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# 6,7-Dihydroxy-4-methylcoumarin

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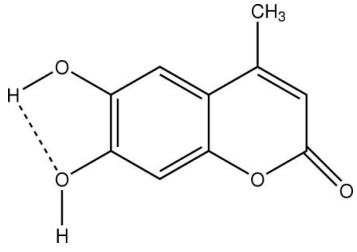
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.006 Å; $R$ factor = 0.095; $wR$ factor = 0.295; data-to-parameter ratio = 10.8.

In the title compound, $C_{10}H_8O_4$, one intramolecular O—H···O hydrogen bond defines an $S(5)$ pattern. The molecules are linked by one O—H···O and one C—H···O hydrogen bond, forming a centrosymmetric dimer with an edge-fused $R_2^2(8)R_2^2(16)[R_2^2(16)]$ motif; the dimers are linked by a pairs of O—H···O hydrogen bond into a [001] ribbon. Adjacent ribbons are linked by $\pi$–$\pi$ stacking interactions with centroid–centroid distances of 3.687 (3) and 3.753 (3) Å.

## Related literature

For related literature, see: Allen *et al.* (1987); Brühlmann *et al.* (2001); García-Báez*et al.* (2002); Rollinger *et al.* (2004); Sharma *et al.* (2005); Shen & Zeng (2006); Zhang *et al.* (2006).




## Experimental

### Crystal data

$C_{10}H_8O_4$
$M_r$ = 192.16
Triclinic, $P\overline{1}$
$a$ = 6.839 (2) Å
$b$ = 7.143 (3) Å
$c$ = 9.549 (3) Å
$\alpha$ = 68.233 (3)°
$\beta$ = 85.262 (3)°
$\gamma$ = 69.443 (3)°
$V$ = 405.0 (2) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 0.12 mm$^{-1}$
$T$ = 298 (2) K
0.56 × 0.15 × 0.13 mm

### Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.934, $T_{max}$ = 0.984
2098 measured reflections
1397 independent reflections
807 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.029

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.095
$wR(F^2)$ = 0.295
$S$ = 1.04
1397 reflections
129 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.07 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.49 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O3—H3···O4 | 0.82 | 2.30 | 2.737 (4) | 114 |
| O3—H3···O2$^{i}$ | 0.82 | 2.02 | 2.770 (4) | 152 |
| O4—H4···O2$^{ii}$ | 0.82 | 2.10 | 2.917 (4) | 173 |
| C8—H8···O1$^{ii}$ | 0.93 | 2.32 | 3.160 (5) | 150 |

Symmetry codes: (i) $x, y, z+1$; (ii) $-x+1, -y, -z+1$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

We acknowledge the financial support of the Huaihai Institute of Technology Science Foundation.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2332).

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# supplementary materials

*Acta Cryst.* (2007). E**63**, o4785 [ **doi:10.1107/S1600536807059272** ]

## 6,7-Dihydroxy-4-methylcoumarin

**S.-P. Yang, L.-J. Han, D.-Q. Wang and H.-T. Xia**

### Comment

7-Hydroxycoumarin derivatives are known to have a broad range of biological activities, including inhibition of Acetylcholinesterase and Monoamine Oxidase (Rollinger *et al.*,2004; Brühlmann *et al.*, 2001), antioxidants (Sharma *et al.*, 2005). The crystal structures of some 7-hydroxycoumarin derivatives (Zhang *et al.*, 2006; Shen *et al.*, 2006) have been described. Here we report the molecular structure of 6,7-dihydroxy-4-methyl-2*H*-1-benzopyran-2-one, (I).

In the molecule of (I), one intramolecular O—H···O hydrogen bond defines an *S*(5) pattern (García-Báez *et al.*, 2002) (Fig. 1, Table 1). The molecule is almost planar, the dihedral angle between the benzene and pyran rings is 3.13 (3) Å. The geometric parameters for (I) are normal (Allen *et al.*, 1987).

