(S)-(2,2-Dimethyl-5-oxo-1,3-dioxolan-4-yl)acetic acid

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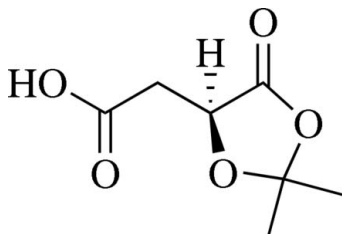
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The title compound, $C_7H_{10}O_5$, was obtained from the reaction of (S)-malic acid and 2,2-dimethoxypropane using p-TsOH as acid catalyst. The molecule is enantiomerically pure, as determined from optical rotation. The dioxolanone ring is a slightly distorted plane with the methylenecarboxy group equatorial. The carboxy group is *syn* to the face of the ring and *anti* to the ring H atom. Molecules are linked by O—H···O hydrogen bonds between the hydroxy group of the carboxyl group and the dioxolane carbonyl O atom, generating helices parallel to *b*. Only the *S* enantiomer is present in the crystal structure, which is consistent with the starting material and its synthetic sequence.

Related literature

The crystal structures of racemic malic acid and the (−)-enantiomer are known (van der Sluis & Kroon, 1985, 1989). While the space group of the (−)-enantiomer is $P2_1$, its absolute configuration could not be determined from anomalous dispersion. The crystal structures of at least one simple dioxolanone derivative of (−)-malic acid is also known (Pang *et al.*, 1997). For related literature, see: Green *et al.* (1995); Kim *et al.* (1997); Mulzer *et al.* (2000); Ohfune *et al.* (1981); Oida *et al.* (1989); Shioiri *et al.* (1995, 1997); Stocksdale *et al.* (2005).

Experimental

Crystal data

$C_7H_{10}O_5$	$V = 397.37$ (14) Å^3
$M_r = 174.15$	$Z = 2$
Monoclinic, $P2_1$	Cu $K\alpha$ radiation
$a = 5.2406$ (11) Å	$\mu = 1.09$ mm^{-1}
$b = 7.8236$ (14) Å	$T = 100$ (2) K
$c = 9.718$ (2) Å	$0.28 \times 0.19 \times 0.12$ mm
$\beta = 94.20$ (2)°	

Data collection

Oxford Diffraction Gemini Ultra diffractometer	1262 independent reflections
Absorption correction: analytical (*CrysAlis*; Oxford Diffraction, 2004)	1213 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.041$
$T_{min} = 0.762$, $T_{max} = 0.891$	2 standard reflections every 50 reflections intensity decay: <2%
7654 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.025$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.064$	
$S = 1.13$	$\Delta\rho_{max} = 0.14$ e Å^{-3}
1262 reflections	$\Delta\rho_{min} = -0.2$ e Å^{-3}
115 parameters	Absolute structure: Flack (1983), with 575 Friedel pairs
1 restraint	Flack parameter: 0.00 (18)

Table 1
Selected torsion angles (°).

O1—C1—C2—O5	13.89 (17)	C2—C3—C4—O3	38.3 (2)
O5—C2—C3—C4	54.09 (17)	C2—C1—O1—C5	−1.06 (17)
C1—C2—C3—C4	−61.72 (19)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H41···O2[i]	0.89 (3)	1.86 (3)	2.7067 (16)	156 (2)

Symmetry code: (i) $-x + 1, y + \frac{1}{2}, -z + 1$.

Data collection: *CrysAlis* (Oxford Diffraction, 2004); cell refinement: *CrysAlis*; data reduction: *CrysAlis*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2053).

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supplementary materials

(*S*)-(2,2-Dimethyl-5-oxo-1,3-dioxolan-4-yl)acetic acid

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Comment

(S)-Malic acid is a convenient starting material from the chiral pool and has been used in a variety of important natural and unnatural synthetic targets (Green *et al.*, 1995; Kim *et al.*, 1997; Mulzer *et al.*, 2000). The reported syntheses of many phytosiderophores and their analogs have utilized the title compound (I) (Ohfune *et al.*, 1981; Shioiri *et al.*, 1995; Shioiri *et al.*, 1997). We are interested in the preparation of a variety of phytosiderophores and their analogs for our ongoing transport studies (Stocksdale *et al.*, 2005). Stereospecific requirements of phytosiderophores on iron-uptake by rice plants have been studied. Enantiomers of the natural phytosiderophores resulted in significantly less iron-uptake (Oida *et al.*, 1989). Thus, absolute configuration of the title compound was important in our continued transport studies. Our preparation of the title compound was adapted from the literature (Green *et al.*, 1995).

