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Synthesis and crystal structure of 5-(8-(((2-carboxyethyl)ammonio)methyl)-7-hydroxy-4-oxo-4*H*-chromen-3-yl)-2-hydroxybenzenesulfonate trihydrate, C₁₉H₂₃NO₁₂S

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Abstract

C₁₉H₂₃NO₁₂S, triclinic, $P\bar{1}$ (no. 2), $a = 8.3926(9)$ Å, $b = 9.0469(6)$ Å, $c = 15.3442(15)$ Å, $\alpha = 78.195(7)^\circ$, $\beta = 74.352(9)^\circ$, $\gamma = 70.169(8)^\circ$, $V = 1047.08(18)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0538$, $wR_{\text{ref}}(F^2) = 0.1289$, $T = 293(2)$ K.

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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 title compound was synthesized *via* a Mannich reaction. Formaldehyde solution (10 mL, 37%) and sodium 2-hydroxy-5-(7-hydroxy-4-oxo-4*H*-chromen-3-yl)benzenesulfonate (3.56 g, 0.01 mol) were added to ethanol (200 mL, 95%) and stirred for 0.5 h at 328 K. Then, the saturated solution of 3-aminopropionic acid (0.89 g, 0.01 mol) was added to the mixture. Hot water was added until a transparent solution was obtained. After 10 h reaction time, the mix-

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.24 × 0.20 × 0.20 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.5 mm ⁻¹
Diffractometer, scan mode:	Bruker SMART, φ and ω -scans
θ_{max} , completeness:	25°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	7313, 3665, 0.040
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2399
$N(\text{param})_{\text{refined}}$:	298
Programs:	Bruker programs [1], SHELX [2, 3]

ture was filtered. The residue was dried at 383 K. Sodium 5-(8-(((2-carboxyethyl)ammonio)methyl)-7-hydroxy-4-oxo-4*H*-chromen-3-yl)-2-hydroxybenzenesulfonate (2.301 g) was obtained. This sodium salt (0.06 g) was added to a mixed solvent (methanol : tetrahydrofuran = 1 : 1, v/v) (60 mL) and sonicated for 10 min. After filtration, a transparent solution was obtained. After 3 days, colorless block crystals of the title compound were obtained.

Experimental details

H atoms were placed in calculated positions and were included in the refinement in the riding model approximation, with $U_{\text{iso}}(\text{H})$ set to 1.2 $U_{\text{eq}}(\text{C})$. According to Table 2 they are unrefined.

