organic papers

2,3-Dihydroxybenzoic acid

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Key indicators

Single-crystal X-ray study
$T = 296$ K
Mean σ(C–C) = 0.004 Å
R factor = 0.044
wR factor = 0.175
Data-to-parameter ratio = 8.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_7H_6O_4$, crystallizes with two independent molecules in the asymmetric unit and forms a two-dimensional structure in the solid state. This is facilitated by a network of hydrogen-bonding interactions. There are two intramolecular hydrogen bonds, one between adjacent hydroxyl groups and the other between between the hydroxyl group and the carbonyl O atom. The crystal structure is stabilized both by carboxylic acid dimer formation and by interactions between the carboxyl and hydroxyl groups.

Comment

The title compound, (I), is a salicylate metabolite (Liu *et al.*, 1999). It is also one of the naturally occurring polyphenols analogous to 3,4-dihydroxybenzoic acid and 3,4,5-trihydroxy-benzoic acid (gallic acid) which have antioxidative activity and also apoptosis characterized by DNA cleavage (Kawase *et al.*, 1998). The title compound enhances Fenton-type reactions in the presence of hydrogen peroxide and metal ions: $M^{(n-1)} + H_2O_2 \rightarrow M^{(n-1)+} + OH^- + OH^{\cdot}$ (Rodríguez *et al.*, 1999; Samuni *et al.*, 1983). The OH$^{\cdot}$ radicals produced in this reaction are responsible for gallic acid induced cell death (Sakaguchi *et al.*, 1998). As a result of the interest in the biological chemistry of this compound, we determined the structure of (I). The asymmetric unit of (I) comprises two similar but independent molecules (Fig. 1 and Table 1). The most significant differences between these planar molecules appear to relate to their intermolecular hydrogen-bonding modes. One of the molecules (Fig. 1) forms a carboxylic acid dimer motif, whereas the carboxylic acid group of the second molecule forms interactions with hydroxyl groups (Fig. 2) of the surrounding molecules (Table 2). Both molecules form similar intramolecular hydrogen bonds. One of these occurs between hydroxyl groups and another occurs between the hydroxyl group and the carbonyl O atom. In the crystal structure, the hydrogen-bonding network extends in the *ac* plane.
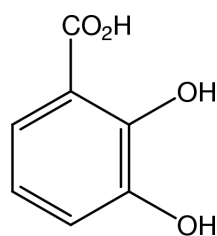
(I)
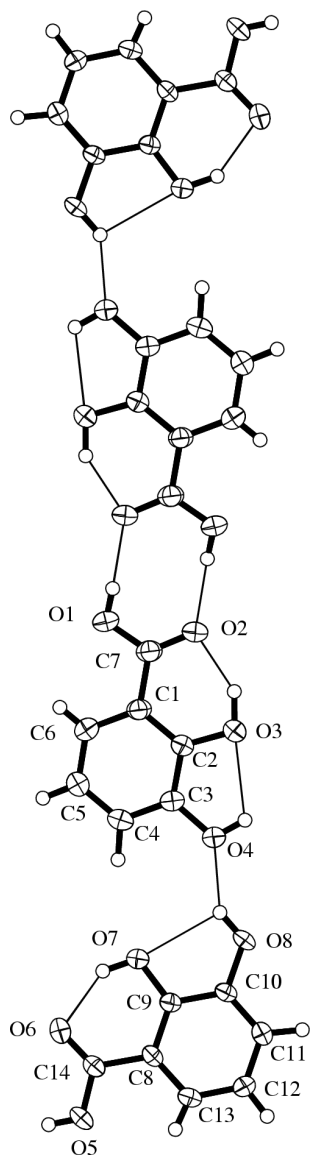
Figure 1
*ORTEP*II (Johnson, 1976) drawing of the structure, showing the atomic numbering scheme and hydrogen-bond interactions. Ellipsoids for non-H atoms correspond to the 50% probability level.

Experimental

The light-yellow prismatic crystal used for analysis was obtained by slow evaporation from an aqueous solution of the compound.

