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Crystal structure of 3-acetyl-6-hydroxy-2*H*-chromen-2-one monohydrate, $C_{11}H_{10}O_5$

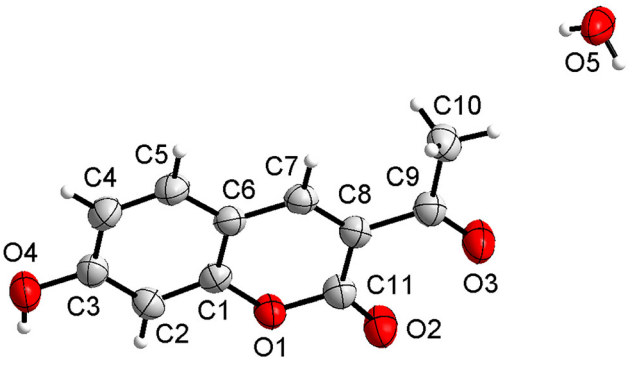

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.22 × 0.18 × 0.14 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.12 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-2, φ and ω-scans
θ_{max}, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7350, 1863, 0.028
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1602
$N(param)_{refined}$:	156
Programs:	Bruker programs [1], SHELX [2, 3], DIAMOND [4]

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Abstract

$[C_{11}H_{10}O_5]$, monoclinic, $P2_1/n$, $a = 7.041(3)$ Å, $b = 9.339(4)$ Å, $c = 15.614(6)$ Å, $\beta = 103.03°$, $V = 1000.2(7)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0337$, w$R_{ref}(F^2) = 0.0994$, T = 296(2) K.

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The crystal 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 materials

2,4–Dihydroxybenzaldehyde (0.69 g, 5 mmol) and ethyl acetoacetate (2.61 g, 20 mmol) were dissolved ethanol (100 mL). Piperidine (0.043 g, 0.5 mmol) and acetic acid (0.018 g, 0.03 mmol) were added dropwise to the solution and refluxed (monitored by TLC). After completion of 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–ethanol, and dried in vacuo to give the title compound. **m.p.** 234–236 °C. **Elemental Anal.** Calcd. (%) for $C_{11}H_8O_4$ (204.18): C, 64.71; H, 3.95. Found (%): C, 63.59; H, 4.08. **IR** (KBr, cm^{-1}): 3486, 3070.8, 2983.2, 1724.9, 1663.2, 1608.1, 1455.7, 1384.3, 1215.7, 927.03.

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 derivatives are well-known natural heterocyclic compounds with a core structure of a benzo-*a*-pyranone. Coumarin is an important structural subunit of many drugs and bioactive compounds [5–8]. There are many coumarin derivatives, such as dicoumarol, Osthole, warfarin, 8–Methoxypsoralen and Psoralen, etc. [9, 10]. Coumarin and its derivatives also have excellent antiviral, antioxidation antibacterial, many other physiological activities and optical properties [11–16]. The synthesis of

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.74949 (13)	0.34547 (9)	1.05587 (6)	0.0437 (3)
O2	0.67556 (17)	0.14944 (10)	0.97957 (7)	0.0582 (3)
O3	0.61438 (19)	0.16768 (11)	0.80055 (7)	0.0657 (3)
O4	0.91200 (18)	0.75279 (11)	1.23927 (6)	0.0580 (3)
H4A	0.9245	0.6911	1.2775	0.087*
O5	0.9441 (2)	0.56954 (13)	0.36617 (8)	0.0645 (4)
H1W	0.906 (3)	0.587 (2)	0.4106 (15)	0.084 (7)*
H2W	1.008 (3)	0.497 (3)	0.3737 (15)	0.101 (8)*
C1	0.78081 (17)	0.49077 (13)	1.06464 (8)	0.0366 (3)
C2	0.82995 (18)	0.54412 (14)	1.14887 (8)	0.0410 (3)
H2	0.8407	0.4840	1.1972	0.049*
C3	0.86312 (19)	0.69068 (15)	1.15975 (9)	0.0430 (3)
C4	0.8470 (2)	0.77999 (15)	1.08616 (10)	0.0488 (4)
H4	0.8702	0.8777	1.0938	0.059*
C5	0.7975 (2)	0.72383 (14)	1.00346 (9)	0.0469 (3)
H5	0.7869	0.7841	0.9552	0.056*
C6	0.76208 (17)	0.57637 (13)	0.98994 (8)	0.0386 (3)
C7	0.70984 (18)	0.50902 (14)	0.90658 (8)	0.0401 (3)
H7	0.6962	0.5652	0.8564	0.048*
C8	0.67881 (17)	0.36563 (14)	0.89704 (8)	0.0380 (3)
C9	0.62521 (19)	0.29659 (14)	0.80899 (9)	0.0425 (3)
C10	0.5842 (3)	0.39028 (16)	0.72915 (9)	0.0556 (4)
H10A	0.5380	0.3326	0.6778	0.083*
H10B	0.7015	0.4387	0.7243	0.083*
H10C	0.4866	0.4596	0.7342	0.083*
C11	0.69916 (18)	0.27724 (14)	0.97565 (8)	0.0412 (3)

coumarin and its derivatives have attracted increasing attention, due to their extensive biological applications and their wide applications [12–18]. In this paper, we report the synthesis and crystal structure of 3-acetyl-6-hydroxy-2H-chromen-2-one as an important intermediate.

