organic compounds

(E)-Phenethyl 3-(3,4-dihydroxy-5-nitro-phenyl)acrylate

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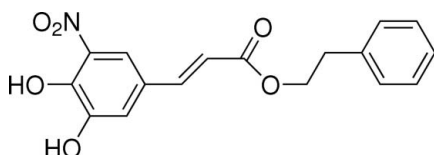Correspondence e-mail: huyang@mail.hz.zj.cn

The title compound, also known as 5-nitrocaffeic acid phenethyl ester, $C_{17}H_{15}NO_6$, was prepared by the condensation reaction of 3,4-dihydroxy-5-nitrobenzaldehyde, Meldrum's acid and 2-phenylethanol. The dihedral angle between the phenyl and benzene rings is 78.12 (5)°. Inter- and intramolecular hydrogen bonds help to stabilize the crystal structure.

Related literature

For related literature, see: Chen *et al.* (1999); Hu *et al.* (2006); Son & Lewis (2002); Son *et al.* (2001).

Experimental

Crystal data

$C_{17}H_{15}NO_6$	V = 1562.8 (5) Å^3
M_r = 329.30	Z = 4
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
a = 8.5840 (17) Å	μ = 0.11 mm^{-1}
b = 5.3725 (11) Å	T = 296 (2) K
c = 33.904 (7) Å	$0.25 \times 0.20 \times 0.10$ mm
β = 91.757 (3)°	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	9258 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	3509 independent reflections
	2268 reflections with $I > 2\sigma(I)$
T_{min} = 0.974, T_{max} = 0.986	R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.124	
S = 1.06	
3509 reflections	$\Delta\rho_{max}$ = 0.16 e Å^{-3}
226 parameters	$\Delta\rho_{min}$ = −0.16 e Å^{-3}
3 restraints	

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O3—H3X$\cdots$O2	0.878 (15)	1.810 (18)	2.5807 (19)	145.3 (19)
O3—H3X$\cdots$N1	0.878 (15)	2.43 (2)	2.914 (2)	115.5 (16)
O4—H4X$\cdots$O5^i	0.826 (15)	1.886 (15)	2.7088 (18)	174 (2)
C6—H6$\cdots$O5^i	0.93	2.48	3.180 (2)	132
C7—H7$\cdots$O1^{ii}	0.93	2.54	3.404 (2)	156
C15—H15$\cdots$O4^{iii}	0.93	2.60	3.507 (2)	166

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $-x+2, -y+2, -z$; (iii) $x, -y+\frac{1}{2}, z+\frac{1}{2}$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2005); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WN2218).

References

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supplementary materials

(*E*)-Phenethyl 3-(3,4-dihydroxy-5-nitrophenyl)acrylate

C.-N. Xia, W.-X. Hu and W. Zhou

Comment

Caffeic acid and its derivatives are widely distributed in the plant kingdom (Chen *et al.*, 1999). The compounds are known to have anti-atherosclerotic, antibacterial, anti-inflammatory, antiproliferative, immunostimulatory, anti-oxidative, antiviral, and neuroprotective properties (Son *et al.*, 2002). In a continuation of our work on the structure-activity relationship of caffeic acid derivatives, we have obtained, by a one-pot method (Hu *et al.*, 2006), the title compound, 5-nitroCAPE, as light brown crystals.

The molecular structure of 5-nitroCAPE is illustrated in Fig. 1. The molecule displays an E configuration, with the benzene ring and carboxylate group located on opposite sides of the C7═C8 double bond. The bond lengths and angles are similar to those of caffeic acid phenethyl ester (CAPE), reported by Son *et al.* (2001). Atoms C1—C9, N1 and O1—O5 are essentially coplanar, with a mean deviation from the least-squares plane of 0.052 (1) Å; atom C10 deviates from this plane by 0.211 (2) Å. The crystal packing (Fig. 2) is stabilized by intramolecular O—H⋯O and O—H⋯N hydrogen bonds; the crystal structure also involves intermolecular C—H⋯O hydrogen bonds (Table 1). The molecules of 5-nitroCAPE form stacks along the *b* axis in a head-to-tail manner forming a dimeric structure; this differs from the head-to-head stacking found in CAPE.