The asymmetric unit of the structure comprises one crystallographically independent molecule of S absolute configuration. The Flack parameter, which refined to 0.00 (18), is not inconsistent with the know absolute configuration of the starting material, (S)-malic acid, and our synthetic sequence should have maintained this stereocenter.

Inspection of the crystal structure reveals molecules linked along the unique axis, b, by O—H⋯O hydrogen bonds. The network along the *b* axis is a helix and, as expected from the space goup, two molecular units form one turn of the helix. Each molecule has two sites for hydrogen bonding: the hydroxy group of the carboxylic acid, O4–H41, and the dioxolanone carbonyl, O2. The O2–O4' intermolecular distance is 2.707 Å.

Experimental

p-Toluenesulfonic acid (0.600 g, 3.2 mmol) was added to a room temperature stirred suspension of (S)-malic acid (30.0 g, 224 mmol) in 2,2-dimethoxypropane (75 ml, 610 mmol). After 30 minutes, the reaction mixture was diluted with CH_2Cl_2 (75 ml) and water (75 ml). The resulting organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 *x* 50 ml). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated to give a white solid. Recrystallization with 2:1 ethyl acetate/hexanes gave 21.8 g (56%) of compound I as colorless needles. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (br s, 1H), 4.69 (dd, 1H, J = 6.7 Hz, J = 3.7 Hz), 2.98 (dd, 1H, J = 17.4 Hz, J = 3.7 Hz), 2.84 (dd, 1H, J = 17.4 Hz, J = 6.7 Hz), 1.60 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.93, 171.87, 111.38, 70.35, 35.94, 26.71, 25.80; IR (TF) 3270, 3000, 2940, 1765, 1740, 1385 cm^{-1}; mp 380 − 382 K (lit. (Green *et al.*, 1995) 388 − 390 K); $[\alpha]_D^{293}$ = +7.2 (0.93, $CHCl_3$) (lit. (Green *et al.*, 1995) $[\alpha]_D^{295}$ = +6.9 (0.94, $CHCl_3$).

supplementary materials

Refinement

Data was collected to the collision limits of the Oxford Diffraction Gemini Ultra with Sapphire 3 detector. The carboxy hydrogen (H41) was located in a difference electron-density map and the isotropic atomic displacement parameters were refined independently. A riding model was used for the all other hydrogen atoms.
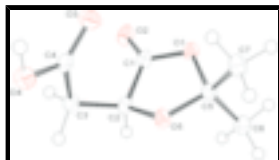
Figures

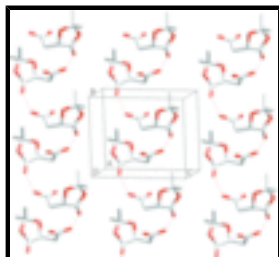Fig. 1. View of (I) (50% probability displacement ellipsoids).

Fig. 2. A view of the packing of (I) and the helical hydrogen-bonded network.

(*S*)-(2,2-Dimethyl-5-oxo-1,3-dioxolan-4-yl)acetic acid

Crystal data

$C_7H_{10}O_5$	$F_{000} = 184$
$M_r = 174.15$	$D_x = 1.455$ Mg m^{-3}
Monoclinic, $P2_1$	Cu $K\alpha$ radiation $\lambda = 1.54184$ Å
Hall symbol: P 2yb	Cell parameters from 1522 reflections
$a = 5.2406$ (11) Å	$\theta = 4.4–57.7°$
$b = 7.8236$ (14) Å	$\mu = 1.09$ mm^{-1}
$c = 9.718$ (2) Å	$T = 100$ (2) K
$\beta = 94.20$ (2)°	Prism, colourless
$V = 397.37$ (14) Å^3	$0.28 \times 0.19 \times 0.12$ mm
$Z = 2$	

