Table 5. *Close intermolecular contacts* (Å)

Orange G/Adenine		Orange G/Cytosine	
O(1)···N(4)	2.742 (4)	O(1)···O(8W)	2.920 (2)
O(2)···N(3)	2.809 (4)	O(2)···N(6)	2.857 (2)
O(3)···O(12W^i)	2.850 (5)	O(3)···N(7)	2.740 (2)
O(3)···O(10W^i)	2.988 (5)	O(4)···N(6^{iv})	2.803 (2)
O(4)···O(12W^i)	2.778 (5)	O(5)···N(4^{vii})	2.971 (2)
O(5)···N(3^{ii})	2.824 (5)	O(6)···N(3)	2.837 (2)
O(6)···O(10W)	2.774 (4)	O(7)···N(5^{viii})	2.740 (2)
O(7)···O(11W^{iii})	2.928 (4)	O(8W)···N(8^{ix})	2.761 (2)
O(8W)···N(6)	2.873 (4)	O(8W)···O(9^{ix})	2.873 (2)
O(9W)···N(11)	2.760 (5)	O(10)···N(4)	2.699 (2)
O(9W)···N(5^v)	2.878 (5)	O(10)···N(3)	2.915 (3)
O(10W)···N(8)	2.855 (4)		
O(11W)···O(12W^v)	2.635 (7)		
O(11W)···N(9)	2.694 (4)		
N(8)···N(12^{vi})	2.882 (5)		

Symmetry codes: (i) $1 + x, y, z$; (ii) $x, 1 + y, z$; (iii) $-x, 1 - y, -z$; (iv) $-1 + x, -1 + y, z$; (v) $x, -1 + y, z$; (vi) $-1 - x, 1 - y, 1 - z$; (vii) $-x, 2 - y, 2 - z$; (viii) $1 + x, y, -1 + z$; (ix) $1 - x, 3 - y, 2 - z$.

In both structures, H atoms bonded to C atoms were placed in calculated positions and were not refined. H atoms bonded to N atoms in Orange G/adenine were located in difference maps and their positional parameters were refined. Peaks were also found near the water O atoms, but their positions were not considered chemically reasonable and were left unassigned. H atoms bonded to N atoms and to the water O atom in Orange G/cytosine were located and their positional parameters were refined. Refinement of a secondary extinction coefficient (Zachariasen, 1963) was considered warranted only in the case of Orange G/cytosine. Data collection and cell determination were carried out using Enraf–Nonius CAD-4 software. Data reduction and structure refinement used the *TEXSAN* software package (Molecular Structure Corporation, 1985). Structure solution was accomplished using *SHELXS86* (Sheldrick, 1985). Molecular graphics were prepared using *ORTEPII* (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978).

References

Conroy, M. J. & Lovrien, R. E. (1992). *J. Cryst. Growth*, **122**, 213–222.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.

Ojala, W. H., Lu, L. K., Albers, K. E., Gleason, W. B., Richardson, T. I., Lovrien, R. E. & Sudbeck, E. A. (1994). *Acta Cryst.* B50. In the press.

Olivieri, A. C., Wilson, R. B., Paul, I. C. & Curtin, D. Y. (1989). *J. Am. Chem.Soc.* **111**, 5525–5532.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Weaver, J. L., Pine, P. S., Anand, R., Bell, S. & Aszalos, A. (1992). *Antivir. Chem. Chemother.* **3**, 147–151.

Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Sorbic Acid

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Abstract

The crystal and molecular structure of sorbic acid [(*E,E*)-2,4-hexadienoic acid], $C_6H_8O_2$, has been determined. There appears to be no delocalization of the C_{sp^2}—C_{sp^2} bonds, arranged in an *E,E* configuration, which have lengths of 1.328 (2) and 1.335 (2) Å (double) and 1.442 (2)–1.487 (2) Å (single). Dimers are formed in the crystal with an intermolecular O···O separation of 2.632 (2) Å; O—H 0.99 (2), H···O 1.65 (2) Å, O—H···O 174 (2)°.