Experimental

5-NitroCAPE was obtained by the method of Hu *et al.* (2006). Crystals suitable for structure analysis were obtained by slow evaporation of a solution of a mixture of tetrahydrofuran and acetone (2:1, *v/v*) as light brown crystalline prisms.

Refinement

Carbon-bound H atoms were included at calculated positions and refined using a riding model; C—H = 0.97 Å for methylene and 0.93 Å for Csp^2; $U_{iso}(H) = 1.2U_{eq}(C)$. The hydroxy atoms H3X and H4X were located in difference Fourier maps and refined isotropically with the O—H restraints of 0.88 (2) and 0.83 (2) Å, respectively.
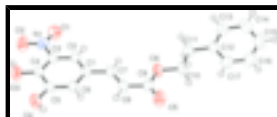
Figures

Fig. 1. The molecular structure of 5-nitroCAPE, shown with 50% probability displacement ellipsoids.
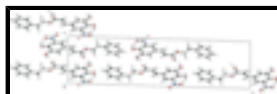

Fig. 2. Packing diagram of 5-nitroCAPE, viewed along the *b* axis. Dashed lines indicate hydrogen bonds.

(*E*)-Phenethyl 3-(3,4-dihydroxy-5-nitrophenyl)acrylate

Crystal data

$C_{17}H_{15}NO_6$	$F_{000} = 688$
$M_r = 329.30$	$D_x = 1.400$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
	$\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 2071 reflections
$a = 8.5840$ (17) Å	$\theta = 2.4$–24.2º
$b = 5.3725$ (11) Å	$\mu = 0.11$ mm^{-1}
$c = 33.904$ (7) Å	$T = 296$ (2) K
$\beta = 91.757$ (3)º	Prismatic, light brown
$V = 1562.8$ (5) Å^3	$0.25 \times 0.20 \times 0.10$ mm
$Z = 4$	

Data collection

Bruker SMART APEXII CCD area-detector diffractometer	3509 independent reflections
Radiation source: fine-focus sealed tube	2268 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.026$
$T = 296(2)$ K	$\theta_{max} = 27.5$º
φ and ω scans	$\theta_{min} = 2.4$º
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -10 \rightarrow 6$
$T_{min} = 0.974$, $T_{max} = 0.986$	$k = -6 \rightarrow 6$
9258 measured reflections	$l = -43 \rightarrow 43$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.043$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.124$	$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 0.128P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
3509 reflections	$\Delta\rho_{max} = 0.16$ e Å^{-3}
226 parameters	$\Delta\rho_{min} = -0.16$ e Å^{-3}
3 restraints	Extinction correction: SHELXL, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0046 (16)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
O1	1.02260 (16)	1.0979 (2)	−0.05897 (4)	0.0718 (4)
O2	0.95350 (17)	1.0519 (2)	−0.12012 (4)	0.0732 (4)
O3	0.76239 (17)	0.7050 (3)	−0.14242 (3)	0.0665 (4)
H3X	0.826 (2)	0.831 (3)	−0.1453 (6)	0.088 (7)*
O4	0.59294 (16)	0.3310 (3)	−0.12109 (3)	0.0649 (4)
H4X	0.538 (2)	0.223 (4)	−0.1112 (6)	0.085 (7)*
O5	0.57612 (18)	0.0167 (3)	0.08346 (3)	0.0802 (5)
O6	0.73569 (15)	0.3321 (2)	0.09845 (3)	0.0581 (3)
N1	0.94801 (17)	0.9898 (3)	−0.08490 (4)	0.0550 (4)
C1	0.75303 (18)	0.5211 (3)	−0.02353 (4)	0.0439 (4)
C2	0.84387 (18)	0.7183 (3)	−0.03486 (4)	0.0461 (4)
H2	0.9009	0.8087	−0.0160	0.055*
C3	0.85022 (18)	0.7820 (3)	−0.07455 (4)	0.0445 (4)
C4	0.76560 (19)	0.6537 (3)	−0.10382 (4)	0.0464 (4)
C5	0.67344 (18)	0.4518 (3)	−0.09193 (4)	0.0466 (4)
C6	0.66815 (18)	0.3901 (3)	−0.05288 (4)	0.0466 (4)
H6	0.6063	0.2568	−0.0455	0.056*
C7	0.74503 (18)	0.4516 (3)	0.01813 (4)	0.0481 (4)
H7	0.7963	0.5539	0.0365	0.058*
C8	0.6712 (2)	0.2558 (3)	0.03185 (4)	0.0545 (4)
H8	0.6240	0.1503	0.0133	0.065*
C9	0.6564 (2)	0.1890 (3)	0.07324 (4)	0.0535 (4)
C10	0.7142 (2)	0.2802 (3)	0.14011 (4)	0.0560 (5)
H10A	0.7480	0.1120	0.1464	0.067*
H10B	0.6051	0.2955	0.1463	0.067*
C11	0.8094 (2)	0.4642 (4)	0.16361 (4)	0.0614 (5)
H11A	0.7801	0.6320	0.1559	0.074*
H11B	0.9190	0.4416	0.1584	0.074*
C12	0.7826 (2)	0.4277 (3)	0.20708 (4)	0.0518 (4)
C13	0.6843 (2)	0.5827 (4)	0.22689 (5)	0.0674 (5)
H13	0.6373	0.7156	0.2136	0.081*
C14	0.6541 (3)	0.5445 (4)	0.26612 (6)	0.0820 (7)
H14	0.5878	0.6519	0.2791	0.098*

