

N(1) and N(2) are not coplanar, and although C(1) and C(2) are located approximately on the mean plane of the six atoms, the displacements of N(1), C(21), N(2) and C(11) are 0.234 (3), 0.235 (3), -0.255 (3) and -0.244 (3) Å, respectively. The two phenyl groups are tilted by about 60° from the mean plane of the molecular backbone.

The plane of the nitro group O(1)—N(1)—O(2) is tilted by about 24° from the plane of N(1)—C(1)—C(11) with O(1) lying 0.453 (3) Å above and O(2) 0.405 (3) Å below this plane (see Fig. 1).

The conformation of the morpholine ring is a regular chair form: C(3), C(4), C(5) and C(6) are coplanar within 0.007 (3) Å and N(2) and O(3) deviate by -0.632 (3) and 0.638 (3) Å from this plane. In conclusion, the striking aspects of the molecule are that the C=C bond is twisted by 23.3°, the nitro group is twisted by about 24° and the two phenyl groups are tilted by 60°, resulting in loss of

significant delocalization energy to relieve the steric hindrance.

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Ethyl 7-Hydroxy-4-coumarinacetate

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Abstract. C₁₃H₁₂O₅, *M_r* = 248.23, monoclinic, *P*2₁, *a* = 4.698 (5), *b* = 10.277 (3), *c* = 12.009 (2) Å, β = 99.58 (1)°, *V* = 571.7 (6) Å³, *Z* = 2, *D_x* = 1.442 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ = 8.98 cm⁻¹, *F*(000) = 260, *T* = 298 K, final *R* = 0.037 for 1098 observed reflections. The coumarin moiety is planar and the plane of the ethyl acetate group makes an angle of 88.1 (1)° to it. The crystal structure is stabilized by O—H...O hydrogen bonds: O(7)...O(2ⁱ) = 2.765 (3) Å, O(7)—H...O(2ⁱ) = 156° [(i) 1 - *x*, *y* - 0.5, 2 - *z*].

Introduction. Coumarin derivatives have been found to be useful in solid-state photochemical reactions (Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985), dye laser studies (Masilamani, 1979) and in a variety of biological studies (Crombie, Jones & Palmer, 1985; Bravic & Bideau, 1978; Valente, Trager & Jensen, 1975). The present study is part of our investigations on coumarin derivatives

involved in photochemical reactions and dye laser activity.

Experimental. Needle-shaped transparent crystals from a mixture of ethanol and chloroform; crystal size 0.5 × 0.3 × 0.3 mm; Enraf-Nonius CAD-4 diffractometer; graphite-monochromated Cu Kα radiation; cell parameters from least-squares treatment of setting angles of 25 reflections with 25 < θ < 35°, ω/2θ scan technique; intensity variation of two standard reflections monitored every 98 reflections less than 3%; total number of reflections measured 1551 with 2θ ≤ 140°, 1098 observed reflections with *I* > 3σ(*I*); range of *hkl*: *h* 0 → 5, *k* 0 → 12 and *l* - 14 → 14; *L_p* correction but absorption ignored; structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); refinement on *F* by full-matrix least-squares method; H atoms from difference Fourier map; anisotropic thermal parameters for

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors

$B_{eq} = (8\pi^2/3) \text{ trace } U.$				
	x	y	z	$B_{eq}(\text{\AA}^2)$
O(1)	0.4074 (3)	0.1413	0.8744 (1)	3.37 (4)
C(2)	0.2570 (5)	0.2362 (3)	0.8113 (2)	3.34 (5)
O(2)	0.0876 (4)	0.2995 (3)	0.8565 (1)	3.92 (4)
C(3)	0.3131 (5)	0.2560 (3)	0.6980 (2)	3.52 (5)
C(4)	0.4997 (5)	0.1793 (3)	0.6528 (2)	3.24 (5)
C(5)	0.8461 (5)	-0.0112 (3)	0.6844 (2)	3.49 (5)
C(6)	0.9848 (6)	-0.1028 (3)	0.7554 (2)	3.70 (5)
C(7)	0.9325 (5)	-0.1134 (3)	0.8664 (2)	3.52 (5)
O(7)	1.0792 (5)	-0.2044 (3)	0.9333 (2)	4.56 (5)
C(8)	0.7337 (5)	-0.0305 (3)	0.9039 (2)	3.37 (6)
C(9)	0.5963 (4)	0.0614 (3)	0.8310 (2)	3.01 (5)
C(10)	0.6460 (5)	0.0754 (3)	0.7196 (2)	3.08 (5)
C(11)	0.5509 (6)	0.2027 (3)	0.5338 (2)	3.84 (6)
C(12)	0.3737 (4)	0.1138 (3)	0.4490 (2)	3.18 (5)
O(12)	0.1880 (5)	0.0405 (3)	0.4683 (2)	6.02 (7)
O(13)	0.4494 (3)	0.1268 (2)	0.3487 (1)	3.77 (4)
C(14)	0.2690 (5)	0.0586 (3)	0.2557 (2)	3.76 (6)
C(15)	0.4200 (5)	0.0674 (4)	0.1556 (2)	4.47 (7)

