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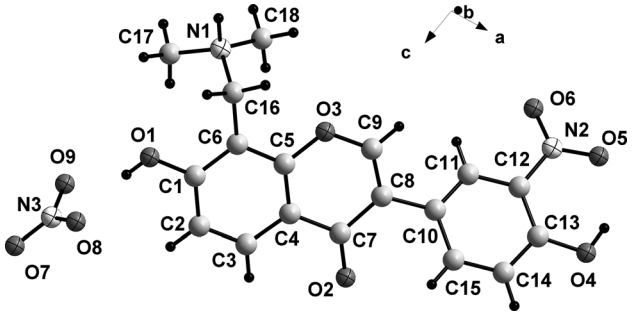
Synthesis and crystal structure of 1-(7-hydroxy-3-(4-hydroxy-3-nitrophenyl)-4-oxo-4*H*-chromen-8-yl)-*N*,*N*-dimethylmethanaminiumnitrate, $C_{18}H_{17}N_3O_9$



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Abstract

$C_{18}H_{17}N_3O_9$, monoclinic, $P2_1/c$ (no. 14), a = 15.3768(3) Å, b = 7.4510(2) Å, c = 15.6673(5) Å, β = 102.700(3)°, V = 1751.13(8) Å^3, Z = 4, $R_{gt}(F)$ = 0.0405, $wR_{ref}(F^2)$ = 0.1157, T = 100 K.

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The molecular structure is shown in the figure. 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:	Yellow needle
Size:	0.20 × 0.15 × 0.13 mm
Wavelength:	Cu *K*α radiation (1.54178 Å)
μ:	1.12 mm^{-1}
Diffractometer, scan mode:	φ and ω
θ_{max}, completeness:	75.5°, 96 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8608, 3365, 0.031
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2867
$N(param)_{refined}$:	275
Programs:	Rigaku [1], Diamond [2], SHELX [3, 4]

1 Source of materials

All reagents and chemicals were purchased from commercial sources and used without further purification. The 8-((dimethylamino)methyl)-7-hydroxy-3-(4-hydroxyphenyl)-4*H*-chromen-4-one was synthesized *via* a Mannich reaction. In a typical experiment a formaldehyde solution (10 mL, 37 %), dimethylamine water solution (30 mL, 40 %) and daidzein (6.4 g, 0.025 mol) were added to ethanol (350 mL, 99 %) and stirred for 2 h at 328 K. After cooling, most of the volatile solvents were removed under vacuum on a rotatory evaporator at 308 K. After cooling for 30 min, the mixture was filtered and the residue was washed with water. Then the residue was dried at 383 K. The crude product (4.3 g) was obtained. The crude product was purified by thin layer chromatography (DMSO as solvent, $CHCl_3$–CH_3OH = 1:1, *v*/*v*). 8-((dimethylamino)methyl)-7-hydroxy-3-(4-hydroxyphenyl)-4*H*-chromen-4-one was obtained. A mixture of Mannich base described before (0.016 g), sodium nitrite (0.041 g), 6 mol/L nitric acid (0.50 mL) and water (8 mL) was sealed in a 20 mL vial and stood for 10 min. The mixture was sonicated for 1 min. The colour of the mixture turned to green. Then the mixture was heated at 363 K for 3 h. Yellow needle crystals of 1-(7-hydroxy-3-(4-hydroxy-3-nitrophenyl)-4-oxo-4*H*-chromen-8-yl)-N,N-dimethylmethanaminium nitrate were obtained. ^{1}**H NMR** (400 MHz, DMSO-d_6) δ: 11.83 (s, 1H, H4), 11.19 (s, 1H, H1), 8.53 (s, 1H,H9), 8.16 (d, J = 2.1 Hz, 1H, H11), 8.10 (d, J = 8.9 Hz, 1H,H3), 7.75 (dd, J = 8.7, 2.1 Hz, 1H, H15), 7.21 (d, J = 8.7 Hz, 1H, H14), 7.14 (d, J = 8.9 Hz, 1H, H2), 4.45 (s, 2H, H16A, H16B), 2.85 (s, 6H, H18A, H18B, H18C, H17A, H17B, H17C).^{13}**C NMR** (100 MHz, DMSO-d_6) δ:174.76(C7), 162.52(C1), 156.62(C5), 154.17(C9), 152.32(C13), 137.02(C12), 135.93(C15), 129.25(C10), 125.73(C3), 123.17(C8), 122.06(C11), 119.45(C14), 116.94(C4), 115.11(C6), 104.77(C2), 49.37(C16), 43.26(C17, C18). **IR spectra** (potassium bromide pellet) were recorded on a Nicolet 6700. **IR** (ν/cm^{-1}): 3286, 3089, 1646, 1626, 1600, 1536, 1469, 1430, 1385, 1311, 1220, 1163, 1138, 1083, 1048, 1037, 1000, 970, 951, 924, 892, 862, 848, 806, 798, 779, 763, 752, 706, 658, 641, 578, 558, 538.

