Crystal structure of methylammonium 4′,7-dimethoxyisoflavone-3′-sulfonate monohydrate, $(CH_3NH_3)(C_{17}H_{13}O_4SO_3) \cdot H_2O$

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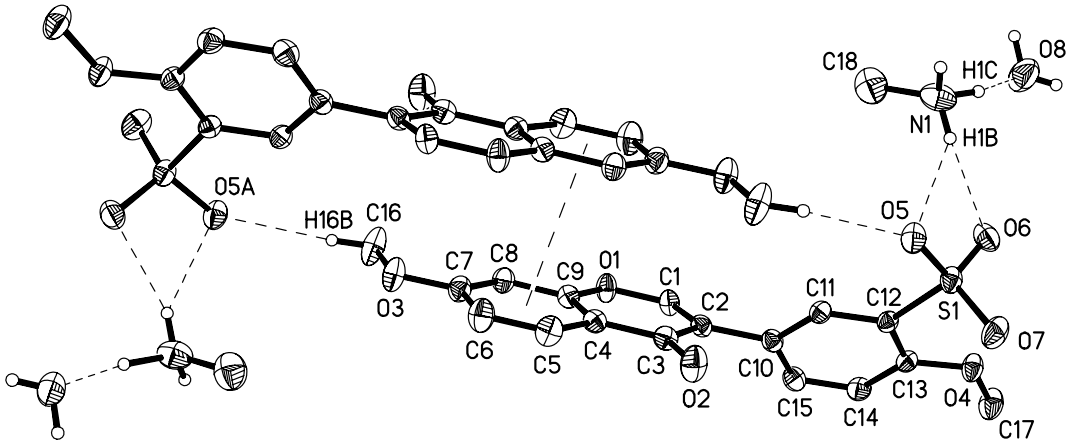
Received February 23, 2006, accepted and available on-line March 7, 2006; CCDC no. 1267/1738



Abstract

$C_{18}H_{21}NO_8S$, monoclinic, $P12_1/c1$ (no. 14), a = 21.069(5) Å, b = 11.494(3) Å, c = 7.996(2) Å, β = 97.257(3)°, V = 1920.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.044, $wR_{ref}(F^2)$ = 0.124, T = 298 K.

Source of material

Sodium 4′,7-dimethoxyisoflavone-3′-sulfonate (1 g) prepared according [1] was dissolved in water (10 ml). The solution was mixed with a saturated $(CH_3NH_3)Cl$ solution (5 ml). Crystals of the title compound were obtained after 24 h at RT. Single crystals suitable for X-ray diffraction were obtained by recrystallization from water and slow evaporation at RT.

Discussion

Dimethoxydaidzein (4′,7-dimethoxyisoflavone) mainly exists in the *Leguminosae* plants such as the *Wisteria brachybotrys* [2], the root of *Glycyrrhiza pallidiflora Maxim* [3] and the fruits of *Amorpha fruticosa* [4]. It has been pharmacologically shown to inhibit the phosphodiesterase [4] and Epstein-Barr virus [2]. Oka et al. [5] also found that dimethoxydaidzein can be used as a good medicine to inhibit the cancer cells. The biological utilization rate of isoflavonid is low and the dose is high for its poor solubility. So, it is necessary to synthesize water-soluble derivatives of dimethoxydaidzein, such $Na(H_2O)_2]X$ and $[M(H_2O)_6]X_2 \cdot 8H_2O$ (M = Cu [6], Ni [1], Co [7], Fe [8]; X = 4′,7-dimethoxyisoflavone-3′-sulfonate) have been reported. Water-soluble derivatives $Na(H_2O)_2]X$ and $[Cu(H_2O)_6]X_2 \cdot 8H_2O$ have been tested that they possess better biological activities than the parent compound [6]. The title compound, methylammonium 4′,7-dimethoxyisoflavone-3′-sulfonate monohydrate, is a water-soluble derivative of daidzein.

