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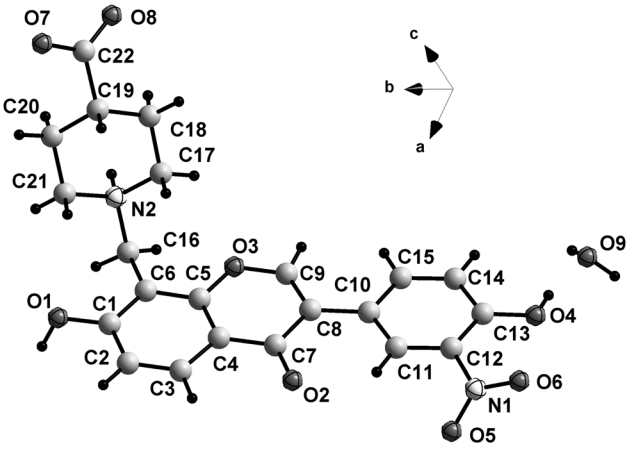
Synthesis and crystal structure of 1-((7-hydroxy-3-(4-hydroxy-3-nitrophenyl)-4-oxo-4*H*-chromen-8-yl) methyl)piperidin-1-ium-4-carboxylate monohydrate, $C_{22}H_{22}N_2O_9$



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Abstract

$C_{22}H_{22}N_2O_9$, monoclinic, $P2_1/c$ (no. 14), a = 7.7374(3) Å, b = 29.1082(11) Å, c = 8.7595(3) Å, β = 96.853 (3)°, V = 1958.74(13) Å^3, Z = 4, $R_{gt}(F)$ = 0.0520, wR_{ref} (F^2) = 0.1501, T = 100 K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.13 × 0.12 × 0.10 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.12 mm^{-1}
Diffractometer, scan mode:	ROD, Synergy Custom DW system, ω
θ_{max}, completeness:	29.3°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	14766, 4372, 0.028
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 σ(I_{obs}), 3383
N(param)$_{refined}$:	318
Programs:	CrysAlis^{PRO} [1], Diamond [2], SHELX [3, 4]

1 Source of materials

All reagents and chemicals were purchased from commercial sources and used without further purification. A mixture of 7-hydroxy-3-(4-hydroxyphenyl)-4*H*-chromen-4-one (0.013 g), sodium nitrite (0.035 g), 6 mol/L nitric acid (1.0 mL) and water (10 mL) was sealed in a 20 mL vial and stood for 10 min. The mixture was sonicated for 1 min. The mixture was heated at 363 K for 24 h. The mixture was filtered and the residue was washed with water. The residue was dried at 353 K. 7-hydroxy-3-(4-hydroxy-3-nitrophenyl)-4*H*-chromen-4-one (0.015 g) was obtained. A mixture of nitro compound described before (0.015 g), piperidine-4-carboxylic acid (0.026 g), N,N-dimethyl formamide (1 mL), methanol (3 mL) and formaldehyde solution (20 µL, 37 %) was sealed in a 20 mL vial and sonicated for 10 min. Then the mixture was heated at 363 K for 24 h. The mixture evaporated for one day at room temperature. Red block shape crystals of 1-((7-hydroxy-3-(4-hydroxy-3-nitrophenyl)-4-oxo-4*H*-chromen-8-yl) methyl)piperidin-1-ium-4-carboxylate monohydrate were obtained. ^{1}H NMR (400 MHz, DMSO-d_6) δ:8.50 (s, 1H, H9), 8.16 (d, J = 2.1 Hz, 1H, H11), 7.92 (d, J = 8.8 Hz, 1H, H3), 7.73 (dd, J = 8.7, 2.1 Hz, 1H, H15), 7.16 (d, J = 8.7 Hz, 1H, H14), 6.91 (d, J = 8.8 Hz, 1H, H2) 3.97 (s, 2H, H16A and H16B), 2.92 (m, 3H, H17B, H21B, H19), 2.32 (m, 2H, H17A, H21A), 1.87 (m, 2H, H18B, H20A), 1.59 (m, 2H, H18A, H20B). ^{13}C NMR (100 MHz, DMSO-d_6) δ:175.74 (C7), 174.47 (C22), 163.45 (C1), 155.16 (C5), 153.67 (C9), 152.30 (C13), 136.57 (C12), 135.43 (C15), 125.77 (C3), 125.26 (C10), 122.68 (C8), 121.20 (C11), 119.14 (C14), 116.05 (C4), 115.34 (C6), 108.37 (C2), 52.05 (C16), 51.76 (C17 and C21), 39.73 (C19), 27.75 (C18 and C20). IR spectra (potassium bromide pellet) were

