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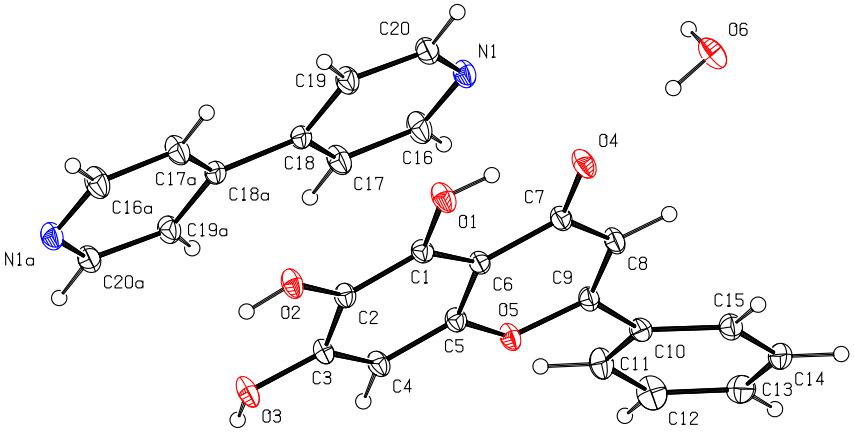
The crystal structure of 4,4′-bipyridine-5,6,7-trihydroxy-2-phenyl-4*H*-chromen-4-one-water (1/2/2), $C_{40}H_{32}N_2O_{12}$



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Abstract

$C_{40}H_{32}N_2O_{12}$, triclinic, $P\bar{1}$ (no. 2), a = 7.403(3) Å, b = 8.275(3) Å, c = 14.571(4) Å, α = 106.115(15)°, β = 98.239(16)°, γ = 95.054(19)°, V = 840.9(5) Å^3, Z = 1, $R_{gt}(F)$ = 0.0353, w$R_{ref}(F^2)$ = 0.0980, T = 170 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 block
Size:	0.45 × 0.36 × 0.23 mm
Wavelength:	MoKα radiation (0.71073 Å)
μ:	0.11 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture Ims3.0, φ and ω
θ_{max}, completeness:	27.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10499, 3690, 0.019
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3355
$N(param)_{refined}$:	253
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

Source of material

Cocrystals of Baicalein (5,6,7-trihydroxy-2-phenyl-4*H*-chromen-4-one) and 4,4′-bipyridine were prepared by dissolving Baicalein (27 mg, 0.1 mmol) and 4,4′-bipyridine (31 mg, 0.2 mmol) in 10 mL acetonitrile. Then the solution vials were treated with shaking or ultrasonic method at 35–40 min, then filter. The solvents were evaporated from the filtrate at ambient temperature, yellow block crystals were obtained after seven days.

Experimental details

Absorption corrections were applied by using multi-scan program [1]. Using Olex2 [2], the structure was solved with the ShelXT [3] structure solution program and refined with the ShelXL [4] refinement package.

