Refinement

Refinement on F
$R = 0.045$
$wR = 0.043$
$S = 0.76$
1098 reflections
145 parameters
Unit weights applied
$(\Delta/\sigma)_{\max} = 0.00014$
$\Delta\rho_{\max} = 0.12$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
N1	0.4286 (4)	0.2827 (2)	−0.1504 (4)	5.66 (9)
N2	0.8457 (4)	0.3047 (1)	0.2060 (3)	3.55 (6)
N3	0.9199 (4)	0.2034 (1)	0.3383 (4)	4.27 (7)
N4	0.5004 (4)	0.4662 (2)	−0.2117 (4)	5.51 (9)
N5	0.8922 (4)	0.4414 (1)	0.1704 (3)	3.46 (6)
N6	1.0184 (4)	0.5439 (1)	0.2638 (4)	4.26 (8)
C1	0.5564 (5)	0.3099 (2)	−0.0570 (4)	3.90 (9)
C2	0.7210 (4)	0.3404 (2)	0.0716 (4)	3.39 (8)
C3	0.8128 (4)	0.2425 (2)	0.2130 (4)	3.88 (8)
C4	0.8711 (6)	0.1348 (2)	0.3419 (6)	7.3 (1)
C5	1.0810 (5)	0.2278 (2)	0.4829 (5)	4.9 (1)
C6	0.6040 (5)	0.4387 (2)	−0.0962 (4)	3.90 (8)
C7	0.7438 (4)	0.4062 (2)	0.0533 (4)	3.41 (8)
C8	0.8909 (5)	0.5044 (2)	0.1546 (4)	4.09 (9)
C9	1.0004 (6)	0.6147 (2)	0.2419 (6)	6.6 (1)
C10	1.1707 (5)	0.5195 (2)	0.4160 (5)	4.8 (1)

Table 2. *Selected geometric parameters (Å, °)*

N1—C1	1.137 (4)	N5—C8	1.291 (5)
N2—C2	1.373 (4)	N6—C8	1.326 (5)
N2—C3	1.299 (5)	N6—C9	1.457 (5)
N3—C3	1.323 (4)	N6—C10	1.446 (5)
N3—C4	1.452 (5)	C1—C2	1.449 (5)
N3—C5	1.447 (4)	C2—C7	1.370 (5)
N4—C6	1.135 (4)	C6—C7	1.457 (5)
N5—C7	1.385 (4)		
C2—N2—C3	118.0 (3)	N2—C2—C1	120.9 (4)
C3—N3—C4	120.8 (3)	N2—C2—C7	122.2 (3)
C3—N3—C5	121.7 (3)	C1—C2—C7	116.9 (3)
C4—N3—C5	117.4 (3)	N2—C3—N3	123.6 (3)
C7—N5—C8	118.2 (3)	N4—C6—C7	177.1 (5)
C8—N6—C9	120.6 (4)	N5—C7—C2	122.4 (3)
C8—N6—C10	122.0 (3)	N5—C7—C6	120.3 (4)
C9—N6—C10	117.3 (3)	C2—C7—C6	117.2 (4)
N1—C1—C2	175.6 (4)	N5—C8—N6	124.1 (4)

All H atoms were taken from difference maps and assigned $U_{\rm iso}$ values equal to $1.3U_{\rm eq}$ of the parent atoms. A riding model was adopted.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN SIR*. Program(s) used to refine structure: *MolEN LSFM*. Molecular graphics: *MolEN ORTEP* (Johnson, 1965). Software used to prepare material for publication: *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: SK1005). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Coumurrayin

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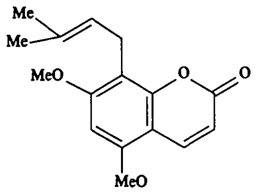
Abstract

In the title compound, 5,7-dimethoxy-8-(3-methyl-2-butenyl)-2*H*-1-benzopyran-2-one, $C_{16}H_{18}O_4$, the coumarin ring system is planar. The methoxy groups at C5 and C7 are coplanar with the coumarin moiety. The side group located at C8 is planar and at an angle of 108.29 (7)° with respect to the coumarin nucleus. The crystal structure is stabilized by van der Waals interactions.