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	0.72325 (18)	0.70755 (5)	0.94430 (15)	0.0302 (3)
H1	0.803283	0.721655	0.907218	0.045*
O2	0.41933 (19)	0.58657 (5)	0.37145 (15)	0.0312 (3)
O3	0.40939 (19)	0.57135 (5)	0.83217 (15)	0.0304 (3)
O4	0.0145 (2)	0.39433 (5)	0.22159 (16)	0.0334 (4)
H4	−0.011104	0.372950	0.279297	0.050*
O7	−0.03272 (19)	0.75635 (5)	1.31442 (16)	0.0327 (3)
O8	−0.11739 (19)	0.68461 (5)	1.34302 (17)	0.0363 (4)
N1	0.1660 (3)	0.46773 (6)	0.0737 (2)	0.0410 (5)
N2	0.4231 (2)	0.64722 (5)	1.13785 (17)	0.0226 (3)
H2	0.432622	0.632606	1.241837	0.027*
C1	0.6465 (2)	0.67838 (7)	0.8397 (2)	0.0243 (4)
C2	0.6499 (2)	0.68551 (7)	0.6804 (2)	0.0259 (4)
H2A	0.702946	0.712403	0.645884	0.031*
C3	0.5784 (2)	0.65445 (7)	0.5765 (2)	0.0254 (4)
H3	0.586891	0.659318	0.470431	0.031*
C4	0.4914 (2)	0.61496 (6)	0.6218 (2)	0.0224 (4)
C5	0.4873 (2)	0.60924 (6)	0.7792 (2)	0.0229 (4)
C6	0.5627 (2)	0.63967 (6)	0.8910 (2)	0.0233 (4)
C7	0.4152 (2)	0.58126 (6)	0.5124 (2)	0.0230 (4)
C8	0.3358 (2)	0.54101 (6)	0.5772 (2)	0.0225 (4)
C9	0.3394 (3)	0.53978 (7)	0.7309 (2)	0.0310 (5)
H9	0.289 (4)	0.5194 (10)	0.790 (3)	0.055 (8)*
C10	0.2544 (2)	0.50264 (6)	0.4835 (2)	0.0225 (4)
C11	0.2428 (3)	0.50196 (7)	0.3246 (2)	0.0288 (4)
H11	0.290664	0.526699	0.272712	0.035*
C12	0.1626 (3)	0.46591 (7)	0.2390 (2)	0.0291 (4)
C13	0.0898 (2)	0.42847 (6)	0.3068 (2)	0.0259 (4)
C14	0.1054 (3)	0.42864 (7)	0.4681 (2)	0.0273 (4)
H14	0.060505	0.403487	0.520180	0.033*
C15	0.1839 (3)	0.46423 (7)	0.5524 (2)	0.0263 (4)
H15	0.192 (3)	0.4620 (8)	0.664 (3)	0.037 (6)*
C16	0.5716 (2)	0.62845 (7)	1.0600 (2)	0.0254 (4)
H16A	0.574308	0.594636	1.072184	0.031*
H16B	0.682111	0.640710	1.113133	0.031*
C17	0.2475 (2)	0.63375 (7)	1.0573 (2)	0.0271 (4)
H17A	0.243384	0.600068	1.041725	0.033*
H17B	0.228892	0.648679	0.955154	0.033*
C18	0.1055 (3)	0.64802 (7)	1.1511 (2)	0.0288 (4)
H18A	0.118402	0.630865	1.249356	0.035*
H18B	−0.009066	0.640030	1.094522	0.035*
C19	0.1110 (2)	0.69905 (7)	1.1843 (2)	0.0255 (4)
H19	0.086793	0.715777	1.084340	0.031*
C20	0.2929 (3)	0.71344 (7)	1.2601 (2)	0.0277 (4)
H20A	0.297033	0.747265	1.271701	0.033*
H20B	0.314549	0.699651	1.363923	0.033*
C21	0.4343 (3)	0.69811 (6)	1.1647 (2)	0.0258 (4)
H21A	0.420425	0.714404	1.064811	0.031*
H21B	0.550000	0.705980	1.219211	0.031*
C22	−0.0265 (2)	0.71368 (7)	1.2880 (2)	0.0267 (4)
O5[a]	0.2909 (3)	0.48698 (8)	0.0261 (2)	0.0538 (6)
O6[a]	0.0492 (4)	0.44931 (7)	−0.0124 (2)	0.0544 (7)
O5A[b]	0.184 (4)	0.5090 (7)	0.019 (3)	0.0538 (6)
O6A[b]	0.166 (5)	0.4382 (7)	−0.017 (2)	0.0544 (7)
O9	−0.0796 (2)	0.32321 (5)	0.36681 (18)	0.0378 (4)
H9A	−0.058854	0.300415	0.307328	0.057*
H9B	−0.019356	0.316840	0.454620	0.057*

recorded on a Nicolet 6700. IR (ν/cm^{-1}): 3005, 2856, 2704, 1625, 1573, 1525, 1445, 1423, 1396, 1373, 1343, 1308, 1265, 1244, 1211, 1183, 1644, 1094, 1077, 1041, 962, 926, 823, 802, 785, 764, 717, 687, 640, 551, 495, 456, 428.

2 Experimental details

Carbon-bound H atoms with the exception of H15 and H9 were placed in calculated positions and were included in the refinement in the riding model approximation, with U_{iso}(H) set to 1.2 U_{eq}(C). The oxygen-bound, nitrogen-bound H atoms, H15 and H9 were located on a difference Fourier map. The O5 and O6 atoms were disordered.

3 Comment

Numerous publications describe the nitrated derivatives and Mannich base derivatives of flavonoids [5, 6]. Some derivatives of flavonoids possess important biological activities. Our previous investigations showed that daizein Mannich base derivatives of amino acid or aliphatic amine react with nitrating agent [7–9]. To extend this research, we investigated a new synthetic route. Nitro group was first introduced on the 3'-position of ring B of daidzein. Then we used the intermediate to react with piperidine-4-carboxylic acid by Mannich reaction and got the title compound. The presence of several groups in daizein derivatives expands the capability of studying their biological activity.

The title structure contains one zwitterion and one water molecule in the asymmetric unit (cf. the figure). The bond distances and bond angles are in normal ranges [7–9]. The dihedral angle between planar rings B (C10–C15) and C (C7–C9/O3/C5/C4) is 1.59°. There are two π-π stacking interactions between phenyl rings from adjacent molecules. The centroid-centroid distance of C1–C6 phenyl rings and C10–C15 phenyl rings is 4.05 Å. The centroid-centroid distance of C10–C15 phenyl rings is 3.97 Å. The nitrogen atom N2 is protonated. There exist various O–H···O and N–H···O hydrogen bonds. Together with hydrogen bonds interactions and π-π stacking interactions a three dimensional network is obtained.

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