Comment

Sorbic acid, (I), exhibits antibacterial and antifungal properties (Martindale, 1993) and has been used to prevent spoilage of syrup by moulds (Richards, 1972). The structures of numerous simple carboxylic acids have been determined and many involve intermolecular hydrogen bonding (Speakman, 1972; CSSR, 1993). It is difficult to obtain well formed crystals of sorbic acid and attempts to determine the cell dimensions by X-ray powder diffraction from a commercial crystalline sample (99 + %, Sigma) were unsuccessful. After repeated crystallizations from ethanol only one specimen was considered suitable for data collection.

(I)
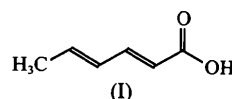
The study shows that dimers form in the crystal with intermolecular hydrogen bonding around a centre of symmetry. The short O···O separation is

achieved by transposing the coordinates of O(2) in Table 1 by $1 - x$, $-y$, $1 - z$. The planar nature of the molecule is shown by the torsion angles and the C_{sp^2}—C_{sp^2} bond lengths compare favourably with values for formal single (1.46 Å) and double bonds (1.34 Å) (Ladd & Palmer, 1993). The crystal structures of several compounds similar to sorbic acid, where the molecules differ only at C(1), have been studied and show very similar intermolecular hydrogen-bonding patterns. These include mono-methyl *trans,trans*-muconate (Rabinovich & Schmidt, 1967), *trans,trans*-muconic acid (Bernstein & Leiserowitz, 1972) and 5-phenyl-2,4-pentadienoic acid (Kashino & Haisa, 1980).
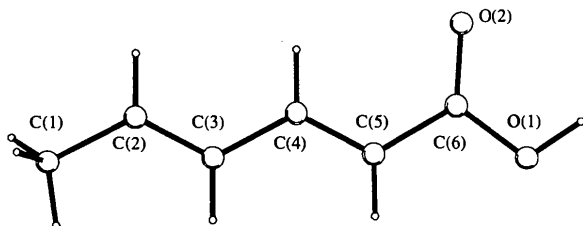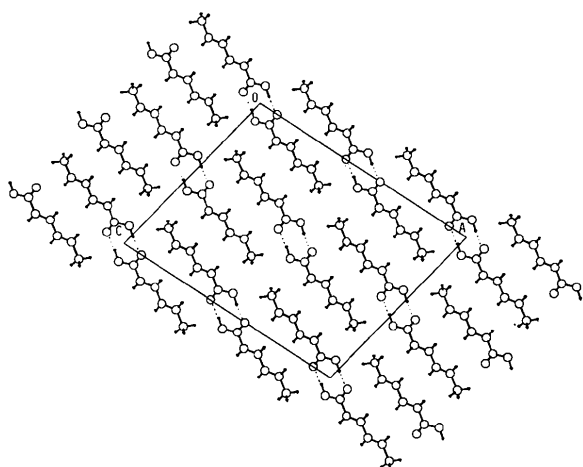

Fig. 1. The atomic arrangement in the molecule.

Fig. 2. The crystal packing viewed on the (010) plane.

Experimental

Crystal data

$C_6H_8O_2$	Mo $K\alpha$ radiation
$M_r = 112.12$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 250
$C2/c$	reflections
$a = 19.749$ (3) Å	$\theta = 2.1–25.2°$
$b = 3.9355$ (5) Å	$\mu = 0.093$ mm^{-1}
$c = 15.649$ (2) Å	$T = 150$ K
$\beta = 101.66$ (1)°	Square plate
$V = 1191.2$ (3) Å^3	0.25 × 0.25 × 0.05 mm
$Z = 8$	Colourless
$D_x = 1.250$ Mg m^{-3}	

