marin moiety. The plane of the ethyl acetate group makes an angle of 88·13 (7)° with the coumarin plane. This value (~90°) 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^i) = 2·765 (3), H(7)···O(2^i) = 2·05 (2) Å, O(7)—H(7)···O(2^i) = 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

By K. Sivakumar, F. Jesurethinam, K. Subramanian and S. Natarajan

Department of Physics, Anna University, Madras 600 025, India

Abstract. $C_{11}H_8O_5.H_2O$, $M_r = 238·2$, monoclinic, $P2_1$, $a = 4·394$ (5), $b = 10·367$ (3), $c = 11·657$ (2) Å, $\beta = 95·13$ (1)°, $V = 528·9$ (6) Å^3, $Z = 2$, $D_x = 1·496$ g cm^{-3}, λ(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)° 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 × 0·4 × 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 < θ < 35°; $\omega/2\theta$ scan technique; intensity variation of two standard reflections monitored every 98 reflections is less than 3%; total number of reflections measured 1167 with $2\theta \leq 140$°; 1017 observed reflections with $I > 3\sigma(I)$; range of *hkl*: *h* 0→5, *k* 0→12 and *l* −14→14; Lp 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;

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

$B_{eq} = (8\pi^2/3)$ trace U.

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1)	0.4018 (4)	0.9782	0.3693 (1)	2.82 (4)
C(2)	0.2816 (5)	0.8791 (3)	0.3047 (2)	2.80 (5)
O(2)	0.1048 (4)	0.8096 (3)	0.3520 (2)	3.41 (4)
C(3)	0.3720 (6)	0.8635 (3)	0.1902 (2)	2.87 (5)
C(4)	0.5597 (5)	0.9471 (3)	0.1442 (2)	2.58 (5)
C(5)	0.8682 (5)	1.1529 (4)	0.1749 (2)	2.95 (5)
C(6)	0.9752 (6)	1.2504 (3)	0.2467 (2)	3.27 (6)
C(7)	0.8884 (5)	1.2555 (3)	0.3599 (2)	2.88 (6)
O(7)	1.0060 (5)	1.3549 (3)	0.4266 (2)	3.91 (6)
C(8)	0.6999 (5)	1.1633 (3)	0.4002 (2)	2.82 (6)
C(9)	0.5941 (5)	1.0658 (3)	0.3249 (2)	2.45 (5)
C(10)	0.6765 (5)	1.0559 (3)	0.2123 (2)	2.52 (6)
C(11)	0.6478 (6)	0.9282 (3)	0.0237 (2)	2.88 (6)
C(12)	0.4860 (5)	1.0160 (3)	−0.0648 (2)	2.62 (5)
O(12)	0.2978 (5)	1.0947 (3)	−0.0457 (2)	4.15 (5)
O(13)	0.5809 (5)	0.9956 (3)	−0.1665 (2)	4.32 (6)
O(W)	0.2710 (6)	1.0943 (3)	−0.3443 (2)	4.52 (6)

Table 2. *Bond lengths (Å) and bond angles (°) involving non-H atoms*

O(1)—C(2)	1.353 (3)	C(6)—C(7)	1.407 (3)
O(1)—C(9)	1.373 (3)	C(7)—O(7)	1.364 (4)
C(2)—O(2)	1.226 (4)	C(7)—C(8)	1.375 (4)
C(2)—C(3)	1.435 (3)	C(8)—C(9)	1.391 (4)
C(3)—C(4)	1.341 (4)	C(9)—C(10)	1.396 (3)
C(4)—C(10)	1.447 (4)	C(11)—C(12)	1.506 (4)
C(4)—C(11)	1.503 (3)	C(12)—O(12)	1.197 (4)
C(5)—C(6)	1.368 (4)	C(12)—O(13)	1.309 (3)
C(5)—C(10)	1.406 (4)		

C(2)—O(1)—C(9)	121.0 (1)	O(7)—C(7)—C(8)	122.6 (2)
O(1)—C(2)—C(3)	118.4 (2)	C(7)—C(8)—C(9)	117.8 (2)
O(1)—C(2)—O(2)	115.3 (2)	O(1)—C(9)—C(8)	115.1 (2)
O(2)—C(2)—C(3)	126.2 (3)	C(8)—C(9)—C(10)	123.1 (3)
C(2)—C(3)—C(4)	122.0 (2)	O(1)—C(9)—C(10)	121.7 (2)
C(3)—C(4)—C(11)	120.6 (2)	C(5)—C(10)—C(9)	116.8 (2)
C(3)—C(4)—C(10)	119.0 (2)	C(4)—C(10)—C(9)	117.6 (2)
C(10)—C(4)—C(11)	120.4 (2)	C(4)—C(10)—C(5)	125.5 (2)
C(6)—C(5)—C(10)	121.4 (2)	C(4)—C(11)—C(12)	114.6 (2)
C(5)—C(6)—C(7)	119.6 (3)	C(11)—C(12)—O(13)	110.7 (2)
C(6)—C(7)—C(8)	121.1 (2)	C(11)—C(12)—O(12)	125.2 (2)
C(6)—C(7)—O(7)	116.2 (2)	O(12)—C(12)—O(13)	124.0 (3)

atomic scattering factors for all atoms as in *SHELX*76 (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 bond lengths and angles are given in Table 2. The numbering scheme for the molecule

* 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 52718 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

is shown in Fig. 1, drawn using *ORTEP* (Johnson, 1976).

