Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Setzer, W. N., Afshar, S., Burns, N. L., Ferrante, L. A., Hester, A. M., Meehan, E. J. Jr, Grant, G. J., Isaac, S. M., Laudemann, C. P., Lewis, C. M. & VanDerveer, D. G. (1990). *Heteroatom Chem.* **1**, 375–387.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1995). *SHELXTL/PC*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Stoe & Cie (1996*a*). *STADI4. Data Collection Program for Windows.* Version 1.06a. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1996*b*). *X-RED. Data Reduction Program for Windows.* Version 1.08. Stoe & Cie, Darmstadt, Germany.
Sutton, L. R., Blake, A. J., Li, W.-S. & Schröder, M. (1998). *J. Chem. Soc. Dalton Trans.* In the press.

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2′-Hydroxy-3′-methoxy-5′-flavonesulfonic Acid Trihydrate: a New Zwitterion

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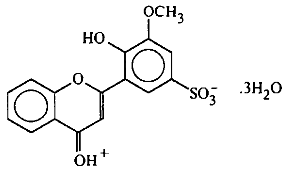
Abstract

The title compound, $C_{16}H_{12}O_7S.3H_2O$, displays an anionic part, the deprotonated sulfonic acid group, and a cationic part, the protonated carbonyl group, indicative of a zwitterionic structure. These two parts in different molecules are linked by hydrogen bonding involving three water molecules.

Comment

Amino acids are well known zwitterions. Substitution of a carboxylic acid group by a sulfonic acid group gives another type of zwitterion, for example, in sulfanilic acid. Substitution of an amino group by a carbonyl group also gives zwitterions, provided that the carbonyl group is basic enough. This is the case for 2′,6′-dimethoxyflavone which can accept Brønsted (Wallet, Gaydou & Baldy, 1989; Tinant, Declercq, Wallet, Gaydou & Baldy, 1991; Wallet, Cody, Wojtczak & Blessing, 1993; Wallet, Cody & Wojtczak, 1994) as well as Lewis acids (Maniukiewicz, Molins, Miravitlles, Wallet & Gaydou, 1996). In the title compound, (I), similar S—O lengths [1.441 (2), 1.443 (2) and 1.445 (2) Å] and O—S—O bond angles [111.92 (10), 112.91 (11) and 112.96 (11)°] clearly show the deprotonation of the sulfonic acid group. An H atom (H4) was located near the carbonyl O atom as the highest peak in a difference Fourier map. To assure this assignment, its isotropic displacement was refined independently (0.077 Å^2). The structure contains an anionic part, the deprotonated sulfonic acid group, and a cationic part, the protonated carbonyl group.



(I)

Molecules are not directly bound through carbonyl and sulfonic acid groups. The bonding is mediated by hydrogen bonding in the three water molecules. Each water molecule is engaged in three hydrogen bonds. O*W*1 is bound to two sulfuryl O atoms belonging to two different flavone molecules and also to a water molecule. O*W*2 is involved in a similar hydrogen-bonding scheme. O*W*3 is bound to O*W*2 and O*W*1, and to the carbonyl O atom. The sulfonyl O atoms are engaged in different hydrogen bonds, O51 has only one bond with O*W*2, O52 is hydrogen bonded to two water molecules, and O53 is bound to the water molecule O*W*1 and to the hydroxyl group of the flavone. Hydrates of sulfonic acids form various cationic water species. In the case of trihydrates, $H_7O_3^+$ (Mootz & Fayos, 1970;

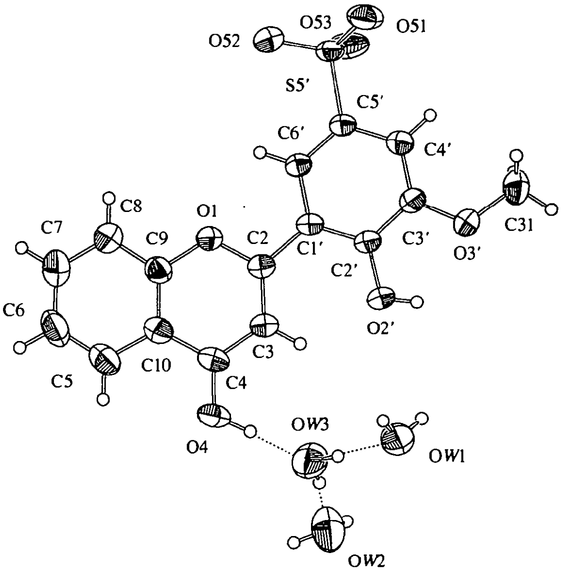


Fig. 1. The molecular structure of the title compound showing 50% probability displacement ellipsoids.

