Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Pomiferin

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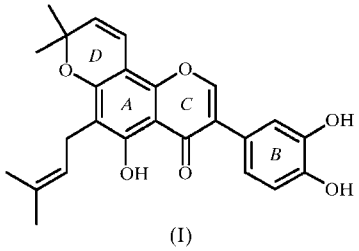
Received 15 January 2003
Accepted 27 January 2003
Online 18 February 2003

The crystal structure of pomiferin, 3-(3,4-dihydroxyphenyl)-5-hydroxy-8,8-dimethyl-6-(3-methylbut-2-enyl)-4*H*,8*H*-pyrano-[2,3-*h*]chromen-4-one, $C_{25}H_{24}O_6$, has been determined. The benzopyranone ring system is nearly planar and the dihedral angle between the phenyl ring and the benzopyranone moiety is 40.85 (4)°. The crystal structure is stabilized by a one-dimensional chain of inter- and intramolecular O—H···O hydrogen bonds, with O···O distances in the range 2.5546 (15)–2.7999 (16) Å.

Comment

The title compound, (I), was originally isolated from the fruit of *Maclura pomifera* Balf. (Moraceae), the Osage orange, a hardwood tree native to the southwestern United States (Wolfrom *et al.*, 1946). Several flavonoids have also been isolated from the root bark (Delle Monache *et al.*, 1984) and heartwood (Deshpande *et al.*, 1973; Gerber, 1986) of the plant, while xanthones (Wolfrom *et al.*, 1965; Cotterile & Scheimann, 1975) and stilbenes (Gerber, 1986) have been obtained from the root bark and the heartwood, respectively. The fruit extract, which contains pomiferin, has displayed interesting antimicrobial activity (Mahmoud, 1981).



(I)

The structure of pomiferin, a prenylated isoflavone, has been established by spectroscopic methods (Wolfrom *et al.*, 1946; Delle Monache *et al.*, 1984, 1994). Due to its significant antifungal activity and relatively low toxicity, it has been widely used as the potent proprietary remedy 'Yeast Ease' against candida-type yeast infections. We have reisolated (I) and have determined its X-ray structure in the course of our work on the biochemistry of prenylated isoflavonoids, which have recently been found to be very interesting compounds because of their potential antioxidative and anticancer activities (Comte *et al.*, 2001).

The main part of the molecule of (I) is the isoflavone molecular fragment, consisting mainly of the six-membered rings *A*, *C* and *B* (see *Scheme*), where the benzopyranone part of the molecule is fused with ring *D* to form the tricyclic ring system *D*/*A*/*C*. The benzopyranone fragment *A*/*C* and ring *B* are nearly planar (the average deviations of contributing atoms from the least-squares planes are 0.03 and 0.004 Å, respectively), but six-membered ring *D* is in a deformed half-chair conformation, with Cremer–Pople puckering parameters (Cremer & Pople, 1975) Q = 0.417 (2) Å, θ = 112.6 (3)° and φ_2 = −19.5 (2)°. The dihedral angle between the benzopyranone moiety *A*/*C* and the phenyl ring *B* is 40.85 (4)°. Surprisingly, the most structurally similar compound to (I) in the Cambridge Structural Database (Version 5.23.3; Allen, 2002) is not an isoflavone, but di-*O*-methylscandenin (Mehdi & Ravikumar, 1992), a complex derivative of 4-hydroxy-3-phenylcoumarin with a completely different chemical genesis.

The hydroxyl group O4 has a *gauche* arrangement with respect to the H4—O4—C5—C4 torsion angle, giving rise to a short [1.67 (2) Å] intramolecular contact between the H atom

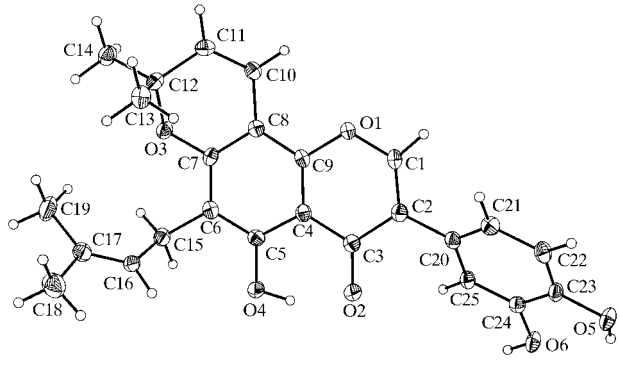


Figure 1
A view of the molecule of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

