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7-Acetoxy-4-(1-chloroethyl)coumarin

William Errington,[a]* Virinder S. Parmar,[b] Amarjit Singh[b] and Ishwar Singh[b]

[a]Department of Chemistry, University of Warwick, Coventry CV4 7AL, England, and [b]Department of Chemistry, University of Delhi, Delhi 110 007, India

Correspondence e-mail: w.errington@warwick.ac.uk

Key indicators

Single-crystal X-ray study
T = 200 K
Mean σ(C–C) = 0.003 Å
R factor = 0.042
wR factor = 0.118
Data-to-parameter ratio = 12.2

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

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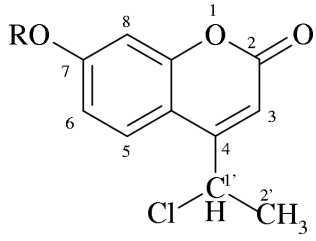
The title compound, $C_{13}H_{11}ClO_4$, a previously unknown coumarin, has the acetoxy and chloroethyl substituents aligned at angles of 65.76 (7) and 63.52 (9)°, respectively, from the plane of the coumarin rings.

Comment

Coumarins are of considerable general importance (Campbell, 1959) and are prominent in natural products chemistry (Dean, 1963; Murray *et al.*, 1982). They have been found to possess a wide variety of uses in the perfumery industry, as flavour enhancers, sunscreens, laser dyes (Khalfan *et al.*, 1987) and in the pharmaceutical industry (Hooper *et al.*, 1982; Morris & Russell, 1971). Our recent work showed pronounced activity of 4-methylcoumarins against Herpes simplex and vascular stomatitis viruses (Parmar *et al.*, 1996). Encouraged by these findings, we have synthesized a series of coumarins for structure–activity studies. This paper reports the synthesis and structure of the new coumarin, 7-acetoxy-4-(1-chloroethyl)-coumarin, (I).



(I) R = $COCH_3$

(II) R = H

The molecular structure of (I) is illustrated in Fig. 1. All bond lengths and angles are largely unremarkable. The inclinations of the planes of the acetoxy and chloroethyl substituents (defined by the O3/C11/O4/C12 and Cl1/C1′/C2′ atoms) with respect to the coumarin ring system are 65.76 (7) and 63.52 (9)°, respectively.

Experimental

The previously unknown 4-(1-chloroethyl)-7-hydroxycoumarin, (II), was prepared by the addition of resorcinol (25.41 g, 0.231 mol) and ethyl 2-(2-chloropropionyl)-2-ethoxycarbonyl acetate (58.0 g, 0.231 mol) to ice-cooled concentrated H_2SO_4 (45 ml). The reaction mixture was maintained at room temperature for 20 h and ice-cooled water was added. (II) precipitated out, was filtered off and crystallized from alcohol as colourless needles (16.5 g, 32% yield), m.p. 429–431 K. The title compound (I) (560 mg, 91% yield) was obtained by

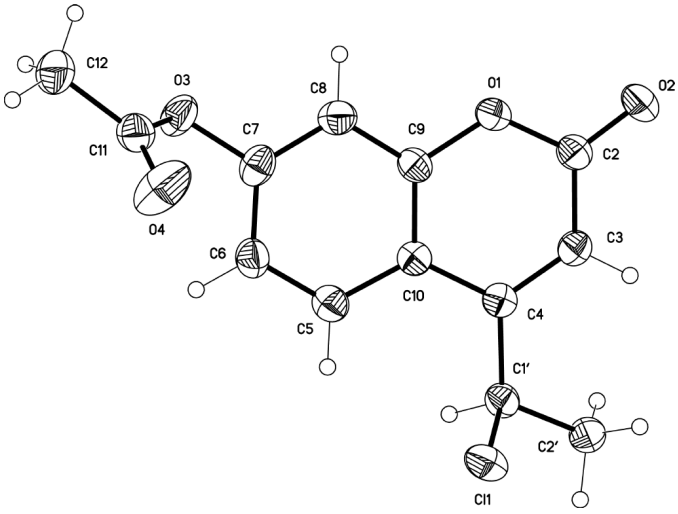


Figure 1
View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level for non-H atoms. H atoms are shown as spheres of arbitrary radii.

the acetylation of (II) (500 mg, 0.228 mol) using acetic anhydride and pyridine. It crystallized from ethyl acetate/petroleum ether as colourless needles, m.p. 410 K.

Crystal data

$C_{13}H_{11}ClO_4$
$M_r = 266.67$
Triclinic, $P\overline{1}$
$a = 4.1204\ (6)$ Å
$b = 10.7106\ (17)$ Å
$c = 13.842\ (2)$ Å
$\alpha = 97.450\ (4)^\circ$
$\beta = 94.291\ (4)^\circ$
$\gamma = 97.184\ (4)^\circ$
$V = 598.39\ (16)$ Å^3
$Z = 2$
$D_x = 1.480$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1852 reflections
$\theta = 1.5$–25.1°
$\mu = 0.32$ mm^{-1}
$T = 200\ (2)$ K
Plate, colourless
0.40 × 0.24 × 0.06 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.882$, $T_{max} = 0.981$
2931 measured reflections
2010 independent reflections
1570 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 25.1^\circ$
$h = -4 \rightarrow 4$
$k = -8 \rightarrow 12$
$l = -16 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.118$
$S = 1.00$
2010 reflections
165 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0746P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

Table 1
Selected torsion angles (°).

C11—O3—C7—C8	−116.4 (2)	C10—C4—C1′—C2′	167.4 (2)
C7—O3—C11—O4	0.1 (4)	C10—C4—C1′—Cl1	−69.7 (2)
C7—O3—C11—C12	178.8 (2)		

The temperature of the crystal during the X-ray diffraction experiment was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of their parent atoms.

Data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL/PC* (Siemens, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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