Discussion

Sodium 2-hydroxy-5-(7-hydroxy-4-oxo-4*H*-chromen-3-yl)benzenesulfonate (DSS) is a strongly water-soluble substance, produced by modifying the structure of daidzein [4]. Some studies have shown that DSS possessed excellent biological activities [5–7]. The Mannich reaction has been considered as an effective method in introducing aminomethyl substituents into the desired flavonoid molecules to improve their biological activities [8–14]. Our previous investigations showed that DSS can react with glycine, L-proline, L-threonine by Mannich reaction [15–17]. The reaction takes place without a catalyst. When the sulfo-groups and carboxyl groups are introduced to daidzein, they can coordinate with some metal ions directly in intriguing ways. In this paper, we report a 3-aminopropanoic acid derivative of DSS.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
N1	0.1652(3)	0.2549(3)	0.63368(15)	0.0360(6)
H1A	0.275170	0.201954	0.658044	0.054*
H1B	0.144870	0.368254	0.628144	0.054*
O1	−0.2068(3)	0.4878(3)	0.72199(14)	0.0566(7)
H1	−0.288727	0.573323	0.730965	0.085*
O2	0.0467(3)	0.2301(3)	1.09163(15)	0.0601(8)
O3	0.1771(3)	0.0475(2)	0.85275(13)	0.0414(6)
O4	0.6291(3)	−0.3417(2)	1.26093(13)	0.0398(6)
H13	0.701981	−0.428234	1.244576	0.060*
O5	0.5232(3)	−0.0285(2)	1.33179(14)	0.0422(6)
O7	0.3207(3)	−0.1802(2)	1.39644(14)	0.0488(6)
O6	0.2214(3)	0.0909(2)	1.32889(14)	0.0491(7)
O8	0.1849(3)	0.5319(3)	0.51596(16)	0.0600(7)
O9	0.4292(3)	0.4971(2)	0.40956(15)	0.0511(6)
H9A	0.411838	0.596426	0.403738	0.077*
O10	0.5012(3)	0.7197(2)	0.77250(14)	0.0547(7)
H10A	0.421056	0.682049	0.772626	0.082*
H10B	0.489866	0.810949	0.742016	0.082*
O11	0.7902(3)	0.3579(2)	0.23602(16)	0.0604(8)
H11A	0.882934	0.334163	0.195233	0.091*
H11B	0.814034	0.305573	0.286023	0.091*
O12	0.8613(3)	0.1729(3)	0.39217(16)	0.0712(8)
H12A	0.970769	0.147992	0.385195	0.107*
H12B	0.834769	0.233743	0.432725	0.107*
S1	0.36284(11)	−0.05436(9)	1.32767(5)	0.0366(3)
C1	−0.1380(4)	0.4145(4)	0.7949(2)	0.0396(8)
C2	−0.1838(4)	0.4855(4)	0.8745(2)	0.0483(9)
H2	−0.264961	0.585219	0.878628	0.058*
C3	−0.1090(4)	0.4076(4)	0.9460(2)	0.0442(9)
H3	−0.140002	0.455558	0.998768	0.053*
C4	0.0131(4)	0.2577(3)	0.94238(19)	0.0331(7)
C5	0.0565(4)	0.1921(3)	0.8619(2)	0.0333(7)
C6	−0.0188(4)	0.2666(3)	0.78747(19)	0.0340(7)
C7	0.0929(4)	0.1729(3)	1.0191(2)	0.0371(8)
C8	0.2261(4)	0.0219(3)	1.00335(19)	0.0320(7)
C9	0.2563(4)	−0.0275(4)	0.9222(2)	0.0412(8)
H9	0.341153	−0.124012	0.912699	0.049*
C10	0.3275(4)	−0.0765(3)	1.07268(19)	0.0325(7)
C11	0.3053(4)	−0.0288(3)	1.15695(19)	0.0331(7)
H11	0.223041	0.066830	1.171306	0.040*
C12	0.4024(4)	−0.1198(3)	1.22034(19)	0.0323(7)
C13	0.5295(4)	−0.2610(3)	1.1997(2)	0.0334(7)
C14	0.5482(4)	−0.3119(4)	1.1179(2)	0.0419(8)
H14	0.628400	−0.409000	1.104434	0.050*
C15	0.4514(4)	−0.2227(4)	1.0559(2)	0.0435(9)
H15	0.468445	−0.260388	1.000999	0.052*
C16	0.0291(4)	0.1941(3)	0.7008(2)	0.0380(8)
H16A	0.072343	0.079780	0.713493	0.046*
H16B	−0.072721	0.220470	0.675527	0.046*
C17	0.2037(4)	0.2102(3)	0.5401(2)	0.0416(8)
H17A	0.100547	0.255263	0.514939	0.050*
H17B	0.236951	0.095883	0.543056	0.050*
C18	0.3483(4)	0.2698(3)	0.4792(2)	0.0443(9)
H18A	0.371514	0.238950	0.418980	0.053*
H18B	0.452433	0.219080	0.503064	0.053*
C19	0.3100(4)	0.4464(4)	0.4705(2)	0.0397(8)

The title compound contains one zwitterion and three water molecules in the asymmetric unit (*cf.* the figure). The bond distances and bond angles are in normal ranges [15–17]. The atoms of the chromen moiety constitute planar rings A (C1–C6) and C (C7–C9/O3/C5/C4) [mean out-of plane deviations are 0.0056 and 0.0144 Å, respectively], with an interplanar angle of 1.9°. There are $\pi \cdots \pi$ stacking interactions between C1–C6 phenyl rings and C10–C15 phenyl rings from adjacent compounds. The centroid-centroid distance is 3.8656(3) Å and the dihedral angle between the two phenyl least square planes is 4.25°. The C19–C18–C17–N1 torsion angle is −58.84°. The compounds shows an intramolecular N1–H1B $\cdots$ O8 hydrogen bond of length 2.062 Å. There exist various O–H $\cdots$ O and N–H $\cdots$ O hydrogen bonds. In the crystal the ylidic title compound and water molecules interact via hydrogen bonds. Together with the $\pi \cdots \pi$ stacking interactions a three-dimensional network is obtained.

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