0.96	2.58	3.523 (4)	168
C20—H20*A*···*Cg*^{iii}	0.96	2.60	3.534 (3)	165

Symmetry codes: (i) $x - \frac{1}{2}$, $-y - \frac{1}{2}$, $z + \frac{1}{2}$; (ii) x, $-y$, $z - \frac{1}{2}$; (iii) $x + \frac{1}{2}$, $y + \frac{1}{2}$, z.

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Since the most electron-rich atom is oxygen, the absolute structure could not be determined using the diffraction data. Therefore, Friedel pairs were averaged before refinement. All H atoms were positioned stereochemically and were refined with fixed individual displacement parameters [$U_{iso}(H) = 1.2U_{eq}(C$ or O) or $1.5U_{eq}$(aromatic C)] using a riding model, with C—H = 0.93–0.97 Å and O—H = 0.82 Å.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *enCIFer* (Allen *et al.*, 2004).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3017). Services for accessing these data are described at the back of the journal.

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