Williams & Peterson, 1972; Lundgren & Lundin, 1972; Lundgren, 1972) and $H_5O_2^+/H_2O$ (Attig & Mootz, 1976) species have been reported. In the present structure, the formation of such species is prevented by the presence of the carbonyl O atom with its strong basic character. The O*W*1···O*W*3 and O*W*2···O*W*3 hydrogen bonds are of similar length, 2.618 (3) and 2.665 (3) Å, respectively. The hydrogen bond between O*W*3 and the carbonyl O atom is shorter, 2.446 (3) Å. The C4—O4 bond distance is in the range of bond distances for protonated ketones and the C10—C4—O4 bond angle [118.4 (2)°] *anti* to the hydrogen bonding is significantly smaller than the angle C3—C4—O4 [123.2 (2)°; Childs, Kostyk, Lock & Mahendran, 1990]. The zwitterion is essentially planar, O1—C2—C1′—C2′ being 177.6 (2)°. This is in good agreement with the contribution of a hydrogen bond to a more planar molecule (Wallet, Cody & Wojtczak, 1994).

Experimental

2′-Hydroxy-3′methoxy-5′-flavonesulfonic acid trihydrate was obtained by heating (358 K) 2′,3′-dimethoxyflavone dissolved in concentrated sulfuric acid (96%) for 5 h. After cooling, water was added until complete precipitation had occurred. Recrystallization was from aqueous solution.

Crystal data

$C_{16}H_{12}O_7S.3H_2O$
$M_r = 402.36$
Monoclinic
$P2_1/c$
$a = 8.665$ (1) Å
$b = 12.503$ (2) Å
$c = 16.306$ (2) Å
$\beta = 94.03$ (1)°
$V = 1762.2$ (4) Å^3
$Z = 4$
$D_x = 1.517$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 13–20°$
$\mu = 0.239$ mm^{-1}
$T = 293$ (2) K
Prismatic
0.56 × 0.28 × 0.15 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: empirical *via* ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.983$, $T_{\max} = 1.000$
4927 measured reflections
4645 independent reflections

2392 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.021$
$\theta_{\max} = 30.40°$
$h = -12 \rightarrow 0$
$k = -17 \rightarrow 0$
$l = -23 \rightarrow 23$
3 standard reflections
frequency: 60 min
intensity decay: 0.4%

Refinement

Refinement on F^2
$R = 0.041$
$wR = 0.101$
$S = 0.944$
4645 reflections
270 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o)^2 + (0.0106P)^2]$ where $P = [\max(0,F_o^2) + 2F_c^2]/3$

$(\Delta/\sigma)_{\max} = 0.041$
$\Delta\rho_{\max} = 0.293$ e Å^{-3}
$\Delta\rho_{\min} = -0.399$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

O1—C2	1.353 (2)	C3—C4	1.400 (3)
O1—C9	1.371 (2)	C4—O4	1.288 (2)
C2—C3	1.372 (2)	C4—C10	1.434 (3)
C2—C1′	1.463 (3)		
C2—O1—C9	121.1 (2)	C2—C3—C4	121.0 (2)
O1—C2—C3	120.3 (2)	O4—C4—C3	123.2 (2)
O1—C2—C1′	112.03 (14)	O4—C4—C10	118.4 (2)
C3—C2—C1′	127.7 (2)	C3—C4—C10	118.3 (2)
O1—C2—C1′—C6′	−3.5 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2′—H2′···O3′	0.82 (3)	2.15 (2)	2.613 (2)	116 (3)
O2′—H2′···O53$^{\rm i}$	0.82 (3)	1.95 (2)	2.654 (2)	144 (3)
O4—H4···O*W*3$^{\rm i}$	0.91 (3)	1.53 (3)	2.446 (3)	177 (3)
O*W*1—H11···O52$^{\rm ii}$	0.82 (3)	2.02 (3)	2.826 (3)	167 (3)
O*W*1—H12···O53	0.82 (3)	2.01 (3)	2.815 (3)	167 (3)
O*W*2—H21···O51$^{\rm iii}$	0.86 (3)	2.03 (3)	2.872 (3)	165 (3)
O*W*2—H22···O52$^{\rm iv}$	0.87 (3)	1.93 (3)	2.796 (3)	176 (3)
O*W*3—H31···O*W*1	0.88 (3)	1.74 (3)	2.618 (3)	173 (3)
O*W*3—H32···O*W*2	0.79 (3)	1.88 (3)	2.665 (3)	171 (3)
C3—H3···O2′	0.93	2.14	2.774 (3)	124 (3)
C6′—H6′···O1	0.93	2.31	2.655 (2)	102 (3)
C6′—H6′···O52	0.93	2.59	2.954 (2)	104 (3)

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

H atoms bonded to C atoms and O2′ were constrained; coordinates for those on O4 and those of the water molecules were freely refined. $U_{\rm iso}$(H) parameters were refined for groups of atoms, *i.e.* H4 (on O4) alone, CH_3 and H_2O, and the remainder.

Data collection: *CAD*-4 *Operations Manual* (Enraf–Nonius, 1977). Cell refinement: *CAD*-4 *Operations Manual*. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai & Pritzkow, 1994).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1187). Services for accessing these data are described at the back of the journal.