In the molecule of the title compound (Fig.), bond lengths and angles within coumarin are very similar to those given in the literature for coumarin derivatives [17–19]. The coumarin ring is approximately planar. The dihedral angles between the coumarin moiety and the plane of the acety group (C10–C9–O3) is 6.9(1)°. The torsion angles of C6–C7–C8–C9, C7–C8–C9–C10, C7–C8–C9–O3, and C7–C8–C11–O2 are –179.6(1)°, –6.5(2)°, 173.4(1)° and 179.3(1)°, respectively. Intermolecular O–H···O hydrogen bonds between water molecules and oxygen atoms (carboxyl oxygen atoms (O1, O2) and hydroxyl oxygen atoms (O4)) of title compound link the molecules into a two-dimensional hydrogen bonded network.

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

References

1. Bruker. APEX2, SAINT and SADABS; Brucker AXS Inc.: Madison, Wisconsin, USA, 2009.
2. Sheldrick G. M. A short history of *SHELX*. *Acta Crystallogr.* 2008, *A64*, 112–122.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Brandenburg K. *DIAMOND. Visual Crystal Structure Information System. Ver. 4.0*; Crystal Impact: Bonn, Germany, 2015.
5. Kumar V., Ahemd D., Verma A., Anwar F., Ali M., Mujeeb M. Umbelliferone β–D-galactopyranoside from Aegle marmelos (L.) corr. an ethnomedicinal plant with antidiabetic, antihyperlipidemic and antioxidative activity. *BMC Compl. Alternative Med.* 2013, *13*, 273–292.
6. Chu Q. B., Zhu Y. F., Cao T. J., Zhang Y., Chang Z. C., Liu Y., Lu J. H., Zhang Y. Z. Studies on the neuroprotection of osthole on glutamate-induced apoptotic cells and an alzheimer's disease mouse model *via* modulation oxidative stress. *Appl. Biochem. Biotechnol.* 2019, *190*, 634–644.
7. Kostova I. Synthetic and natural coumarins as antioxidants. *Mini Rev. Med. Chem.* 2006, *6*, 365–374.
8. Parfenov E. A., Smirnov L. D. Pharmacological potential of antioxidants derived from coumarin (Review). *Khim.-Farm. Zh.* 1988, *22*, 1438–1448.
9. Daru J., Stirling A. Mechanism of the Pechmann reaction: a theoretical study. *J. Org. Chem.* 2011, *76*, 8749–8755.
10. Liu S. Y., Ren D., Li L. H., Cao R. X., Qian S. Synthesis, spectral properties and biological activity of 7–N-substituted coumarin derivatives. *Chin. J. Anhui Agric. Univ.* 2020, *47*, 135–140.
11. Liu L., Song D. W., Liu G. L., Shan L. P., Qiu T. X., Chen J. Hydroxycoumarin efficiently inhibits spring viraemia of carp virus infection *in vitro* and *in vivo*. *Sci. Zool. Res.* 2020, *41*, 395–409.
12. Nicolaides D. N., Gautam D. R., Litinas K. E., Hadjipavlou-Litina D. J., Fylaktakidou K. C. Synthesis and evaluation of the antioxidant and antiinflammatory activities of some benzo[l] khellactone derivatives and analogues. *Sci. Eur. J. Med. Chem.* 2004, *39*, 323–332.
13. Wang Y. H., Jiang S. C., Chen Y., Guo T., Xia R. J., Tang X., He M., Xue W. Synthesis and antibacterial activity of novel chalcone derivatives bearing a coumarin moiety. *Sci. Chem. Pap.* 2019, *73*, 2493–2500.
14. Jardosh H. H., Patel M. P. Microwave-assisted CAN-catalyzed solvent-free synthesis of N-allyl quinolone-based pyrano [4, 3-*b*] chromene and benzopyrano [3, 2-*c*] chromene derivatives and

their antimicrobial activity. *Sci. Med. Chem. Res.* 2013, *22*, 905–915.
15. Goud N. S., Pooladanda V., Mahammad G. S., Jakkula P., Gatreddi S., Qureshi I. A., Chandraiah Godugu R. A., Alvala M. Synthesis and biological evaluation of morpholines linked coumarin-triazole hybrids as anticancer agents. *Sci. Chem. Biol. Drug Des.* 2019, *94*, 1919–1929.
16. Ren X., Kondakova M. E., Giesen D. J., Rajeswaran M., Madaras M., Lenhart W. C. Coumarin-based, electron-trapping iridium complexes as highly efficient and stable phosphorescent emitters for organic light-emitting diodes. *Sci. Inorg. Chem.* 2010, *49*, 1301–1303.
17. Gu J., Xiao P. L., Wang J., Zhong L., Nie X. L., Peng D. Y. Synthesis, crystal structure, spectroscopic characterization and anti-fungal activity of ethyl 2–Oxo-2*H*-chromene-3-carboxylate derivatives. *J. Mol. Struct.* 2022, *1257*, 132576.
18. Zeng F. X., Nie X. L., Shang-Guan X. C., Yin Z. P., Peng D. Y. Crystal structure of 3-methyl-2H-chromen-2-one, $C_{10}H_8O_2$. *Z. Kristallogr. N. Cryst. Struct.* 2016, *231*, 975–976.
19. Wang J., Luo L. S., Deng Y. C., Li Z. C., Peng D. Y. Crystal structure of 6-methyl-3-(pyrrolidine-1-carbonyl)-2*H*-chromen-2-one, $C_{15}H_{15}N_1O_3$. *Z. Kristallogr. N. Cryst. Struct.* 2022, *237*, 331–333.