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Chains of edge-fused hydrogen-bonded $R_3^3(22)$ rings in 5,3′-dihydroxy-3,6,7,4′,5′-pentamethoxyflavone

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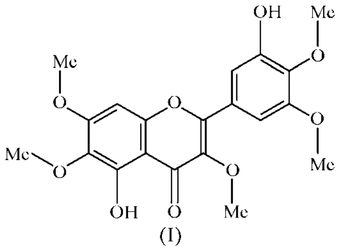
The title compound [systematic name: 5-hydroxy-2-(3-hydroxy-4,5-dimethoxyphenyl)-3,6,7-trimethoxy-4*H*-chromen-4-one], $C_{20}H_{20}O_9$, was isolated from the seeds of *Cleom viscosa* Linn. Two independent molecules (*A* and *B*) are present in the asymmetric unit with almost similar conformations. The dihedral angles between the fused chromene ring system and the benzene ring bonded to it in molecules *A* and *B* are 4.2 (1) and 12.7 (1)°, respectively. The hydroxy O atoms are involved in intramolecular hydrogen bonding. The molecules are linked by C—H···O and O—H···O interactions into chains of edge-fused $R_3^3(22)$ rings. Aromatic π–π and weak C—H···π(arene) interactions are also observed.

Comment

Cleome viscosa Linn (Capparaceae) is a bushy and sticky aromatic herb with secretory glandular trichomes (Adams, 1972). The leaves and stem of this herb are not eaten by herbivores because of their waxy aromatic odorous chemical mixture, which may be derived from the glandular trichomes. The ethanolic extracts of the leaves, flowers and stem of this plant have been tested for antimicrobial (Sudhakar *et al.*, 2006), insecticidal and nemeticidal (Williams *et al.*, 2003) activities. The seeds of this plant are said to be anthelmintic and are useful in treating fever, diarrhoea and infantile convulsions (Asolkar *et al.*, 1992). As the whole plant, it is useful in treating liver diseases, chronic painful joints and mental disorders (Chatterjee & Pakrashi, 1991). Furthermore, *C. Viscosa* Linn. has also been studied for its psychopharmacological effects in rat and mouse models (Parimala *et al.*, 2004). In view of the above important properties, the extract of the seeds of this plant has been studied and a number of compounds have been isolated (Mahender, 2006). The title compound, (I), is one of these, and we report its structure here.



(I)

In compound (I), two independent molecules, *A* and *B*, are present in the asymmetric unit and have similar conformations (Fig. 1). The bond lengths and angles show normal values and are comparable with those observed in 5,3′-dihydroxy-3,7,4′,5′-tetramethoxyflavone (Etti *et al.*, 2005) and calycopterin (Vijayalakshmi *et al.*, 1986). The geometric parameters in the main skeletons of molecules *A* and *B* show no significant differences, but they are distinguished by some bond rotations (Table 1). The dihedral angles between the chromene ring system (C1*n*–C9*n*/O1*n*, *n* = *A* or *B*) and the benzene ring (C13*n*–C18*n*) are 4.2 (1) and 12.7 (1)° for molecules *A* and *B*, respectively. We understand from the literature (Krishnaiah *et al.*, 2005) that there is a correlation (directly proportional) between the dihedral angle between the benzene ring and the chromene ring system and the C—C bond length joining them. However, this may not necessarily be true, because in (I) the bond length C8*n*—C13*n* is approximately the same in the two molecules [1.475 (2) Å in *A* and 1.472 (2) Å in *B*], despite them having different dihedral angles. Furthermore, Wallet and co-workers (Wallet *et al.*, 1988, 1990; Cody, 1988) reported that there is no relationship between the dihedral angle and the bond distance. The double bonds C1*n*═O2*n* and the multiple-character bonds C8*n*—C9*n*, which are generally responsible for the photoactivity of coumarins (Song &

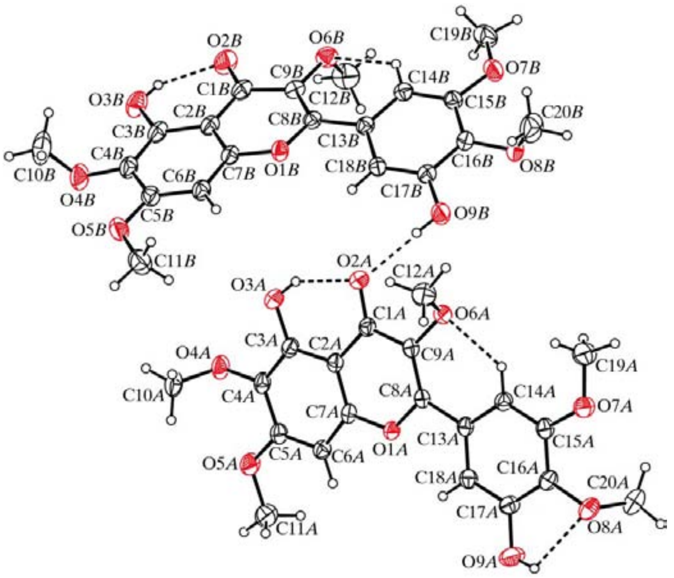


Figure 1
The asymmetric unit of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds.