References

Attig, R. & Mootz, D. (1976). *Acta Cryst.* **B32**, 435–439.
Childs, R. E, Kostyk, M. D., Lock, C. J. L. & Mahendran, M. (1990). *J. Am. Chem. Soc.* **112**, 8912–8920.
Enraf–Nonius (1977). *CAD*-4 *Operations Manual*. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Lundgren, J.-O. (1972). *Acta Cryst.* **B28**, 475–481.
Lundgren, J.-O. & Lundin, P. (1972). *Acta Cryst.* **B28**, 486–491.

Maniukiewicz, W., Molins, E., Miravitlles, C., Wallet, J.-C. & Gaydou, E. M. (1996). *J. Chem. Crystallogr.* **26**, 691–694.
Mootz, D. & Fayos, J. (1970). *Acta Cryst.* B**26**, 2046–2054.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Tinant, B., Declercq, J.-P., Wallet, J.-C., Gaydou, E. M. & Baldy, A. (1991). *Bull. Soc. Chim. Belg.* **100**, 329–338.
Wallet, J.-C., Cody, V. & Wojtczak, A. (1994). *Struct. Chem.* **5**, 361–366.
Wallet, J.-C., Cody, V., Wojtczak, A. & Blessing, R. H. (1993). *Anti-Cancer Drug Des.* **8**, 325–332.
Wallet, J.-C., Gaydou, E. M. & Baldy, A. (1989). *Acta Cryst.* C**45**, 512–515.
Williams, J. M. & Peterson, S. W. (1972). *Am. Crystallogr. Assoc. Winter Meet.*, Albuquerque, NM, USA. Abstract I7, p. 51.
Zsolnai, L. & Pritzkow, H. (1994). *ZORTEP. ORTEP for a PC.* University of Heidelberg, Germany.

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5,5-Dihydroxyethylbarbituric Acid

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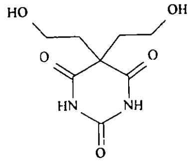
Abstract

The title compound, $C_8H_{12}N_2O_5$, does not show conformational symmetry in the crystal. It is stabilized by intermolecular hydrogen bonds producing a three-dimensional network of hydrogen bonds. The two molecules in the asymmetric unit differ in the conformation of the six-membered ring and the way in which each participates in the hydrogen-bonding network.

Comment

The title molecule, (I), was prepared as a preliminary step in the synthesis of a new achiral nucleotide analogue (Barbier *et al.*, 1993). The crystal structure was studied as part of a program to examine the packing characteristics of barbiturates containing 5,5-polar substituents which can be involved in hydrogen bonding.



(I)

The asymmetric unit of the title structure contains two non-equivalent molecules. The two molecules are pseudo-related by $x_A = x_B + \frac{1}{2}$, $y_A = \frac{1}{2} - y_B$, $z_A = z_B$, which together with the crystal symmetry, suggests the pseudo-translation vector $[\frac{1}{2},0,\frac{1}{2}]$. This is a non-crystallographic translation symmetry because 295 reflections with $h + l = 2n + 1$ have $I > 10\sigma(I)$ [802 have $I > 3\sigma(I)$].

The main differences between the two molecules are in the conformation of the six-membered ring and the hydrogen bonds formed by the hydroxyl groups. The six-membered ring of molecule *A* has a twist-boat form with the N1—C1—C4—C3, N2—C3—C4—C1 and C1—N1—C2—N2 torsion angles equal to −7.2 (3), −1.8 (3) and −7.3 (3)°, respectively, while that of molecule *B* has a boat form with corresponding torsion angles of 3.2 (3), 5.8 (3) and 11.4 (3)°. Only one hydroxyl group of molecule *A* is involved in a hydrogen bond (O5*A*···O4*A*), while both hydroxyl groups of molecule *B* are involved in hydrogen bonds with O atoms of molecule *A*. These hydrogen bonds produce a two-dimensional network in the *ab* plane.

A search of the Cambridge Structural Database (Allen & Kennard, 1993) for 5,5-disubstituted barbiturates yielded 68 compounds for which crystal structures have been determined. All compounds, including the title

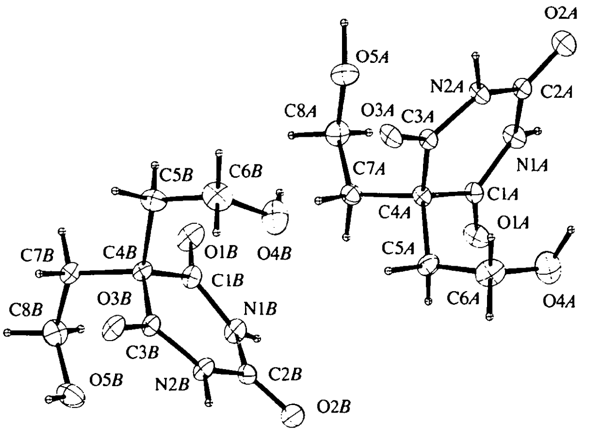


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.