The molecules of (I) are linked by one O—H···O and one C—H···O hydrogen bonds into a centrosymmetric dimer of $R_2^2(8)R_2^2(16)[R_2^2(16)]$ (García-Báez *et al.*, 2002) ring centred at (1/2, 0, 1/2)(Fig. 2 and Table 1). Atoms O4 and C8 in the molecule at (*x*, *y*, *z*) act as a hydrogen-bond donor to atoms O2 and O1 in the molecule at (1 − *x*, −*y*,1 − *z*), respectively. These dimers are connected by a pair of O—H···O hydrogen bonds into a ribbon in the [0 0 1] direction (Fig. 2 and Table 1). Atoms O3 in the molecules at (*x*, *y*, *z*) and (1 − *x*, −*y*, 2 − *z*) act as a hydrogen-bond donors to atoms O2 in the molecules at (*x*, *y*, 1 + *z*) and (1 − *x*, −*y*,1 − *z*), respectively. These adjacent ribbons are linked by π···π interacions into three-dimensional structure [$Cg1\cdots Cg2^{i}$= 3.687 (3) Å, $Cg1\cdots Cg2^{ii}$= 3.753 (3) Å; symmetry codes: (i)-*x*,1 − *y*,1 − *z*; (ii)1 − *x*,1 − *y*.1 − *z*; where *Cg*1 is centroid of the ring O1/C1—C4/C9 and *Cg*2 is centroid of the ring C4—C9.]

### Experimental

The reaction mixture containing 2,3,4-triacetoxy benzene (2.52 g, 10 mmol), acetoacetic ester (1.3 ml, 10 mmol) and phosphoric acid (5.3 ml) was stirred at 363–373 K for 12 h, and then poured into the water. The solid obtained was filtered off, washed with water and dried at room temperature. Colourless crystals of (I) suitable for X-ray structure analysis were obtained by slow evaporation of a ethanol solution with the crude product over three days. (M·P.555–557 K).

### Refinement

All H atoms were positioned geometrically and refined as riding on their parent atoms, with C—H = 0.96Å (methyl), O—H = 0.82Å (hydroxy) and $U_{iso}$(H)= 1.5$U_{eq}$(C,*O*), and C—H = 0.93Å and $U_{iso}$(H) = 1.2$U_{eq}$(C) for all other H atoms. The residual peaks ($\Delta\rho_{max}$ = 1.07 e Å$^{-3}$) and *R* (*wR*($F^2$) = 0.295) values are high because of poor crystal quality.

## Figures

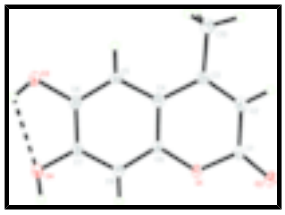

Fig. 1. The molecular structure of (I), showing the atom-labelling scheme and intramolecular hydrogen-bonded S(6) ring. Displacement ellipsoids are drawn at the 30% probability level. Dashed line indicate hydrogen bonds.

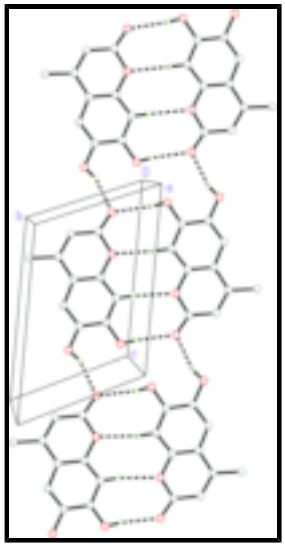

Fig. 2. Part of the crystal structure of (I), showing the formation of a [0 0 1] ribbon. For clarity, H atoms not involved in the motifs have been omitted. Dashed lines indicate hydrogen bonds.

## 6,7-Dihydroxy-4-methylcoumarin

*Crystal data*

| | |
|---|---|
| $C_{10}H_8O_4$ | $Z = 2$ |
| $M_r = 192.16$ | $F_{000} = 200$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.576$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Melting point: 555 K |
| $a = 6.839$ (2) Å | Mo $K\alpha$ radiation<br>$\lambda = 0.71073$ Å |
| $b = 7.143$ (3) Å | Cell parameters from 520 reflections |
| $c = 9.549$ (3) Å | $\theta = 2.3$–$26.9$º |
| $\alpha = 68.233$ (3)º | $\mu = 0.12$ mm$^{-1}$ |
| $\beta = 85.262$ (3)º | $T = 298$ (2) K |
| $\gamma = 69.443$ (3)º | Prism, colourless |
| $V = 405.0$ (2) Å$^3$ | 0.56 × 0.15 × 0.13 mm |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 1397 independent reflections |
| Radiation source: fine-focus sealed tube | 807 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.029$ |