Data collection

Delft Instruments FAST	$R_{int} = 0.048$
diffractometer	$\theta_{max} = 25.2°$
Area detector	$h = -19 \rightarrow 21$
Absorption correction:	$k = -3 \rightarrow 4$
none	$l = -17 \rightarrow 9$
1744 measured reflections	Standard reflections not
908 independent reflections	applicable to FAST area
658 observed reflections	detection data collection
$[I > 2\sigma I]$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.01$
$R(F) = 0.039$	$\Delta\rho_{max} = 0.20$ e Å^{-3}
$wR(F^2) = 0.096$	$\Delta\rho_{min} = -0.16$ e Å^{-3}
$S = 0.508$	Extinction correction: none
908 reflections	Atomic scattering factors
85 parameters	from *SHELXL*93
$w = 1/[\sigma^2(F_o^2) + (0.0132P)^2]$	(Sheldrick, 1993)
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

U_{iso} for H atoms; $U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for others.

	x	y	z	U_{iso}/U_{eq}
O(1)	0.4644 (1)	0.2581 (3)	0.4074 (1)	0.036 (1)
O(2)	0.4164 (1)	−0.0584 (3)	0.4985 (1)	0.034 (1)
C(1)	0.0880 (1)	0.1738 (5)	0.3066 (1)	0.033 (1)
C(2)	0.1573 (1)	0.0909 (4)	0.3597 (1)	0.029 (1)
C(3)	0.2171 (1)	0.2111 (4)	0.3460 (1)	0.026 (1)
C(4)	0.2839 (1)	0.1218 (4)	0.3970 (1)	0.026 (1)
C(5)	0.3442 (1)	0.2344 (4)	0.3819 (1)	0.027 (1)
C(6)	0.4106 (1)	0.1308 (4)	0.4348 (1)	0.027 (1)
H(1)	0.5074 (12)	0.1804 (50)	0.4458 (16)	0.068 (7)
H(1A)	0.0590	0.2708	0.3443	0.069 (7)
H(1B)	0.0664	−0.0336	0.2790	0.041 (5)
H(1C)	0.0930	0.3389	0.2614	0.045 (6)
H(2)	0.1590	−0.0606	0.4073	0.032 (5)
H(3)	0.2156	0.3670	0.2993	0.024 (4)
H(4)	0.2852	−0.0282	0.4448	0.018 (4)
H(5)	0.3439	0.3878	0.3349	0.025 (4)

Table 2. *Selected geometric parameters* (Å, °)

O(1)—C(6)	1.322 (2)	C(3)—C(4)	1.442 (2)
O(2)—C(6)	1.231 (2)	C(4)—C(5)	1.335 (2)
C(1)—C(2)	1.487 (2)	C(5)—C(6)	1.460 (2)
C(2)—C(3)	1.328 (2)		
C(3)—C(2)—C(1)	125.4 (2)	O(2)—C(6)—O(1)	122.8 (2)
C(2)—C(3)—C(4)	124.6 (2)	O(2)—C(6)—C(5)	123.7 (2)
C(5)—C(4)—C(3)	124.8 (2)	O(1)—C(6)—C(5)	113.5 (2)
C(4)—C(5)—C(6)	122.5 (2)		
C(1)—C(2)—C(3)—C(4)	−178.5 (2)	C(4)—C(5)—C(6)—O(2)	−2.3 (3)
C(2)—C(3)—C(4)—C(5)	178.0 (2)	C(4)—C(5)—C(6)—O(1)	177.32 (14)
C(3)—C(4)—C(5)—C(6)	−178.89 (14)		

Atom H(1) was freely refined with all other H atoms riding. All H-atom U's were refined. Computer programs used were *SHELXS*86 (Sheldrick, 1990), *SHELXL*93 (Sheldrick, 1993) and *SNOOPI* (Davies, 1983).

References

Bernstein, J. & Leiserowitz, L. (1972). *Isr. J. Chem.* **10**, 601–612.

CSSR (1993). *Crystal Structure Search and Retrieval Instruction Manual.* Chemical Classes 1 and 2. SERC, Daresbury Laboratory, Warrington, England.

Davies, K. (1983). *SNOOPI. CHEMGRAF User Guide.* The CHEMGRAF Suite. Chemical Crystallography Laboratory, Oxford, England.