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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	0.94867 (10)	0.89829 (11)	0.82872 (7)	0.0307 (2)
H1	0.988601	0.983549	0.813317	0.046*
O2	0.76496 (10)	0.62978 (10)	0.86385 (6)	0.02723 (19)
H2	0.691517	0.554641	0.872857	0.041*
O3	0.39419 (11)	0.55105 (10)	0.80231 (7)	0.0303 (2)
H3	0.279595	0.542886	0.785407	0.045*
O4	0.93414 (11)	1.15262 (11)	0.75616 (7)	0.0308 (2)
O5	0.37962 (10)	1.00223 (10)	0.65973 (6)	0.02491 (18)
C1	0.76339 (14)	0.86129 (14)	0.79752 (8)	0.0220 (2)
C2	0.66863 (14)	0.72389 (13)	0.81530 (8)	0.0218 (2)
C3	0.47640 (14)	0.68537 (13)	0.78222 (8)	0.0228 (2)
C4	0.37994 (14)	0.78123 (14)	0.73176 (8)	0.0242 (2)
H4	0.250514	0.754696	0.710396	0.029*
C5	0.47835 (14)	0.91592 (14)	0.71381 (8)	0.0218 (2)
C6	0.66897 (14)	0.96069 (13)	0.74618 (8)	0.0211 (2)
C7	0.76319 (15)	1.10366 (14)	0.72543 (8)	0.0238 (2)
C8	0.65104 (16)	1.18496 (14)	0.66733 (9)	0.0261 (2)
H8	0.706366	1.278759	0.650909	0.031*
C9	0.46889 (15)	1.13137 (13)	0.63547 (8)	0.0226 (2)
C10	0.34468 (15)	1.19984 (13)	0.57115 (8)	0.0236 (2)
C11	0.15473 (16)	1.18406 (16)	0.57044 (10)	0.0312 (3)
H11	0.103759	1.129688	0.612183	0.037*
C12	0.04065 (18)	1.24813 (18)	0.50852 (11)	0.0380 (3)
H12	−0.088265	1.237280	0.508262	0.046*
C13	0.11336 (18)	1.32789 (16)	0.44700 (9)	0.0335 (3)
H13	0.034755	1.372028	0.405184	0.040*
C14	0.30180 (18)	1.34258 (15)	0.44712 (9)	0.0306 (3)
H14	0.351984	1.396443	0.404949	0.037*
C15	0.41719 (16)	1.27905 (15)	0.50847 (8)	0.0273 (2)
H15	0.545846	1.289312	0.507957	0.033*
O6	1.03629 (12)	1.48787 (11)	0.75882 (7)	0.0342 (2)
H6A	0.969 (2)	1.545 (2)	0.7971 (12)	0.057*
H6B	1.005930	1.382993	0.757191	0.051*
N1	0.62077 (14)	1.36142 (12)	0.92075 (7)	0.0287 (2)
C16	0.44584 (18)	1.28870 (16)	0.90706 (10)	0.0341 (3)
H16	0.352437	1.335375	0.874825	0.041*
C17	0.39335 (17)	1.14928 (15)	0.93723 (9)	0.0309 (3)
H17	0.267047	1.103724	0.925832	0.037*
C18	0.52599 (15)	1.07617 (13)	0.98425 (8)	0.0231 (2)
C19	0.70821 (16)	1.15344 (15)	1.00010 (9)	0.0286 (2)
H19	0.804382	1.110495	1.032873	0.034*
C20	0.74785 (17)	1.29329 (15)	0.96769 (9)	0.0295 (3)
H20	0.872601	1.343588	0.979544	0.035*

Comment

Baicalein (BE) is one of the most important bioactive flavonoids isolated from the well-known traditional Chinese medicine called “Huang Qin”. Cocrystals of Baicalein with caffffeine (CCDC: 1522878, KAMQOH), and theophylline (CCDC: 1522877, KAMQIB) [5], Baicalein nicotinamide (CCDC: 893495, GAZWUB) [6], baicalein-temozolomide (CCDC: 1842673, JIJWIL) [7], baicalein-oxaliplatin (CCDC: 1998709, UJIHUT) [8] were obtained. The O–H···N heterosynthon can be the most competitive synthon in cocrystallizing phenolic compounds. Zhang’s group [9] chose 4,4′-bipyridine (BPY) as conformer. The structural analyses show that baicalein molecules are linked by water molecules in the same fashion, by hydrogen bonding patterns as BE·2BPY·H_2O (CCDC: 1561425, ODAJOW). BE·2BPY·H_2O was prepared as follows: Baicalein (13.5 mg, 0.05 mmol) and 4,4′-bipyridine dihydrate (19.2 mg, 0.10 mmol) were combined in 8.0 mL ethanol and 2.0 mL acetone and stirred at 25 °C for 2 h. The solvents were evaporated from the filtrate at ambient temperature and yellow block crystals were obtained after 10 days. However, in another solvent, acetonitrile, we obtained a co-crystal of a different composition (2BE·BPY·2H_2O, CCDC: 2171759, LAYTOY).

The asymmetric unit of the title structure contais one half of a bipyridine moleule, one baicaleine, and one water molecule (see the figure). The 4,4′-bipyridine molecules in the title structure are π–π stacked and arranged along the 1D baicalein water chain to which they are linked via classical intermolecular hydrogen bonds [O7–H7–N2 (1.87 Å) and O8–H8B–N4 (1.97 Å)] on one side, generating a zipper-type architecture. On the other side of the hydrogen-bonded BE/water layer chain, the 4,4′-bipyridine molecules are linked to baicalein molecules via non-classical hydrogen bonds [C12–H12–N1 (2.69 Å) and C13–H13–N3 (2.59 Å)].

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

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