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2,3-Dihydro-7,8-dihydroxy-3-[(4-methoxyphenyl)methylene]-4*H*-1-benzopyran-4-one

Suchada Chantrapromma,[a]* Sompong Boonsri,[a] Hoong-Kun Fun,[b]* Shazia Anjum[c] and Akkharawit Kanjana-opas[d]

[a]Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand, [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, [c]HEJ Research Institute of Chemistry, International Center for Chemical Sciences, University of Karachi, Karachi 75270, Pakistan, and [d]Department of Industrial Biotechnology, Faculty of Agro-Industry, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand

Correspondence e-mail: suchada.c@psu.ac.th, hkfun@usm.my

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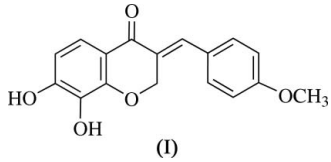
The title compound, also known as intricatinol, $C_{17}H_{14}O_5$, is a homoisoflavanoid that was isolated for the first time from the twigs and stems of *Caesalpinia digyna* Rottler. The pyran ring is in an envelope form. O—H···O intramolecular hydrogen bonds are observed. Symmetry-related molecules are linked *via* O—H···O intermolecular interactions to form infinite one-dimensional chains. These chains are interconnected to form a three-dimensional molecular network.

Comment

Caesalpinia digyna Rottler, known in Thai as kamchai, belongs to the Leguminosae-Caesalpinioideae family (Smitinand, 2001). Several members of the species *Caesalpinia* have exhibited inhibitory (Reddy *et al.*, 2003), antitumor (Gupta *et al.*, 2004), antiflammatory (Rao *et al.*, 2005), antimalarial (Linn *et al.*, 2005) and antiviral activities (Jiang *et al.*, 2002).



(I)

In a previous study, we have reported the crystal structure and activity of bonducellin, a homoisoflavanoid isolated from *C. digyna* (Boonsri *et al.*, 2005). Our further investigation of the chemical components of this plant has led to the isolation of the title compound, (I). The crystal structure of (I) was determined in order to relate the biological activity to the structural properties, which will be further investigated. The title compound, intricatinol, was previously isolated from *Hoffmanosseggia intricata* (Wall *et al.*, 1989) but we have isolated (I) (Fig. 1) for the first time from the twigs and stems of *C. digyna*. Our studies of the antimicrobial activity of (I) have shown that it is active against *Bacillus subsitilis* and *Staphylococcus aureus*.

The bond distances and angles in (I) (Fig. 1 and Table 1) show normal values (Allen *et al.*, 1987) and are comparable to those observed in 2,3-dihydro-7-hydroxy-3-[(4-methoxyphenyl)methylene]-4*H*-1-benzopyran-4-one (Boonsri *et al.*, 2005). In the structure, the pyran ring (C1/C6–C9/O1) is in an envelope form with puckering parameters $Q = 0.299\ (2)$ Å, $\theta = 61.9\ (4)^\circ$ and $\varphi = 319.0\ (3)^\circ$. The flap atom C9 has the maximum deviation of 0.199 (2) Å. The (4-methoxyphenyl)methylene substituent (C10–C17/O5) is twisted away from the benzopyran-4-one plane, the dihedral angle between the C1–C6 and C11–C16 benzene planes being 34.88 (7)°. The C7—C8—C10—C11 torsion angle is −177.21 (15)°, indicating a (−)-anti-periplanar conformation (Fig. 1). Owing to the

Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.002 Å
R factor = 0.042
wR factor = 0.110
Data-to-parameter ratio = 13.2

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

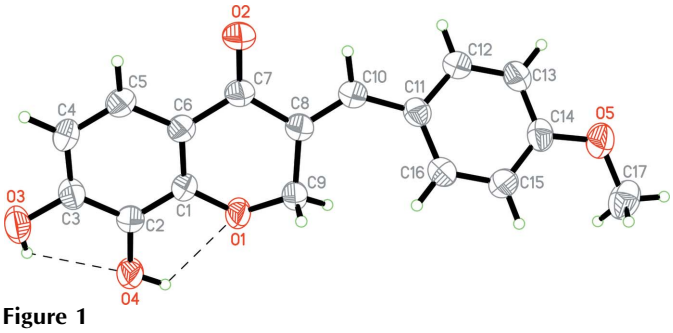


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atomic numbering. Hydrogen bonds are shown as dashed lines.

