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7-Hydroxy-4-(hydroxymethyl)coumarin

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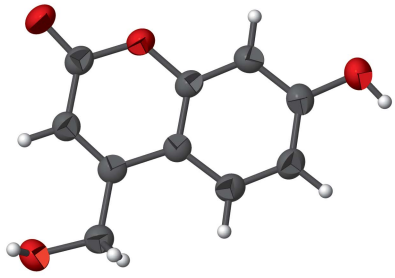
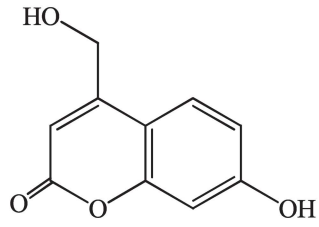
In the title compound, $C_{10}H_8O_4$, the almost planar coumarin ring system (r.m.s. deviation = 0.0216 Å from the plane through all 11 non-H atoms of the system) has hydroxymethyl and hydroxyl substituents at the 4- and 7-positions, respectively. In the crystal, two classical O—H···O hydrogen bonds generate a three-dimensional network structure.

3D view



Chemical scheme



Structure description

The design and synthesis of coumarin derivatives have attracted considerable attention because of their diverse pharmaceutical applications, including antivirus, anti-HIV and anti-neoplasm activities (Cherng *et al.*, 2008; Nawrot-Modranka *et al.*, 2007; Nakagawa-Goto *et al.*, 2007). In 2008, Zhang and co-workers described the preparation of 3-(*p*-methoxyphenyl)-4-hydroxymethyl-6-bromo-7-hydroxycoumarin co-crystallized from methanol (Jiang *et al.*, 2008). It is well known that variations in substituent groups can alter the biological properties and we have therefore synthesized the title coumarin derivative and report its structure here.

In the title coumarin derivative (Fig. 1), the C1–C5/C11 and O2/C4/C5/C7C9 rings are inclined to one another at an angle of 0.77 (4)°. The C10 and O4 atoms of the hydroxymethyl and the O1 atom of the hydroxyl substituent all lie close to the plane of the ring system with a maximum deviation of 0.055 (1) Å for O4. Bond lengths and angles observed here are closely similar to those found for 3-(*p*-methoxyphenyl)-4-hydroxymethyl-6-bromo-7-hydroxycoumarin (Jiang *et al.*, 2008). In the crystal, adjacent molecules are aggregated into a three-dimensional supramolecular network by O—H···O hydrogen bonds (Table 1 and Fig. 2).

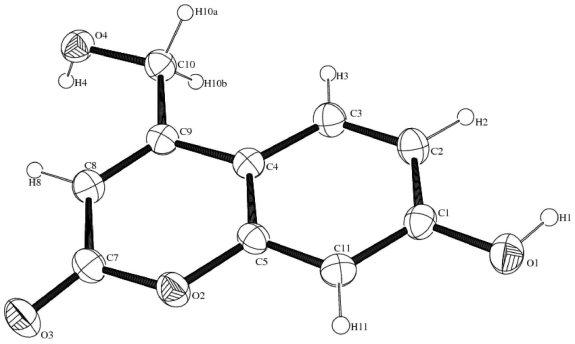


Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level.

Synthesis and crystallization

Freshly prepared acetyl chloride (1.10 g, 14.02 mmol) was added dropwise to a mixture of 1-(2,4-dihydroxyphenyl)-2-chloroethanone (1.03 g, 5.61 mmol) and K_2CO_3 (7.73 g, 56.1 mmol) in acetonitrile (70 ml). The mixture was filtered after refluxing for 6 h. The filtrate was neutralized with 2*M* HCl and extracted with ethyl acetate. The organic layer was washed with Na_2CO_3 (aq.) and water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to yield a yellow oil. The crude product was purified by chromatography to give the title compound as white solid. Colorless crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of this solid in methanol at room temperature for 5 days (yield 0.51 g, 45%).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

