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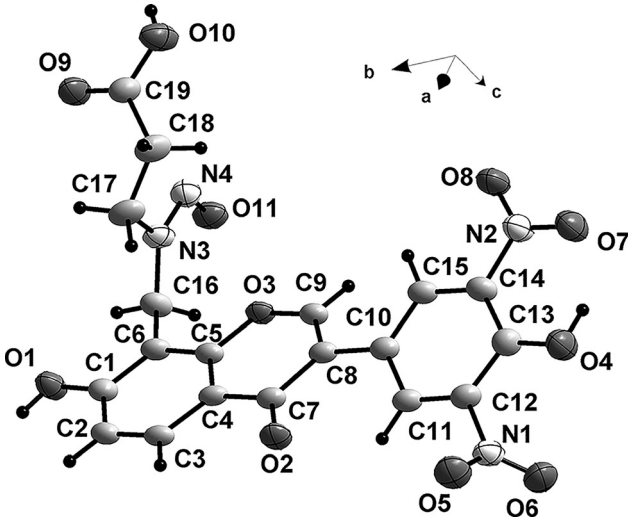
Synthesis and crystal structure of 3-(((7-hydroxy-3-(4-hydroxy-3,5-dinitrophenyl)-4-oxo-4*H*-chromen-8-yl)methyl)(nitroso)amino)propanoic acid, $C_{19}H_{14}N_4O_{11}$



https://doi.org/10.1515/ncrs-2022-0352
Received July 11, 2022; accepted August 16, 2022; published online September 2, 2022

Abstract

$C_{19}H_{14}N_4O_{11}$, monoclinic, *C*2/*c* (no. 15), a = 17.855(4) Å, b = 18.214(4) Å, c = 14.193(3) Å, β = 124.32(3)°, V = 3812.3(17) Å^3, Z = 8, $R_{gt}(F)$ = 0.0639, w$R_{ref}(F^2)$ = 0.1897, T = 100.01(10) K.

CCDC no.: 2201784

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:	0.16 × 0.15 × 0.13 mm
Wavelength:	Cu *K*α radiation (1.54184 Å)
μ:	1.21 mm^{-1}
Diffractometer, scan mode:	ROD, Synergy Custom DW system, HyPix, ω
θ_{max}, completeness:	76.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	22401, 3922, 0.036
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2 $\sigma(I_{obs})$, 3642
$N(param)_{refined}$:	310
Programs:	CrysAlis^{PRO} [1], Diamond [2], SHELX [3, 4]

Source of material

All reagents and chemicals were purchased from commercial sources and used without further purification. The starting material sodium 5-(8-(((2-carboxyethyl)amino)methyl)-7-hydroxy-4-oxo-4*H*-chromen-3-yl)-2-hydroxybenzenesulfonate was synthesized following the literature procedures [5]. A mixture of sodium salt described before (0.022 g), sodium nitrite (0.035 g), 6 mol/L nitric acid (0.4 mL) and water (3 mL) was sealed in a 20 mL vial and sonicated for 5 min. Then the mixture was heated at 363 K for three days. Yellow needle crystals of 3-(((7-hydroxy-3-(4-hydroxy-3,5-dinitrophenyl)-4-oxo-4*H*-chromen-8-yl)methyl)(nitroso)amino)propanoic acid were obtained. ^{1}**H–NMR** (400 MHz, DMSO-d_6) δ:11.37 (s, 1H, H4), 8.68 (s, 1H, H9), 8.51 (s, 2H, H11, H15), 7.98 (d, J = 8.8 Hz, 1H, H3), 7.07 (d, J = 8.8 Hz, 1H, H2), 4.92 (s, 2H, H16A, H16B), 4.22 (s, 2H, H17A, H17B), 2.74 (s, 2H, H18A, H18B). ^{13}**C–NMR** (100 MHz, DMSO-d_6) δ:174.10 (C7), 172.06 (C19), 161.30 (C1), 155.56