Kashino, S. & Haisa, M. (1980). *Acta Cryst.* B**36**, 346–353.

Ladd, M. F. C. & Palmer, R. A. (1993). *Structure Determination by X-ray Crystallography*, 3rd ed., p. 434. New York: Plenum.

Martindale (1993). *The Extra Pharmacopoeia.* 30th ed. London: Pharmaceutical Press.

Rabinovich, D. & Schmidt, G. M. J. (1967). *J. Chem. Soc. B*, pp. 286–289.

Richards, R. M. E. (1972). *Pharm. J.* **2**, 91.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.

Speakman, J. C. (1972). *Structure and Bonding*, Vol. 12, pp. 141–199. Berlin: Springer-Verlag.

γ-Resorcylic Acid, its Monohydrate and its Pyridinium Complex

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Abstract

The crystal structures of γ-resorcylic acid (2,6-dihydroxybenzoic acid), $C_7H_6O_4$, (I), γ-resorcylic acid monohydrate, $C_7H_6O_4 \cdot H_2O$, (II), and pyridinium γ-resorcylate, $C_5H_6N^+ \cdot C_7H_5O_4^-$, (III), have been determined. In (I) and (II), the carboxyl group of the γ-resorcylic acid molecule is in an *anti* conformation and the carboxylic OH group is involved as a donor in an O—H···O intramolecular hydrogen bond. This bond is part of an infinite hydrogen-bonded chain with mixed σ- and π-bond cooperativity. Structure (II) is disordered and may be considered to result from the superposition

of two lower-symmetry structures related by a mirror plane. Structure (III) consists of discrete complex units formed from the anion and cation by means of an N—H···O hydrogen bond.

Comment

γ-Resorcylic acid is one of the strongest carboxylic acids ($pK_a = 1.3$). It is also an interesting example of a molecule with two possible intramolecular hydrogen-bond systems, one with two phenolic OH groups and another with one phenolic and one carboxylic OH group involved as donors in intramolecular hydrogen bonds; these two forms, *A* and *B*, are shown in the scheme below.

(*A*)   (*B*)
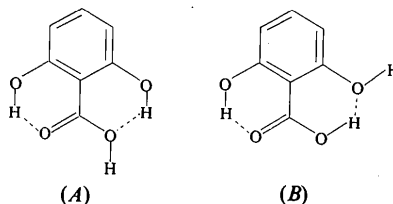
Solution ^1H NMR studies of this acid in the presence of bases of different proton-acceptor ability show that structure *A* prevails and that an intermolecular hydrogen-bond interaction with the base occurs through the carboxylic OH group (Golubev & Denisov, 1992). Some strengthening of the intramolecular hydrogen bonds was observed as the proton-acceptor ability of the base increased. In order to study the hydrogen-bond interactions of γ-resorcylic acid in the solid state, it was recrystallized from solvents of different proton-acceptor and proton-donor ability. The only forms obtained were anhydrous γ-resorcylic acid, γ-resorcylic acid monohydrate and, where a strong base was present in the crystallization mixture, an $A^- \cdots H—B^+$ complex. This paper presents X-ray structure analyses of γ-resorcylic acid (I), its monohydrate (II) and its pyridinium salt (III).

The carboxyl group of the γ-resorcylic acid molecule in (I) is in an *anti* conformation as a result of the intramolecular hydrogen bond with the hydroxyl group at O4. Unlike the structure in solution, the molecular structure in the crystal corresponds to form *B*, in which one phenolic OH group acts as an intra- and the other as intermolecular hydrogen-bond donor. The molecules are linked by hydrogen bonds to form infinite chains along [01$\bar{1}$]. Intra- and intermolecular hydrogen bonds form a chain with alternating σ- and π-bond cooperativity (Jeffrey & Saenger, 1991) (Fig. 1). The energy of the H atoms involved in the hydrogen bonds along this chain can be considered to be characterized by double-minimum potentials. A concerted proton-transfer process induced along this chain would cause a transformation from form *B* to form *A*. The two minima are of different energies and only molecules of form *B*