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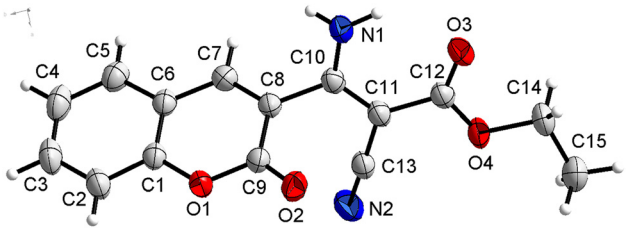
Crystal structure of ethyl (*Z*)-3-amino-2-cyano-3-(2-oxo-2*H*-chromen-3-yl)acrylate, $C_{15}H_{12}N_2O_4$



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Abstract

$C_{15}H_{12}N_2O_4$, monoclinic, $P2_1/c$ (no. 14), a = 5.4588(5) Å, b = 29.629(3) Å, c = 8.1217(8) Å, β = 93.157(1)°, V = 1311.6(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.0346, w$R_{ref}(F^2)$ = 0.0925, T = 296(2) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The starting materials 2-hydroxybenzaldehyde (0.61 g, 5 mmol) and ethyl acetoacetate (2.46 g, 20 mmol) were dissolved in absolute ethanol (100 mL). Piperidine (0.043 g, 0.5 mmol) and acetic acid (0.018 g, 0.03 mmol) were added dropwise to the above solution and refluxed.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.22 × 0.16 × 0.12 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.11 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	9962, 2432, 0.019
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 2063
$N(param)_{refined}$:	192
Programs:	Bruker [1], SHELX [2, 3], Diamond [4]

Reactions were monitored by TLC. After the reaction, the mixture was cooled to room temperature and then 10 mL water was added. The mixture was placed at 3 °C to crystallize. After suction filtration, the filter residue was washed with 50% ice – C_2H_5OH, and dried in vacuo to give the title compound. The crystals were obtained after one week of slow volatilization at room temperature. **Elemental Anal.** Calcd. (%) for $C_{15}H_{12}N_2O_4$ (284.27): C, 63.38; H, 4.26; N, 9.85. Found (%): C, 62.39; H, 4.36; N, 9.70.

Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with C–H = 0.90–0.97 Å with U_{iso}(H) = 1.5 U_{eq}(C) for methyl H atoms and 1.2 U_{eq}(C) for all other H atoms.

Comment

Coumarin is one of phenylpropanoid compounds, which is a natural heterocyclic compound with core structure of enzo-*a*-pyranone [5, 6]. Coumarin compounds have a mild, sweet smell similar to vanilla, so they are often added to shower gels, perfumes, oils, and other cosmetics to add flavor [7]. But some coumarin compounds such as cyclocoumarin, 4-methyl-7-ethoxy coumarins, dihydrocoumarins, are forbidden to be used in cosmetics, because of its certain hepatotoxicity, allergenic and carcinogenic risks. At present, the detection method of coumarin is high-performance liquid chromatography, which has the disadvantages of few components,

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.8504 (3)	0.74098 (5)	0.52205 (18)	0.0353 (3)
C2	0.9041 (3)	0.78594 (5)	0.4984 (2)	0.0445 (4)
H2	1.0416	0.7944	0.4432	0.053*
C3	0.7495 (4)	0.81795 (5)	0.5582 (2)	0.0528 (5)
H3	0.7818	0.8484	0.5420	0.063*
C4	0.5469 (4)	0.80539 (6)	0.6422 (2)	0.0523 (4)
H4	0.4435	0.8274	0.6814	0.063*
C5	0.4976 (3)	0.76059 (5)	0.6679 (2)	0.0445 (4)
H5	0.3629	0.7524	0.7266	0.053*
C6	0.6491 (3)	0.72714 (5)	0.60612 (18)	0.0350 (3)
C7	0.6114 (3)	0.67973 (5)	0.62548 (18)	0.0358 (3)
H7	0.4797	0.6697	0.6836	0.043*
C8	0.7625 (2)	0.64933 (5)	0.56134 (17)	0.0326 (3)
C9	0.9684 (3)	0.66425 (5)	0.46827 (18)	0.0345 (3)
C10	0.7300 (2)	0.59955 (5)	0.57958 (17)	0.0337 (3)
C11	0.9011 (3)	0.57515 (5)	0.67514 (18)	0.0348 (3)
C12	0.8917 (3)	0.52615 (5)	0.68742 (18)	0.0355 (3)
C13	1.0850 (3)	0.59921 (5)	0.77001 (18)	0.0369 (3)
C14	1.0815 (3)	0.46132 (5)	0.8100 (2)	0.0466 (4)
H14A	1.0678	0.4463	0.7038	0.056*
H14B	0.9483	0.4512	0.8751	0.056*
C15	1.3245 (3)	0.45101 (6)	0.8972 (2)	0.0556 (5)
H15A	1.4542	0.4618	0.8324	0.083*
H15B	1.3405	0.4190	0.9122	0.083*
H15C	1.3342	0.4657	1.0028	0.083*
N1	0.5365 (2)	0.58189 (4)	0.49965 (17)	0.0436 (3)
H1A	0.5099	0.5533	0.5048	0.052*
H1B	0.4369	0.5989	0.4423	0.052*
N2	1.2273 (3)	0.61946 (5)	0.84796 (19)	0.0537 (4)
O1	1.00627 (18)	0.70976 (3)	0.45731 (13)	0.0398 (3)
O2	1.1085 (2)	0.64009 (4)	0.39952 (14)	0.0462 (3)
O3	0.7397 (2)	0.50266 (4)	0.61457 (15)	0.0482 (3)
O4	1.07164 (19)	0.50996 (3)	0.78872 (13)	0.0427 (3)

scattered detection methods and complex operation [8]. Therefore, it is necessary to establish the detection methods with more uniform and cover more coumarin compounds. As a food and drug safety practitioners, we are committed to the detection and regulation of cosmetics. In order to strengthen the supervision of coumarin and its derivatives, and establish a quick and convenient detection method, a series of coumarin derivatives were synthesized [9–11].

In the molecule of the title compound (see the Figure), bond lengths and angles within coumarin are very similar to those given in the literature for coumarin derivatives [9–11]. In the molecules the coumarin moiety is approximately planar. The dihedral angle between the planes of the benzo and pyranosyl moiety is 1.2°. The dihedral angles formed by the plane of C1–C6, the plane of C8–C10–C11–C13, and the plane of the carboxylate group (O3–C12–O4) are 70.64(4)° and 70.21(4)°, respectively. The torsion angles of C7–C8–C10–N1, C7–C8–C10–C11, C8–C10–C11–C13, C10–C11–C13–N2, C11–C12–O4–C14 and C12–O4–C14–C15 are 68.6(2)°, –112.05(16)°, 8.03(2)°, 45.23(5)°, –179.68(12)° and 168.0(2)°, respectively.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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