C15	0.7209 (3)	0.3504 (4)	0.28595 (5)	0.0778 (6)
H15	0.6997	0.3239	0.3124	0.093*
C16	0.8195 (3)	0.1940 (4)	0.26687 (6)	0.0781 (6)
H16	0.8659	0.0613	0.2804	0.094*
C17	0.8500 (2)	0.2332 (4)	0.22766 (5)	0.0674 (5)
H17	0.9173	0.1263	0.2149	0.081*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0780 (9)	0.0685 (9)	0.0685 (8)	−0.0313 (7)	−0.0021 (7)	−0.0013 (6)
O2	0.0860 (9)	0.0773 (9)	0.0565 (7)	−0.0254 (8)	0.0078 (7)	0.0172 (6)
O3	0.0834 (10)	0.0783 (9)	0.0378 (6)	−0.0229 (8)	0.0016 (6)	0.0106 (6)
O4	0.0823 (9)	0.0784 (9)	0.0338 (6)	−0.0338 (8)	−0.0015 (6)	−0.0013 (6)
O5	0.1063 (11)	0.0848 (9)	0.0495 (7)	−0.0534 (9)	0.0003 (7)	0.0065 (6)
O6	0.0772 (8)	0.0644 (8)	0.0328 (5)	−0.0260 (6)	0.0032 (5)	−0.0010 (5)
N1	0.0568 (9)	0.0536 (8)	0.0549 (8)	−0.0082 (7)	0.0065 (7)	0.0045 (7)
C1	0.0467 (9)	0.0500 (9)	0.0350 (7)	−0.0057 (7)	0.0024 (6)	−0.0028 (6)
C2	0.0484 (9)	0.0505 (9)	0.0396 (8)	−0.0078 (8)	0.0007 (7)	−0.0044 (7)
C3	0.0446 (9)	0.0452 (9)	0.0440 (8)	−0.0079 (7)	0.0057 (7)	0.0019 (7)
C4	0.0498 (9)	0.0538 (10)	0.0359 (8)	−0.0032 (8)	0.0043 (7)	0.0024 (7)
C5	0.0512 (9)	0.0531 (9)	0.0356 (8)	−0.0085 (8)	0.0013 (7)	−0.0028 (7)
C6	0.0510 (9)	0.0499 (9)	0.0389 (8)	−0.0115 (8)	0.0037 (7)	0.0007 (7)
C7	0.0528 (10)	0.0554 (10)	0.0362 (8)	−0.0103 (8)	0.0017 (7)	−0.0047 (7)
C8	0.0662 (11)	0.0606 (10)	0.0365 (8)	−0.0194 (9)	−0.0004 (7)	−0.0036 (7)
C9	0.0624 (11)	0.0579 (10)	0.0400 (8)	−0.0158 (9)	0.0011 (8)	0.0003 (7)
C10	0.0725 (12)	0.0637 (11)	0.0318 (8)	−0.0157 (9)	0.0033 (7)	0.0045 (7)
C11	0.0797 (13)	0.0640 (11)	0.0406 (9)	−0.0193 (10)	0.0048 (8)	−0.0016 (8)
C12	0.0616 (11)	0.0551 (10)	0.0386 (8)	−0.0129 (9)	−0.0006 (7)	−0.0033 (7)
C13	0.0867 (14)	0.0624 (12)	0.0532 (10)	0.0046 (11)	0.0041 (10)	0.0006 (9)
C14	0.1038 (17)	0.0859 (15)	0.0573 (12)	0.0011 (13)	0.0190 (11)	−0.0158 (11)
C15	0.0981 (16)	0.0972 (16)	0.0382 (9)	−0.0266 (14)	0.0022 (10)	−0.0002 (10)
C16	0.0931 (16)	0.0859 (15)	0.0542 (11)	−0.0053 (13)	−0.0156 (11)	0.0169 (11)
C17	0.0723 (13)	0.0701 (13)	0.0598 (11)	0.0063 (10)	0.0004 (9)	0.0009 (9)