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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	0.12061 (7)	0.69595 (17)	0.37594 (7)	0.0244 (3)
H1	0.113052	0.634840	0.418784	0.037*
O2	0.53339 (7)	0.58249 (16)	0.39153 (7)	0.0235 (3)
O3	0.32749 (6)	0.75673 (15)	0.19759 (7)	0.0198 (2)
O4	0.82537 (7)	0.70179 (17)	0.16493 (8)	0.0256 (3)
H4	0.823354	0.693987	0.111048	0.038*
O5	0.73960 (7)	0.64011 (19)	0.00372 (8)	0.0322 (3)
O6	0.60442 (8)	0.54183 (19)	−0.02255 (8)	0.0316 (3)
N1	0.09657 (8)	0.68739 (18)	0.15205 (8)	0.0192 (3)
H1A	0.052415	0.763503	0.111274	0.023*
N2	0.66921 (8)	0.6071 (2)	0.02719 (9)	0.0238 (3)
C1	0.20526 (9)	0.6755 (2)	0.36637 (10)	0.0200 (3)
C2	0.27290 (10)	0.6086 (2)	0.43455 (10)	0.0216 (3)
H2	0.259206	0.572554	0.488261	0.026*
C3	0.35888 (9)	0.5956 (2)	0.42317 (10)	0.0202 (3)
H3	0.404482	0.551862	0.469589	0.024*
C4	0.38002 (9)	0.6459 (2)	0.34403 (10)	0.0186 (3)
C5	0.31153 (9)	0.7085 (2)	0.27698 (10)	0.0175 (3)
C6	0.22313 (9)	0.7269 (2)	0.28627 (10)	0.0181 (3)
C7	0.47196 (9)	0.6341 (2)	0.33206 (10)	0.0190 (3)
C8	0.48336 (9)	0.6853 (2)	0.24492 (10)	0.0187 (3)
C9	0.41175 (9)	0.7431 (2)	0.18478 (10)	0.0198 (3)
H9	0.421175	0.776801	0.129042	0.024*
C10	0.57229 (9)	0.6802 (2)	0.22197 (10)	0.0191 (3)
C11	0.58094 (9)	0.6404 (2)	0.13793 (10)	0.0204 (3)
H11	0.529840	0.607637	0.094657	0.024*
C12	0.66455 (10)	0.6481 (2)	0.11624 (10)	0.0207 (3)
C13	0.74188 (9)	0.6910 (2)	0.17902 (11)	0.0209 (3)
C14	0.73261 (9)	0.7221 (2)	0.26399 (10)	0.0214 (3)
H14	0.784233	0.745257	0.308495	0.026*
C15	0.65004 (10)	0.7203 (2)	0.28530 (10)	0.0209 (3)
H15	0.645691	0.746403	0.343561	0.025*
C16	0.15256 (9)	0.8146 (2)	0.21697 (10)	0.0189 (3)
H16A	0.181891	0.901023	0.184356	0.023*
H16B	0.112438	0.883870	0.246167	0.023*
C17	0.04345 (10)	0.5584 (2)	0.19292 (11)	0.0239 (3)
H17A	0.083930	0.480001	0.233581	0.036*
H17B	0.005840	0.485584	0.147187	0.036*
H17C	0.005735	0.625112	0.224820	0.036*
C18	0.14978 (10)	0.5927 (2)	0.09690 (10)	0.0217 (3)
H18A	0.180231	0.681185	0.067531	0.033*
H18B	0.110018	0.519481	0.052959	0.033*
H18C	0.194055	0.515220	0.133985	0.033*
O7	0.06716 (7)	0.31052 (18)	0.59633 (8)	0.0300 (3)
O8	0.10530 (7)	0.53271 (16)	0.52423 (7)	0.0242 (3)
O9	0.06919 (7)	0.27676 (18)	0.45887 (8)	0.0297 (3)
N3	0.08034 (7)	0.37109 (18)	0.52690 (9)	0.0213 (3)

2 Experimental details

Carbon-bound H atoms 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 and nitrogen-bound H atoms were located on a difference Fourier map.

