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Crystal structure of (*E*)-3-(3,4-dihydroxyphenyl)-*N*-ethylacrylamide, $C_{11}H_{13}NO_3$, *a caffeic acid imide*

Fa-Yan Meng, Bing-Li Jiang, Li Wang and Cui-Wu Lin*

Guangxi University, College of Chemistry and Chemical Engineering, Guangxi 530004, P. R. China

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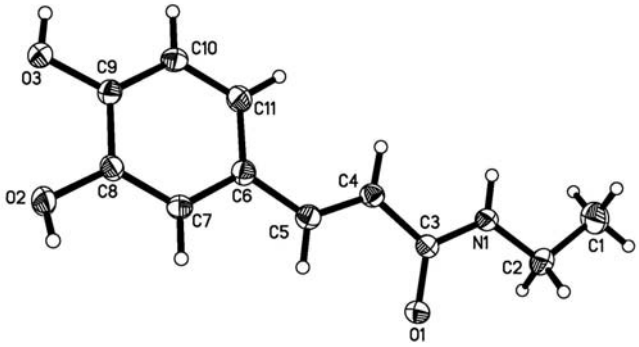

Abstract

$C_{11}H_{13}NO_3$, monoclinic, $P2_1/n$ (no. 14), a = 6.780(2) Å, b = 11.397(3) Å, c = 13.849(4) Å, β = 96.743(4)°, V = 1062.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.039, $wR_{ref}(F^2)$ = 0.117, T = 296 K.

Source of material

To a stirred tetrahydrofuran solution (15 ml) of chlorogenic acid (0.354 g, 1 mmol) was added *N*,*N*′-dicyclohexylcarbodiimide (DCC, 1.5 mmol) in tetrahydrofuran (5 mL) at 0 °C. The reaction mixture was stirred for 2 h at 0 °C and overnight at room temperature. The precipitated dicyclohexylurea was filtered and washed with tetrahydrofuran. The combined filtrates were evaporated, the residue was extracted with EtOAc, and the extract was washed with 1 N $NaHCO_3$, H_2O and 1 N HCl, dried over Na_2SO_4, and filtered, the solvents were concentrated by evaporation. The resulting crude product was further purified by column chromatography on silica gel (4 × 40 cm) with petroleum ether/ethylacetate (1:4, *v*/*v*). The product was recrystallized with ethanol to give pale yellow block-shaped crystals.

Experimental details

All the H atoms were positioned geometrically with d(C—H) = 0.97 Å and refined as riding with U_{iso}(H) = 1.2 U_{eq}(C).

Discussion

The genus *Blumea riparia* (Bl.) DC., a traditional chinese medicinal herb, has been used to treat gynecological diseases including menorrhagia, puerperal metrorrhagia, peripheral edema, infertility and vulvar ulcer [1]. Recent research showed that the phenolic compounds are widely present in medicinal plants, exhibiting antioxidant, antivirus, immunomodulatory, antiallergic, and other types of pharmacological activity [2-5]. Up to now, about 20 phenolic compounds such as caffeic acid, chlorogenic acid and hydroxycinnamic acid have been isolated from *Blumea riparia* DC. Our previous investigations showed that some of the phenolic compounds obtained from *Blumea riparia* DC. play significant role at antiplatelet activity, and the caffeic acid can remarkable strengthen uterine contraction [6]. In order to improve the procoagulant activity of the phenolic acid extracted from *Blumea riparia* (Bl.) DC. we synthetized further derivatives.

In the title crystal structure, the bond lengths C8—O2 and C9—O3 are almost equal (1.363(2) and 1.370(2) Å, respectively), which is similar in the heptyl 3-(3,4-dihydroxyphenyl)-2-propenoate [7]. The benzene ring is almost planar with maximal deviation of 0.010(1) Å and it makes a dihedral angle of 13.5° with the linker (C3–C4–C5–O1). The presence of an ethylenic spacer allows the formation of a conjugated system, strongly stabilized through π-electron delocalization. C4=C5 is a *trans*-double bond as in caffeic esters [7].

The crystal packing is stabilized by intermolecular O–H···O, N–H···O and C–H···O hydrogen bonds. The molecules of the caffeic acid amide form chains through N–H···O hydrogen bonds along [100] in a head-to-tail manner [8]. The chains interact via C–H···O and O–H···O hydrogen bonds to form a three-dimensional network.

Table 1. Data collection and handling.

