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Flemiculosin, a novel chalcone

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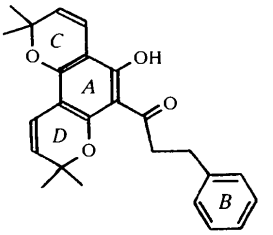
Abstract

The title compound, 6-cinnamoyl-5-hydroxy-2,2,8,8-tetramethyl-2*H*,8*H*-pyrano[2,3-*f*]chromene, $C_{25}H_{24}O_4$, is an angular benzodipyran system. It contains a central tricyclic core and a peripheral aromatic ring. The central ring of the tricyclic core is fully substituted while the pyran rings on either side are each unsubstituted at two sites. The central fully substituted ring is planar within 0.014 Å. One pyran ring is planar to within 0.041 Å, but the second pyran ring is only planar to within 0.156 Å; this may be attributed to an intramolecular C—H···O contact of 2.30 Å. The structure is stabilized by intramolecular O—H···O hydrogen bonds.

Comment

The genus *Flemingia* is notable for including a variety of flavanoids, particularly stromenochalcones; a number of *Flemingia* species have been examined chemically (Adityachaudhury *et al.*, 1970; Adityachaudhury & Gupta, 1970; Bhatt, 1975). Flemiculosin, (I), a novel chalcone with an angular benzodipyran system, has been studied chemically, and NMR and spectroscopic studies have been carried out by Khattri *et al.* (1984). We report here the X-ray structure determination of flemiculosin undertaken to provide more details of the structure.



(I)

The title compound has been isolated from the leaves of *Flemingia* fruticulose wall. (Leguminosae). Flemiculosin is unique among chalcones being the first member of the flavanoid class of compounds to have a benzodipyran unit. It is a 2′-hydroxychalcone in which ring *B* is unsubstituted and ring *A* is completely substituted as part of the benzodipyran system. The oxygen substitution pattern of ring *A* is also biogenetically consistent as prenyl substituents in flavonoids and other related carbo-aromatic compounds are mostly found between two oxygen substituents. The benzodipyran system is not planar: ring *A* makes angles of 1.94 (7) and 6.36 (6)° with rings *C* and *D*, respectively. In the cinnamoyl moiety, the least-squares plane through atoms C6—C11—C12—C13 makes an angle of 20.4 (2)° with the benzene ring, *B*. This plane is not coplanar with ring *A*, as shown by the torsion angles C5—C6—C11—C12 [167.4 (2)] and C4′—C6—C11—C12 [−14.6 (3)°]. In the same moiety, O25 lies 0.340 (2) Å above the C6—C11—C12—C13 plane. O24 is nearly coplanar with ring *A*. The central double bond (C12=C13) has a *trans* configuration and the length of the C11=C25 bond is similar to that seen in related chalcones such as the two nitro-α-methoxy-*trans*-chalcones described

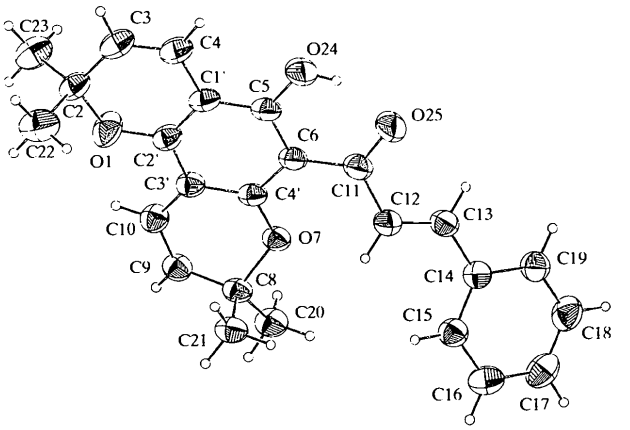


Fig. 1. Structure of the title compound showing 30% probability displacement ellipsoids and atom numbering. H atoms are shown with an arbitrary radius.

by Bolte *et al.* (1996) and in (*E*)-5-methylthio-1,5-diphenyl-1-penten-3-one (Tokuno *et al.*, 1986).

