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Osajin

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.004 Å
R factor = 0.049
wR factor = 0.125
Data-to-parameter ratio = 12.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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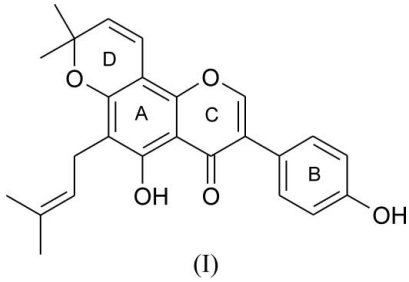
Osajin [systematic name: 5-hydroxy-3-(3-hydroxyphenyl)-8,8-dimethyl-6-(3-methylbut-2-enyl)-4*H*,8*H*-pyrano[2,3-*h*]chromen-4-one, $C_{25}H_{24}O_5$, crystallizes with two independent molecules in the asymmetric unit. The benzopyranone ring system is nearly planar in both molecules and they differ significantly only in the orientation of the benzene rings, which are rotated by 56.27 (7) and 44.16 (7)° with respect to the benzopyranone systems. In the crystal structure, intermolecular O—H···O hydrogen bonds link the molecules into dimers.

Comment

The title compound, (I), and previously described pomiferin (Marek *et al.*, 2003) are the two main prenylisoflavones isolated from the fruits of *Maclura pomifera*, the Osage orange (Moraceae). This small deciduous tree is native to North America, especially to an area centered on Arkansas, southern Oklahoma and northern Texas (Burton, 2002). Several types of compounds have been isolated from *Maclura pomifera*. Prenylated and non-prenylated flavonoids have been obtained from the fruits (Monache *et al.*, 1994; Mahmoud, 1981), leaves, heartwood and root bark (Monache *et al.*, 1994). Xanthones (Wolfrom *et al.*, 1946) and stilbenes (Djapic *et al.*, 2003) have been isolated from the root bark and heartwood, respectively.



(I)

Osajin included in the alcoholic fruit extract exhibited interesting antibacterial activity, being more active against *Salmonella gallinarum* (Mahmoud, 1981) than streptomycin. The molecular structure of osajin has been established by derivatization and spectroscopic methods (Wolfrom *et al.*, 1964). The bioactive compounds, isolated from the Osage orange are of interest especially for their anticancer, antioxidant (Veselá *et al.*, 2004), antimicrobial and antiviral activities. Osajin could be used directly, but interesting pharmaceutical effects are related also with synthetically modified osajin derivatives used as ligands for trace metal complexation and supplementation. In this study, we reisolated and determined the crystal structure of osajin, (I), one of the major

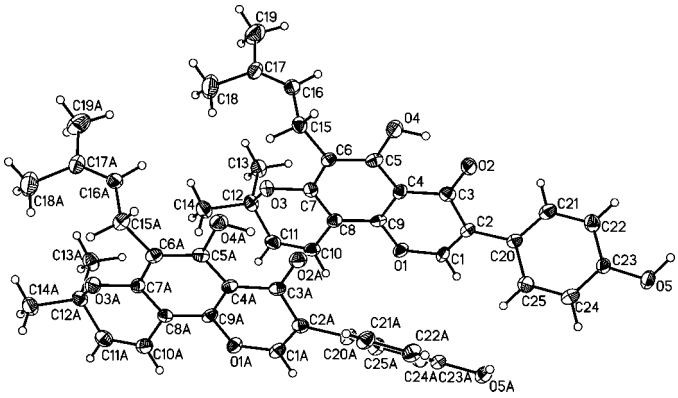


Figure 1
A view of the two independent molecules of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

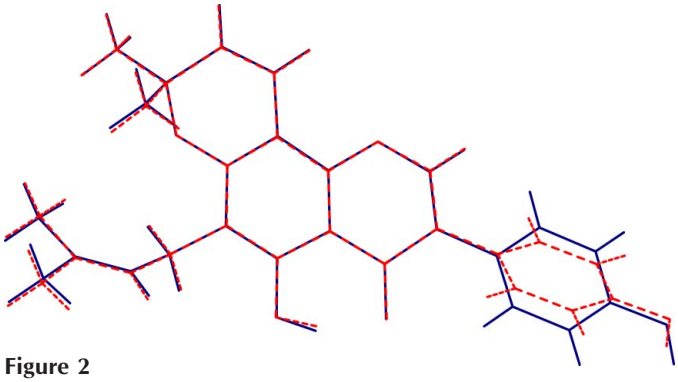


Figure 2
A view of the least-squares overlay of the two independent molecules of (I).

compounds of the ethanolic extract of the fruits of *Maclura pomifera*.