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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	0.41842 (12)	0.75141 (10)	0.59460 (17)	0.0433 (5)
H1	0.459174	0.781386	0.608362	0.065*
O2	0.61633 (11)	0.44611 (10)	0.66783 (16)	0.0386 (4)
O3	0.36247 (10)	0.49885 (9)	0.57871 (13)	0.0311 (4)
O4	0.55097 (13)	0.10154 (11)	0.65625 (19)	0.0520 (5)
H4	0.504685	0.074731	0.620907	0.078*
O5	0.74165 (13)	0.22064 (12)	0.7455 (2)	0.0540 (5)
O6	0.70933 (14)	0.15637 (13)	0.8465 (2)	0.0632 (6)
O7	0.37366 (14)	0.08431 (11)	0.5171 (2)	0.0539 (5)
O8	0.28466 (13)	0.17743 (12)	0.43951 (19)	0.0536 (5)
O9	0.06091 (12)	0.65749 (11)	0.16331 (19)	0.0522 (5)
O10	0.01959 (13)	0.54286 (12)	0.10801 (19)	0.0532 (5)
H10	−0.032897	0.557603	0.083855	0.080*
O11	0.14065 (12)	0.59314 (12)	0.50754 (16)	0.0450 (5)
N1	0.69023 (14)	0.19739 (12)	0.76802 (19)	0.0407 (5)
N2	0.35914 (14)	0.15051 (13)	0.5052 (2)	0.0430 (5)
N3	0.22516 (13)	0.61294 (12)	0.44628 (18)	0.0367 (5)
N4	0.14853 (14)	0.59104 (12)	0.42407 (19)	0.0392 (5)
C1	0.44960 (15)	0.68240 (14)	0.60597 (19)	0.0338 (5)
C2	0.53806 (15)	0.66754 (14)	0.63625 (19)	0.0336 (5)
H2	0.577899	0.706906	0.649847	0.040*
C3	0.56669 (14)	0.59649 (14)	0.64611 (18)	0.0312 (5)
H3	0.626299	0.587052	0.666068	0.037*
C4	0.50916 (14)	0.53725 (13)	0.62712 (18)	0.0299 (5)
C5	0.42220 (14)	0.55376 (13)	0.59781 (18)	0.0296 (5)
C6	0.39035 (14)	0.62511 (14)	0.58651 (19)	0.0324 (5)
C7	0.53902 (14)	0.46122 (14)	0.63885 (18)	0.0306 (5)
C8	0.47051 (14)	0.40536 (14)	0.61473 (18)	0.0303 (5)
C9	0.38864 (15)	0.42859 (14)	0.58833 (19)	0.0316 (5)
H9	0.346022	0.391905	0.575502	0.038*
C10	0.49002 (14)	0.32579 (14)	0.62129 (19)	0.0321 (5)
C11	0.57895 (15)	0.29840 (14)	0.6874 (2)	0.0343 (5)
H11	0.628579	0.331499	0.726628	0.041*
C12	0.59472 (16)	0.22430 (15)	0.6958 (2)	0.0373 (5)
C13	0.52612 (17)	0.17105 (15)	0.6409 (2)	0.0385 (5)
C14	0.43715 (16)	0.20018 (15)	0.5716 (2)	0.0372 (5)
C15	0.42013 (15)	0.27468 (14)	0.5618 (2)	0.0339 (5)
H15	0.359401	0.291583	0.513389	0.041*
C16	0.29740 (15)	0.63892 (15)	0.5603 (2)	0.0379 (5)
H16A	0.291928	0.613779	0.617953	0.046*
H16B	0.289668	0.692242	0.565652	0.046*
C17	0.23513 (17)	0.61555 (18)	0.3510 (2)	0.0469 (7)
H17A	0.298798	0.603827	0.379912	0.056*
H17B	0.222922	0.666290	0.320750	0.056*
C18	0.17316 (18)	0.56341 (17)	0.2535 (2)	0.0456 (6)
H18A	0.200362	0.552822	0.210502	0.055*
H18B	0.169127	0.516519	0.285670	0.055*
C19	0.07842 (16)	0.59348 (15)	0.1720 (2)	0.0380 (5)

(C5), 154.97 (C13), 145.51 (C9), 139.90 (C12, C14), 129.58 (C11, C15), 129.54 (C3), 126.68 (C10) 119.50 (C8), 116.30 (C4), 114.71 (C6), 107.53 (C2), 47.25 (C17), 36.16 (C16), 32.93 (C18).

IR spectra (potassium bromide pellet) were recorded on a Nicolet 6700. **IR** (ν/cm^{-1}): 3437, 1625, 1543, 1444, 1345, 1311, 1261, 1173, 1128, 1033, 917, 903, 849, 785, 746, 730, 689, 649, 547, 502.

Experimental details

All the 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) or 1.5 U_{eq}(O).

Comment

Numerous publications describe the nitration of flavonoids [6–9]. Some of nitro derivatives of flavonoids possess various biological activities such as antioxidant, anti-inflammatory, and anti-cancer [9]. The goal of our work is to synthesize nitro derivatives of daidzein to improve its' biological activity. In this paper, we used sodium 5-(8-(((2-carboxyethyl)amino)methyl)-7-hydroxy-4-oxo-4*H*-chromen-3-yl)-2-hydroxybenzenesulfonate to react with nitrating agent and got the title compound. The molecular structure contains a nitrosamine group. Studies of the pharmacological activities of the title compound are in progress. The asymmetric unit of the title structure has one 3-(((7-hydroxy-3-(4-hydroxy-3,5-dinitrophenyl)-4-oxo-4*H*-chromen-8-yl)methyl)(nitroso)amino)propanoic acid molecule (cf. the figure). The dihedral angle between planar rings B (C10—C15) and C (C7—C9/O3/C5/C4) is 23.92°. The molecule shows an intramolecular O4—H4···O7 hydrogen bond of length 1.946 Å. There exist various O—H···O hydrogen bonds. There are two π–π stacking interactions between phenyl rings from adjacent molecules. The centroid-centroid distance of C1—C6 phenyl rings is 3.4246(15) Å and the centroid-centroid distance of C10—C15 phenyl rings is 3.5776(17) Å. Together with intermolecular hydrogen bonds and $\pi \cdots \pi$ stacking interactions a two-dimensional layer is obtained.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This work was financially supported by Guangxi Natural Science Foundation of China (No. 2020GXNSFBA297138) and 2021 High-Level Talents Scientific Research Startup Fund of Hechi University (No. 2021GCC021).

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

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