non-H and isotropic for H atoms, H-atom positions not refined; final $R = 0.037$, $wR = 0.045$, $w = 1/[\sigma^2(F_o) + 0.00246F_o^2]$, $S = 1.53$, $(\Delta/\sigma)_{\text{max}} = 0.02$; final difference map was essentially featureless with max. and min. peak heights of 0.20 and $-0.25 \text{ e } \text{\AA}^{-3}$; no correction for secondary extinction; atomic scattering factors for all atoms as in *SHELX76* (Sheldrick, 1976); other geometrical calculations using *PARST* (Nardelli, 1983); an IBM 360/44 computer was used.

Discussion. Table 1* lists the final atomic coordinates and equivalent isotropic temperature factors of non-H atoms. The values of the bond lengths and angles are given in Table 2. Atom numbering is illustrated in Fig. 1 and the molecular packing in the unit cell viewed down the a axis is shown in Fig. 2.

Bond lengths and angles in the present structure are in good agreement, within experimental error, with those observed in other related coumarin derivatives (Murthy, Ramamurthy & Venkatesan, 1988; Ramasubbu, Gnanaguru, Venkatesan & Ramamurthy, 1982; Ueno & Saito, 1977). The double bond $C(3)=C(4)$ is confirmed by the distance $1.357(4) \text{ \AA}$.

The 2-pyrone ring in the coumarin moiety is planar with a maximum deviation of $0.026(3) \text{ \AA}$ for $C(2)$, and the benzene ring is also planar ($\chi^2 = 9.0$). The dihedral angle between these two planes, $1.50(7)^\circ$, confirms the overall planarity of the cou-

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, distances and angles involving H atoms, torsion angles and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52717 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) involving non-H atoms

O(1)—C(2)	1.359 (3)	C(7)—O(7)	1.346 (4)
O(1)—C(9)	1.374 (3)	C(7)—C(8)	1.393 (4)
C(2)—O(2)	1.222 (4)	C(8)—C(9)	1.374 (4)
C(2)—C(3)	1.443 (4)	C(9)—C(10)	1.403 (3)
C(3)—C(4)	1.358 (4)	C(11)—C(12)	1.511 (4)
C(4)—C(10)	1.440 (4)	C(12)—O(12)	1.204 (4)
C(5)—C(11)	1.507 (4)	C(12)—O(13)	1.318 (3)
C(5)—C(6)	1.361 (4)	O(13)—C(14)	1.463 (3)
C(5)—C(10)	1.409 (4)	C(14)—C(15)	1.497 (4)
C(6)—C(7)	1.399 (3)		
C(2)—O(1)—C(9)	121.7 (2)	C(7)—C(8)—C(9)	118.9 (2)
O(1)—C(2)—C(3)	117.9 (2)	O(1)—C(9)—C(8)	115.7 (2)
O(1)—C(2)—O(2)	116.8 (2)	C(8)—C(9)—C(10)	122.9 (3)
O(2)—C(2)—C(3)	125.3 (3)	O(1)—C(9)—C(10)	121.4 (2)
C(2)—C(3)—C(4)	121.8 (2)	C(5)—C(10)—C(9)	116.5 (2)
C(3)—C(4)—C(11)	120.1 (2)	C(4)—C(10)—C(9)	117.9 (2)
C(3)—C(4)—C(10)	119.2 (2)	C(4)—C(10)—C(5)	125.6 (2)
C(10)—C(4)—C(11)	120.6 (2)	C(4)—C(11)—C(12)	112.7 (2)
C(6)—C(5)—C(10)	121.5 (2)	C(11)—C(12)—O(13)	110.6 (2)
C(5)—C(6)—C(7)	120.6 (3)	C(11)—C(12)—O(12)	125.7 (2)
C(6)—C(7)—C(8)	119.6 (2)	O(12)—C(12)—O(13)	123.6 (2)
C(6)—C(7)—O(7)	117.9 (2)	C(12)—O(13)—C(14)	116.0 (2)
O(7)—C(7)—C(8)	122.4 (2)	O(13)—C(14)—C(15)	107.0 (2)

