

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

3,5-Dihydroxy-2-methyl-4H-pyran-4-one

Cheng-Ming Dong,^a Shou-Cheng Pu^b and Wen-Yuan Gao^{b*}

^aDepartment of Pharmaceutical Science, Henan College of Traditional Chinese Medicine, Zhengzhou 450008, People's Republic of China, and ^bSchool of Pharmaceutical Science & Technology, Tianjin University, Tianjin 300072, People's Republic of China

Correspondence e-mail: pharimgao@tju.edu.cn

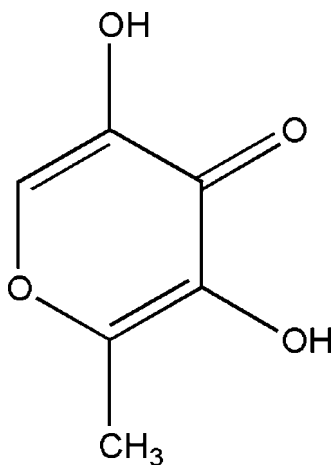
Received 18 March 2008; accepted 19 April 2008

Key indicators: single-crystal X-ray study; $T = 113$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.032; wR factor = 0.097; data-to-parameter ratio = 12.0.

In the title compound, $\text{C}_6\text{H}_6\text{O}_4$, inter- and intramolecular hydrogen bonds are observed which help to establish the crystal structure. There are weak π - π interactions between pyran rings separated by 3.5692 (9) Å.

Related literature

For general background, see: Shinoda *et al.* (2004). For related structures, see: Yao *et al.* (2005); Gibbons *et al.* (2000).



Experimental

Crystal data

$\text{C}_6\text{H}_6\text{O}_4$
 $M_r = 142.11$
 Monoclinic, $P2_1/n$
 $a = 6.9400$ (14) Å
 $b = 6.0648$ (12) Å
 $c = 14.008$ (3) Å
 $\beta = 92.77$ (3)°

$V = 588.9$ (2) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.14$ mm⁻¹
 $T = 113$ (2) K
 $0.14 \times 0.12 \times 0.10$ mm

Data collection

Rigaku Saturn diffractometer
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku/MS, 2005)
 $T_{\min} = 0.981$, $T_{\max} = 0.986$

3970 measured reflections
 1381 independent reflections
 1166 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.096$
 $S = 1.10$
 1381 reflections

115 parameters
 All H-atom parameters refined
 $\Delta\rho_{\max} = 0.37$ e Å⁻³
 $\Delta\rho_{\min} = -0.24$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------------------|------------|-------------|-------------|---------------|
| O4—H6 \cdots O3 ⁱ | 0.838 (18) | 1.89 (2) | 2.6902 (12) | 159.6 (13) |
| O2—H5 \cdots O3 ⁱⁱ | 0.94 (2) | 1.75 (2) | 2.6596 (12) | 162.6 (17) |
| O4—H6 \cdots O3 | 0.838 (18) | 2.44 (2) | 2.7820 (12) | 105.4 (10) |
| C1—H3 \cdots O4 | 1.005 (15) | 2.537 (14) | 2.8957 (15) | 100.5 (9) |
| C6—H4 \cdots O2 ⁱⁱⁱ | 0.936 (14) | 2.412 (13) | 3.3354 (14) | 169.4 (12) |

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

Data collection: *CrystalClear* (Rigaku/MS, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PV2074).

References

- Gibbons, S., Denny, B. J., Ali-Amine, S., Mathew, K. T., Skelton, B. W., White, A. H. & Gray, A. I. (2000). *J. Nat. Prod.* **63**, 839–840.
 Rigaku/MS. (2005). *CrystalClear*. Rigaku/MS, The Woodlands, Texas, USA.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Shinoda, Y., Murata, M., Homma, S. & Komura, H. (2004). *Biosci. Biotechnol. Biochem.* **68**, 529–536.
 Yao, G.-M., Wang, Y.-B., Wang, L.-Q. & Qin, G.-W. (2005). *Acta Cryst.* **E61**, o1403–o1405.

supplementary materials

Acta Cryst. (2008). E64, o1032 [doi:10.1107/S1600536808010957]

3,5-Dihydroxy-2-methyl-4*H*-pyran-4-one

C.-M. Dong, S.-C Pu and W.-Y. Gao

Comment

The title compound, 3,5-dihydroxy-2-methyl-pyran-4-one, (I) was identified as a decomposition product in the stored solution of orange juice (Shinoda, *et al.*, 2004). We report here the crystal structure of the title compound (Fig. 1) which was isolated from *Hydrocotyle sibthorpoioides* Lam. The structure of (I) is stabilized by two strong intermolecular hydrogen bonds of the type O—H...O and a weak intermolecular interaction of the type C—H...O. Intramolecular interactions are also observed which result in five membered rings; details are given in Table 1. There is indication of π - π interactions between the pyran rings lying about inversion centers with minimum separation of 3.5692 (9) Å. The crystal structures of 2-hydroxy-methyl analogue (Yao *et al.*, 2005) and 5-hydroxy-3-methoxy-pyran-4-one (Gibbons *et al.*, 2000) have been reported.