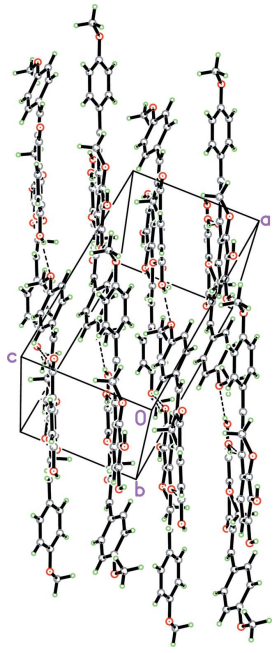


Figure 2
The crystal packing of (I), showing the packing of one-dimensional chains. Hydrogen bonds are shown as dashed lines.

steric effect between the benzopyran-4-one (C1–C9/O1–O4) and 4-methoxyphenyl (C11–C17/O5) systems, the C*sp*^{1} angle at C10 is widened to 132.27°. The methoxy group attached at atom C14 is slightly twisted from the benzene ring [C17—O5—C14—C13 = 172.68 (15)° and C17—O5—C14—C15 = −8.6 (2)°]. Selected bond distances and angles are given in Table 1. The two hydroxy groups are involved in intramolecular hydrogen bonds.

In the crystal packing, atoms O3 and O4 are involved in both intramolecular and intermolecular O—H···O hydrogen bonds, while atom O2 is involved in an intramolecular C—H···O weak interaction (Table 2). Symmetry-related molecules are linked *via* O—H···O intermolecular interactions to form infinite one-dimensional chains along the *b* axis. These chains are linked together to form a three-dimensional molecular network (Fig. 2).

Experimental

Air-dried twigs and stems of *C. digyna* from Songkhla province in the southern part of Thailand were extracted with CH_2Cl_2 (15 l × 3) at room temperature. The CH_2Cl_2 extract (14.52 g) was fractionated by quick column chromatography (QCC) with an acetone–hexane gradient system to give 12 fractions (F1–F12). Fraction F10 (1.32 g) was rechromatographed on a silica gel column with 5% acetone/$CHCl_3$ to afford seven subfractions (F10*A*–F10*G*). Subfraction F10*E* was recrystallized from CH_2Cl_2/CH_3OH (4:1 *v*/*v*), yielding yellow single crystals of (I) after several days (m.p. 457–459 K).

Crystal data

$C_{17}H_{14}O_5$
M_r = 298.28
Monoclinic, $P2_1/c$
a = 12.886 (3) Å
b = 13.896 (3) Å
c = 7.680 (2) Å
β = 95.905 (4)°
V = 1367.9 (5) Å^3
Z = 4
D_x = 1.448 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2699 reflections
θ = 1.6–26.0°
μ = 0.11 mm^{-1}
T = 297 (2) K
Needle, yellow
0.51 × 0.11 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.947, T_{max} = 0.989
7637 measured reflections
2687 independent reflections
2291 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 26.0°
$h = -15 \rightarrow 14$
$k = -17 \rightarrow 17$
$l = -8 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.110
S = 1.05
2687 reflections
203 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.3706P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0049 (9)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3610 (18)	O4—C2	1.3654 (18)
O1—C9	1.4332 (19)	O5—C14	1.3725 (19)
O2—C7	1.2280 (18)	C8—C10	1.338 (2)
O3—C3	1.3589 (18)		
C1—O1—C9	117.30 (12)	C8—C10—C11	132.27 (15)
C14—O5—C17	118.42 (14)		
C7—C8—C10—C11	−177.21 (15)	C17—O5—C14—C15	−8.6 (2)
C17—O5—C14—C13	172.68 (15)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···O4	0.82	2.27	2.706 (2)	113
O3—H3*A*···O5^{i}	0.82	2.13	2.802 (2)	138
O4—H4*A*···O1	0.82	2.35	2.762 (2)	112
O4—H4*A*···O2^{ii}	0.82	2.06	2.796 (2)	148
C10—H10···O2	0.93	2.34	2.755 (2)	107

Symmetry codes: (i) $x-1, y, z-1$; (ii) $-x, y+\frac{1}{2}, -z+\frac{3}{2}$.

H atoms were placed in calculated positions, with O—H distances of 0.82 Å and C—H distances in the range 0.93–0.96 Å. The U_{iso} values were constrained to be $1.5U_{eq}$ of the carrier atom for hydroxy and methyl H atoms and $1.2U_{eq}$ for the remaining H atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

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