| | |
|---|---|
| $T$ = 298(2) K | $\theta_{max}$ = 25.0º |
| φ and ω scans | $\theta_{min}$ = 2.3º |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $h$ = −7→8 |
| $T_{min}$ = 0.934, $T_{max}$ = 0.984 | $k$ = −8→8 |
| 2098 measured reflections | $l$ = −11→9 |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.095 | H-atom parameters constrained |
| $wR(F^2)$ = 0.295 | $w = 1/[\sigma^2(F_o^2) + (0.1927P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S$ = 1.04 | $(\Delta/\sigma)_{max} < 0.001$ |
| 1397 reflections | $\Delta\rho_{max}$ = 1.07 e Å$^{-3}$ |
| 129 parameters | $\Delta\rho_{min}$ = −0.49 e Å$^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: none |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.3392 (5) | 0.2706 (4) | 0.3419 (3) | 0.0317 (9) |
| O2 | 0.3742 (5) | 0.3077 (5) | 0.1047 (3) | 0.0387 (10) |
| O3 | 0.2139 (6) | 0.5590 (5) | 0.8112 (3) | 0.0457 (11) |
| H3 | 0.2451 | 0.4563 | 0.8916 | 0.069* |
| O4 | 0.3620 (5) | 0.1277 (5) | 0.8662 (3) | 0.0381 (10) |
| H4 | 0.4299 | 0.0067 | 0.8680 | 0.057* |
| C1 | 0.3200 (7) | 0.4023 (7) | 0.1939 (4) | 0.0293 (11) |
| C2 | 0.2386 (7) | 0.6265 (7) | 0.1609 (5) | 0.0330 (12) |
| H2 | 0.2153 | 0.7185 | 0.0602 | 0.040* |
| C3 | 0.1929 (7) | 0.7131 (7) | 0.2691 (5) | 0.0257 (11) |
| C4 | 0.2277 (6) | 0.5693 (6) | 0.4254 (4) | 0.0238 (11) |
| C5 | 0.1990 (7) | 0.6340 (6) | 0.5502 (4) | 0.0245 (11) |