Comment

Coumarin derivatives are biologically important (Michel & Durant, 1976; Schmalle, Jarchow, Hausen & Schulz, 1982). The structure of coumurrayin, (I), a coumarin isolated from the roots of *Seseli Sibiricum* Benth. (Kumar, Gupta, Banerjee & Atal, 1978), is presented in this paper as a part of our programme on the crystal structure analysis of some naturally occurring coumarins (Rajnikant, Goswami, Yadava & Padmanabhan, 1991, 1993; Rajnikant, Goswami, Yadava, Padmanabhan, Gupta & Banerjee, 1993; Gupta *et al.*, 1993; Magotra, Gupta, Rajnikant, Goswami & Thappa, 1995).



(I)

An *ORTEP*II (Johnson, 1976) drawing of the molecule with atomic labelling is shown in Fig. 1. The coumarin moiety is planar, as found in other simple coumarin derivatives, and the methoxy groups are coplanar with it. Coplanarity of this kind results in a close approach between C6 and C11 [2.785 (3) Å], and C6 and C12 [2.790 (4) Å] which causes expansion of angles C6—C5—O3 [124.1 (2)°] and C6—C7—O4 [122.7 (2)°], and contraction of angles C8—C7—O4 [115.0 (2)°] and C10—C5—O3 [114.9 (2)°]. The side group (C1′–C5′) located at C8 is nearly planar and is oriented at 108.29 (7)° with respect to the plane of coumarin nucleus. The angles C8—C9—O1 and C4—C10—C5 at the junction of the phenyl and pyrone rings differ significantly from 120° (Table 2).

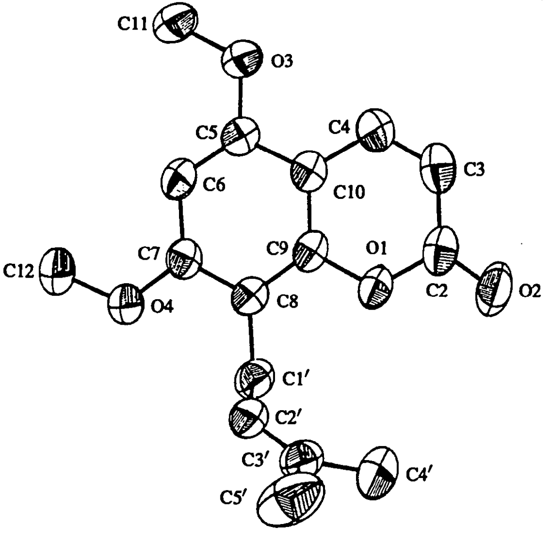


Fig. 1. *ORTEP*II (Johnson, 1976) view of the molecule with displacement ellipsoids drawn at the 50% probability level.

Experimental

The roots of *Seseli Sibiricum* were successively extracted with hexane and benzene. The hexane extract on chromatography yielded coumurrayin which was crystallized from Me_2CO–hexane as thick needles (m.p. 428–429 K).

Crystal data

$C_{16}H_{18}O_4$
$M_r = 274.3$
Triclinic
$P\bar{1}$
$a = 7.085\ (1)$ Å
$b = 9.836\ (1)$ Å
$c = 10.704\ (1)$ Å
$\alpha = 102.95\ (1)°$
$\beta = 95.58\ (1)°$
$\gamma = 98.54\ (1)°$
$V = 712.3$ Å^3
$Z = 2$
$D_x = 1.279$ Mg m^{-3}
$D_m = 1.288$ Mg m^{-3}
D_m measured by flotation in *n*-hexane and CCl_4

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 4.8$–$13.2°$
$\mu = 0.091$ mm^{-1}
$T = 293$ K
Needle
0.30 × 0.15 × 0.10 mm
White transparent

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2504 measured reflections
2306 independent reflections
1900 observed reflections [$F > 4\sigma(F)$]

