Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

[6a,16b]-*cis*-7,7-Dimethyl-6,6a,7,16b-tetrahydrochromeno[4′,3′:3,4]pyrano-[3,2-*c*]-*α*-naphthocoumarin

R. Krishna,[a] S. Selvanayagam,[a] M. Yogavel,[a] D. Velmurugan[a]* and S. Manikandan[b]

[a]Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India, and [b]Department of Organic Chemistry, University of Madras, Guindy Campus, Chennai 600 025, India

Correspondence e-mail: d_velu@yahoo.com

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.049
wR factor = 0.153
Data-to-parameter ratio = 14.4

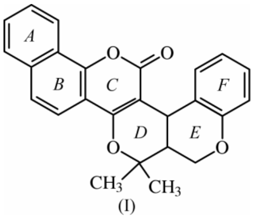
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 3 April 2003
Accepted 8 April 2003
Online 23 April 2003

In the title compound, $C_{25}H_{20}O_4$, the dihydropyran rings adopt distorted sofa conformations. The molecule comprises two planar regions which form a dihedral angle of 62.56 (3)°. C—H$\cdots\pi$ interactions link the molecules to form centrosymmetric dimeric pairs. The dimers are interlinked along the [101] direction by C—H$\cdots$O hydrogen bonds.

Comment

Coumarin derivatives occurring in plants have different biological activities (Cisowski, 1983, 1984). These derivatives are used in oral anticoagulation therapy (Cole *et al.*, 1988; Greenfield, 1988). Coumarin derivatives have been found to be useful in solid-state photochemical reactions (Gnanaguru *et al.*, 1985) and in dye lasers (Masilamani, 1979). Coumarin substrates are also used in enzyme determination (Michel & Durant, 1976). The title compound, (I), was chosen for this crystallographic study to determine its structure and conformation.



(I)

The title molecule (Fig. 1) consists of three benzene rings (*A*, *B* and *F*), one pyran ring (C) and two dihydropyran rings (*D* and *E*). The molecule contains two planar regions, one comprising atoms in rings *A*, *B*, *C* and *D* and the other containing atoms in rings *E* and *F*. The weighted least-squares planes through these two parts (excluding C17), form a dihedral angle of 62.56 (3)°. The H17—C17—C26—H26 torsion angle at the *D*/*E* ring junction is −46.6 (2)°. Both the dihydropyran rings, *D* and *E*, adopt distorted sofa conformations, with ΔC_s(C17) asymmetry parameters of 0.070 (1) and 0.026 (1), respectively (Nardelli, 1983); the deviation of C17 from the C3—C4—O15—C16—C26 and C18—O19—C20—C25—C26 planes is 0.623 (2) and 0.633 (2) Å, respectively. All the C—C bond lengths in the title compound agree well with the mean values (Allen *et al.*, 1987). The C2—O1 [1.381 (2) Å], C14—O1 [1.371 (2) Å] and C2—O29 [1.216 (2) Å] distances in the pyran ring agree well with those reported in related structures (Chinnakali *et al.*, 1998, 1999).

In the crystal structure, inversion-related molecules are linked to form dimeric pairs by C—H$\cdots\pi$ interactions (Table 2), C28—H28*A*$\cdots$*CgA*, where *CgA* is the centroid of the

DOI: 10.1107/S160053680300789X

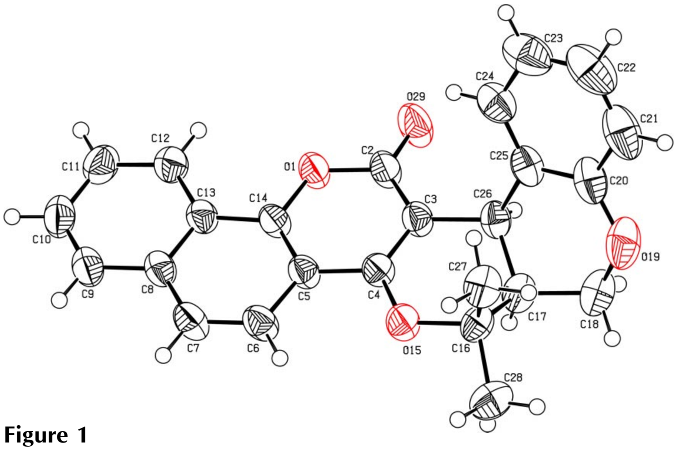


Figure 1
The molecular structure of the title compound, showing 50% probability displacement ellipsoids and the atom-numbering scheme.

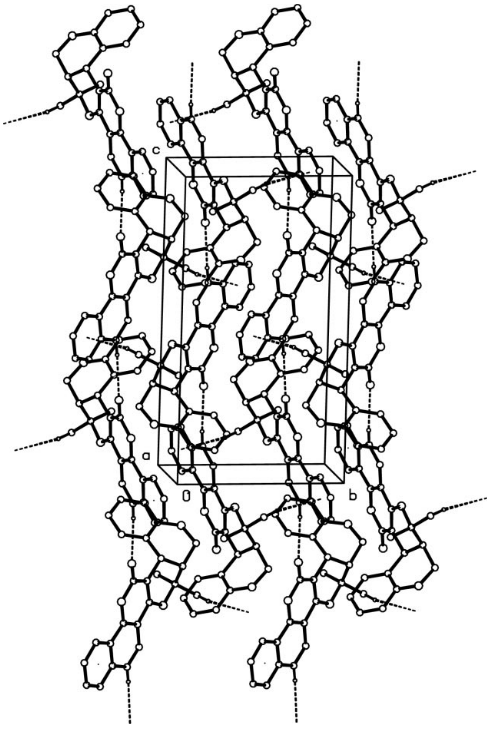


Figure 2
Packing of the molecules in the title compound, viewed down the *a* axis. For clarity, H atoms not involved in hydrogen bonding have been omitted.

benzene ring *A* (C9–C13) of the symmetry-related molecule at $(1 - x, 1 - y, -z)$. The dimeric pairs are interlinked by C7—H7$\cdots$O29$^{\rm ii}$ [symmetry code:(ii) $x - \frac{1}{2}, \frac{3}{2} - y, z - \frac{1}{2}$] hydrogen bonds along the [101] direction.