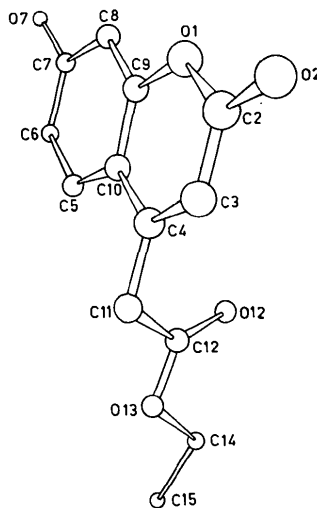
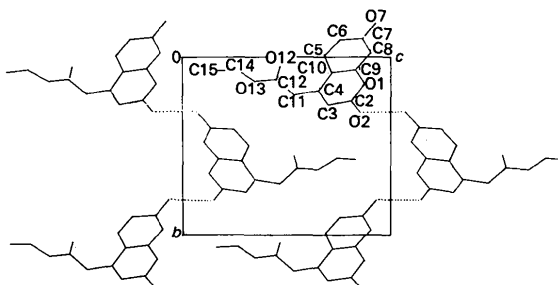


Fig. 1. Perspective view of the title compound.

Fig. 2. Molecular packing of the title compound in the unit cell viewed down the a axis.

marin moiety. The plane of the ethyl acetate group makes an angle of $88.13(7)^\circ$ with the coumarin plane. This value ($\sim 90^\circ$) is typical of observations of the out-of-plane twist in other crystal structures (Murthy, Ramamurthy & Venkatesan, 1988; Sivakumar, 1987; Schweizer & Dunitz, 1982).

The crystal packing in this structure is stabilized by the presence of O—H...O hydrogen bonds. O(7)...O(2) = 2.765 (3), H(7)...O(2) = 2.05 (2) Å, O(7)—H(7)...O(2) = 156° [symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + 2$]. Hydrogen bonding of this type is a common feature in 7-hydroxycoumarins (Ueno & Saito, 1976, 1977).

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7-Hydroxy-4-coumarinacetic Acid Monohydrate

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Abstract. $C_{11}H_8O_5 \cdot H_2O$, $M_r = 238.2$, monoclinic, $P2_1$, $a = 4.394(5)$, $b = 10.367(3)$, $c = 11.657(2)$ Å, $\beta = 95.13(1)^\circ$, $V = 528.9(6)$ Å³, $Z = 2$, $D_x = 1.496$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 10.18$ cm⁻¹, $F(000) = 248$, $T = 298$ K, $R = 0.039$ for 1017 observed reflections. The coumarin moiety is planar and the plane of the acetic acid group makes an angle of $77.35(8)^\circ$ with it. The crystal structure is stabilized by extensive O—H...O hydrogen bonding involving the water molecule and the hydroxy, keto and acid groups of the coumarin moiety.

Introduction. Coumarin derivatives have been found to be useful in solid-state photochemical reactions (Gnanaguru, Ramasubbu, Venkatesan & Ramamurthy, 1985), dye laser studies (Masilamani, 1979) and in a variety of biological studies (Crombie, Jones & Palmer, 1985; Bravic & Bideau, 1978; Valente, Trager & Jensen, 1975). The present study is part of our investigations on coumarin derivatives involved in photochemical reactions and dye laser activity.

Experimental. Colourless needle-shaped crystals from a mixture of aqueous ethanol and chloroform;

preliminary cell parameters and space group from Weissenberg and precession photographs, crystal size $0.5 \times 0.4 \times 0.4$ mm; Enraf-Nonius CAD-4 diffractometer; graphite-monochromated Cu $K\alpha$ radiation; accurate cell parameters from the least-squares treatment of the setting angles of 25 reflections with $25 < \theta < 35^\circ$; $\omega/2\theta$ scan technique; intensity variation of two standard reflections monitored every 98 reflections is less than 3%; total number of reflections measured 1167 with $2\theta \leq 140^\circ$; 1017 observed reflections with $I > 3\sigma(I)$; range of hkl : $h 0 \rightarrow 5$, $k 0 \rightarrow 12$ and $l -14 \rightarrow 14$; L_p correction but absorption ignored; structure solved by direct methods using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); refinement on F by full-matrix least-squares method using *SHELX76* (Sheldrick, 1976); all H atoms except one water H atom were located from difference Fourier map; anisotropic thermal parameters for non-H and isotropic for H atoms, H-atom positions not refined; final $R = 0.039$, $wR = 0.044$, $w = 1/[\sigma^2(|F_o|) + 0.00606F_o^2]$, $S = 1.46$, $(\Delta/\sigma)_{\max} = 0.07$; final difference map was featureless within $\Delta\rho = \pm 0.2$ e Å⁻³; no correction for secondary extinction;