The structure of Osajin consists of the isoflavone fragment containing the six-membered ring *B* (see scheme) and benzopyranone system *A*/*C* fused with ring *D* to form the tricyclic ring system *D*/*A*/*C*. The overall geometry of both independently refined molecules of (I) is similar to that of other natural compounds containing benzopyranone ring systems, *e.g.* the prenylated isoflavone pomiferin (Marek *et al.*, 2003) or phenylcoumarin derivatives scandenin (Ravikumar *et al.*, 2005) and di-*O*-methylscandenin (Mehdi & Ravikumar, 1992). Rings *A*, *B* and *C* are each nearly planar, while ring *D* is in a deformed half-chair conformation in both molecules; atoms C12 and C12*A* lie 0.516 (3) and 0.533 (3) Å out of the mean planes C7/C8/C10/C11/O2 and C7*A*/C8*A*/C10*A*/C11*A*/O2*A*, respectively. The Cremer–Pople puckering parameters (Cremer & Pople, 1975) for *D* rings in both molecules are Q = 0.368 (2) Å, Θ = 113.4 (4)° and φ_2 = −23.2 (4)°, and Q = 0.383 (2) Å, Θ = 112.3 (4)°, φ_2 = −23.2 (4)°.

The bond lengths and angles in the two independent molecules are similar (Table 1), and a least-squares overlay of atoms from the *D*/*A*/*C* ring system in both molecules is 0.043 Å. The r.m.s. deviation between the osajin and pomiferin molecules is 0.084 Å. The two independent molecules of (I) differ significantly only in the orientation of the *B* rings

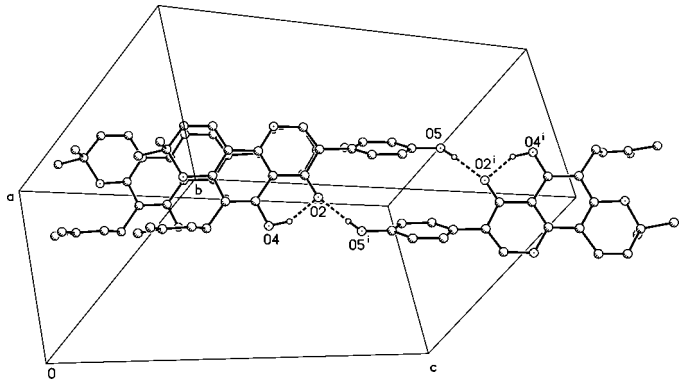


Figure 3
Perspective view of the molecular packing of (I), showing the the stacking interaction between rings *C* and *D* and the formation of the hydrogen-bonded (dashed lines) dimer. C-bound H atoms have been omitted for clarity. [Symmetry code: (i) $-x, 2-y, 1-z$].

(Fig. 2), which are rotated by 56.27 (7) and 44.16 (7)° with respect to the *A*/*C* plane.

In the crystal structure, the molecules are linked into dimers by O—H···O hydrogen bonds (Fig. 3 and Table 2). The distance between the centroid of ring *C* (O1/C1/C2/C3/C4/C9) and plane C7*A*/C8*A*/C10*A*/C11*A*/O3*A* is 3.5941 (2) Å, while the distance between the centroid of ring *D* and the plane of ring *C* is 3.5755 (2) Å, demonstrating that the molecular packing is further stabilized by stacking interactions between the *C* and *D* rings of the two independent molecules.

Experimental

The title compound, (I), together with other substances like pomiferin (Marek *et al.*, 2003), 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 osajin was isolated. The purity was proven using high-performance liquid chromatography (HP 1100, DAD detector). The compounds were identifed by comparing the melting points and the UV, MS, FTIR and ^{1}H and ^{13}C NMR spectra. The spectroscopic data agreed with those reported in the literature (Monache *et al.*, 1994). Crystals of (I) were prepared by the vapour diffusion method, whereby a saturated solution of osajin in ethyl acetate was equilibrated against petroleum ether at room temperature. After four weeks, large yellow crystals of (I) were obtained. Analysis (Carlo–Erba 1180 instrument) calculated for $C_{25}H_{24}O_5$: C 74.24, H 5.98%; found: C 74.05, H 6.03%.