Experimental

To a refluxing solution of 4-hydroxy-α-naphthocoumarin (1 mmol) in 10 ml of dry ethanol, 2-(3-methyl-2-butenyloxy)benzaldehyde (1 mmol) was added and the reaction mixture was refluxed for 7 h; evaporation of the solvent and flash column chromatography (hexane/ethyl acetate) afforded the title compound as a colourless solid, in 22% yield. Single crystals were grown by slow evaporation of a solution in methanol–chloroform (1:1).

Crystal data

$C_{25}H_{20}O_4$
$M_r = 384.41$
Monoclinic, $P2_1/n$
$a = 12.172$ (1) Å
$b = 9.140$ (1) Å
$c = 18.081$ (1) Å
$\beta = 106.58$ (1)°
$V = 1927.9$ (3) Å^3
$Z = 4$

$D_x = 1.324$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 15$–35°
$\mu = 0.72$ mm^{-1}
$T = 293$ (2) K
Block, colourless
$0.30 \times 0.25 \times 0.20$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
3967 measured reflections
3783 independent reflections
2686 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$

$\theta_{\rm max} = 71.9°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 11$
$l = -22 \rightarrow 21$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.153$
$S = 1.02$
3783 reflections
263 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0905P)^2 + 0.3018P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0045 (5)

Table 1
Selected geometric parameters (Å, °).

O1—C14	1.371 (2)	C16—C27	1.505 (3)
O1—C2	1.381 (2)	C16—C28	1.518 (3)
C2—O29	1.216 (2)	C16—C17	1.540 (3)
C2—C3	1.427 (2)	C17—C18	1.522 (3)
C3—C4	1.361 (2)	C17—C26	1.535 (3)
C3—C26	1.508 (2)	C18—O19	1.422 (3)
C4—O15	1.336 (2)	O19—C20	1.370 (3)
C4—C5	1.443 (2)	C21—C22	1.370 (4)
C5—C14	1.368 (2)	C25—C26	1.523 (3)
O15—C16	1.476 (2)		
C14—O1—C2	121.31 (14)	C5—C14—O1	121.47 (16)
O29—C2—O1	115.36 (16)	C4—O15—C16	119.77 (13)
O29—C2—C3	125.78 (17)	O15—C16—C27	106.10 (15)
O1—C2—C3	118.86 (15)	O15—C16—C28	102.94 (15)
O15—C4—C3	124.88 (16)	O19—C20—C21	115.4 (2)
O15—C4—C5	114.00 (14)	O19—C20—C25	123.34 (19)
C26—C3—C4—C5	−175.5 (2)	C4—O15—C16—C28	−153.9 (2)
C6—C5—C14—O1	−179.4 (2)	O19—C20—C25—C24	174.3 (2)
C4—O15—C16—C27	90.5 (2)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C28—H28$A\cdots CgA^{\rm i}$	0.96	2.60	3.530 (3)	163
C7—H7$\cdots$O29$^{\rm ii}$	0.93	2.49	3.306 (2)	147

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

The H atoms were positioned geometrically and were treated as riding on their parent C atoms; they were refined isotropically with phenyl C—H distance of 0.93 Å, methyl C—H distance of 0.96 Å, methylene C—H distance of 0.98 Å and ethylene C—H distance of 0.97 Å.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *PLATON* (Spek, 1990); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

SSN and DV thank the University Grants Commission (UGC), New Delhi, for financial support under the Herbal Sciences Programme.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Chinnakali, K., Fun, H.-K., Sriraghavan, K. & Ramakrishnan, V. T. (1998). *Acta Cryst.* C**54**, 542–544.

Chinnakali, K., Fun, H.-K., Sriraghavan, K. & Ramakrishnan, V. T. (1999). *Acta Cryst.* C**55**, 946–948.

Cisowski, W. (1983). *Herba Pol.* **29**, 301–318.

Cisowski, W. (1984). *Herba Pol.* **30**, 71–79.

Cole, M. S., Minifee, P. K. & Wolma, F. J. (1988). *Surgery*, **103**, 271–277.

Enraf–Nonius (1994). *CAD*-4 *EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Gnanaguru, K., Ramasubbu, N., Venkatesan, K. & Ramamurthy, V. (1985). *J. Org. Chem.* **50**, 2337–2346.

Greenfield, L. J. (1988). *Surgery*, **103**, 386–387.

Harms, K. & Wocadlo, S. (1995). *XCAD*4. University of Marburg, Germany.

Masilamani, V. (1979). PhD thesis, Indian Institute of Technology, Madras, India.

Michel, A. G. & Durant, F. (1976). *Acta Cryst.* B**32**, 321–323.

Nardelli, M. (1983). *Acta Cryst.* C**39**, 1141–1142.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.