Data collection

Oxford Diffraction Gemini Ultra diffractometer	$\theta_{max} = 63.1°$
φ and ω scans	$\theta_{min} = 4.6°$
Absorption correction: analytical (CrysAlisRED; Oxford Diffraction, 2004)	$h = -6 \rightarrow 6$
$T_{min} = 0.762$, $T_{max} = 0.891$	$k = -8 \rightarrow 9$
7654 measured reflections	$l = -11 \rightarrow 11$

1262 independent reflections	2 standard reflections
1213 reflections with $I > 2\sigma(I)$	every 50 reflections
$R_{int} = 0.041$	intensity decay: <2%

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2 + 0.0537P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.025$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.064$	$\Delta\rho_{max} = 0.14$ e Å^{-3}
$S = 1.13$	$\Delta\rho_{min} = -0.2$ e Å^{-3}
1262 reflections	Extinction correction: none
115 parameters	Absolute structure: Flack (1983), with 575 Friedel pairs
1 restraint	Flack parameter: 0.00 (18)

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.

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

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.6680 (3)	0.1093 (2)	0.21710 (16)	0.0198 (3)
C2	0.9076 (3)	0.1467 (2)	0.30831 (18)	0.0192 (4)
H2	1.0549	0.0825	0.2736	0.023*
C3	0.8910 (3)	0.1093 (2)	0.46061 (15)	0.0205 (3)
H3A	0.8504	−0.0131	0.4729	0.025*
H3B	1.0587	0.1326	0.5108	0.025*
C4	0.6886 (3)	0.2171 (2)	0.52035 (17)	0.0195 (3)
C5	0.8131 (3)	0.3752 (2)	0.16201 (16)	0.0193 (3)
C6	0.9868 (3)	0.3752 (2)	0.04477 (16)	0.0245 (4)
H6A	1.1133	0.467	0.0589	0.037*
H6B	0.8849	0.3937	−0.0426	0.037*
H6C	1.075	0.265	0.0419	0.037*
C7	0.6774 (3)	0.5421 (2)	0.18230 (17)	0.0248 (4)
H7A	0.5539	0.5277	0.2525	0.037*
H7B	0.5871	0.5774	0.095	0.037*
H7C	0.8027	0.6298	0.2126	0.037*
O1	0.61925 (19)	0.24126 (16)	0.13314 (10)	0.0207 (3)
O2	0.5412 (2)	−0.02001 (15)	0.21109 (12)	0.0264 (3)
O3	0.4856 (2)	0.25122 (18)	0.45951 (10)	0.0276 (3)
O4	0.7556 (2)	0.26832 (15)	0.64876 (11)	0.0232 (3)

O5	0.9441 (2)	0.32571 (14)	0.28877 (12)	0.0201 (3)
H41	0.623 (5)	0.326 (3)	0.679 (2)	0.046 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0251 (8)	0.0160 (8)	0.0188 (7)	−0.0001 (7)	0.0058 (6)	−0.0011 (6)
C2	0.0230 (7)	0.0129 (9)	0.0220 (8)	0.0007 (6)	0.0028 (6)	0.0007 (7)
C3	0.0229 (8)	0.0159 (8)	0.0224 (8)	0.0001 (7)	0.0008 (6)	0.0019 (6)
C4	0.0233 (8)	0.0136 (8)	0.0218 (7)	−0.0048 (6)	0.0027 (6)	0.0029 (6)
C5	0.0208 (7)	0.0146 (9)	0.0220 (8)	−0.0030 (6)	−0.0016 (6)	0.0011 (6)
C6	0.0264 (8)	0.0228 (9)	0.0241 (8)	−0.0001 (7)	0.0015 (7)	0.0005 (7)
C7	0.0299 (8)	0.0186 (9)	0.0257 (8)	0.0033 (7)	0.0013 (7)	0.0005 (7)
O1	0.0237 (6)	0.0172 (5)	0.0208 (5)	−0.0038 (5)	−0.0008 (4)	0.0017 (5)
O2	0.0357 (6)	0.0187 (6)	0.0249 (6)	−0.0088 (5)	0.0027 (5)	−0.0004 (5)
O3	0.0218 (6)	0.0343 (7)	0.0263 (6)	0.0046 (6)	−0.0001 (5)	−0.0022 (6)
O4	0.0263 (6)	0.0212 (7)	0.0220 (5)	0.0004 (5)	0.0015 (4)	−0.0034 (5)
O5	0.0242 (6)	0.0139 (6)	0.0214 (5)	−0.0028 (4)	−0.0030 (4)	0.0017 (4)

