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Crystal structure of 5,4'-dihydroxy-7,3'-dimethoxyflavanone, C₁₇H₁₆O₆

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.19 × 0.14 × 0.04 mm
Wavelength:	Cu K α radiation (1.54178 Å)
μ :	0.91 mm ⁻¹
Diffractometer, scan mode:	Bruker AXS D8-Venture, φ and ω -scans
$2\theta_{\max}$, completeness:	65.1°, 99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13241, 2450, 0.078
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1913
$N(\text{param})_{\text{refined}}$:	213
Programs:	Bruker [1], Olex2 [2], SHELX [3]

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Abstract

C₁₇H₁₆O₆, orthorhombic, $P2_12_12_1$ (no. 19), $a = 5.2601(3)$ Å, $b = 12.7161(6)$ Å, $c = 22.0116(11)$ Å, $V = 1472.31(13)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0430$, $wR_{\text{ref}}(F^2) = 0.1089$, $T = 296(2)$ K.

CCDC no.: 1889566

The crystal structure of the title compound (systematic name: 5-hydroxy-2-(4-hydroxy-3-methoxyphenyl)-7-methoxychroman-4-one) is shown in the figure. 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 C₁₇H₁₆O₆ was isolated using medium pressure column chromatography (MPCC). In a continuation of our program for the chemical study of the Atacama Desert

Flora [4–9], dried aerial parts of *Parastrephia quadrangularis* (1030 g) collected in april 2015 in El Tatio, Atacama Desert, Northern Chile. This medicinal plant used by the *Aymara* Amerindians [10, 11], a known producer of several flavonoids and benzoic acid derivatives with antioxidant activity [12–15]. This plant was defatted with hexane (3 liters, 3 times in the dark, 24 h each time) and 180.0 g were obtained after evaporation of the solvent. Then the plant material was extracted with ethyl acetate (3 liters, 3 times in the dark, 24 h each time). After evaporation of the solvent under vacuo at 35 °C, 245.0 g of a dark gummy extract was obtained. A portion of the extract (30.0 g) was filtered and submitted to a medium pressure column chromatography system composed of an 2.5 cm × 48 cm medium pressure column (Aceglass inc, Vineland, NY, USA) packed with silica gel (Kieselgel 60 H, 55 μ m particle size, Merck, Darmstadt, Germany) using an isocratic solvent system of *n*-hexane-ethyl acetate (8.0:2.0 v/v) pumped with a medium pressure pump (FMI lab pump, Syosset, NY, USA) with a flow rate of 10 mL/min. The collected fractions (62) were combined according to TLC analysis (Kieselgel F254 plates, developed with hexane: EtOAc 1:1 v/v, and spots visualized by spraying with vanillin:sulfuric acid 2% in ethanol and heating). From fractions 8–15, the flavonoid compound 5,4'-dihydroxy-7,3'-dimethoxyflavanone [16] (86.3 mg) was obtained and the fractions 20–35, 11-(*p*-coumaroyloxy)-tremetone [17] (230 mg). The NMR data for both compounds are consistent with literature. Recrystallization of this 5,4'-dihydroxy-7,3'-dimethoxyflavanone from *n*-hexane:

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

Atom	x	y	z	U_{iso}^*/U_{eq}
O1	0.7090(5)	0.55661(14)	0.60334(9)	0.0379(6)
O2	1.2438(5)	0.47584(19)	0.72976(10)	0.0527(7)
O3	1.0560(6)	0.28635(18)	0.73128(11)	0.0556(7)
H3	1.142319	0.336090	0.742953	0.083*
O4	0.4042(5)	0.20609(16)	0.59569(11)	0.0534(7)
O5	0.4164(6)	0.98624(18)	0.62207(12)	0.0620(8)
O6	0.7169(6)	1.03341(18)	0.53237(11)	0.0593(8)
H6	0.614584	1.068408	0.551901	0.089*
C1'	0.7885(7)	0.7407(2)	0.61315(13)	0.0326(8)
C2	0.8130(7)	0.6365(2)	0.64417(14)	0.0341(8)
H2	0.708930	0.637972	0.681086	0.041*
C2'	0.6072(7)	0.8119(2)	0.63413(14)	0.0354(8)
H2'	0.502294	0.794106	0.666560	0.042*
C3	1.0809(7)	0.6058(2)	0.66175(14)	0.0401(8)
H3A	1.187890	0.605775	0.625856	0.048*
H3B	1.148636	0.657107	0.690024	0.048*
C3'	0.5841(7)	0.9087(2)	0.60660(15)	0.0383(8)
C4	1.0867(7)	0.4987(2)	0.69054(14)	0.0376(8)
C4'	0.7406(7)	0.9359(2)	0.55820(13)	0.0393(9)
C5	0.8902(7)	0.3197(3)	0.68867(14)	0.0392(9)
C5'	0.9166(8)	0.8660(2)	0.53704(14)	0.0441(9)
H5'	1.019912	0.883854	0.504339	0.053*
C6	0.7214(8)	0.2495(2)	0.66430(13)	0.0427(9)
H6A	0.716834	0.180409	0.678062	0.051*
C6'	0.9411(8)	0.7683(2)	0.56445(14)	0.0416(9)
H6'	1.061121	0.720803	0.549962	0.050*
C7	0.5571(8)	0.2826(2)	0.61884(14)	0.0388(8)
C7'	0.2502(8)	0.9706(3)	0.67157(16)	0.0539(11)
H7'A	0.144734	0.910471	0.663837	0.081*
H7'B	0.145278	1.031718	0.676727	0.081*
H7'C	0.347636	0.958976	0.707839	0.081*
C8	0.5531(7)	0.3855(2)	0.59816(14)	0.0340(8)
H8	0.440790	0.406362	0.567837	0.041*
C9	0.7214(7)	0.4562(2)	0.62401(13)	0.0313(8)
C10	0.8969(7)	0.4261(2)	0.66894(12)	0.0339(8)
C11	0.2103(8)	0.2330(3)	0.55408(15)	0.0482(10)
H11A	0.285386	0.257371	0.516921	0.072*
H11B	0.106283	0.287573	0.571107	0.072*
H11C	0.107338	0.172234	0.545955	0.072*