Crystal:	yellow block, size 0.12 × 0.18 × 0.33 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.95 cm^{-1}
Diffractometer, scan mode:	multiwire proportional, φ/ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5817, 1970
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1614
$N(param)_{refined}$:	136
Programs:	SHELXS-97, SHELXL-97 [9]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1D)	4*e*	–0.0859	0.4861	1.2476	0.044
H(1A)	4*e*	–0.0727	0.3372	1.4627	0.105
H(1B)	4*e*	–0.2140	0.3510	1.3653	0.105
H(1C)	4*e*	–0.1362	0.4626	1.4241	0.105
H(2A)	4*e*	0.1855	0.4212	1.3912	0.057
H(2B)	4*e*	0.1073	0.3096	1.3322	0.057
H(4A)	4*e*	–0.0206	0.5949	1.1150	0.041
H(5A)	4*e*	0.3557	0.5568	1.0681	0.043
H(7A)	4*e*	0.4528	0.6298	0.9215	0.042
H(10A)	4*e*	–0.0947	0.8715	0.8705	0.052
H(11A)	4*e*	–0.0661	0.7424	0.9993	0.053
H(2C)	4*e*	0.5240	0.6989	0.7691	0.078
H(3A)	4*e*	0.0540	0.9461	0.7400	0.062

* Correspondence author (e-mail: cuiwulin@yahoo.com.cn)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	4*e*	0.0327(2)	0.4600(1)	1.26263(8)	0.0322(6)	0.0411(7)	0.0369(6)	0.0039(5)	0.0068(5)	0.0077(5)
C(1)	4*e*	–0.1032(3)	0.3845(2)	1.4055(1)	0.064(1)	0.096(2)	0.052(1)	–0.001(1)	0.0170(9)	0.029(1)
C(2)	4*e*	0.0730(2)	0.3887(2)	1.3501(1)	0.0503(9)	0.0481(9)	0.0439(9)	0.0032(7)	0.0077(7)	0.0136(7)
C(3)	4*e*	0.1688(2)	0.4866(1)	1.20528(9)	0.0309(7)	0.0266(6)	0.0331(7)	–0.0010(5)	0.0053(5)	–0.0056(5)
C(4)	4*e*	0.1076(2)	0.5645(1)	1.12269(9)	0.0336(7)	0.0351(7)	0.0340(7)	0.0033(5)	0.0066(5)	–0.0016(5)
C(5)	4*e*	0.2315(2)	0.5925(1)	1.0588(1)	0.0378(7)	0.0336(7)	0.0361(7)	0.0033(6)	0.0072(6)	–0.0023(6)
C(6)	4*e*	0.1980(2)	0.6722(1)	0.9755(1)	0.0369(7)	0.0327(7)	0.0341(7)	0.0010(5)	0.0083(5)	–0.0014(5)
C(7)	4*e*	0.3418(2)	0.6781(1)	0.9111(1)	0.0341(7)	0.0321(7)	0.0399(7)	0.0056(5)	0.0078(6)	0.0012(6)
C(8)	4*e*	0.3241(2)	0.7534(1)	0.8324(1)	0.0327(7)	0.0317(7)	0.0397(7)	0.0001(5)	0.0109(6)	0.0010(6)
C(9)	4*e*	0.1599(2)	0.8282(1)	0.8177(1)	0.0340(7)	0.0318(7)	0.0372(7)	–0.0013(5)	0.0034(5)	0.0032(5)
C(10)	4*e*	0.0156(2)	0.8226(1)	0.8806(1)	0.0364(8)	0.0450(9)	0.0506(9)	0.0137(6)	0.0120(6)	0.0087(7)
C(11)	4*e*	0.0330(2)	0.7454(1)	0.9583(1)	0.0410(8)	0.0492(9)	0.0450(8)	0.0090(7)	0.0186(6)	0.0069(7)
O(1)	4*e*	0.3435(1)	0.44807(8)	1.22254(7)	0.0322(5)	0.0368(5)	0.0482(6)	0.0032(4)	0.0069(4)	0.0030(4)
O(2)	4*e*	0.4616(2)	0.7606(1)	0.76840(8)	0.0510(6)	0.0481(7)	0.0616(7)	0.0159(5)	0.0300(5)	0.0207(5)
O(3)	4*e*	0.1518(1)	0.90369(9)	0.74037(7)	0.0363(5)	0.0418(6)	0.0475(6)	0.0064(4)	0.0094(4)	0.0138(4)

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