Bond lengths and angles in the present structure are in good agreement, within experimental error, with those observed in other related coumarin derivatives (Subramanian, Sivakumar, Natarajan & Parthasarathy, 1990; Murthy, Ramamurthy & Venkatesan, 1988; Ramasubbu, Gnanaguru, Venkatesan & Ramamurthy, 1982). The double bonds C(2)=O(2) and C(3)=C(4), which are responsible for the photoactivity of coumarins, are confirmed by their respective distances of 1.226 (4) and 1.341 (4) Å (Song & Gordon, 1970).

The coumarin ring system is planar [the dihedral angle between the planes of the 2-pyrone and benzene rings is 1.51 (8)°]. The plane of the acetic acid group makes an angle of 77.35 (8)° with the coumarin plane. Such substituent groups normally assume a conformation nearly perpendicular to the plane of the coumarin skeleton (Subramanian, Sivakumar, Natarajan & Parthasarathy, 1990; Murthy, Ramamurthy & Venkatesan, 1988; Schweizer & Dunitz, 1982).
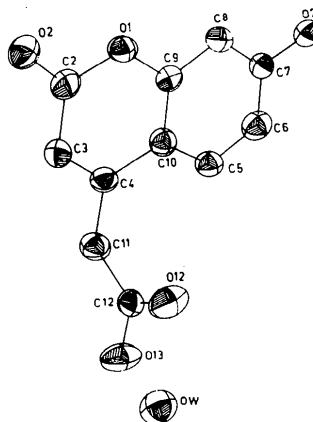
Fig. 1. Numbering of atoms in the molecule drawn using *OPTEP*.
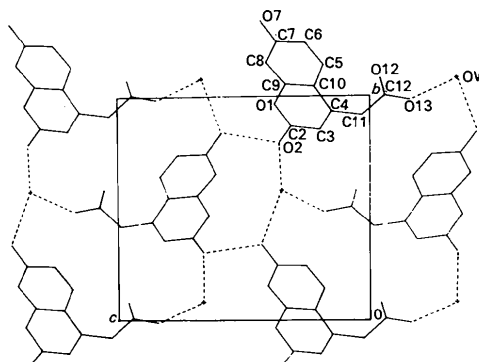
Fig. 2. Molecular packing of the title compound in the unit cell viewed down the *a* axis.

Crystal packing is stabilized by O—H⋯O hydrogen bonding (Fig. 2). The water molecule is H bonded with the coumarin molecule of the same asymmetric unit [O(13)⋯OW = 2·587 (4), O(13)—H = 0·86 Å, O(13)—H⋯OW = 173·2 (2)°]. In addition, the water molecule is also involved in an intermolecular hydrogen bond with the glide-related coumarin molecule {OW⋯O(2^i) = 2·773 (4), OW—H(OW) = 0·96 Å, OW—H⋯O(2^i) = 151·5 (2)° [symmetry code: (i) $-x$, $\frac{1}{2} + y$, $-z$]}. Yet another possible H bond is present between the water molecule and the 7-hydroxy group but could not be fully characterized owing to the non-location of the second H atom on the water molecule from the difference maps {the short contact is OW⋯O(7^{ii}) = 2·890 (4) Å [symmetry code: (ii) $-x+1$, $y-\frac{1}{2}$, $-z$]}. The characteristic O—H⋯O hydrogen bond observed in 7-hydroxycoumarins, between the hydroxyl O(7) atom and the keto O(2) atom is also present {O(7)⋯O(2^{iii}) = 2·710 (3), O(7)—H = 0·94 Å, O(7)—H(7)⋯O(2^{iii}) = 177·7 (2)° [symmetry code: (iii) $-x+1$, $y+\frac{1}{2}$, $-z+1$]} [see, for example, Subramanian, Sivakumar, Natarajan & Parthasarathy (1990) and Ueno & Saito (1976, 1977)].

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Trihydrate Structure of a Multisubstrate Inhibitor of L-DOPA Decarboxylase*

BY J. M. GULBIS AND M. F. MACKAY

Department of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia

AND M. M. ILES, M. N. ISKANDER AND P. R. ANDREWS†

School of Pharmaceutical Chemistry, Victorian College of Pharmacy Ltd, 381 Royal Parade, Parkville, Victoria 3052, Australia

Abstract. $C_{17}H_{18}N_2O_6.3H_2O$, $M_r = 400·4$, monoclinic, $P2_1$, $a = 4·872$ (1), $b = 17·824$ (2), $c = 11·149$ (2) Å, $\beta = 107·09$ (1)°, $V = 925·4$ (3) Å^3, $Z = 2$, D_m(flotation) = 1·44 (1), $D_x = 1·437$ Mg m^{-3}, $F(000) = 424$, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0·90$ mm^{-1}, $T = 289$ (1) K. Final $R = 0·062$ for 1096 observed data. The bridged diphenyl moiety comprising rings A and C linked through C(1) has a twist conformation, with the hydroxymethyl substituent at C(5′) and the phenolic oxygen at C(3′) in distal and proximal orientations respectively. The hydroxypyridine moiety is in the 1,3-dipolar ionic form and the isoquinoline ring nitrogen, N(2), is protonated with ionization at the carboxylate group.

Introduction. In the search for specific reversible inhibitors of L-DOPA decarboxylase (EC4.1.1.38) we