Geometric parameters (Å, °)

O1—N1	1.2189 (17)	C7—H7	0.9300
O2—N1	1.2420 (17)	C8—C9	1.458 (2)
O3—C4	1.3366 (18)	C8—H8	0.9300
O3—H3X	0.878 (15)	C10—C11	1.496 (2)
O4—C5	1.3544 (18)	C10—H10A	0.9700
O4—H4X	0.826 (15)	C10—H10B	0.9700
O5—C9	1.2105 (19)	C11—C12	1.511 (2)
O6—C9	1.3227 (19)	C11—H11A	0.9700
O6—C10	1.4569 (16)	C11—H11B	0.9700
N1—C3	1.447 (2)	C12—C17	1.374 (2)
C1—C2	1.377 (2)	C12—C13	1.375 (2)
C1—C6	1.404 (2)	C13—C14	1.378 (2)

C1—C7	1.465 (2)	C13—H13	0.9300
C2—C3	1.391 (2)	C14—C15	1.358 (3)
C2—H2	0.9300	C14—H14	0.9300
C3—C4	1.394 (2)	C15—C16	1.369 (3)
C4—C5	1.408 (2)	C15—H15	0.9300
C5—C6	1.367 (2)	C16—C17	1.379 (2)
C6—H6	0.9300	C16—H16	0.9300
C7—C8	1.320 (2)	C17—H17	0.9300
C4—O3—H3X	105.9 (14)	O6—C9—C8	114.86 (14)
C5—O4—H4X	109.0 (14)	O6—C10—C11	107.86 (13)
C9—O6—C10	115.93 (12)	O6—C10—H10A	110.1
O1—N1—O2	122.06 (14)	C11—C10—H10A	110.1
O1—N1—C3	119.26 (13)	O6—C10—H10B	110.1
O2—N1—C3	118.68 (14)	C11—C10—H10B	110.1
C2—C1—C6	118.29 (13)	H10A—C10—H10B	108.4
C2—C1—C7	120.60 (14)	C10—C11—C12	109.68 (14)
C6—C1—C7	121.11 (14)	C10—C11—H11A	109.7
C1—C2—C3	119.89 (14)	C12—C11—H11A	109.7
C1—C2—H2	120.1	C10—C11—H11B	109.7
C3—C2—H2	120.1	C12—C11—H11B	109.7
C2—C3—C4	122.14 (14)	H11A—C11—H11B	108.2
C2—C3—N1	117.69 (14)	C17—C12—C13	117.88 (15)
C4—C3—N1	120.17 (13)	C17—C12—C11	121.29 (16)
O3—C4—C3	126.12 (14)	C13—C12—C11	120.77 (16)
O3—C4—C5	116.37 (14)	C12—C13—C14	121.15 (19)
C3—C4—C5	117.51 (13)	C12—C13—H13	119.4
O4—C5—C6	124.00 (14)	C14—C13—H13	119.4
O4—C5—C4	116.01 (13)	C15—C14—C13	120.2 (2)
C6—C5—C4	119.99 (14)	C15—C14—H14	119.9
C5—C6—C1	122.18 (14)	C13—C14—H14	119.9
C5—C6—H6	118.9	C14—C15—C16	119.68 (18)
C1—C6—H6	118.9	C14—C15—H15	120.2