Experimental

Dried powder of *Hydrocotyle sibthorpoioides* Lam was exacted with EtOH and the extract was concentrated *in vacuo*. The residue was subjected to silical-gel coloumn chromatography. Elution with chloroform-methanol (95:5 *v/v*) yielded the title compound. Crystals suitable for XRD study were grwon from a solution of methanol at room temperature by slow evaporation.

Refinement

All H atoms were located from difference map and allowed to refine freely.

Figures

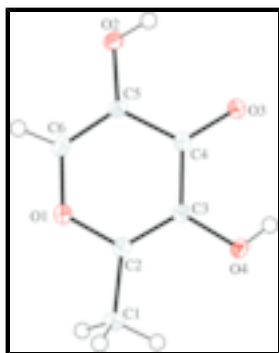


Fig. 1. A view of the molecule of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

3,5-Dihydroxy-2-methyl-4*H*-pyran-4-one

Crystal data

C₆H₆O₄

$F_{000} = 296$

supplementary materials

$M_r = 142.11$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 6.9400$ (14) Å

$b = 6.0648$ (12) Å

$c = 14.008$ (3) Å

$\beta = 92.77$ (3)°

$V = 588.9$ (2) Å³

$Z = 4$

$D_x = 1.603$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1620 reflections

$\theta = 1.5$ – 27.9 °

$\mu = 0.14$ mm⁻¹

$T = 113$ (2) K

Block, colorless

$0.14 \times 0.12 \times 0.10$ mm

Data collection

Rigaku Saturn
diffractometer

Radiation source: rotating anode

Monochromator: confocal

$T = 113$ (2) K

ω scans

Absorption correction: multi-scan
(CrystalClear; Rigaku/MSC, 2005)

$T_{\min} = 0.981$, $T_{\max} = 0.986$

3970 measured reflections

1381 independent reflections

1166 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\text{max}} = 27.9$ °

$\theta_{\text{min}} = 2.9$ °

$h = -9 \rightarrow 9$

$k = -7 \rightarrow 7$

$l = -10 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.096$

$S = 1.11$

1381 reflections

115 parameters

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.0654P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.37$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.24$ e Å⁻³

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|--------------|--------------|-------------|----------------------------------|
| O3 | 0.27997 (10) | 1.01120 (11) | 0.27250 (5) | 0.0149 (2) |
| O1 | 0.76427 (10) | 1.05517 (12) | 0.44524 (5) | 0.0157 (2) |
| O4 | 0.56909 (12) | 0.69576 (12) | 0.26153 (5) | 0.0171 (2) |
| O2 | 0.32648 (11) | 1.36372 (12) | 0.40092 (5) | 0.0173 (2) |
| C4 | 0.43152 (15) | 1.02588 (15) | 0.32615 (7) | 0.0124 (2) |
| C5 | 0.46324 (15) | 1.20540 (16) | 0.39217 (7) | 0.0132 (2) |
| C3 | 0.58183 (15) | 0.86536 (16) | 0.32479 (7) | 0.0127 (2) |
| C2 | 0.74196 (15) | 0.88197 (16) | 0.38483 (7) | 0.0139 (2) |
| C6 | 0.62774 (16) | 1.21333 (17) | 0.44749 (7) | 0.0157 (2) |
| C1 | 0.90601 (15) | 0.72547 (19) | 0.39113 (8) | 0.0174 (3) |
| H4 | 0.656 (2) | 1.323 (2) | 0.4929 (10) | 0.021 (3)* |
| H3 | 0.871 (2) | 0.582 (2) | 0.3585 (10) | 0.028 (3)* |
| H1 | 1.017 (2) | 0.782 (2) | 0.3616 (11) | 0.037 (4)* |
| H2 | 0.940 (2) | 0.689 (2) | 0.4591 (10) | 0.025 (3)* |
| H5 | 0.271 (3) | 1.393 (3) | 0.3397 (14) | 0.054 (5)* |
| H6 | 0.454 (3) | 0.669 (2) | 0.2453 (11) | 0.037 (4)* |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|------------|------------|------------|-------------|-------------|-------------|
| O3 | 0.0141 (4) | 0.0150 (4) | 0.0153 (4) | 0.0004 (3) | -0.0022 (3) | -0.0013 (3) |
| O1 | 0.0155 (4) | 0.0165 (4) | 0.0148 (4) | -0.0005 (3) | -0.0020 (3) | -0.0020 (3) |
| O4 | 0.0136 (4) | 0.0163 (4) | 0.0211 (4) | 0.0004 (3) | -0.0008 (3) | -0.0080 (3) |
| O2 | 0.0233 (4) | 0.0142 (4) | 0.0142 (4) | 0.0058 (3) | -0.0018 (3) | -0.0018 (3) |
| C4 | 0.0142 (5) | 0.0125 (5) | 0.0105 (4) | -0.0022 (4) | 0.0016 (4) | 0.0017 (3) |
| C5 | 0.0177 (5) | 0.0106 (5) | 0.0116 (4) | 0.0007 (4) | 0.0021 (4) | 0.0008 (3) |
| C3 | 0.0138 (5) | 0.0118 (5) | 0.0128 (5) | -0.0019 (4) | 0.0023 (4) | -0.0011 (3) |
| C2 | 0.0145 (5) | 0.0141 (5) | 0.0132 (4) | -0.0017 (4) | 0.0024 (4) | -0.0003 (3) |
| C6 | 0.0200 (6) | 0.0133 (5) | 0.0139 (5) | -0.0012 (4) | 0.0006 (4) | -0.0020 (4) |
| C1 | 0.0126 (5) | 0.0200 (6) | 0.0195 (5) | 0.0013 (4) | 0.0001 (4) | -0.0010 (4) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|----------|-------------|----------|-------------|
| O3—C4 | 1.2659 (13) | C4—C5 | 1.4386 (13) |
| O1—C6 | 1.3497 (13) | C5—C6 | 1.3494 (16) |
| O1—C2 | 1.3531 (12) | C3—C2 | 1.3646 (15) |
| O4—C3 | 1.3577 (12) | C2—C1 | 1.4816 (15) |
| O4—H6 | 0.838 (18) | C6—H4 | 0.936 (14) |
| O2—C5 | 1.3598 (12) | C1—H3 | 1.005 (15) |
| O2—H5 | 0.94 (2) | C1—H1 | 0.956 (17) |
| C4—C3 | 1.4276 (14) | C1—H2 | 0.996 (15) |
| C6—O1—C2 | 120.47 (8) | O1—C2—C3 | 120.53 (9) |