Crystal data

$C_7H_6O_4$	$Z = 4$
$M_r = 154.12$	$D_x = 1.546$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 9.431$ (2) Å	Cell parameters from 25
$b = 10.307$ (2) Å	reflections
$c = 8.291$ (1) Å	$\theta = 14.3–15.0°$
$\alpha = 110.29$ (1)°	$\mu = 0.13$ mm^{-1}
$\beta = 113.75$ (1)°	$T = 296$ K
$\gamma = 67.10$ (2)°	Plate, light brown
$V = 662.0$ (2) Å^3	$0.30 \times 0.20 \times 0.10$ mm

Data collection

Rigaku AFC-5R diffractometer	$h = 0 \rightarrow 12$
ω–2θ scans	$k = -12 \rightarrow 13$
3221 measured reflections	$l = -10 \rightarrow 9$
3037 independent reflections	3 standard reflections
1763 reflections with $I > 2\sigma(I)$	every 150 reflections
$R_{int} = 0.020$	intensity decay: 1.0%
$\theta_{max} = 27.5°$	

Refinement

Refinement on F^2	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)] = 0.044$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
$wR(F^2) = 0.175$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
1763 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
199 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.310 (2)	C2—C3	1.399 (4)
O2—C7	1.238 (4)	C3—C4	1.375 (4)
O3—C2	1.359 (3)	C4—C5	1.382 (3)
O4—C3	1.372 (2)	C5—C6	1.378 (4)
O5—C14	1.325 (4)	C8—C9	1.399 (4)
O6—C14	1.217 (3)	C8—C13	1.389 (3)
O7—C9	1.357 (2)	C8—C14	1.468 (3)
O8—C10	1.375 (3)	C9—C10	1.397 (3)
C1—C2	1.398 (3)	C10—C11	1.369 (3)
C1—C6	1.401 (4)	C11—C12	1.382 (4)
C1—C7	1.468 (4)	C12—C13	1.379 (4)
C2—C1—C6	119.7 (3)	C9—C8—C13	119.7 (2)
C2—C1—C7	119.6 (2)	C9—C8—C14	118.5 (2)
C6—C1—C7	120.7 (2)	C13—C8—C14	121.8 (2)
O3—C2—C1	124.7 (3)	O7—C9—C8	124.7 (2)
O3—C2—C3	116.3 (2)	O7—C9—C10	116.5 (2)
C1—C2—C3	119.0 (2)	C8—C9—C10	118.8 (2)
O4—C3—C2	120.6 (2)	O8—C10—C9	119.6 (2)
O4—C3—C4	118.7 (3)	O8—C10—C11	119.6 (2)
C2—C3—C4	120.7 (2)	C9—C10—C11	120.8 (2)
C3—C4—C5	120.2 (3)	C10—C11—C12	120.2 (2)
C4—C5—C6	120.3 (3)	C11—C12—C13	120.0 (2)
C1—C6—C5	120.1 (2)	C8—C13—C12	120.4 (3)
O1—C7—O2	122.7 (3)	O5—C14—O6	122.6 (2)
O1—C7—C1	114.6 (2)	O5—C14—C8	113.8 (2)
O2—C7—C1	122.7 (2)	O6—C14—C8	123.6 (3)
O1—C7—C1—C2	−178.3 (2)	O8—C10—C9—C8	179.6 (2)
O1—C7—C1—C6	2.0 (4)	O8—C10—C11—C12	−179.7 (3)
O2—C7—C1—C2	1.1 (4)	C1—C2—C3—C4	−1.3 (4)
O2—C7—C1—C6	−178.6 (3)	C1—C6—C5—C4	−0.2 (4)
O3—C2—C1—C6	−178.7 (2)	C2—C1—C6—C5	−0.7 (4)
O3—C2—C1—C7	1.6 (4)	C2—C3—C4—C5	0.4 (4)
O3—C2—C3—O4	−1.6 (3)	C3—C2—C1—C6	1.5 (4)
O3—C2—C3—C4	178.8 (2)	C3—C2—C1—C7	−178.2 (2)
O4—C3—C2—C1	178.3 (2)	C3—C4—C5—C6	0.4 (4)
O4—C3—C4—C5	−179.2 (2)	C5—C6—C1—C7	179.0 (3)
O5—C14—C8—C9	173.6 (2)	C8—C9—C10—C11	−0.5 (4)
O5—C14—C8—C13	−7.2 (4)	C8—C13—C12—C11	−0.3 (4)
O6—C14—C8—C9	−6.3 (4)	C9—C8—C13—C12	0.1 (4)
O6—C14—C8—C13	172.9 (3)	C9—C10—C11—C12	0.4 (4)
O7—C9—C8—C13	−179.9 (2)	C10—C9—C8—C13	0.3 (4)
O7—C9—C8—C14	−0.7 (4)	C10—C9—C8—C14	179.5 (2)
O7—C9—C10—O8	−0.3 (4)	C10—C11—C12—C13	0.0 (5)
O7—C9—C10—C11	179.6 (2)	C12—C13—C8—C14	−179.1 (3)