3 Comment

In the past decades, much attention has been focused on the nitration of flavonoids [5–8]. Some of nitro derivatives of flavonoids possess important biological activities. Our previous investigations showed that Daizein Mannich base derivatives of amino acid react with nitrating agent [9, 10]. To extend this research, we used the Daizein Mannich base derivative of an aliphatic amine to react with a nitrating agent and got the title compound. In this study, the title compound was obtained from 8-((dimethylamino)methyl)-7-hydroxy-3-(4-hydroxyphenyl)-4*H*-chromen-4-one *via* a nitration substitution reaction.

The title compound contains one cation and one nitrate ion in the asymmetric unit (cf. the figure). The bond distances and bond angles are in normal ranges [9, 10]. The dihedral angle between planar rings B (C10–C15) and C (C7–C9/O3/C5/C4) is 34.05°. The nitrogen atom N1 is protonated. The molecule shows an intramolecular O4–H4···O5 hydrogen bond of length 1.922 Å. There exist various O–H···O and N–H···O hydrogen bonds. There are π···π stacking interactions between C1–C6 phenyl rings and C10–C15 phenyl rings from adjacent compounds. The centroid-centroid distance is 3.78 Å. Together with hydrogen bonds interactions and π···π stacking interactions a three-dimensional network is obtained.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Rigaku. *CrysAlis^{PRO}*; Rigaku Corporation: Yarnton, Oxfordshire, England, 2023.
2. Brandenburg K. *DIAMOND. Visual Crystal Structure Information System. Ver. 3.2*; Crystal Impact: Bonn, Germany, 2012.
3. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
4. Sheldrick G. M. *SHELXTL* – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.

5. Tan D.-J., Zhang Z.-T. Crystal structure of 3′-nitro-4′,7-dihydroxyisoflavone, $C_{15}H_9NO_6$. *Z. Kristallogr. N. Cryst. Struct.* 2007, *222*, 293–294.
6. Lewin G., Jullian J.-C., Rodrigo J. Unexpected B-ring regioselective di-nitration of diosmetin, a Citrus flavonoid. *Tetrahedron Lett.* 2010, *51*, 1145–1148.
7. Patoilo D. T., Silva A. M. S., Cavaleiro J. A. S. Regioselective 3-nitration of flavones: a new synthesis of 3-nitro-and 3-aminoflavones. *Synlett* 2010, *2010*, 1381–1385.
8. Tavera-Hernández R., Jiménez-Estrada M., Alvarado-Sansininea J. J., Nieto-Camacho A., López-Muñoz H., Sánchez-Sánchez L., Escobar L. M. Synthesis of chrysin, quercetin and naringin nitroderivatives: antiproliferative, anti-inflammatory and antioxidant activity. *Lett. Drug Des. Discov.* 2021, *18*, 795–805.
9. Chen H.-L., Yao D.-M., Luo Z.-P., Wang Y.-P., Luo L.-S. Synthesis and crystal structure of 3-(((7-hydroxy-3-(4-hydroxy-3,5-dinitrophenyl)-4-oxo-4*H*-chromen-8-yl)methyl)(nitroso)amino)propanoic acid, $C_{19}H_{14}N_4O_{11}$. *Z. Kristallogr. N. Cryst. Struct.* 2022, *237*, 1029–1031.
10. Chen H.-L., Wang Y.-P., Pan L.-W., Wei Z., Tang L.-C. Synthesis and crystal structure of 5-(8-(((5-carboxypentyl)ammonio)methyl)-7-hydroxy-4-oxo-4*H*-chromen-3-yl)-2-hydroxy-3-nitrobenzenesulfonate monohydrate, $C_{22}H_{24}N_2O_{12}S$. *Z. Kristallogr. N. Cryst. Struct.* 2023, *238*, 217–219.