Geometric parameters (Å, °)

C1—O2	1.209 (2)	C5—O5	1.4196 (19)
C1—O1	1.329 (2)	C5—O1	1.4720 (19)
C1—C2	1.512 (2)	C5—C7	1.507 (2)
C2—O5	1.4281 (18)	C5—C6	1.510 (2)
C2—C3	1.518 (2)	C6—H6A	0.98
C2—H2	1	C6—H6B	0.98
C3—C4	1.505 (2)	C6—H6C	0.98
C3—H3A	0.99	C7—H7A	0.98
C3—H3B	0.99	C7—H7B	0.98
C4—O3	1.208 (2)	C7—H7C	0.98
C4—O4	1.333 (2)	O4—H41	0.89 (3)
O2—C1—O1	122.66 (14)	O1—C5—C7	108.44 (12)
O2—C1—C2	128.34 (15)	O5—C5—C6	112.02 (12)
O1—C1—C2	108.89 (13)	O1—C5—C6	107.58 (12)
O5—C2—C1	103.03 (14)	C7—C5—C6	114.54 (14)
O5—C2—C3	109.67 (14)	C5—C6—H6A	109.5
C1—C2—C3	115.47 (13)	C5—C6—H6B	109.5
O5—C2—H2	109.5	H6A—C6—H6B	109.5
C1—C2—H2	109.5	C5—C6—H6C	109.5
C3—C2—H2	109.5	H6A—C6—H6C	109.5
C4—C3—C2	111.14 (13)	H6B—C6—H6C	109.5
C4—C3—H3A	109.4	C5—C7—H7A	109.5
C2—C3—H3A	109.4	C5—C7—H7B	109.5
C4—C3—H3B	109.4	H7A—C7—H7B	109.5
C2—C3—H3B	109.4	C5—C7—H7C	109.5
H3A—C3—H3B	108	H7A—C7—H7C	109.5
O3—C4—O4	123.61 (16)	H7B—C7—H7C	109.5

O3—C4—C3	123.72 (15)	C1—O1—C5	109.70 (11)
O4—C4—C3	112.65 (13)	C4—O4—H41	107.5 (15)
O5—C5—O1	104.73 (12)	C5—O5—C2	108.79 (13)
O5—C5—C7	109.01 (12)		
O2—C1—C2—O5	−169.91 (16)	C2—C1—O1—C5	−1.06 (17)
O1—C1—C2—O5	13.89 (17)	O5—C5—O1—C1	−12.36 (15)
O2—C1—C2—C3	−50.4 (2)	C7—C5—O1—C1	−128.64 (13)
O1—C1—C2—C3	133.42 (15)	C6—C5—O1—C1	106.97 (14)
O5—C2—C3—C4	54.09 (17)	O1—C5—O5—C2	21.49 (15)
C1—C2—C3—C4	−61.72 (19)	C7—C5—O5—C2	137.37 (14)
C2—C3—C4—O3	38.3 (2)	C6—C5—O5—C2	−94.81 (15)
C2—C3—C4—O4	−142.86 (14)	C1—C2—O5—C5	−21.72 (15)
O2—C1—O1—C5	−177.52 (14)	C3—C2—O5—C5	−145.19 (12)

Hydrogen-bond geometry (Å, °)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O4—H41⋯O2[i]	0.89 (3)	1.86 (3)	2.7067 (16)	156 (2)

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

Fig. 1

Fig. 2