C8—C7—C1	125.48 (15)	C16—C15—H15	120.2
C8—C7—H7	117.3	C15—C16—C17	120.0 (2)
C1—C7—H7	117.3	C15—C16—H16	120.0
C7—C8—C9	126.34 (15)	C17—C16—H16	120.0
C7—C8—H8	116.8	C12—C17—C16	121.07 (19)
C9—C8—H8	116.8	C12—C17—H17	119.5
O5—C9—O6	123.07 (14)	C16—C17—H17	119.5
O5—C9—C8	122.07 (15)		
C6—C1—C2—C3	−0.3 (2)	C2—C1—C7—C8	−174.75 (17)
C7—C1—C2—C3	180.00 (15)	C6—C1—C7—C8	5.6 (3)
C1—C2—C3—C4	0.7 (2)	C1—C7—C8—C9	−177.28 (17)
C1—C2—C3—N1	−179.69 (14)	C10—O6—C9—O5	−3.5 (3)
O1—N1—C3—C2	1.2 (2)	C10—O6—C9—C8	175.86 (15)
O2—N1—C3—C2	−178.96 (15)	C7—C8—C9—O5	174.04 (19)
O1—N1—C3—C4	−179.13 (15)	C7—C8—C9—O6	−5.3 (3)
O2—N1—C3—C4	0.7 (2)	C9—O6—C10—C11	−178.53 (15)

C2—C3—C4—O3	178.60 (16)	O6—C10—C11—C12	176.41 (15)
N1—C3—C4—O3	−1.0 (3)	C10—C11—C12—C17	76.2 (2)
C2—C3—C4—C5	−0.9 (2)	C10—C11—C12—C13	−101.0 (2)
N1—C3—C4—C5	179.52 (14)	C17—C12—C13—C14	0.0 (3)
O3—C4—C5—O4	0.6 (2)	C11—C12—C13—C14	177.26 (18)
C3—C4—C5—O4	−179.90 (14)	C12—C13—C14—C15	−0.4 (3)
O3—C4—C5—C6	−178.84 (15)	C13—C14—C15—C16	0.6 (3)
C3—C4—C5—C6	0.7 (2)	C14—C15—C16—C17	−0.3 (3)
O4—C5—C6—C1	−179.71 (15)	C13—C12—C17—C16	0.3 (3)
C4—C5—C6—C1	−0.3 (3)	C11—C12—C17—C16	−176.97 (18)
C2—C1—C6—C5	0.1 (2)	C15—C16—C17—C12	−0.1 (3)
C7—C1—C6—C5	179.84 (15)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3X···O2	0.878 (15)	1.810 (18)	2.5807 (19)	145.3 (19)
O3—H3X···N1	0.878 (15)	2.43 (2)	2.914 (2)	115.5 (16)
O4—H4X···O5[i]	0.826 (15)	1.886 (15)	2.7088 (18)	174 (2)
C6—H6···O5[i]	0.93	2.48	3.180 (2)	132
C7—H7···O1[ii]	0.93	2.54	3.404 (2)	156
C15—H15···O4[iii]	0.93	2.60	3.507 (2)	166

Symmetry codes: (i) −*x*+1, −*y*, −*z*; (ii) −*x*+2, −*y*+2, −*z*; (iii) *x*, −*y*+1/2, *z*+1/2.

Fig. 1

Fig. 2