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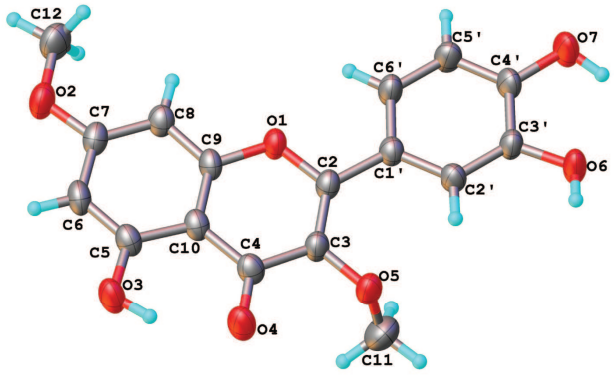
Crystal structure of 3′,4′,5-trihydroxy-3,7-dimethoxyflavone, $C_{17}H_{14}O_7$



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Abstract

$C_{17}H_{14}O_7$, monoclinic, $P2_1/c$ (no. 14), $a = 11.6670(4)$ Å, $b = 11.3338(4)$ Å, $c = 11.6415(4)$ Å, $\beta = 110.269(1)$ Å, $V = 1444.05(9)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.038$, $wR_{ref}(F^2) = 0.117$, $T = 296$ K.

CCDC no.: 1447966

The crystal structure is shown in the figure. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

Plant material of *Heliotropium taltalense* (Phil.) I. M. Johnst. (aerial parts) were collected in Quebrada de Paposo in April 2011. Voucher herbarium specimens are kept at the Natural Products Laboratory of Universidad de Antofagasta under reference number: Heltal20110406. Extraction and isolation: Dried aerial parts of *H. taltalense* (1.8 kg) were immersed in ethyl acetate (EtOAc) for 1 min (2 L) in order to obtain an extract from the exudate. The extract was immediately concentrated *in vacuo* and the resulting dark brown syrup (47 g) was added to 50 g of silicagel 60 G (Merck Darmstadt, Germany) and slurred onto the top of a column containing silica gel 60 H (0.5 kg), partitioned using a medium pressure

Table 1: Data collection and handling.

Crystal:	Yellow, block, size 0.26×0.27×0.33 mm
Wavelength:	Cu K_α radiation (1.54178 Å)
μ:	10.15 cm^{-1}
Diffractometer, scan mode:	Bruker AXS D8-Venture,Triumph-IμS-Cu, ω
$2\theta_{max}$:	133.34°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13590, 2472
$N(param)_{refined}$:	228
Programs:	SHELX [11], Bruker programs [12], OLEX2 [13]

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

Atom	Site	x	y	z	U_{iso}
H(3)	4e	0.0807	0.4768	0.1723	0.045
H(7)	4e	0.6317	0.3480	0.2055	0.046
H(9A)	4e	0.8304	0.3656	0.2298	0.087
H(9B)	4e	0.9160	0.2756	0.1965	0.087
H(9C)	4e	0.8024	0.2301	0.2260	0.087
H(10)	4e	0.4318	0.4080	0.3703	0.049
H(11)	4e	0.3932	0.4461	0.5467	0.056
H(12)	4e	0.6090	0.3124	−0.1461	0.050
H(17A)	4e	0.0439	0.2523	−0.0760	0.103
H(17B)	4e	−0.0550	0.3122	−0.0323	0.103
H(17C)	4e	0.0645	0.2609	0.0641	0.103
H(1)	4e	0.117(2)	0.515(2)	0.561(2)	0.092
H(4)	4e	−0.043(2)	0.548(2)	0.288(2)	0.077
H(19)	4e	0.308(2)	0.370(2)	−0.259(2)	0.062

