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Crystal structure of 3-methyl-3-(2,4,5-trimethyl-3,6-dioxocyclohexa-1,4-dien-1-yl)butanoic acid, $C_{14}H_{18}O_4$

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.28 × 0.25 × 0.22 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.09 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω -scans
$\theta_{\max}$, completeness:	27.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	20424, 3061, 0.027
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2407
$N(\text{param})_{\text{refined}}$:	169
Programs:	Bruker programs [1], SHELX [2]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.20494(17)	0.19897(14)	0.48372(13)	0.0845(5)
O2	−0.09537(11)	0.58243(12)	0.31963(13)	0.0681(4)
O3	0.07579(13)	0.49527(11)	0.13188(8)	0.0589(4)
O4	−0.01756(13)	0.67250(12)	0.04006(9)	0.0621(4)
H4	−0.0331	0.6188	−0.0104	0.093*
C1	0.13686(17)	0.28628(16)	0.43255(12)	0.0494(4)
C2	0.00797(17)	0.25228(15)	0.36745(12)	0.0475(4)
C3	−0.06884(14)	0.35098(15)	0.31959(12)	0.0448(4)
C4	−0.02018(13)	0.48984(14)	0.33162(12)	0.0408(3)
C5	0.11873(13)	0.51761(13)	0.36460(10)	0.0347(3)
C6	0.18939(14)	0.42483(15)	0.43062(11)	0.0413(3)
C7	−0.0307(2)	0.10764(18)	0.36174(18)	0.0717(6)
H7A	−0.0462	0.0767	0.2880	0.108*
H7B	−0.1068	0.0982	0.3860	0.108*
H7C	0.0361	0.0555	0.4076	0.108*
C8	−0.20470(18)	0.3347(2)	0.2580(2)	0.0732(6)
H8A	−0.2568	0.3940	0.2874	0.110*
H8B	−0.2308	0.2439	0.2643	0.110*
H8C	−0.2138	0.3558	0.1827	0.110*
C9	0.32038(17)	0.4417(2)	0.50423(14)	0.0639(5)
H9A	0.3820	0.4113	0.4675	0.096*
H9B	0.3279	0.3900	0.5693	0.096*
H9C	0.3350	0.5345	0.5230	0.096*
C10	0.16511(13)	0.65228(14)	0.33161(11)	0.0384(3)
C11	0.16429(17)	0.75826(17)	0.41938(13)	0.0533(4)
H11A	0.0795	0.7682	0.4274	0.080*
H11B	0.1932	0.8423	0.3980	0.080*
H11C	0.2197	0.7303	0.4874	0.080*
C12	0.29931(15)	0.64082(19)	0.31379(14)	0.0546(4)

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Abstract

$C_{14}H_{18}O_4$, monoclinic, $P2_1/n$ (no. 14), $a = 10.8905(6)$ Å, $b = 9.9903(5)$ Å, $c = 12.7101(6)$ Å, $\beta = 104.912(2)^\circ$, $V = 1336.28(12)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0502$, $wR_{\text{ref}}(F^2) = 0.1504$, $T = 296(2)$ 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.

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Table 2 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
H12A	0.3593	0.6222	0.3820	0.082*
H12B	0.3214	0.7235	0.2849	0.082*
H12C	0.3009	0.5696	0.2634	0.082*
C13	0.07851(16)	0.70655(14)	0.22413(12)	0.0462(4)
H13A	−0.0006	0.7358	0.2385	0.055*
H13B	0.1190	0.7850	0.2032	0.055*
C14	0.04680(14)	0.61291(15)	0.12877(11)	0.0431(3)

Source of material

6-Hydroxy-4,4,5,7,8-pentamethylchroman-2-one (0.5 g, 2.18 mmol) was dissolved in CH₃CN–H₂O (1:9, v/v, 30 mL). To this mixture, *N*-bromosuccinimide (0.4 g, 2.25 mmol) in CH₃CN (15 mL) was added dropwise. The reaction solution was stirring at room temperature for 1 h. After completion of the reaction, the mixture was diluted with water (50 mL), and extracted with dichloromethane (50 mL) three times. The organic layer was washed with water (100 mL) and brine (100 mL) and dried over anhydrous Na₂SO₄. The solvent was removed in vacuum. The crude product was recrystallized in petroleum ether/dichloromethane to afford crystals of the title compound.

Experimental details

The hydrogen atoms were placed in calculated positions riding on attached atoms with *U*_{iso} 1.2 times those of their carrier atoms. The *U*_{iso} values of the hydrogen atoms of methyl groups and oxygen were set to 1.5*U*_{eq}(C, O).

Discussion

The title compound is an important intermediate for the design of anticancer prodrug [3–5] and fluorescence probe [6–9] which response to DT-diaphorase, a kind of overexpressed enzyme in some cancer cells. The title compound should work a trigger group of anticancer prodrug; the quinone moiety can be reduced by DT-diaphorase into hydroquinone to release active drug for cancer treatment. On the other hand, the quinone group of the title compound as electron-deficient group, it can quench fluorescence of fluorophore *via* photoinduced electron transfer [10, 11], and after the quinone group being reduced, the fluorescence of fluorophore restore. However, to the best of our knowledge, there have been no reports of the crystal structure of the title compound. In our group continuing efforts to study the derivatives of the title compound, and in this context, we report the title crystal structure. In the molecule, the C1–O1, C1–C2, C1–C6, C2–C3, C2–C7, C3–C4, C3–C8, C4–O2, C4–C5, C5–C6, C5–C10, C6–C9, C10–C12, C10–C11, C10–C13, C13–C14, C14–O3 and C14–O4 bond lengths

are found to be 1.219(2) Å, 1.474(3) Å, 1.500(2) Å, 1.334(2) Å, 1.502(2) Å, 1.479(2) Å, 1.494(2) Å, 1.2187(18) Å, 1.4882(19) Å, 1.3502(19) Å, 1.5330(19) Å, 1.501(2) Å, 1.540(2) Å, 1.540(2) Å, 1.5448(19) Å, 1.499(2) Å, 1.2150(18) Å and 1.3078(17) Å respectively, which are nearly equal to those derived from a closely related structure [10]. The bond angles are all in the typical ranges (see electronic supplement). There is one weak intramolecular hydrogen bond C13–H13A···O2 in the molecule. Two symmetry-related intermolecular hydrogen bonds connect adjacent molecules pairwise, which is a typical motif for many carboxylic acids.

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