| | | | | |
|---|---|---|---|---|
| H5 | 0.1499 | 0.7798 | 0.5341 | 0.029* |
| C6 | 0.2419 (7) | 0.4867 (7) | 0.6950 (4) | 0.0283 (11) |
| C7 | 0.3178 (7) | 0.2672 (7) | 0.7203 (4) | 0.0261 (11) |
| C8 | 0.3444 (7) | 0.1995 (7) | 0.6007 (4) | 0.0267 (11) |
| H8 | 0.3898 | 0.0538 | 0.6168 | 0.032* |
| C9 | 0.3021 (6) | 0.3523 (6) | 0.4558 (4) | 0.0230 (11) |
| C10 | 0.1105 (8) | 0.9506 (7) | 0.2279 (5) | 0.0376 (13) |
| H10A | 0.1870 | 0.9891 | 0.2861 | 0.056* |
| H10B | −0.0349 | 0.9960 | 0.2486 | 0.056* |
| H10C | 0.1263 | 1.0196 | 0.1223 | 0.056* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| O1 | 0.048 (2) | 0.0257 (16) | 0.0158 (15) | −0.0051 (14) | 0.0024 (13) | −0.0091 (12) |
| O2 | 0.058 (2) | 0.0340 (18) | 0.0220 (17) | −0.0101 (16) | 0.0045 (15) | −0.0136 (14) |
| O3 | 0.075 (3) | 0.0332 (19) | 0.0191 (17) | −0.0023 (17) | −0.0025 (16) | −0.0135 (14) |
| O4 | 0.055 (2) | 0.0313 (17) | 0.0167 (16) | −0.0054 (16) | 0.0010 (14) | −0.0057 (13) |
| C1 | 0.039 (3) | 0.031 (2) | 0.014 (2) | −0.009 (2) | 0.0021 (18) | −0.0073 (18) |
| C2 | 0.039 (3) | 0.031 (2) | 0.021 (2) | −0.008 (2) | −0.001 (2) | −0.0036 (19) |
| C3 | 0.024 (2) | 0.024 (2) | 0.024 (2) | −0.0048 (18) | 0.0008 (17) | −0.0061 (17) |
| C4 | 0.019 (2) | 0.030 (2) | 0.022 (2) | −0.0075 (18) | 0.0028 (17) | −0.0098 (19) |
| C5 | 0.026 (3) | 0.018 (2) | 0.027 (2) | −0.0034 (17) | 0.0025 (18) | −0.0096 (18) |
| C6 | 0.027 (3) | 0.034 (2) | 0.022 (2) | −0.005 (2) | 0.0029 (18) | −0.0140 (19) |
| C7 | 0.027 (3) | 0.030 (2) | 0.016 (2) | −0.0054 (19) | 0.0024 (17) | −0.0073 (17) |
| C8 | 0.031 (3) | 0.024 (2) | 0.022 (2) | −0.0058 (19) | 0.0035 (18) | −0.0086 (18) |
| C9 | 0.024 (2) | 0.022 (2) | 0.021 (2) | −0.0031 (17) | 0.0014 (17) | −0.0102 (17) |
| C10 | 0.045 (3) | 0.029 (3) | 0.030 (3) | −0.007 (2) | 0.006 (2) | −0.007 (2) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O1—C1 | 1.363 (5) | C4—C9 | 1.372 (6) |
| O1—C9 | 1.382 (5) | C4—C5 | 1.407 (5) |
| O2—C1 | 1.233 (5) | C5—C6 | 1.369 (6) |
| O3—C6 | 1.362 (5) | C5—H5 | 0.9300 |
| O3—H3 | 0.8200 | C6—C7 | 1.398 (6) |
| O4—C7 | 1.361 (5) | C7—C8 | 1.373 (6) |
| O4—H4 | 0.8200 | C8—C9 | 1.384 (6) |
| C1—C2 | 1.415 (6) | C8—H8 | 0.9300 |
| C2—C3 | 1.354 (6) | C10—H10A | 0.9600 |
| C2—H2 | 0.9300 | C10—H10B | 0.9600 |
| C3—C4 | 1.446 (6) | C10—H10C | 0.9600 |
| C3—C10 | 1.490 (6) | | |
| C1—O1—C9 | 121.1 (3) | O3—C6—C5 | 118.7 (4) |
| C6—O3—H3 | 109.5 | O3—C6—C7 | 121.6 (4) |
| C7—O4—H4 | 109.5 | C5—C6—C7 | 119.8 (4) |
| O2—C1—O1 | 114.5 (4) | O4—C7—C8 | 122.5 (4) |
| O2—C1—C2 | 128.1 (4) | O4—C7—C6 | 117.3 (4) |

