3,3'-Benzylidenebis(4-hydroxy-6-methylcoumarin)

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In the title compound, $C_{27}H_{20}O_6$, both benzopyran moieties are slightly distorted from planarity. Intramolecular O—H···O hydrogen bonds are formed between hydroxyl and carbonyl groups of the two hydroxycoumarin moieties.

Comment

The structures of a large number of HIV1 integrase inhibitors have in common two aryl units separated by a central linker. At least one of these aryl moieties must contain dihydroxy substituents in order to exhibit high inhibitory potency. Inclusion of the phenyl ring (similar to title compound) in the horizontal dimer exhibited twofold better inhibitory potency than the corresponding vertical dimer (Zhao *et al.*, 1997). (In the horizontal dimer, the coumarin moieties are attached side-by-side through a phenyl ring whilst in the vertical dimer, the coumarin moieties are attached one below the other through the phenyl ring.) The title compound, (I), is a derivative of 3,3'-benzylidenebis(4-hydroxycoumarin), also known as dicoumarol. In the present investigation, the X-ray structure analysis of (I) was carried out to study its molecular conformation and hydrogen-bonding characteristics.

(I)
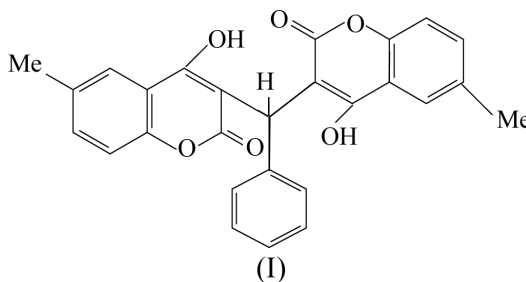
In the title molecule, both benzopyran rings are slightly distorted from planarity. The bond lengths C10—C4 1.447 (2) Å and C4═C3 1.360 (2) Å in one ring system, and C20—C14 1.444 (2) Å and C14═C13 1.363 (2) Å in the other, indicate conjugation (Alcock & Hough, 1972; Vijayalakshmi *et al.*, 2001). The plane of the phenyl ring is inclined at angles of 53.80 (8) and 68.76 (8)° to the benzopyran moieties. The dihedral angle between the two benzopyran moieties is 54.40 (5)°. The orientations of the benzopyrans about C21 may be described in terms of the torsion angles C13—C21—C3—C4 88.7 (2)° and C3—C21—C13—C12 −83.8 (2)°. The bond angles C3—C21—C13 112.3 (1)°, C3—C21—C22 115.7 (1)° and C13—C21—C22 114.7 (1)° at C21 are widened in comparison with normal tetrahedral values. Steric crowding around this atom may be responsible for this feature (Valente & Eggleston, 1989). The C21—C22 distance of 1.534 (2) Å is longer than an unstrained Csp^2—C_{ar} bond, but is in the range

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characteristic of sterically crowded structures (Bernardinelli & Geraldil, 1981; Destro *et al.*, 1980). The exocyclic bond angles at C3 [C2—C3—C21 114.8 (2)° and C4—C3—C21 126.7 (2)°] differ by 11.9°, whereas the corresponding angles at C13 [C12—C13—C21 118.3 (2)° and C14—C13—C21 122.7 (2)°] differ only by 4.4°. This asymmetry may arise from the effects of steric crowding within the molecule or from packing constraints. In general, the geometry of the molecule agrees with closely related structures (Vijayalakshmi *et al.*, 2001; Valente & Eggleston, 1989). In the title molecule, two intra-molecular O—H···O hydrogen bonds, involving the hydroxyl and carbonyl groups, are observed (see Fig. 1 and Table 1).

Experimental

4-Hydroxy-6-methylcoumarin (1.76 g, 0.01 *M*) in absolute ethanol (30 ml) was heated on a boiling water bath, resulting in a clear solution which was then filtered. To this solution, benzaldehyde (0.76 g, 0.005 *M*) was added and the resulting solution was refluxed for 15 h. To this, piperidine (8–10 drops) was added as a catalyst. Excess solvent was distilled off and the solution was cooled gradually to obtain the desired compound. The product was filtered, washed with chilled ethanol, dried and recrystallized from glacial acetic acid (m.p. 493 K and yield 70%).