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

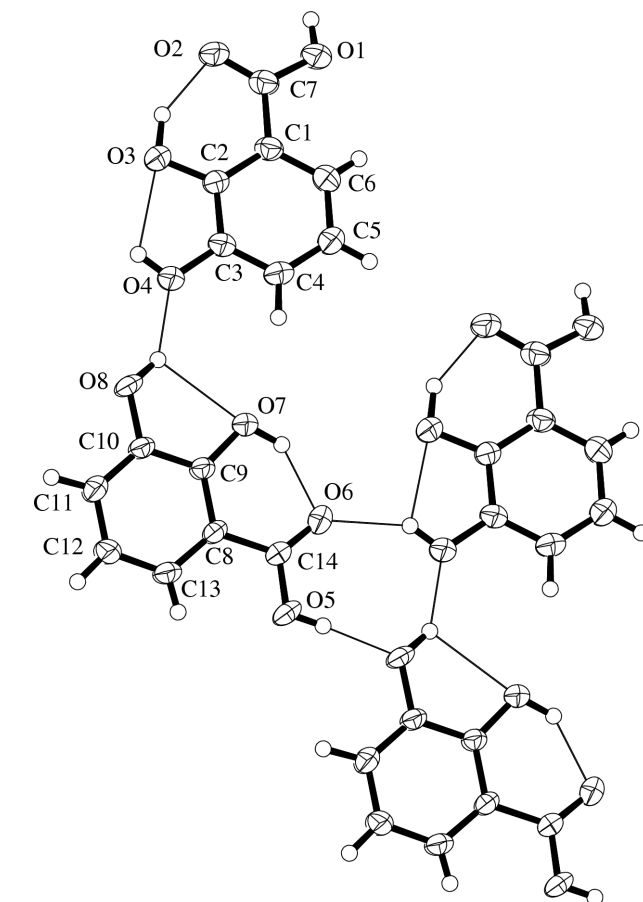| D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O4—H3$\cdots$O3	0.88	2.24	2.700 (3)	113
O3—H2$\cdots$O2	0.98	1.77	2.642 (2)	147
O8—H9$\cdots$O7	0.82	2.26	2.682 (2)	113
O7—H8$\cdots$O6	0.82	1.93	2.625 (2)	143
O1—H1$\cdots$O2^i	0.84	1.85	2.685 (3)	175
O5—H7$\cdots$O8^{ii}	0.83	1.81	2.645 (2)	177
O4—H3$\cdots$O6^{iii}	0.88	2.05	2.809 (2)	144
O8—H9$\cdots$O4	0.82	2.04	2.670 (2)	134

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

All H atoms were located from difference Fourier maps. Those bound to oxygen were fixed in the determined positions and carbon-bound H atoms were included in the riding-model approximation.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation & Rigaku, 1999*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* ((Molecular Structure Corporation & Rigaku, 1999*b*); program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989) and *DIRDIF*94 (Beurskens *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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Figure 2
*ORTEP*II (Johnson, 1976) drawing of the structure, showing the atomic numbering scheme and hydrogen-bond interactions. Ellipsoids for non-H atoms correspond to the 50% probability level.