| | | | |
|---|---|---|---|
| O1—C1—C2 | 117.4 (4) | C8—C7—C6 | 120.1 (4) |
| C3—C2—C1 | 123.0 (4) | C7—C8—C9 | 118.7 (4) |
| C3—C2—H2 | 118.5 | C7—C8—H8 | 120.7 |
| C1—C2—H2 | 118.5 | C9—C8—H8 | 120.7 |
| C2—C3—C4 | 118.3 (4) | C4—C9—O1 | 121.8 (4) |
| C2—C3—C10 | 120.8 (4) | C4—C9—C8 | 123.2 (4) |
| C4—C3—C10 | 120.9 (4) | O1—C9—C8 | 115.0 (3) |
| C9—C4—C5 | 116.8 (4) | C3—C10—H10A | 109.5 |
| C9—C4—C3 | 118.1 (4) | C3—C10—H10B | 109.5 |
| C5—C4—C3 | 125.1 (4) | H10A—C10—H10B | 109.5 |
| C6—C5—C4 | 121.3 (4) | C3—C10—H10C | 109.5 |
| C6—C5—H5 | 119.3 | H10A—C10—H10C | 109.5 |
| C4—C5—H5 | 119.3 | H10B—C10—H10C | 109.5 |
| C9—O1—C1—O2 | 174.3 (4) | O3—C6—C7—O4 | 0.3 (7) |
| C9—O1—C1—C2 | −6.9 (6) | C5—C6—C7—O4 | 178.7 (4) |
| O2—C1—C2—C3 | −176.9 (5) | O3—C6—C7—C8 | −180.0 (4) |
| O1—C1—C2—C3 | 4.4 (7) | C5—C6—C7—C8 | −1.6 (7) |
| C1—C2—C3—C4 | −0.5 (7) | O4—C7—C8—C9 | −177.9 (4) |
| C1—C2—C3—C10 | 179.1 (4) | C6—C7—C8—C9 | 2.4 (7) |
| C2—C3—C4—C9 | −1.0 (6) | C5—C4—C9—O1 | −179.0 (4) |
| C10—C3—C4—C9 | 179.4 (4) | C3—C4—C9—O1 | −1.5 (6) |
| C2—C3—C4—C5 | 176.3 (4) | C5—C4—C9—C8 | 1.4 (6) |
| C10—C3—C4—C5 | −3.2 (7) | C3—C4—C9—C8 | 179.0 (4) |
| C9—C4—C5—C6 | −0.5 (6) | C1—O1—C9—C4 | 5.6 (6) |
| C3—C4—C5—C6 | −177.9 (4) | C1—O1—C9—C8 | −174.8 (4) |
| C4—C5—C6—O3 | 179.1 (4) | C7—C8—C9—C4 | −2.4 (7) |
| C4—C5—C6—C7 | 0.6 (7) | C7—C8—C9—O1 | 178.0 (4) |

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H3···O4 | 0.82 | 2.30 | 2.737 (4) | 114 |
| O3—H3···O2$^{i}$ | 0.82 | 2.02 | 2.770 (4) | 152 |
| O4—H4···O2$^{ii}$ | 0.82 | 2.10 | 2.917 (4) | 173 |
| C8—H8···O1$^{ii}$ | 0.93 | 2.32 | 3.160 (5) | 150 |

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

**Fig. 1**

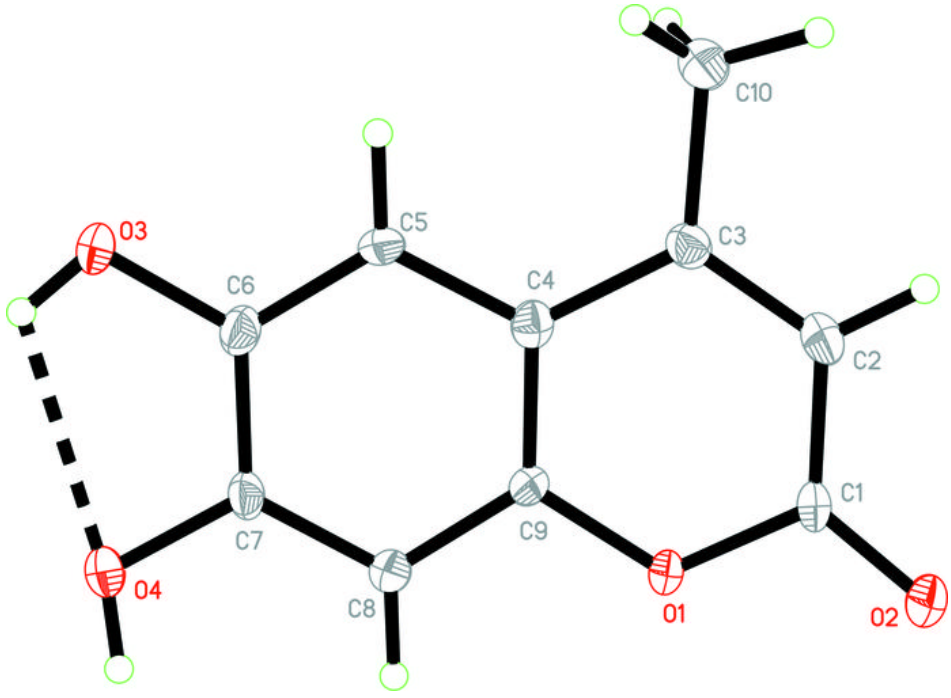

**Fig. 2**