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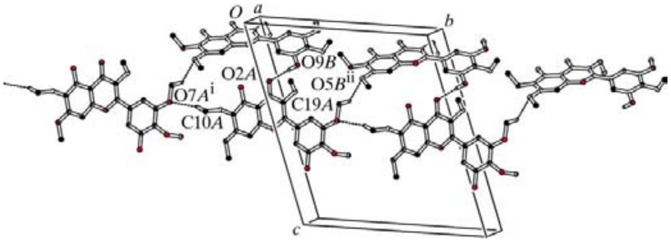

Figure 2
Part of the crystal structure of (I), highlighting the formation of a chain of $R_3^3(22)$ rings along $[\overline{1}10]$. Dashed lines indicate hydrogen bonds. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. [Symmetry codes: (i) 1 + *x*, *y* − 1, *z*; (ii) *x* − 1, 1 + *y*, *z*.]

Gordon, 1970), are confirmed by their respective distances (Table 1). Similarly, the C7*n*—O1*n* and C8*n*—O1*n* bonds (Table 1) exhibit variation in their distances, a feature quite common in furano compounds and simple coumarins (Rajnikanth *et al.*, 1993; Gupta *et al.*, 1993).

In contrast, some relatively large conformational differences are found in the methoxy substituents. With respect to the chromene ring system, the methoxy substituents at C4*n*, C5*n* and C9*n* make angles of 70.7 (1), 6.3 (1) and 72.9 (1)°, respectively, in molecule *A*, and 89.5 (2), 3.4 (1), and 80.5 (2)°, respectively, in molecule *B*. With respect to the benzene ring, the methoxy groups at positions C15*n* and C16*n* make angles of 4.7 (1) and 74.5 (1)°, respectively, in *A*, and 14.8 (1) and 89.8 (1)°, respectively, in *B*.

Within the asymmetric unit, hydroxy atom O9*B* attached to the benzene ring acts as hydrogen-bond donor, *via* atom H9*B*, to ketone atom O2*A* attached to the chromene ring system (Fig. 2). In both molecules, hydroxy atom O3*n* is involved in an intramolecular hydrogen bond with the adjacent ketone O atom, forming a six-membered pseudo-ring (O2*n*/C1*n*/C2*n*/C3*n*/O3*n*/H3*n*) with an *S*(6) pattern (Bernstein *et al.*, 1995). Similarly, in molecule *A*, hydroxy atom O9*A* is involved in an intramolecular hydrogen bond with methoxy atom O8*A*, which completes a five-membered pseudo-ring (O8*A*/C16*A*/C17*A*/O9*A*/H9*A*) with an *S*(5) pattern. Similar interactions have been reported in the literature (Smith *et al.*, 2001). Interestingly, the latter interaction is absent in molecule *B*.

Molecules *A* in (I) are linked into chains by the co-operative action of a C—H···O hydrogen bond of moderate strength (Table 2). Methyl atom C10*A* at (*x*, *y*, *z*) acts as hydrogen-bond donor to methoxy atom O7*A* at (1 + *x*, *y* − 1, *z*), so forming a *C*(13) chain (Bernstein *et al.*, 1995) running along the $[\overline{1}10]$ direction (Fig. 2). Each molecule *B* is linked to two molecules *A* through O—H···O and C—H···O interactions. The combination of these *A* and *B* molecules then generates edge-fused $R_3^3(22)$ rings. Interestingly, only *A* molecules are involved in aromatic *π*–*π* stacking interactions along the *a* axis. The pyrone rings in the fused chromene ring system are stacked with a centre-to-centre distance of 3.556 Å. In addition, the pyrone ring and the C13*A*–C18*A* benzene ring (centroid-to-centroid distance = 3.742 Å), and the six-membered C2*A*–C7*A* ring in the chromene ring system and the C13*A*–C18*A* benzene ring (centroid-to-centroid distance = 3.764 Å) are also involved in similar interactions. The structure is further stabilized by weak C—H···*π* interations (Table 2).

Experimental

The dried and ground seeds of *Cleome viscosa* Linn. (4 kg) were soaked in $CHCl_3$–MeOH (1:1, 8 l) for two weeks. The crude extract was suspended in hexane–ethyl acetate (9:1) and then fractionated by silica-gel chromatography using increasing proportions of hexane–ethyl acetate as eluant to obtain compound (I) (Mahender, 2006). Crystals were grown from an MeOH–water (1:1) solution by slow evaporation.