supplementary materials

| | | | |
|-------------|-------------|-------------|------------|
| C3—O4—H6 | 110.7 (11) | O1—C2—C1 | 113.31 (9) |
| C5—O2—H5 | 107.9 (12) | C3—C2—C1 | 126.15 (9) |
| O3—C4—C3 | 122.06 (9) | C5—C6—O1 | 122.45 (9) |
| O3—C4—C5 | 122.13 (9) | C5—C6—H4 | 124.0 (8) |
| C3—C4—C5 | 115.82 (9) | O1—C6—H4 | 113.5 (8) |
| C6—C5—O2 | 119.86 (9) | C2—C1—H3 | 111.1 (8) |
| C6—C5—C4 | 119.68 (10) | C2—C1—H1 | 112.2 (9) |
| O2—C5—C4 | 120.44 (9) | H3—C1—H1 | 107.1 (13) |
| O4—C3—C2 | 118.92 (9) | C2—C1—H2 | 110.3 (8) |
| O4—C3—C4 | 120.04 (9) | H3—C1—H2 | 106.4 (12) |
| C2—C3—C4 | 121.01 (9) | H1—C1—H2 | 109.5 (13) |
| O3—C4—C5—C6 | -179.79 (9) | C6—O1—C2—C1 | 179.47 (9) |
| C3—C4—C5—C6 | 0.12 (14) | O4—C3—C2—O1 | 176.47 (9) |
| O3—C4—C5—O2 | 1.94 (15) | C4—C3—C2—O1 | -1.93 (15) |
| C3—C4—C5—O2 | -178.15 (8) | O4—C3—C2—C1 | -2.39 (16) |
| O3—C4—C3—O4 | 3.12 (15) | C4—C3—C2—C1 | 179.21 (9) |
| C5—C4—C3—O4 | -176.78 (8) | O2—C5—C6—O1 | 176.71 (9) |
| O3—C4—C3—C2 | -178.50 (9) | C4—C5—C6—O1 | -1.58 (15) |
| C5—C4—C3—C2 | 1.59 (14) | C2—O1—C6—C5 | 1.32 (15) |
| C6—O1—C2—C3 | 0.47 (15) | | |

Hydrogen-bond geometry (\AA , $^\circ$)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|----------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O4—H6 \cdots O3 ⁱ | 0.838 (18) | 1.89 (2) | 2.6902 (12) | 159.6 (13) |
| O2—H5 \cdots O3 ⁱⁱ | 0.94 (2) | 1.75 (2) | 2.6596 (12) | 162.6 (17) |
| O4—H6 \cdots O3 | 0.838 (18) | 2.44 (2) | 2.7820 (12) | 105.4 (10) |
| C1—H3 \cdots O4 | 1.005 (15) | 2.537 (14) | 2.8957 (15) | 100.5 (9) |
| C6—H4 \cdots O2 ⁱⁱⁱ | 0.936 (14) | 2.412 (13) | 3.3354 (14) | 169.4 (12) |

Symmetry codes: (i) $-x+1/2, y-1/2, -z+1/2$; (ii) $-x+1/2, y+1/2, -z+1/2$; (iii) $-x+1, -y+3, -z+1$.

Fig. 1