The central, fully substituted ring (*A*) of the tricyclic core is planar to within 0.014 Å. The first pyran ring (*C*) is planar to within 0.041 Å, but the second pyran ring (*D*) is only planar to within 0.156 Å. This deviation may be due to the steric hindrance between C12 and O7 [2.733 (3) Å]: the H12···O7 distance is only 2.30 Å.

An intramolecular hydrogen bond exists between O25 of the cinnamoyl moiety and O24 of the benzodipyran system [O24···O25 2.493 (2) Å, O24—H24···O25 149 (2)°].

Experimental

Crystals of the title compound were obtained by chromatographic resolution of the petroleum ether extract of the leaves of *F.* fruticulose, followed by slow evaporation of a hexane solution at room temperature.

Crystal data

$C_{25}H_{24}O_4$
M_r = 388.44
Monoclinic
$P2_1/c$
a = 12.316 (2) Å
b = 9.606 (2) Å
c = 18.296 (3) Å
β = 103.77 (2)°
V = 2102.3 (7) Å^3
Z = 4
D_x = 1.227 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.54178 Å
Cell parameters from 35 reflections
θ = 10–15°
μ = 0.662 mm^{-1}
T = 293 (2) K
Tablet
0.25 × 0.22 × 0.10 mm
Red

Data collection

Siemens AED diffractometer
ω–2θ scans
Absorption correction:
ψ scan (North *et al.*, 1968)
T_{min} = 0.758, T_{max} = 0.936
4104 measured reflections
3983 independent reflections
2951 reflections with $I > 2\sigma(I)$

R_{int} = 0.034
θ_{max} = 70.02°
$h = -15 \rightarrow 14$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 22$
1 standard reflection
every 100 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.184
S = 1.103
3950 reflections
268 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.1226P)^2 + 0.3428P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.04

$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Extinction correction:
*SHELXL*93 (Sheldrick, 1993)
Extinction coefficient:
0.0051 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C2′	1.345 (3)	O7—C8	1.471 (2)
O1—C2	1.466 (2)	C8—C21	1.517 (3)
C2—C23	1.503 (3)	C8—C20	1.525 (3)
C2—C22	1.515 (4)	C11—O25	1.247 (3)
C5—O24	1.344 (2)	C11—C12	1.476 (3)
C6—C11	1.463 (3)	C12—C13	1.317 (3)
O7—C4′	1.360 (2)	C13—C14	1.464 (3)
O1—C2—C3	111.6 (2)	O25—C11—C12	118.1 (2)
C23—C2—C22	111.1 (2)	C6—C11—C12	122.0 (2)
O24—C5—C1′	117.6 (2)	C13—C12—C11	122.0 (2)
O24—C5—C6	120.3 (2)	C12—C13—C14	126.8 (2)
C4′—O7—C8	117.22 (13)	C19—C14—C13	119.6 (2)
C21—C8—C20	111.1 (2)	C15—C14—C13	122.3 (2)
O25—C11—C6	119.9 (2)		
C2′—O1—C2—C23	134.2 (3)	C5—C6—C11—C12	167.4 (2)
C2′—O1—C2—C22	−108.5 (3)	O25—C11—C12—C13	−26.4 (4)
C22—C2—C3—C4	108.5 (3)	C11—C12—C13—C14	−178.0 (2)
C4′—O7—C8—C20	167.8 (2)	C12—C13—C14—C19	173.2 (2)
C21—C8—C9—C10	84.0 (2)	C12—C13—C14—C15	−7.3 (4)
C4′—C6—C11—O25	167.4 (2)	O24—C5—C1′—C2′	178.0 (2)
C5—C6—C11—O25	−10.6 (3)	C5—C1′—C2′—C3′	0.8 (3)
C4′—C6—C11—C12	−14.6 (3)		

Table 2. *Ring puckering parameters (Å, °)*

Ring	q_2	q_3	Q_T	θ
A	0.038 (2)	−0.007 (2)	0.038 (2)	101 (3)
C	0.095 (2)	−0.039 (2)	0.102 (2)	112.5 (13)
D	0.372 (2)	−0.152 (2)	0.402 (2)	112.2 (3)

H atoms were inserted at geometrically calculated positions, except for those of the hydroxyl (H24 on O24) and methyl groups. They were found from a circular difference Fourier synthesis. The H atoms were then allowed to ride on their parent atoms with U_{iso}(H) = nU_{eq}(parent), where n = 1.5 for hydroxyl- and methyl-H atoms, and 1.2 for all others.