Crystal data

$C_{25}H_{24}O_5$
M_r = 404.44
Triclinic, $P\overline{1}$
a = 8.8220 (11) Å
b = 11.641 (2) Å
c = 21.504 (3) Å
α = 75.865 (11)°
β = 87.731 (10)°
γ = 72.474 (12)°
V = 2040.7 (5) Å^3
Z = 4
D_x = 1.316 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2831 reflections
θ = 2.0–27.6°
μ = 0.09 mm^{-1}
T = 120 (2) K
Prism, yellow
0.50 × 0.50 × 0.40 mm

Data collection

Kuma KM-4 CCD diffractometer	$R_{int} = 0.042$
ω scans	$\theta_{max} = 25.0°$
Absorption correction: none	$h = -10 \rightarrow 10$
14158 measured reflections	$k = -11 \rightarrow 13$
7159 independent reflections	$l = -25 \rightarrow 25$
3734 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 0.01P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.125$	$\Delta\rho_{max} = 0.37$ e Å^{-3}
$S = 1.02$	$\Delta\rho_{min} = -0.23$ e Å^{-3}
7159 reflections	
563 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.353 (3)	O1*A*—C1*A*	1.359 (3)
O1—C9	1.369 (3)	O1*A*—C9*A*	1.373 (3)
O3—C7	1.370 (3)	O3*A*—C7*A*	1.359 (3)
O3—C12	1.463 (3)	O3*A*—C12*A*	1.466 (3)
O4—C5	1.358 (3)	O4*A*—C5*A*	1.357 (3)
O5—C23	1.378 (3)	O5*A*—C23*A*	1.375 (3)
C1—O1—C9	118.5 (2)	C1*A*—O1*A*—C9*A*	118.6 (2)
C7—O3—C12	116.7 (2)	C7*A*—O3*A*—C12*A*	117.0 (2)
C2—C1—O1	126.1 (3)	C2*A*—C1*A*—O1*A*	124.9 (3)
O2—C3—C2	123.5 (3)	O2*A*—C3*A*—C4*A*	121.5 (3)
O2—C3—C4	120.6 (3)	O2*A*—C3*A*—C2*A*	122.3 (3)
O3—C12—C11	110.3 (2)	O3*A*—C12*A*—C11*A*	109.7 (2)
O3—C12—C13	107.7 (2)	O3*A*—C12*A*—C13*A*	107.8 (2)
C13—C12—C11—C10	87.8 (3)	C13*A*—C12*A*—C11*A*—C10*A*	87.1 (3)
C14—C12—C11—C10	−147.8 (3)	C14*A*—C12*A*—C11*A*—C10*A*	−148.7 (3)
O2—C3—C4—C5	−5.2 (4)	O2*A*—C3*A*—C4*A*—C5*A*	−7.4 (4)
H4O—O4—C5—C4	−3 (2)	H4*P*—O4*A*—C5*A*—C4*A*	−1.7 (19)
C5—C6—C15—C16	94.0 (3)	C5*A*—C6*A*—C15*A*—C16*A*	93.5 (3)
C6—C15—C16—C17	125.1 (3)	C6*A*—C15*A*—C16*A*—C17*A*	122.9 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4O···O2	0.946 (10)	1.697 (18)	2.567 (3)	151 (3)
O4*A*—H4*P*···O2*A*	0.953 (10)	1.68 (3)	2.596 (3)	162 (3)
O5—H5O···O2^{i}	0.94 (3)	1.805 (19)	2.698 (3)	157 (4)
O5*A*—H5*P*···O2*A*^{ii}	0.95 (4)	2.05 (3)	2.765 (3)	131 (3)

Symmetry codes: (i) $-x, 2-y, 1-z$; (ii) $1-x, 1-y, 1-z$.

C-bound H atoms were positioned geometrically, with C—H = 0.95–0.99 Å and U_{iso}(H) values of $1.2U_{eq}$(C) [$1.5U_{eq}$(C) for methyl groups]. The parameters of the O-bound H atoms were refined, with the O—H distances restrained to 0.95 (1) Å and with freely refined U_{iso}(H) values.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997) and *PARST* (Nardelli, 1995).

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