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Table 3: Atomic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(4')	4e	0.2156(2)	0.4861(2)	0.4667(2)	0.037(1)	0.064(1)	0.028(1)	0.0010(8)	0.0175(8)	−0.0002(8)
C(3')	4e	0.1222(1)	0.4953(2)	0.3534(2)	0.0292(9)	0.054(1)	0.032(1)	0.0042(7)	0.0151(7)	0.0013(7)
C(2')	4e	0.1439(2)	0.4708(2)	0.2473(2)	0.0331(9)	0.053(1)	0.0264(9)	0.0043(7)	0.0110(7)	0.0015(7)
C(1')	4e	0.2610(1)	0.4368(1)	0.2512(2)	0.0324(8)	0.0414(9)	0.0319(9)	0.0026(7)	0.0148(7)	0.0015(7)
C(2)	4e	0.2901(1)	0.4103(1)	0.1406(2)	0.0301(8)	0.0408(9)	0.034(1)	0.0038(7)	0.0153(7)	0.0042(7)
C(9)	4e	0.4616(1)	0.3692(1)	0.0807(2)	0.0368(9)	0.0378(9)	0.0328(9)	0.0040(7)	0.0201(7)	0.0033(7)
C(8)	4e	0.5858(1)	0.3474(2)	0.1223(2)	0.0367(9)	0.046(1)	0.035(1)	0.0054(7)	0.0162(7)	0.0051(7)
C(7)	4e	0.6393(2)	0.3246(1)	0.0355(2)	0.0356(9)	0.0408(9)	0.045(1)	0.0053(7)	0.0213(8)	0.0039(7)
C(12)	4e	0.8332(2)	0.2926(2)	0.1891(2)	0.039(1)	0.079(2)	0.056(1)	0.0147(9)	0.0157(9)	0.003(1)
C(6')	4e	0.3534(2)	0.4293(2)	0.3656(2)	0.0304(9)	0.062(1)	0.033(1)	0.0063(8)	0.0147(7)	0.0025(8)
C(5')	4e	0.3305(2)	0.4527(2)	0.4714(2)	0.0336(9)	0.077(1)	0.028(1)	0.0044(8)	0.0092(7)	0.0026(8)
C(6)	4e	0.5709(2)	0.3265(2)	−0.0892(2)	0.045(1)	0.048(1)	0.042(1)	0.0056(8)	0.0274(8)	−0.0012(8)
C(5)	4e	0.4483(2)	0.3491(2)	−0.1287(2)	0.045(1)	0.042(1)	0.033(1)	0.0057(7)	0.0190(8)	0.0004(7)
C(10)	4e	0.3889(1)	0.3683(1)	−0.0425(2)	0.0394(9)	0.0360(9)	0.033(1)	0.0057(7)	0.0181(7)	0.0033(7)
C(4)	4e	0.2596(1)	0.3849(1)	−0.0767(2)	0.0395(9)	0.042(1)	0.030(1)	0.0079(7)	0.0134(8)	0.0037(7)
C(3)	4e	0.2140(1)	0.4008(2)	0.0226(2)	0.0308(9)	0.046(1)	0.033(1)	0.0062(7)	0.0142(7)	0.0019(7)
C(11)	4e	0.0310(2)	0.3001(2)	−0.0135(2)	0.043(1)	0.095(2)	0.069(2)	−0.015(1)	0.021(1)	−0.016(1)
O(1)	4e	0.1958(1)	0.5101(2)	0.5731(1)	0.0420(7)	0.117(1)	0.0279(8)	0.0095(8)	0.0166(6)	−0.0048(7)
O(2)	4e	0.41309(9)	0.3956(1)	0.1688(1)	0.0311(6)	0.0530(7)	0.0304(6)	0.0052(5)	0.0158(5)	0.0030(5)
O(3)	4e	0.7600(1)	0.3021(1)	0.0630(1)	0.0357(7)	0.0742(9)	0.0491(8)	0.0113(6)	0.0213(6)	0.0023(6)
O(4)	4e	0.0112(1)	0.5295(1)	0.3583(1)	0.0334(7)	0.093(1)	0.0310(7)	0.0155(6)	0.0157(5)	0.0015(6)
O(7)	4e	0.0901(1)	0.4115(1)	−0.0079(1)	0.0308(6)	0.0709(9)	0.0377(7)	0.0081(6)	0.0129(5)	−0.0016(6)
O(6)	4e	0.1893(1)	0.3861(1)	−0.1869(1)	0.0429(7)	0.0790(9)	0.0289(7)	0.0130(6)	0.0129(6)	0.0020(6)
O(5)	4e	0.3846(1)	0.3530(1)	−0.2498(1)	0.0494(8)	0.079(1)	0.0311(7)	0.0159(7)	0.0187(6)	−0.0007(6)