Data collection: local program (Belletti *et al.*, 1993). Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1267). Services for accessing these data are described at the back of the journal.

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(*S*)-2-Hydroxy-3-(1*H*-imidazol-5-yl)-propanoic acid hydrate

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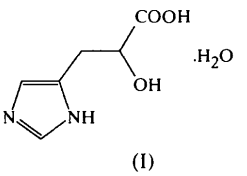
Abstract

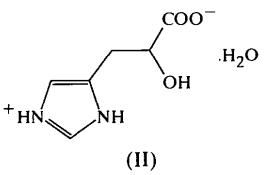
(*S*)-2-Hydroxy-3-(1*H*-imidazol-5-yl)propanoic acid hydrate, $C_6H_8N_2O_3\cdot H_2O$, has a fully extended lactic acid side chain with a *trans* conformation, which is oriented nearly perpendicular to the imidazole plane. The imidazole ring is protonated, and the carboxylate group deprotonated, to give a zwitterionic structure. The molecules are held together by intermolecular hydrogen bonds between the carboxylate, imino and hydroxyl groups, and the water molecules.

Comment

The title compound, (I) is a well known final product of L-histidine catabolism. Patients with liver cirrhosis or histidinemia have high urinary values of (I) (Dubovsky & Dubovska, 1965; Murray *et al.*, 1993). It also has an inhibitory action on cholinesterase and monoamine oxidase (Kurocochi *et al.*, 1956). Accordingly, an accurate crystal structure determination is important for the elucidation of its catabolic pathway and physiological action.



(I)



(II)

The molecular structure of (I) is shown in Fig. 1, with the atomic labelling scheme. The molecule is in a zwitterionic form, *i.e.* (II) rather than (I). The carboxylate group is negatively charged, as evidenced by the similar C—O distances, as well as by the lack of an H atom, and the imidazole ring is positively charged, as evidenced by two imino H atoms. The conformation may be compared with that of histidine hydrochloride (Donohue *et al.*, 1956), because the only difference between the title compound and histidine is the substitution of OH in (I) for the α-amino group in histidine. The chief conformational change involves rotations around the C4—C6 and C6—C7 bonds. The ionized lactic acid side chain of the title compound is fully extended, with a *trans* conformation [C4—C6—C7—C8 −175.2 (2)°], and it is oriented nearly perpendicular to the protonated imidazole plane [C5—C4—C6—C7 92.1 (4)°]. The imidazole ring and the carboxylate group are sited in an *anti* form. The imidazole ring of histidine hydrochloride is also protonated; its side chain is oriented nearly perpendicular, as in (I), but its carboxylate and imidazole groups are in a *cis* form. The other main differences between these compounds are in the bond angles around the asymmetric C atoms. For instance, the O3—C7—C8 angle [112.1 (2)°] of the title compound is larger than that of the corresponding N—C—C angle of 108.4° in histidine. This difference may be caused by the attractive force between the positively charged amino and the negatively charged carboxylate groups of histidine. As a result of the differences of the substituted groups (hydroxyl or amino) at the asymmetric C atom, the C6—C7—C8 angle [108.5 (2)°] of the title compound is smaller than the corresponding value of 115.0° in histidine. No stacking interactions between imidazole rings are observed. The crystal structure is stabilized by hydrogen bonds between the carboxylate, imino and hydroxyl groups and the water molecules, as shown in Table 2.

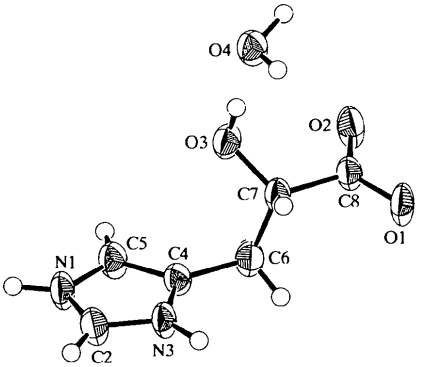


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound, with the atom-numbering scheme for non-H atoms: displacement ellipsoids correspond to 50% probability. H atoms are shown as circles of an arbitrary radius.