EtOAc (7:3 v/v) at room temperature yielded white crystals, which were suitable for X-ray diffraction analysis.

5,4'-dihydroxy-7,3'-dimethoxyflavanone, white crystals, m.p. 172 °C. The molecular weight was determined by orbitrap ESI-MS/MS with a mass spectrometer (Q-exactive Focus, Bremen, Germany) $[M + H]^+$: 317.10440 calcd. for C₁₇H₁₇O₆⁺: 317.10196. ¹H NMR (Bruker Avance 300 MHz, DMSO-d₆) δ ppm: 2.75 (1H, dd, J = 2.9, 17.5 Hz, H-3β), 3.08 (1H, dd, J = 17.5, 12.6 Hz, H-3α), 3.78 (3H, s, OCH₃), 3.90 (3H, s, OCH₃), 5.30 (1H, dd, J = 12.6, 3.0 Hz, H-2), 6.05 (1H, d, J = 2.2 Hz, H-6), 6.08 (1H, d, J = 2.2 Hz, H-8), 6.86–6.98 (3H, m, H-2'/H-5'/H-6'), 12.03 (1H, s, OH-5). ¹³C NMR (¹³C NMR Bruker Avance 300 MHz,

DMSO-d₆) δ ppm: 199.1 (C-4), 168.1 (C-7), 164.2 (C-5), 162.8 (C-9), 146.7 (C-3'), 146.5 (C-4'), 130.4 (C-1'), 119.6 (C-6'), 114.5 (C-5'), 108.8 (C-2'), 103.5 (C-10), 95.4 (C-6), 95.1 (C-8), 79.4 (C-2), 56.0 (O–CH₃), 56.9 (O–CH₃), 43.4 (C-3). These data, together with ESI-MS/MS and correlations observed in the HSQC and HMBC spectra, are consistent with the structure of 5,4'-dihydroxy-7,3'-dimethoxyflavanone confirmed by comparison spectroscopic data with those reported in the literature for similar flavanones [16, 18].

Experimental details

H atoms were located in the difference Fourier map, but refined with fixed individual displacement parameters, using a riding model with C–H distances of 0.93 Å (for aromatic rings), O–H distances of 0.82 Å and C–H distances 0.96 for methyl group with $U(H)$ values of $1.2U_{eq}(C,O)$ and $1.5U_{eq}(C)$ (for CH₃).

Comment

The title compound is a positional isomer of 5,3'-dihydroxy-7,4'-dimethoxyflavanone [18], which was isolated from the Chinese Tibetan medicinal plant *Artemisia sphaerocephala* Kraschen, but the absolute structure could not be established. In the present compound, the absolute configuration has been made probable from the refinement of the Flack parameter, $\chi = 0.04(18)$, which indicate that the correct configuration had been assigned against 967 (95%) CuKα Bijvoet pair. On this basis the absolute configuration was assigned as C2S. The structure of the title compound consists of three rings, including a phenyl ring and a benzopyrone fused ring (the Figure). The methoxy groups on C7 and C3' and the hydroxyl groups on C4' and C5 are equatorially oriented. The conformation is consolidated by one intramolecular O–H...O hydrogen bond. In the crystal, the molecules are linked by one O–H...O hydrogen bond interactions, forming chains along [010], with graph-set notation C₁'(12) [19]. All distances and bond angles are normal and comparable with its positional isomer.

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