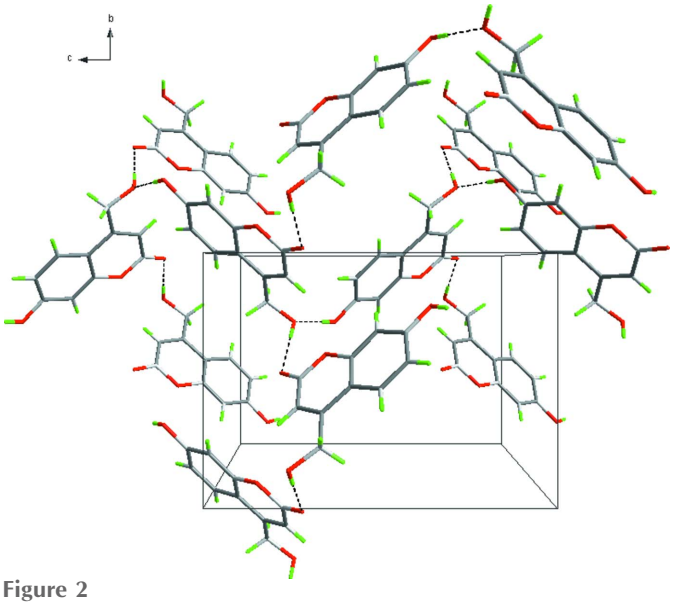


Figure 2
Part of the crystal structure, viewed along *a*, with hydrogen bonds drawn as dashed lines.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O3^{i}	0.82	1.88	2.696 (2)	179
O1—H1···O4^{ii}	0.82	1.83	2.654 (2)	180

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{10}H_8O_4$
M_r	192.16
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	296
a, *b*, *c* (Å)	13.217 (10), 9.831 (7), 13.627 (9)
V (Å^3)	1771 (2)
Z	8
Radiation type	Mo *Kα*
μ (mm^{-1})	0.11
Crystal size (mm)	0.33 × 0.30 × 0.30
Data collection	
Diffractometer	Bruker *SMART APEX* CCD area-detector
Absorption correction	Multi-scan (*SADABS*; Sheldrick, 1996)
T_{min}, T_{max}	0.964, 0.967
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9109, 1543, 1273
R_{int}	0.027
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.033, 0.078, 1.01
No. of reflections	1543
No. of parameters	130
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.15, −0.13

Computer programs: *SMART* and *SAINT* (Bruker, 2007), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008).

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160598 [doi:10.1107/S2414314616005988]

7-Hydroxy-4-(hydroxymethyl)coumarin

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7-Hydroxy-4-(hydroxymethyl)-2-oxo-2*H*-chromene

Crystal data

$C_{10}H_8O_4$
M_r = 192.16
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
a = 13.217 (10) Å
b = 9.831 (7) Å
c = 13.627 (9) Å
V = 1771 (2) Å^3
Z = 8
F(000) = 800
D_x = 1.442 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 2954 reflections
θ = 3.0–26.6°
μ = 0.11 mm^{-1}
T = 296 K
Block, colorless
0.33 × 0.30 × 0.30 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.964, T_{max} = 0.967
9109 measured reflections
1543 independent reflections
1273 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 25.0°, θ_{min} = 3.0°
h = −15→10
k = −11→11
l = −12→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.078
S = 1.01
1543 reflections
130 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0246P)^2 + 0.7759P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.13 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0102 (14)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.37748 (11)	0.30023 (12)	0.36743 (8)	0.0518 (4)
H1	0.3289	0.2962	0.3301	0.078*
O2	0.50816 (9)	0.10367 (10)	0.65278 (7)	0.0422 (3)
O3	0.58112 (10)	0.01787 (12)	0.78346 (8)	0.0520 (4)
O4	0.27929 (10)	−0.28639 (10)	0.74612 (8)	0.0453 (3)
H4	0.3219	−0.3459	0.7377	0.068*
C1	0.36957 (14)	0.20140 (15)	0.43601 (11)	0.0400 (4)
C2	0.29307 (14)	0.10429 (16)	0.43439 (11)	0.0435 (4)
H2	0.2454	0.1051	0.3842	0.052*
C3	0.28770 (14)	0.00731 (16)	0.50660 (11)	0.0417 (4)
H3	0.2360	−0.0568	0.5048	0.050*
C4	0.35857 (13)	0.00311 (14)	0.58290 (10)	0.0348 (4)
C5	0.43436 (12)	0.10092 (15)	0.58148 (10)	0.0355 (4)
C7	0.51031 (14)	0.00963 (16)	0.72671 (11)	0.0406 (4)
C8	0.43095 (14)	−0.08943 (15)	0.72989 (11)	0.0399 (4)
H8	0.4299	−0.1520	0.7811	0.048*
C9	0.35823 (13)	−0.09497 (14)	0.66163 (10)	0.0357 (4)
C10	0.27631 (14)	−0.20065 (15)	0.66317 (11)	0.0413 (4)
H10A	0.2112	−0.1553	0.6612	0.050*
H10B	0.2820	−0.2561	0.6045	0.050*
C11	0.44128 (14)	0.19958 (15)	0.50994 (11)	0.0407 (4)
H11	0.4931	0.2636	0.5113	0.049*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0544 (9)	0.0540 (7)	0.0471 (7)	−0.0047 (6)	−0.0053 (6)	0.0131 (5)
O2	0.0395 (7)	0.0415 (6)	0.0456 (6)	−0.0050 (5)	−0.0093 (5)	0.0024 (5)
O3	0.0456 (8)	0.0535 (7)	0.0569 (7)	−0.0042 (6)	−0.0191 (6)	0.0042 (5)
O4	0.0475 (9)	0.0418 (7)	0.0465 (6)	0.0018 (5)	0.0060 (5)	0.0042 (5)
C1	0.0449 (11)	0.0395 (9)	0.0356 (8)	0.0042 (7)	0.0035 (7)	0.0004 (6)
C2	0.0475 (11)	0.0458 (9)	0.0373 (8)	−0.0010 (8)	−0.0084 (7)	−0.0019 (7)
C3	0.0437 (11)	0.0398 (8)	0.0416 (8)	−0.0042 (8)	−0.0051 (7)	−0.0036 (6)
C4	0.0366 (10)	0.0322 (8)	0.0356 (8)	0.0030 (7)	0.0010 (7)	−0.0045 (6)
C5	0.0322 (9)	0.0378 (8)	0.0366 (8)	0.0040 (7)	−0.0021 (7)	−0.0051 (6)
C7	0.0396 (11)	0.0385 (9)	0.0438 (9)	0.0038 (7)	−0.0052 (8)	−0.0027 (7)
C8	0.0422 (11)	0.0359 (8)	0.0416 (8)	0.0014 (7)	−0.0023 (7)	0.0003 (6)
C9	0.0367 (10)	0.0324 (8)	0.0380 (8)	0.0041 (7)	0.0018 (7)	−0.0063 (6)
C10	0.0404 (11)	0.0399 (9)	0.0437 (8)	−0.0013 (7)	−0.0025 (7)	−0.0002 (7)
C11	0.0385 (11)	0.0394 (9)	0.0441 (8)	−0.0024 (7)	0.0022 (7)	−0.0003 (7)