Crystal data

$C_{20}H_{20}O_9$
$M_r = 404.36$
Triclinic, $P\overline{1}$
$a = 7.5629$ (5) Å
$b = 15.2199$ (9) Å
$c = 17.6543$ (11) Å
$\alpha = 69.621$ (1)°
$\beta = 83.145$ (1)°
$\gamma = 77.760$ (1)°
$V = 1859.3$ (2) Å^3
$Z = 4$
$D_x = 1.445$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.12$ mm^{-1}
$T = 273$ (2) K
Prism, colourless
0.22 × 0.18 × 0.16 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
16152 measured reflections
8323 independent reflections
6127 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.019$
$\theta_{\rm max} = 28.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.131$
$S = 1.02$
8323 reflections
537 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0608P)^2 + 0.4046P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.24$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1*A*—O2*A*	1.257 (2)	C1*B*—O2*B*	1.252 (2)
C3*A*—O3*A*	1.348 (2)	C3*B*—O3*B*	1.352 (2)
C4*A*—O4*A*	1.371 (2)	C4*B*—O4*B*	1.376 (2)
C5*A*—O5*A*	1.351 (2)	C5*B*—O5*B*	1.352 (2)
C7*A*—O1*A*	1.370 (2)	C7*B*—O1*B*	1.366 (2)
C8*A*—O1*A*	1.362 (2)	C8*B*—O1*B*	1.362 (2)
C8*A*—C9*A*	1.365 (2)	C8*B*—C9*B*	1.363 (2)
C9*A*—O6*A*	1.370 (2)	C9*B*—O6*B*	1.366 (2)
C15*A*—O7*A*	1.357 (2)	C15*B*—O7*B*	1.368 (2)
C16*A*—O8*A*	1.380 (2)	C16*B*—O8*B*	1.379 (2)
C17*A*—O9*A*	1.366 (2)	C17*B*—O9*B*	1.360 (2)
C3*A*—C2*A*—C1*A*	122.31 (15)	C3*B*—C2*B*—C1*B*	122.32 (16)
O1*A*—C7*A*—C6*A*	115.89 (14)	O1*B*—C7*B*—C6*B*	116.42 (15)
O1*A*—C8*A*—C13*A*	110.64 (13)	O1*B*—C8*B*—C13*B*	111.59 (14)
C9*A*—C8*A*—C13*A*	129.39 (15)	C9*B*—C8*B*—C13*B*	127.96 (16)
O8*A*—C16*A*—C15*A*	122.71 (16)	O8*B*—C16*B*—C15*B*	120.26 (16)
C1*A*—C2*A*—C7*A*—C6*A*	−174.79 (15)	C9*B*—C8*B*—C13*B*—C18*B*	−164.99 (17)
C9*A*—C8*A*—C13*A*—C18*A*	178.72 (16)	C3*B*—C4*B*—O4*B*—C10*B*	−91.9 (3)
C3*A*—C4*A*—O4*A*—C10*A*	−109.62 (19)	C6*B*—C5*B*—O5*B*—C11*B*	−3.4 (3)
C6*A*—C5*A*—O5*A*—C11*A*	−3.3 (3)	C1*B*—C9*B*—O6*B*—C12*B*	−82.6 (2)
C1*A*—C9*A*—O6*A*—C12*A*	76.84 (19)	C14*B*—C15*B*—O7*B*—C19*B*	−14.0 (3)
C14*A*—C15*A*—O7*A*—C19*A*	−5.1 (3)	C17*B*—C16*B*—O8*B*—C20*B*	−92.5 (2)
C1*B*—C2*B*—C7*B*—C6*B*	−179.56 (17)		

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

*Cg*1 is the centroid of the C2*B*–C7*B* ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3*A*—H3*A*···O2*A*	0.82	1.91	2.6311 (18)	147
O3*B*—H3*B*···O2*B*	0.82	1.87	2.603 (2)	148
O9*A*—H9*A*···O8*A*	0.82	2.26	2.698 (2)	114
O9*B*—H9*B*···O2*A*	0.82	1.96	2.7783 (18)	176
C10*A*—H10*C*···O7*A*^{i}	0.96	2.57	3.495 (2)	162
C14*A*—H14*A*···O6*A*	0.93	2.20	2.863 (2)	128
C14*B*—H14*B*···O6*B*	0.93	2.19	2.824 (2)	125
C19*A*—H19*C*···O5*B*^{ii}	0.96	2.50	3.302 (3)	141
C19*B*—H19*F*···*Cg*1^{iii}	0.96	2.88	3.668	141

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

All H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, with C—H distances of 0.93–0.98 Å, O—H distances of 0.82 Å, and with $U_{\rm iso}$(H) = $1.5U_{\rm eq}$(C,O) for methyl or hydroxy H atoms and $1.2U_{\rm eq}$(C) for all other H atoms.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB3008). Services for accessing these data are described at the back of the journal.

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