pump with an isocratic eluent (*n*-hexane-EtOAc 8:2 v:v), to obtain six partitions (fractions A to F: *n*-hexane, *n*-hexane–EtOAc 95:5, *n*-hexane–EtOAc 90:10, *n*-hexane–EtOAc 80:20, *n*-hexane–EtOAc 50:50 and pure EtOAc). Further purification by a combination of chromatography on silicagel 60 H and permeation through Sephadex LH-20 (eluting with methanol-water 7:3) of the fraction 20% hexane-ethyl acetate (fraction D, 15 g) afforded the phytoalexin 2*S*-sakuranetin [2], Fraction C (10% hexane-ethyl acetate, 5 g) was submitted to successive steps of Sephadex LH-20 permeation (eluting with methanol-water 7:3 v:v) and afforded 39 mg of 7 *O*-methyl-eriodyctiol, and 10 mg of 3,7-Di-O-methyl-quercetin, for which NMR data are consistent with literature [3, 8, 9]. Recrystallization from ethyl acetate at −20 °C yielded yellow crystals of the title compound (0.051 g). Analysis: m.p. 289–291 °C. ESI-MS/MS (HCT-Ultra ETD II, Bruker Daltonics, Germany) $[M-H]^-$: 329.32, $[M+H]^+$: 331.12. ^{1}H NMR (300 MHz, DMSO-d6) δ ppm: 7.65 (1H, d, J = 1.4 Hz, H-2′), 7.55 (1H, dd, J = 1.4, 8.4 Hz, H-6′), 6.97 (1H, d, J = 8.4 Hz, H-5′), 6.77 (1H, d, J = 1.9 Hz, H-8), 6.43 (1H, d, J = 1.9 Hz, H-6), 3.93 (3H, s, OCH3), 3.86 (3H, s, OCH3). ^{13}C NMR (300 MHz, DMSO-d6) δ ppm: 147.92 (C-2), 137.23 (C-3), 177.35 (C-4), 162.54 (C-5), 99.35 (C-6), 165.74 (C-7), 94.4 (C-8), 158.2 (C-9), 104.4 (C-10), 124.13 (C-1′), 116.06 (C-2′), 146.23 (C-3′), 148.75 (C-4′), 116.23 (C-5′), 121.66 (C-6′), 56.92 (7-O—CH_3), 56.95 (3-O—CH_3).

Experimental details

H atoms were refined with fixed individual displacement parameters, using a riding mode with C—H distances of 0.93 Å (for aromatic rings), 0.96 Å (for CH_3), with U_{iso}(H) values of $1.2U_{eq}$(C) (for CH in aromatic), and $1.5U_{eq}$(C) (for methyl group), O—H distances are 0.87(3); 0.88(3) and 0.88(2) Å.

Discussion

H. taltalense (Phil.) Johnst. (Heliotropiaceae) is an endemic species growing in Paposo valley that produces a resinous exudate that covers its foliar surface and stems [1]. The flavonoids S-sakuranetin, naringenin, 3-O-methylgalangin and 7-O-methyl-eriodictiol were the main phenolic constituents reported so far from the exudate [2, 3] which showed important DPPH scavenging activity [3]. Furthermore, several methoxy-flavone derivatives such as quercetin O-methyl ether derivatives showed interesting biological activities such as antioxidant [4], antibacterial [5], antihypercholesterolemic [6] and anti-inflammatory activities [7]. We report in this paper the structure of 3′,4′,5-trihydroxy-3,7-dimethoxyflavone (3,7-di-O-methylquercetin) a further methyl flavonol isolated from this plant, which is a di-O-methyl derivative of quercetin, a common flavonoid present in many fruits and vegetables. The molecule is not planar, with a dihedral angle between

the endocyclic atoms of the pirone ring system and the substituted phenyl ring of only 7.7(3)°. The bond lengths and angles are in the expected ranges. The molecular conformation and the crystal packing is stabilized by an intermolecular O—H···O hydrogen bond, and a weak π-π stacking interaction between phenyl rings with centroid-centroid distance of 3.480 Å (Cg—Cg^{i}: C5/C6/C7/C8/C9/C10) [symmetry code (i) 1−*x*, 1−*y*, −*z*] respectively. In the crystal, molecules are linked by strong intramolecular O—H···O^{ii} [symmetry code (ii) −*x*, 1−*y*, −*z*] hydrogen bonds with set graph-motif $R^2_2(18)$ [10].

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