The title compound is composed of one $CH_3NH_3^+$ cation, one 4′,7-dimethoxylisoflavone-3′-sulfonate anion and one lattice water molecule. In the anion, the bond lengths and angles of isoflavone unit are similar to those of $[Ni(H_2O)_6]X_2 \cdot 8H_2O$ [1], $[Co(H_2O)_6]X_2 \cdot 8H_2O$ [7] and $[Fe(H_2O)_6]X_2 \cdot 8H_2O$ [8] (X is 4′,7-dimethoxyisoflavone-3′-sulfonate). The atoms of benzopyranone moiety containing planar rings A (C4 - C9) and C (C1 - C4/C9/O1) display an almost coplanar configuration, with a mean deviation of 0.008 Å from the least-squares plane and the dihedral angle of 1.05°. To avoid intramolecular steric conflicts, the two rigid ring systems, benzene ring B (C10 - C15) and benzopyranone moiety, are rotated by 55.12° with respect to each other. Paired C16–H16B···O5A(1–x,2–y,1–z) hydrogen bonds make molecules into a centrosymmetric dimer. In the dimer, the isoflavone skeletons are in an anti-parallel mode and π-π stacking interactions exist between their rings A with an offset distance of 0.782 Å and an intercentroid distance of 3.717(5) Å. Methylammonium atom H1B and sulfonate atom O5 are three-centered and trifurcated, respectively, by hydrogen bonds. The C16–H16C···O2(x,5/2–y,1/2+z) and N1–H1A···O5(1–x,2–y,1–z) hydrogen bonds, which exist between the dimers, assemble the isoflavone units into a sheet along (011). The sheets are also crosslinked by paired hydrogen bonds O8–H81···O7(x,y,1+z) and a three-dimensional supramolecular structure is generated.

Table 1. Data collection and handling.

Crystal:	colorless rhomboid, size 0.19 × 0.42 × 0.47 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.15 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9851, 3385
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2252
$N(param)_{refined}$:	258
Programs:	SHELXS-97 [9], SHELXL-97 [10]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	4*e*	0.3433	0.6930	0.3867	0.049
H(5)	4*e*	0.4952	1.0515	0.1735	0.060
H(6)	4*e*	0.5998	1.0216	0.2786	0.067
H(8)	4*e*	0.5518	0.7336	0.5167	0.049
H(11)	4*e*	0.2622	1.0015	0.2842	0.042
H(14)	4*e*	0.1612	0.6811	0.0213	0.050
H(15)	4*e*	0.2701	0.6802	0.0974	0.051
H(16A)	4*e*	0.6471	0.7816	0.6792	0.107
H(16B)	4*e*	0.7142	0.7786	0.6138	0.107
H(16C)	4*e*	0.6581	0.7015	0.5268	0.107
H(17A)	4*e*	0.0623	0.7343	–0.1115	0.093
H(17B)	4*e*	0.0021	0.7680	–0.0252	0.093
H(17C)	4*e*	0.0540	0.6844	0.0669	0.093
H(1A)	4*e*	0.1509	1.2038	0.7172	0.097
H(1B)	4*e*	0.1101	1.1015	0.7099	0.097
H(1C)	4*e*	0.1449	1.1292	0.5694	0.097
H(81)	4*e*	0.0471	1.0235	0.8743	0.080
H(82)	4*e*	0.0020	1.0104	0.7375	0.080
H(18A)	4*e*	0.1914	0.9805	0.7356	0.120
H(18B)	4*e*	0.2065	1.0747	0.8768	0.120
H(18C)	4*e*	0.2380	1.0834	0.7098	0.120

