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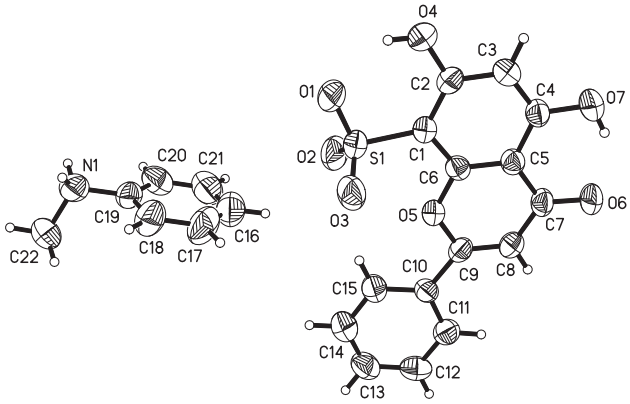
Crystal structure of *N*-methylanilinium 5,7-dihydroxy-4-oxo-2-phenyl-4*H*-chromene-8-sulfonate monohydrate, $C_{22}H_{21}NO_8S$



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Abstract

$C_{22}H_{21}NO_8S$, triclinic, $P\bar{1}$ (no. 2), $a = 7.095(4)$ Å, $b = 11.882(7)$ Å, $c = 13.661(8)$ Å, $\alpha = 95.004(9)°$, $\beta = 104.918(9)°$, $\gamma = 107.323(9)°$, $V = 1045.4(11)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0627$, $wR_{ref}(F^2) = 0.1745$, $T = 296(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The mixture of chrysin (1 g, 3.9 mmol) and concentrated sulfuric acid (5 mL) was stirred at room temperature.

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Table 1: Data collection and handling.

Crystal:	Colourless sheet
Size:	0.37 × 0.25 × 0.11 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.21 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	27.2°, 98%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6155, 4414, 0.034
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1826
$N(param)_{refined}$:	302
Programs:	SHELX [1], Bruker [2]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
S1	0.43830(18)	0.07589(9)	0.30954(8)	0.0551(3)
N1	1.0179(5)	0.7518(3)	0.5597(3)	0.0659(10)
H1A	1.152674	0.766244	0.587640	0.079*
H1B	0.955239	0.728706	0.606784	0.079*
O1	0.5038(5)	0.0609(2)	0.41532(19)	0.0778(10)
O2	0.6022(4)	0.1626(2)	0.2840(2)	0.0712(9)
O3	0.2453(4)	0.1003(2)	0.2835(2)	0.0738(9)
O4	0.4771(5)	−0.1625(2)	0.3806(2)	0.0637(8)
H4	0.487(7)	−0.103(3)	0.4255(17)	0.096*
O5	0.3026(4)	0.0166(2)	0.08827(18)	0.0459(7)
O6	0.1265(4)	−0.2999(2)	−0.10445(19)	0.0609(8)
O7	0.2194(5)	−0.3996(2)	0.0552(2)	0.0672(9)
H7	0.171560	−0.396233	−0.005454	0.101*
O8	0.8422(6)	0.6926(3)	0.7104(3)	0.0740(10)
C1	0.3887(6)	−0.0650(3)	0.2362(3)	0.0433(9)
C2	0.4073(6)	−0.1657(4)	0.2787(3)	0.0472(10)
C3	0.3533(6)	−0.2767(3)	0.2166(3)	0.0543(11)
H3	0.369499	−0.341778	0.246694	0.065*
C4	0.2772(6)	−0.2910(3)	0.1126(3)	0.0471(10)
C5	0.2619(5)	−0.1913(3)	0.0647(3)	0.0428(9)
C6	0.3185(5)	−0.0819(3)	0.1292(3)	0.0402(9)
C7	0.1870(6)	−0.2014(3)	−0.0445(3)	0.0474(10)
C8	0.1890(6)	−0.0917(3)	−0.0800(3)	0.0494(10)
H8	0.152948	−0.091893	−0.150459	0.059*
C9	0.2409(5)	0.0114(3)	−0.0154(3)	0.0443(10)
C10	0.2447(5)	0.1295(3)	−0.0406(3)	0.0432(9)

Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C11	0.1707(6)	0.1419(4)	−0.1425(3)	0.0527(11)
H11	0.119295	0.075104	−0.194632	0.063*
C12	0.1731(6)	0.2526(4)	−0.1666(3)	0.0613(12)
H12	0.128141	0.260979	−0.234912	0.074*
C13	0.2418(7)	0.3503(4)	−0.0894(4)	0.0641(12)
H13	0.241270	0.424688	−0.105444	0.077*
C14	0.3114(7)	0.3386(4)	0.0113(4)	0.0652(12)
H14	0.357511	0.405178	0.063223	0.078*
C15	0.3135(6)	0.2290(3)	0.0360(3)	0.0567(11)
H15	0.361450	0.221899	0.104493	0.068*
C16	0.7869(11)	0.4699(5)	0.3083(4)	0.0866(17)
H16	0.735797	0.406195	0.253408	0.104*
C17	0.6586(9)	0.4978(5)	0.3566(4)	0.0917(17)
H17	0.517976	0.454332	0.333403	0.110*
C18	0.7342(8)	0.5907(4)	0.4406(4)	0.0778(14)
H18	0.646328	0.608942	0.474714	0.093*
C19	0.9403(7)	0.6544(4)	0.4717(3)	0.0572(11)
C20	1.0713(8)	0.6290(4)	0.4228(4)	0.0720(13)
H20	1.211575	0.673432	0.444458	0.086*
C21	0.9907(10)	0.5358(5)	0.3406(4)	0.0852(16)
H21	1.078210	0.517501	0.306318	0.102*
C22	0.9848(7)	0.8652(4)	0.5327(4)	0.0796(15)
H22A	1.065221	0.895924	0.488158	0.119*
H22B	1.026982	0.923302	0.594372	0.119*
H22C	0.840933	0.849301	0.498133	0.119*
H8A	0.904(6)	0.690(4)	0.7694(15)	0.078(17)*
H8B	0.794(9)	0.745(4)	0.722(5)	0.15(3)*

The reactions were monitored by thin-layer chromatography (TLC), which showed the disappearance of chrysin that was indicative of the reaction being complete. Then, the mixture was poured into *N*-methylaniline hydrochloride saturated aqueous solution (55 mL), a white precipitate appeared and was filtered after 5 h. The precipitate was washed with *N*-methylaniline hydrochloride saturated aqueous solution. The single crystals suitable for X-ray diffraction were obtained by slow evaporation of the title compound in a mixture of ethanol/water (1:1, *v*/*v*) solution at room temperature.

Experimental details

All hydrogen atoms were identified in difference Fourier syntheses and placed in geometrically idealized positions. The U_{iso} values of the hydrogen atoms of methyl groups were set to $1.5U_{eq}$(C) and the U_{iso} values of all other hydrogen atons were set to $1.2U_{eq}$(C).

Comment

Chrysin (5,7-dihydroxyflavone) is a bioactive flavone derived from plant extracts such as blue passion flower, propolis, and honey, which are widely used as herb medicine in China. Except its multiple bioactivities in antioxidant [3], antiinflammatory [4] and antibacterial [5], its antitumor potential is also well validated in a variety of human cancer cell lines. Chrysin is demonstrated to exert antitumor effect by inducing cell cycle arrest and apoptosis through different mechanisms, for instance, activation of extrinsic apoptosis pathway [6], alteration of cyclins and CDKs (cyclin-dependent kinases) [7]. In the reported experiments, the efforts were centered mostly on the substitutions on the aromatic rings (either A or C) of the chrysin. These derivatives, compared with their parent compound, displayed significant biological activity [8–10]. Thus, it would be valuable to explore novel chrysin derivatives.

The asymmetric unit of the title structure consists of one chrysin-8-sulfonate anion, one *N*-methylaniline cation and one crystal water molecule (*cf*. the figure; the water molecule is omitted for clarity). The chrysin-8-sulfonate skeleton has an essentially planar conformation, with mean deviation from this plane of 0.0235(3) Å. The bond lengths and angles of anion and cation are similar to those found in literature [11, 12]. In the crystal structure of title compound, hydrogen bonds connect chrysin-8-sulfonate into dimers, and the adjacent dimers are further connected by hydrogen bonds to form one-dimensional chain along the directions of [011], [010] and axis *a*, respectively. The crystal structure also features π−π interactions between pairs of inversion-related chrysin-8-sulfonate skeletons with an interplanar spacing of 3.636(2) Å. π−π interactions link chrysin-8-sulfonate skeleton into one-dimensional chain along *a* axis. Hydrogen bonds and π−π interactions extend the complex into a three-dimensional network.

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