Crystal data

$C_{27}H_{20}O_6$	$D_x = 1.420$ Mg m^{-3}
$M_r = 440.43$	Cu $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
$a = 10.647 (1)$ Å	reflections
$b = 7.595 (1)$ Å	$\theta = 2$–25°
$c = 25.481 (2)$ Å	$\mu = 0.83$ mm^{-1}
$\beta = 90.298 (9)°$	$T = 293 (2)$ K
$V = 2060.43 (37)$ Å^3	Needle, colourless
$Z = 4$	$0.12 \times 0.10 \times 0.08$ mm

Data collection

Enraf–Nonius–CAD-4	$R_{int} = 0.019$
diffractometer	$\theta_{max} = 67.9°$
ω–2θ scans	$h = 0 \rightarrow 12$
Absorption correction: ψ scan	$k = 0 \rightarrow 9$
(North *et al.*, 1968)	$l = -30 \rightarrow 27$
$T_{min} = 0.840$, $T_{max} = 0.941$	2 standard reflections
3901 measured reflections	every 60 reflections
3701 independent reflections	intensity decay: negligible
2788 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.038$	$+ 0.6209P]$
$wR(F^2) = 0.106$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} = 0.001$
3701 reflections	$\Delta\rho_{max} = 0.17$ e Å^{-3}
303 parameters	$\Delta\rho_{min} = -0.17$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.0031 (2)

Table 1
Hydrogen-bonding geometry (Å, °).

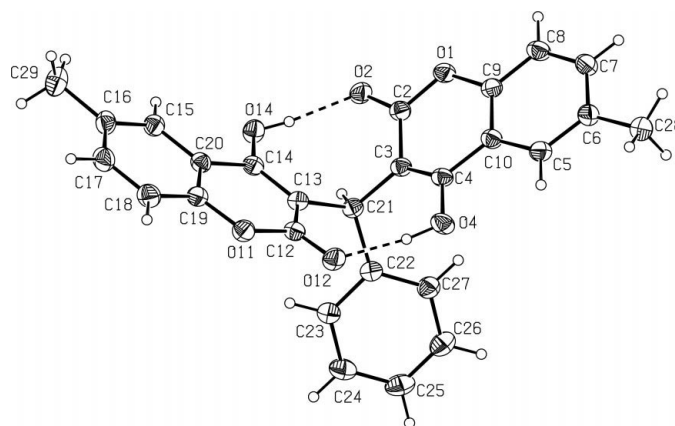| D—H···A	D—H	H···A	D···A	D—H···A
O4—H4···O12	0.90	1.77	2.658 (2)	165
O14—H14···O2	0.85	1.78	2.631 (2)	173

Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

H atoms attached to C atoms were fixed geometrically (0.93–0.98 Å) and allowed to ride on the respective carrier atom. The hydroxyl H atoms were located from a difference Fourier map and their isotropic displacement parameters were refined.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *MolEN* (Fair, 1990); data reduction: *MolEN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP*97 (Zsolnai, 1997); software used to prepare material for publication: *SHELXL*97.

References

Alcock, N. W. & Hough, E. (1972). *Acta Cryst.* B**28**, 1957–1960.
Bernardinelli, G. & Gerdil, R. (1981). *Helv. Chim. Acta*, **64**, 1365–1371.
Destro, R., Pilati, T. & Simonetta, M. (1980). *Acta Cryst.* B**36**, 2495–2497.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1997). *SHELXL*97 and *SHELXS*97. University of Göttingen, Germany.
Valente, E. J. & Eggleston, D. S. (1989). *Acta Cryst.* C**45**, 785–787.
Vijayalakshmi, L., Parthasarathi, V., Vora, V., Desai, B. & Shah, A. (2001). *Acta Cryst.* C**57**, 817–818.
Zhao, H., Neamati, N., Hong, H., Mazumdar, A., Wang, S., Sunder, S., Milne, G. W. A., Pommier, Y. & Burke, T. R. Jr (1997). *J. Med. Chem.* **40**, 242–249.
Zsolnai, L. (1997). *ZORTEP*. University of Heidelberg, Germany.

3,3'-Benzylidenebis(4-hydroxy-6-methylcoumarin). Erratum

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An error in the paper by Vijayalakshmi *et al.* [*Acta Cryst.* (2002), E**58**, o659–o660] is corrected. The last sentence of page o659 should read "The C21—C22 distance of 1.534 (2) Å is longer than an unstrained Csp^3—C_{ar} bond, but is in the range characteristic of sterically crowded structures . . . ".