$R_{\rm int} = 0.008$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 12$
2 standard reflections monitored every 100 reflections
intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.050$
$wR(F^2) = 0.144$
$S = 0.90$
1900 reflections
247 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o)^2 + (0.0776P)^2 + 0.045P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.718$ (for U_{13} of C5′)
$\Delta\rho_{\rm max} = 0.28$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.30$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.2086 (2)	0.2979 (1)	−0.1081 (2)	0.0521 (6)
C2	0.2650 (3)	0.2393 (2)	−0.0079 (3)	0.0571 (9)
O2	0.2560 (3)	0.1127 (2)	−0.0346 (2)	0.0832 (9)
C3	0.3280 (3)	0.3353 (3)	0.1165 (3)	0.0573 (9)
C4	0.3252 (3)	0.4741 (3)	0.1358 (2)	0.0508 (8)
C5	0.2542 (3)	0.6765 (2)	0.0416 (2)	0.0459 (7)
C6	0.1992 (3)	0.7246 (2)	−0.0645 (2)	0.0473 (7)
C7	0.1452 (3)	0.6283 (2)	−0.1847 (2)	0.0459 (8)
C8	0.1439 (3)	0.4836 (2)	−0.2011 (2)	0.0451 (8)
C9	0.2062 (3)	0.4411 (2)	−0.0913 (2)	0.0435 (8)
C10	0.2625 (3)	0.5324 (2)	0.0305 (2)	0.0438 (7)
O3	0.3045 (3)	0.7607 (2)	0.1637 (2)	0.0605 (7)
C11	0.2871 (6)	0.9063 (3)	0.1815 (3)	0.0758 (13)
O4	0.0895 (3)	0.6683 (2)	−0.2943 (2)	0.0598 (6)
C12	0.0841 (6)	0.8137 (3)	−0.2853 (3)	0.0713 (12)
C1′	0.0842 (4)	0.3799 (3)	−0.3316 (3)	0.0547 (9)
C2′	0.2492 (4)	0.3644 (2)	−0.4069 (2)	0.0569 (9)
C3′	0.3308 (4)	0.2517 (2)	−0.4401 (2)	0.0561 (9)
C4′	0.5065 (7)	0.2523 (4)	−0.5079 (4)	0.0995 (17)
C5′	0.2656 (5)	0.1136 (3)	−0.4115 (3)	0.0734 (12)

Table 2. *Selected geometric parameters (Å, °)*

C2—C3	1.435 (4)	C5—O3	1.363 (3)
C4—C10	1.437 (3)	C7—O4	1.360 (3)
C5—C6	1.369 (3)	O3—C11	1.427 (4)
C5—C10	1.406 (3)	O4—C12	1.418 (4)
O1—C2—C3	116.7 (2)	O1—C9—C8	115.9 (2)
O1—C2—O2	116.2 (2)	C8—C9—C10	124.1 (2)
O2—C2—C3	127.0 (2)	C5—C10—C9	117.2 (2)
C7—C8—C9	115.9 (2)	C4—C10—C5	124.5 (2)

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using *SHELXS*86 (Sheldrick, 1985). Isotropic refinement of the structure by least-squares methods using *SHELXL*93 (Sheldrick, 1993) was followed by anisotropic refinement of all the non-H atoms. All H atoms were located from a difference Fourier map and their positions and isotropic displacement parameters were refined (except $U_{\rm iso}$ of the two methyl groups of the side chain located at C8). All calculations were performed on a PC/AT-386 computer.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: locally written program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: VJ1039). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Charge-Transfer Complex 4-(2-Hydroxyethyl)carbazole–2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (1/1) (HEK–DDQ)

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Abstract

The planar donor HEK and the nearly planar acceptor DDQ dimerize to form a face-to-face alternately arranged π–π charge-transfer complex, $C_{14}H_{13}NO.$-$C_8Cl_2N_2O_2$.

Comment

The electron acceptor, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), possesses a uniquely high electron affinity of 3.13 eV (Chen & Wentworth, 1975) and can react with various electron donors to form charge-transfer complexes with different structural types. BPH–DDQ (BPH = benzo[*c*]phenanthrene) adopts a mixed-stack packing motif, with many short intermolecular distances between the parallel molecular planes of two adjacent BPH and DDQ molecules typical of π–π intermolecular interactions (Bernstein, Regev & Herbstein, 1977). PH (PH = phenanthrene) and DDQ in PH–DDQ are arranged in a similar way but with no short intermolecular contacts (Herbstein, Kapon, Rzonzew & Rabinovich, 1978). DAPH (DAPH = diazaphenanthrene) and DDQ in $(DAPH)_2$–DDQ are arranged in segregated sheets with the DAPH and DDQ planes perpendicular to each other, corresponding to an n–π electronic interaction mode, that is coordinating the DAPH lone pair of electrons with the π orbital of DDQ (Shaanan, Shmueli & Colapietro, 1982). Recently, it was reported that 4-(2-