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Ethyl 8-methoxy-2-oxo-2*H*-1-benzopyran-3-carboxylate

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.002 Å
R factor = 0.044
wR factor = 0.148
Data-to-parameter ratio = 11.8

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

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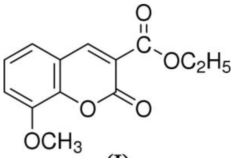
In the title compound, $C_{13}H_{12}O_5$, the ethoxycarbonyl group makes an angle of 60.73 (4)° with the coumarin ring system. There are intermolecular π–π and C—H···π interactions.

Comment

Coumarin is a chemical compound found in many plants, notably in high concentration in the Tonka bean woodruff and bison grass. It has a sweet scent, readily recognized as the scent of newly mown hay. Coumarin derivatives are a useful component for developing new materials such as fluorescent materials and laser dyes, non-linear optical materials and reagents, photorefractive materials, photoresistors, intermediates for drug synthesis, luminescent materials, analytical reagents, *etc*. (Takahashi *et al.*, 2005). Although the fluorescence of coumarin itself is weak, the introduction of a substituent group into coumarin increases the fluorescence intensity (Murov *et al.*, 1993). In order to elucidate the substituent effect of coumarin on the structure and crystal packing, some crystal structures of coumarin (Gavuzzo et al., 1974) and its derivatives have been reported. The crystal structure of coumarin shows intermolecular C—H···O interactions, while intermolecular C—H···O and C—H···π interactions are observed in 8-methoxycoumarin (Gnanaguru *et al.*, 1985), ethyl coumarin-3-carboxylate (Garcia-Baez *et al.*, 2003) and 7-diethylamino-3-dimethylaminocoumarin (Takahashi *et al.*, 2005). The elucidation of the crystal structures of coumarin derivatives has therefore attracted much attention. We now report the crystal structure of the title compound, (I).



(I)

The molecular structure is shown in Fig. 1. The C—C and C—O bond lengths of the coumarin ring system agree with those of coumarin (Gavuzzo *et al.*, 1974). The dihedral angle between the coumarin ring system (defined by atoms O1/O2/C1–C9) and the ethoxycarbonyl group (defined by O3/C10/O4/C11/C12) is 60.73 (4)°, which differs from that of ethyl coumarin-3-carboxylate [14.24 (9)°; Garcia-Baez *et al.*, 2003], while the dihedral angle between the coumarin ring system and the methoxy group (defined by C8/O5/C13) is 7.62 (1)°, similar to that in 8-methoxycoumarin [9.79 (3)°; Gnanaguru *et al.*, 1985].

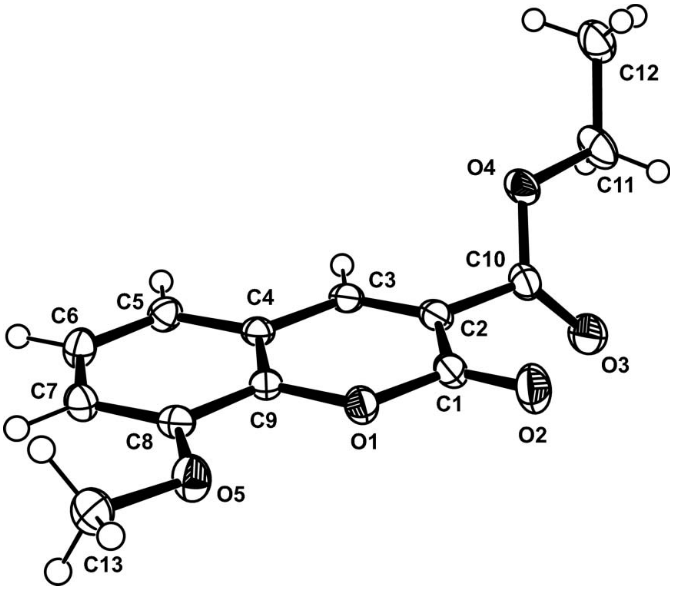


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

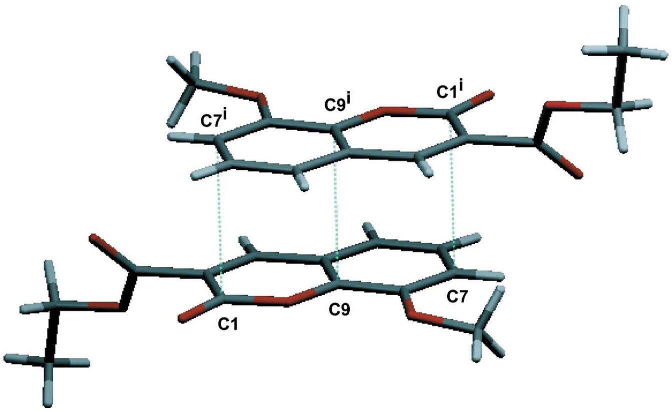


Figure 2
The π–π interactions (dotted lines) in (I). [Symmetry code: (i) $2 - x, -y, 1 - z$.]

Intermolecular π–π interactions between the coumarin planes of (I) are observed (Fig. 2). The distances between the atoms of the coumarin ring systems are 3.3036 (18) Å for C1···C7^{i} [symmetry code: (i) $2 - x, -y, 1 - z$] and 3.2611 (16) Å for C9···C9^{i}, within the range for π–π interactions (3.3–3.8 Å; Prout *et al.*, 1973; Kubo *et al.*, 2001). There are intermolecular C—H···O interactions (Table 1). The shortest H···O distance is similar to that of 2,7-dibromotropone (2.51 Å; Kubo *et al.*, 2005).

Experimental

Compound (I) was synthesized by the Knoevenagel condensation reaction of *o*-vanillin and diethyl malonate (Sugino & Tanaka, 2001). Crystals of (I) were grown by slow evaporation of a chloroform solution.

Crystal data

$C_{13}H_{12}O_5$
$M_r = 248.23$
Monoclinic, $P2_1/n$
$a = 6.8572$ (14) Å
$b = 10.644$ (2) Å
$c = 15.780$ (3) Å
$\beta = 100.153$ (14)°
$V = 1133.6$ (4) Å^3
$Z = 4$
$D_x = 1.454$ Mg m^{-3}
Cu $K\alpha$ radiation
$\mu = 0.95$ mm^{-1}
$T = 173.1$ K
Prism, colorless
0.40 × 0.30 × 0.25 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.608$, $T_{\max} = 0.788$
14613 measured reflections
2061 independent reflections
1860 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int} = 0.027$
$\theta_{\max} = 68.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.148$
$S = 1.00$
2061 reflections
175 parameters
H-atom parameters constrained
$w = 4F_o^2/[0.0041F_o^2 + \sigma(F_o^2)]$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.50$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H1···O3^{i}	0.95	2.72	3.5090 (17)	141
C5—H2···O3^{i}	0.95	2.57	3.4022 (16)	146
C12—H7···O5^{ii}	0.95	2.68	3.3729 (17)	131
C13—H10···O4^{iii}	0.95	2.72	3.6357 (17)	163

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

H atoms were positioned geometrically and refined as riding, with C—H = 0.95 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *CrystalClear* (Rigaku, 1999); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *CrystalStructure*.

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