Crystal structure of (*E*)-3-(3,4-dihydroxyphenyl)-*N*-methylacrylamide, $C_{10}H_{11}NO_3$

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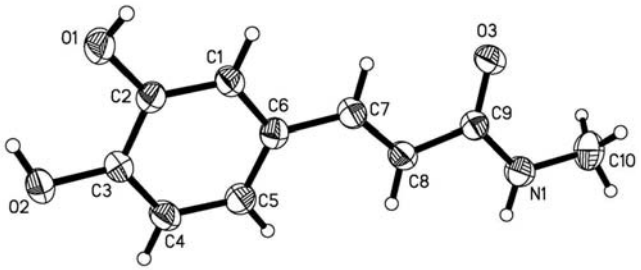

Abstract

$C_{10}H_{11}NO_3$, orthorhombic, *Pbca* (no. 61), $a = 5.053(3)$ Å, $b = 14.685(7)$ Å, $c = 24.87(1)$ Å, $V = 1845.1$ Å^3, $Z = 8$, $R_{gt}(F) = 0.050$, $wR_{ref}(F^2) = 0.150$, $T = 296$ K.

Source of material

The caffeic acid (10 mmol) is dissolved in 20 mL of DMF. The solution is cooled in an ice-water bath, and 10 mmol of the methylamine was added followed by a solution of 10 mmol of EDC in 20 mL of THF. The mixture is stirred at 0 °C for 2 h and then at room temperature for 24 h. THF is removed under reduced pressure, and the solution is diluted with water. The products are extracted with ethyl acetate. The extract is washed successively with 1 N HCl, water, 1 M $NaHCO_3$, water and dried over $MgSO_4$, filtered and evaporated. The residue is purified on a silica gel column (eluent: ethyl acetate/petroleum ether, yield 50 %) [1].

Experimental details

All the H atoms were positioned geometrically with d(N—H) = 0.86 Å, d(O—H) = 0.82 Å, d(C—H) = 0.93 - 0.96 Å and treated as riding with U_{iso}(H) = 1.2 U_{eq}(N,C) and U_{iso}(H) = 1.5 U_{eq}(O).

Discussion

Naturally occurring caffeic acid and its esters and amides attract much attention in biology and medicine [2,3]. These compounds show antiviral, antibacterial, vasoactive, antiatherogenic, antiproliferative, antioxidant and antiinflammatory properties [4-6]. Our previous research showed that the phenolic acids compounds including caffeic, chlorogenic, ferulic, vanillic, syringic and protocatechuic acid from Blumea riparia DC have significant role at antiplatelet activity [7]. This prompted us to synthesize a series of caffeic acid amides and esters to investigate their properties.
In the title crytal structure, all values of the geometric parameters are normal. The benzene ring is planar within experimental deviation and it makes an angle of 12.5° to the linker C2–C3– C4–O2. In the case of caffeic esters, the presence of an ethylenic spacer allows the formation of a conjugated system, strongly stabilized through π-electron delocalization. The bond C7=C8 is a *trans*-double bond. The crystal packing is stabilized by intermolecular hydrogen bonds: O2–H2A···O2′ (d(O2– H2A···O2′) = 2.894(2) Å, ∠O2–H2A···O2′ = 173.4°) and N1–H1A···O3 (d(N1–H1A···O3) = 3.099(3) Å, ∠N1–H1A···O3 = 134.3°).

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.20 × 0.34 × 0.43 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.04 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	56.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	10909, 2239
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1713
$N(param)_{refined}$:	127
Programs:	SHELXS-97, SHELXL-97 [8]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	8*c*	–0.2683	0.8296	0.6207	0.053
H(1B)	8*c*	0.4681	0.9613	0.4298	0.041
H(4A)	8*c*	–0.1982	0.7983	0.3473	0.046
H(5A)	8*c*	–0.1745	0.8020	0.4400	0.044
H(7A)	8*c*	0.3318	0.9132	0.5162	0.040
H(8A)	8*c*	–0.1562	0.8363	0.5311	0.042
H(10A)	8*c*	–0.2468	0.8332	0.7084	0.081
H(10B)	8*c*	–0.0478	0.9143	0.7015	0.081
H(10C)	8*c*	0.0567	0.8138	0.7019	0.081
H(1C)	8*c*	0.5609	1.0135	0.3418	0.066
H(2A)	8*c*	0.2418	0.8750	0.2647	0.070

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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)	8*c*	–0.1191(3)	0.8480(1)	0.63329(6)	0.0385(9)	0.065(1)	0.0299(8)	–0.0108(8)	0.0021(6)	0.0030(7)
C(1)	8*c*	0.3322(4)	0.9290(1)	0.41334(6)	0.0348(9)	0.0381(8)	0.0294(8)	–0.0070(7)	–0.0010(7)	–0.0030(6)
C(2)	8*c*	0.3164(3)	0.9277(1)	0.35779(6)	0.0321(9)	0.0350(8)	0.0299(8)	–0.0024(7)	0.0028(6)	–0.0004(6)
C(3)	8*c*	0.1176(3)	0.8776(1)	0.33309(6)	0.0335(9)	0.0379(8)	0.0280(8)	0.0000(7)	–0.0028(6)	–0.0002(6)
C(4)	8*c*	–0.0644(4)	0.8314(1)	0.36401(7)	0.036(1)	0.0436(9)	0.0340(9)	–0.0097(8)	–0.0050(7)	–0.0013(7)
C(5)	8*c*	–0.0504(4)	0.8336(1)	0.41965(7)	0.037(1)	0.0389(9)	0.0340(9)	–0.0075(7)	0.0024(7)	0.0031(7)
C(6)	8*c*	0.1483(3)	0.8828(1)	0.44515(6)	0.0337(9)	0.0320(8)	0.0293(8)	0.0014(7)	0.0010(6)	0.0007(6)
C(7)	8*c*	0.1748(4)	0.8879(1)	0.50367(7)	0.0371(9)	0.0334(8)	0.0302(8)	–0.0038(7)	–0.0013(7)	0.0000(6)
C(8)	8*c*	0.0055(4)	0.8613(1)	0.54119(7)	0.0333(9)	0.0413(9)	0.0302(8)	–0.0039(7)	–0.0026(7)	0.0004(7)
C(9)	8*c*	0.0702(3)	0.8708(1)	0.59881(7)	0.0331(9)	0.0308(8)	0.0304(8)	–0.0017(7)	0.0003(7)	0.0011(6)
C(10)	8*c*	–0.0865(5)	0.8527(2)	0.69120(8)	0.061(1)	0.071(1)	0.031(1)	–0.001(1)	0.0067(9)	0.0030(9)
O(1)	8*c*	0.4883(3)	0.97258(9)	0.32496(5)	0.0471(8)	0.0541(8)	0.0301(6)	–0.0183(6)	0.0054(5)	–0.0028(5)
O(2)	8*c*	0.0941(3)	0.8749(1)	0.27840(5)	0.0444(8)	0.0692(9)	0.0263(6)	–0.0130(7)	–0.0022(5)	–0.0004(6)
O(3)	8*c*	0.2913(3)	0.8963(1)	0.61421(5)	0.0372(7)	0.0546(8)	0.0368(7)	–0.0116(6)	–0.0021(5)	–0.0032(6)

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