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2-Methyl-2-nitropropyl 3-(3,4-dihydroxyphenyl)-prop-2-enoate

Chun-Nian Xia,* Wei-Xiao Hu and Wei Zhou

College of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China

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

Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.135
Data-to-parameter ratio = 12.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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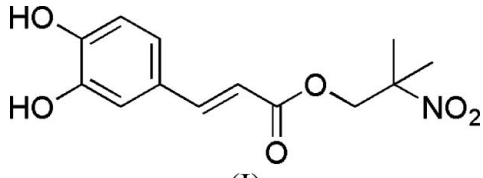
Crystals of the title compound, $C_{13}H_{15}NO_6$, were obtained from the modified Knoevenagel condensation reaction of 3,4-dihydroxybenzaldehyde and mono-2-methyl-2-nitropropyl malonate. The molecule is the *E* isomer with the usual bond lengths and angles. The crystal packing is stabilized by intermolecular O—H···O and C—H···O hydrogen bonds.

Comment

Caffeic acid and its derivatives are widely distributed in the plant kingdom (Chen *et al.*, 1999). These compounds are known to have anti-atherosclerotic, antibacterial, anti-inflammatory, antiproliferative, immunostimulatory, anti-oxidative, antiviral and neuroprotective properties (Son & Lewis, 2002). In a continuation of our research into the structure–activity relationships in caffeic acid derivatives (Xia & Hu, 2005), we have obtained the title compound, (I), as a product of the modified Knoevenagel condensation reaction of 3,4-dihydroxybenzaldehyde and mono-2-methyl-2-nitropropyl malonate.



(I)

The molecular structure of (I) is illustrated in Fig. 1. Its configuration is the *E* form. Selected bond lengths and angles are listed in Table 1. Atoms C1–C9 and O1–O3 are almost coplanar, deviating from the mean plane within 0.054 (2) Å.

The crystal packing (Fig. 2) is stabilized by O—H···O and C—H···O hydrogen bonds (Table 2). The molecules of the caffeic acid ester form stacks along the *a* axis in a head-to-head manner.

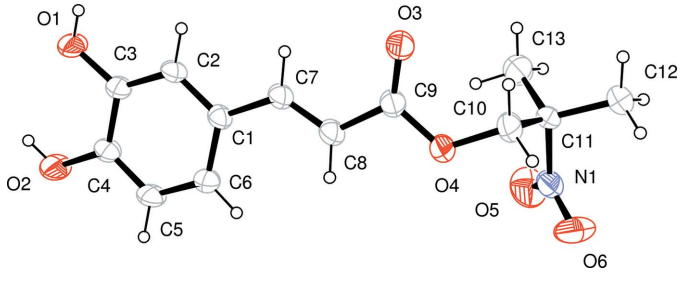


Figure 1
The structure of (I), with 30% probability displacement ellipsoids.

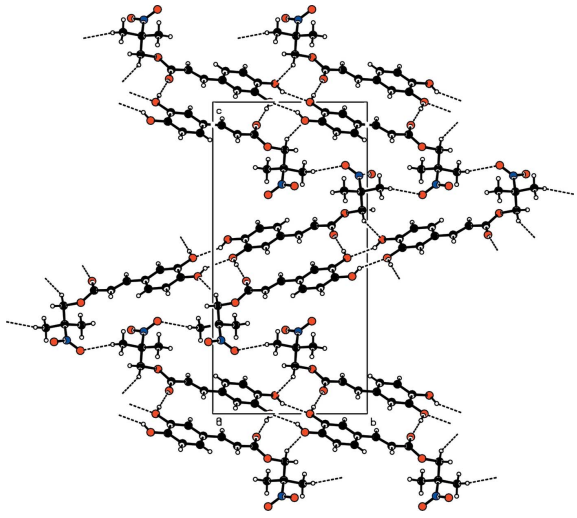


Figure 2
A packing diagram for (I), viewed along the *a* axis. Intermolecular hydrogen bonds are shown as dashed lines.