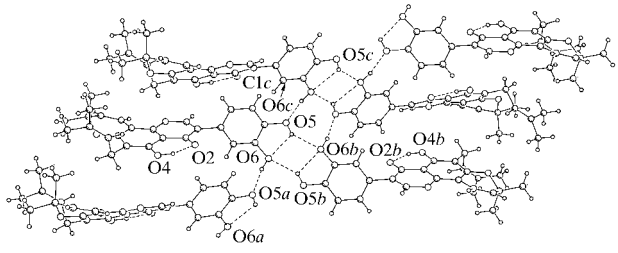


Figure 2
Part of the crystal structure of (I), showing the formation of a molecular chain of edge-fused rings. Atoms with the labels *a*, *b* and *c* are at the symmetry positions (x, $-y$, $\frac{1}{2}+z$), ($-x$, $-y$, $-z$) and (x, $-y$, $z-\frac{1}{2}$), respectively.

 DOI: 10.1107/S0108270103002300

of the O4 hydroxyl group and carbonyl atom O2. Similar structural motifs have also been found in other compounds obtained from natural sources, *e.g.* two isoflavones from *Milletia thonningii* (Kingsford-Adaboh *et al.*, 2001), and the prenylated flavone morusine and its dimethyl ether derivative (Uchida *et al.*, 1996).

In the crystal lattice of (I), the molecular units are linked into a one-dimensional chain of edge-fused rings by relatively strong inter- and intramolecular O—H···O hydrogen bonds (Fig. 2 and Table 2).

Experimental

Pomiferin, together with other substances, was obtained from the fruits of the osage orange (*Maclura pomifera*) by extraction with 95% ethanol. After pre-separation by flash chromatography over a column containing silica gel, pure pomiferin was isolated. The purity was proven using high-performance liquid chromatography (HP1100, DAD detector). The compounds were identified by comparing the melting points and the UV, MS, FT–IR and ^{1}H and ^{13}C NMR spectra. The spectroscopic data agreed with those reported in the literature (Delle Monache *et al.*, 1984, 1994). Crystals of (I) were prepared by vapour diffusion methods, whereby a saturated solution of pomiferin in ethyl acetate was equilibrated against petroleum ether at room temperature. After four weeks, large yellow crystals of (I) were obtained.

Crystal data

$C_{25}H_{24}O_6$
M_r = 420.44
Monoclinic, $C2/c$
a = 29.158 (2) Å
b = 13.9891 (10) Å
c = 9.9578 (7) Å
β = 91.597 (5)°
V = 4060.2 (5) Å^3
Z = 8
D_x = 1.376 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2773 reflections
θ = 3.3–26.5°
μ = 0.10 mm^{-1}
T = 120 (2) K
Prism, yellow
0.5 × 0.5 × 0.3 mm

Data collection

Kuma KM-4 CCD area-detector diffractometer
ω scans
11 311 measured reflections
3869 independent reflections
3409 reflections with $I > 2\sigma(I)$
R_{int} = 0.049
θ_{max} = 25.8°
$h = -35 \rightarrow 35$
$k = -16 \rightarrow 17$
$l = -12 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.095
S = 1.02
3869 reflections
377 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 4.0P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00147 (19)

The H atoms were freely refined with isotropic displacement parameters.

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlisRED* (Oxford Diffraction, 2002); data reduction: *CrysAlisRED*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Johnson & Burnett, 1996); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3578 (18)	O4—C5	1.3519 (18)
O1—C9	1.3736 (17)	O5—C23	1.3809 (18)
O3—C7	1.3645 (18)	O6—C24	1.3803 (18)
C1—O1—C9	118.57 (12)	O2—C3—C2	122.65 (14)
C7—O3—C12	116.27 (11)	O3—C12—C11	108.72 (12)
C2—C1—O1	125.64 (14)	O3—C12—C13	107.83 (13)
O2—C3—C4	121.61 (14)		
C13—C12—C11—C10	81.71 (18)	O2—C3—C4—C5	−0.9 (2)
C14—C12—C11—C10	−153.27 (15)	H4—O4—C5—C4	−0.3 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O2	0.93 (2)	1.68 (2)	2.5546 (15)	154 (2)
O5—H5···O6	0.83 (2)	2.26 (2)	2.6963 (16)	113.0 (17)
O5—H5···O6^{i}	0.83 (2)	2.08 (2)	2.7999 (16)	144 (2)
O6—H6···O5^{ii}	0.88 (2)	1.86 (2)	2.7247 (16)	169 (2)

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

Financial support of this work by the Ministry of Education of the Czech Republic (MŠMT; grant Nos. J07/98:143100008 and J07/98:163700003) and the Grant Agency of the Czech Republic (GAČR; grant No. 203/02/0436) is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1154). Services for accessing these data are described at the back of the journal.

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