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	4*e*	0.43436(8)	0.7346(2)	0.4202(2)	0.033(1)	0.042(1)	0.058(1)	0.0017(8)	0.0041(9)	0.0161(9)
O(2)	4*e*	0.37244(9)	1.0080(2)	0.1176(3)	0.051(1)	0.052(1)	0.080(2)	0.005(1)	0.003(1)	0.029(1)
O(3)	4*e*	0.64954(9)	0.8672(2)	0.4673(3)	0.036(1)	0.056(1)	0.079(2)	–0.0057(9)	–0.006(1)	0.006(1)
O(4)	4*e*	0.08078(8)	0.8491(2)	0.0718(2)	0.035(1)	0.039(1)	0.062(1)	–0.0001(8)	–0.0065(9)	–0.0098(9)
O(5)	4*e*	0.17832(8)	1.1413(2)	0.3278(3)	0.041(1)	0.036(1)	0.068(1)	0.0002(8)	–0.001(1)	–0.0104(9)
O(6)	4*e*	0.08806(9)	1.0186(2)	0.3536(3)	0.043(1)	0.053(1)	0.066(1)	–0.0048(9)	0.018(1)	–0.014(1)
O(7)	4*e*	0.10089(9)	1.1082(2)	0.0853(3)	0.060(1)	0.045(1)	0.063(1)	0.015(1)	–0.013(1)	0.004(1)
S(1)	4*e*	0.13181(3)	1.06054(6)	0.24114(9)	0.0356(4)	0.0318(4)	0.0518(5)	0.0036(3)	–0.0014(3)	–0.0044(3)
C(1)	4*e*	0.3720(1)	0.7490(2)	0.3585(3)	0.031(1)	0.041(2)	0.050(2)	0.002(1)	0.007(1)	0.004(1)
C(2)	4*e*	0.3482(1)	0.8367(2)	0.2605(3)	0.035(1)	0.035(1)	0.037(2)	0.005(1)	0.007(1)	0.000(1)
C(3)	4*e*	0.3913(1)	0.9267(2)	0.2120(3)	0.044(2)	0.035(2)	0.041(2)	0.004(1)	0.007(1)	0.002(1)
C(4)	4*e*	0.4580(1)	0.9108(2)	0.2792(3)	0.040(2)	0.032(1)	0.039(2)	0.000(1)	0.007(1)	–0.002(1)
C(5)	4*e*	0.5061(1)	0.9875(2)	0.2423(4)	0.051(2)	0.041(2)	0.057(2)	–0.004(1)	0.002(2)	0.011(1)
C(6)	4*e*	0.5686(1)	0.9699(3)	0.3054(4)	0.046(2)	0.045(2)	0.075(2)	–0.009(1)	0.006(2)	0.010(2)
C(7)	4*e*	0.5860(1)	0.8751(2)	0.4098(4)	0.039(2)	0.043(2)	0.051(2)	–0.001(1)	0.002(1)	–0.007(1)
C(8)	4*e*	0.5406(1)	0.7974(2)	0.4477(3)	0.039(2)	0.038(2)	0.046(2)	0.001(1)	0.003(1)	0.002(1)
C(9)	4*e*	0.4775(1)	0.8167(2)	0.3802(3)	0.036(1)	0.034(1)	0.040(2)	–0.001(1)	0.007(1)	–0.001(1)
C(10)	4*e*	0.2783(1)	0.8391(2)	0.2017(3)	0.037(1)	0.035(1)	0.038(2)	0.004(1)	0.007(1)	0.003(1)
C(11)	4*e*	0.2419(1)	0.9365(2)	0.2331(3)	0.035(1)	0.032(1)	0.036(2)	–0.000(1)	0.001(1)	0.003(1)
C(12)	4*e*	0.1766(1)	0.9381(2)	0.1898(3)	0.035(1)	0.031(1)	0.032(1)	0.003(1)	0.001(1)	0.002(1)
C(13)	4*e*	0.1451(1)	0.8417(2)	0.1091(3)	0.036(1)	0.036(1)	0.033(2)	0.002(1)	0.000(1)	0.001(1)
C(14)	4*e*	0.1812(1)	0.7455(2)	0.0752(4)	0.044(2)	0.036(2)	0.044(2)	–0.002(1)	0.002(1)	–0.007(1)
C(15)	4*e*	0.2466(1)	0.7453(2)	0.1212(3)	0.045(2)	0.035(1)	0.048(2)	0.006(1)	0.009(1)	–0.001(1)
C(16)	4*e*	0.6688(2)	0.7747(3)	0.5811(5)	0.046(2)	0.062(2)	0.098(3)	–0.002(2)	–0.020(2)	0.008(2)
C(17)	4*e*	0.0470(1)	0.7508(3)	–0.0059(4)	0.045(2)	0.051(2)	0.084(2)	–0.006(1)	–0.009(2)	–0.019(2)
N(1)	4*e*	0.1463(1)	1.1307(2)	0.6810(3)	0.093(2)	0.042(2)	0.062(2)	–0.008(1)	0.024(2)	–0.010(1)
O(8)	4*e*	0.0418(1)	1.0202(2)	0.7673(3)	0.054(1)	0.143(2)	0.063(2)	–0.017(2)	–0.001(1)	0.007(2)
C(18)	4*e*	0.2001(2)	1.0614(3)	0.7573(5)	0.073(3)	0.070(2)	0.097(3)	–0.002(2)	0.012(2)	–0.006(2)

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