Geometric parameters (Å, º)

O1—C1	1.3521 (18)	C3—H3	0.9300
O1—H1	0.8200	C4—C5	1.389 (2)
O2—C7	1.3676 (19)	C4—C9	1.442 (2)
O2—C5	1.377 (2)	C5—C11	1.378 (2)
O3—C7	1.217 (2)	C7—C8	1.432 (3)
O4—C10	1.4106 (19)	C8—C9	1.339 (2)
O4—H4	0.8200	C8—H8	0.9300
C1—C11	1.383 (2)	C9—C10	1.501 (2)
C1—C2	1.391 (3)	C10—H10A	0.9700
C2—C3	1.372 (2)	C10—H10B	0.9700
C2—H2	0.9300	C11—H11	0.9300
C3—C4	1.400 (2)		
C1—O1—H1	109.5	O3—C7—O2	116.05 (15)
C7—O2—C5	121.41 (13)	O3—C7—C8	126.12 (15)
C10—O4—H4	109.5	O2—C7—C8	117.83 (14)
O1—C1—C11	117.37 (15)	C9—C8—C7	122.18 (15)
O1—C1—C2	122.58 (15)	C9—C8—H8	118.9
C11—C1—C2	120.05 (15)	C7—C8—H8	118.9
C3—C2—C1	120.22 (15)	C8—C9—C4	119.16 (15)
C3—C2—H2	119.9	C8—C9—C10	122.45 (14)
C1—C2—H2	119.9	C4—C9—C10	118.38 (14)
C2—C3—C4	121.23 (16)	O4—C10—C9	113.87 (14)
C2—C3—H3	119.4	O4—C10—H10A	108.8
C4—C3—H3	119.4	C9—C10—H10A	108.8
C5—C4—C3	116.87 (14)	O4—C10—H10B	108.8
C5—C4—C9	118.39 (14)	C9—C10—H10B	108.8
C3—C4—C9	124.74 (15)	H10A—C10—H10B	107.7
O2—C5—C11	115.99 (14)	C5—C11—C1	118.60 (15)
O2—C5—C4	120.98 (13)	C5—C11—H11	120.7
C11—C5—C4	123.03 (15)	C1—C11—H11	120.7

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4—H4···O3^{i}	0.82	1.88	2.696 (2)	179
O1—H1···O4^{ii}	0.82	1.83	2.654 (2)	180

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+3/2; (ii) −*x*+1/2, −*y*, *z*−1/2.