Experimental

3,4-Dihydroxybenzaldehyde (1.4 g, 10 mmol) and mono-2-methyl-2-nitropropyl malonate (4.8 g, 25 mmol) were dissolved in a mixture of pyridine (5 ml) and piperidine (0.2 ml). The solution was stirred at room temperature for 12 h and dried *in vacuo* to give a dark-brown mixture. The cooled mixture was dissolved in dry diethyl ether (30 ml), washed twice with a saturated solution of sodium bicarbonate (2 × 20 ml), and then with dilute hydrochloric acid and finally distilled water. The diethyl ether phase was dried over anhydrous $MgSO_4$ overnight. After removal of the drying agent, the solvent was distilled to obtain a light-brown crystalline product (4.0 g, 98%). Recrystallization from a mixture of benzene and diethyl ether (1:1) gave light-brown crystals of (I) (m.p. 417–420 K). Spectroscopic analysis: IR (KBr, ν, cm^{-1}): 3290, 1709, 1686, 1626, 1607, 1592, 1526, 1490, 1182, 1073, 779; ^{1}H NMR (DMSO-d_6, δ, p.p.m.): 9.64 (1H, *s*, OH), 9.13 (1H, *s*, OH), 7.48 (1H, *d*, J = 15.9 Hz, α-H), 7.05 (1H, *d*, J = 1.8 Hz, Ph—H), 7.02 (1H, *dd*, J = 1.8 and 8.1 Hz, Ph—H), 6.75 (1H, *d*, J = 8.1 Hz, Ph—H), 6.25 (1H, *d*, J = 15.9 Hz, β-H), 5.00 (2H, *s*, CH_2), 1.60 (6H, *s*, $2CH_3$).

Crystal data

$C_{13}H_{15}NO_6$
M_r = 281.26
Monoclinic, $P2_1/c$
a = 5.739 (4) Å
b = 10.7660 (17) Å
c = 22.112 (5) Å
β = 100.73 (4)°
V = 1342.3 (11) Å^3
Z = 4
D_x = 1.392 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10.2–12.6°
μ = 0.11 mm^{-1}
T = 295 (2) K
Plate, light brown
0.40 × 0.35 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.958, T_{max} = 0.987
2960 measured reflections
2406 independent reflections
1319 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 25.2°
$h = 0 \rightarrow 6$
$k = -12 \rightarrow 1$
$l = -26 \rightarrow 25$
3 standard reflections
frequency: 60 min
intensity decay: 0.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.135
S = 1.02
2406 reflections
192 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 0.3869P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0107 (18)

Table 1
Selected geometric parameters (Å, °).

O1—C3	1.376 (3)	O5—N1	1.201 (3)
O2—C4	1.358 (3)	O6—N1	1.212 (3)
O3—C9	1.205 (3)	N1—C11	1.537 (3)
O4—C9	1.347 (3)	C7—C8	1.316 (3)
O4—C10	1.445 (3)		
C9—O4—C10	119.1 (2)	O1—C3—C4	116.3 (2)
O5—N1—O6	123.3 (3)	O2—C4—C5	119.1 (2)
O5—N1—C11	118.6 (3)	O3—C9—O4	123.0 (2)
O6—N1—C11	118.0 (3)	O4—C10—C11	110.7 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1X···O3^{i}	0.82 (2)	1.96 (2)	2.779 (3)	175 (4)
C10—H10B···O2^{ii}	0.97	2.50	3.399 (3)	154
C12—H12B···O5^{iii}	0.96	2.50	3.417 (4)	161

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

The hydroxy H atoms were found in a difference Fourier map and refined isotropically, with O—H = 0.83 (1) Å. C-bound H atoms were positioned geometrically and refined as riding, with C—H = 0.93–0.97 Å and U_{iso}(H) = 1.2–1.5 U_{eq}(parent atom).

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4*, *PSI* and *EAC* (Enraf–Nonius, 1994); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1999); software used to prepare material for publication: *SHELXL97*.

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