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Ethyl *p*-Methoxycinnamate from *Kaempferia galanga L.* in Vietnam

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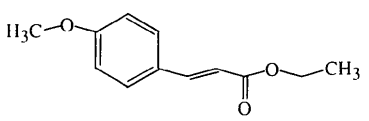
Abstract

The title compound, ethyl (*E*)-3-(4-methoxyphenyl)-propenoate, $C_{12}H_{14}O_3$, was isolated from the rhizomes of the Vietnamese plant *Kaempferia galanga L.* Its chemical identity was confirmed by an X-ray investigation, which established clearly a molecular *trans* configuration. As expected, the molecule is completely planar with a bonding geometry similar to that found in free cinnamic acid and related derivatives.

Comment

Ethyl *p*-methoxycinnamate, (I), was isolated from the essential oil of the fresh rhizomes of the Vietnamese plant *Kaempferia galanga L.* in high yield (3.1%) by steam distillation. The rhizomes of this plant are usually used as food spice. The therapeutic uses of *Kaempferia galanga L.* are well known (Dan *et al.*, 1990; Liangfeng, Yonghua, Baoling, Biyao & Nianhe, 1993). The rhizome is recommended for dyspepsia and is very useful for the treatment of headache, pectoral and abdominal pains due to cold-evil, vomiting and diarrhoea caused by cold-wetness evils, and toothache, functioning by promoting vital energy circulation, warming the middle and alleviating pain. An alcoholic maceration is employed externally through massage for the treatment of rheumatism. The structure of (I) was determined by X-ray diffraction in order to confirm its chemical identity and to establish its spatial structure.



(I)

The molecular structure of (I) is shown in Fig. 1, together with the atom-numbering scheme, confirming the *trans* arrangement with respect to the C7=C8 double bond. Bond lengths and angles are in the expected ranges previously found in non-substituted *trans*-cinnamic acid (Wierda, Feng & Barron, 1989; Bryan & Freyberg, 1975) and in various substituted *cis* and *trans* derivatives (Filippakis, Leiserowitz, Rabinovich & Schmidt, 1972; He, Shi & Su, 1993; Kim, Mang & Suh, 1988). The molecular skeleton is almost completely planar. The only torsion angle involving C and O atoms which differs by more than 3° from either 0 or 180° is C9—O92—C10—C11 of −173.9 (3)°.

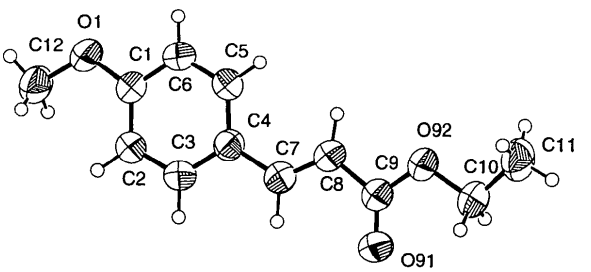


Fig. 1. The molecular structure of ethyl *p*-methoxycinnamate, showing the atomic numbering scheme (*ORTEP*; Johnson, 1965). Displacement ellipsoids are plotted at the 50% probability level.

In the crystal lattice, which displays a herringbone packing arrangement (Fig. 2), no close contacts were found that indicate any relevant intermolecular interaction.

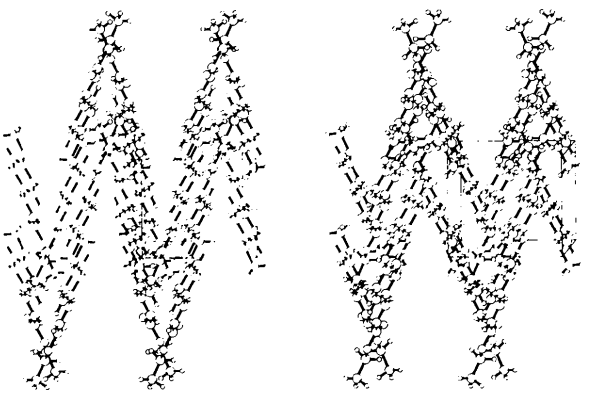


Fig. 2. Stereoscopic view of the molecular packing in a projection of the lattice onto the *yz* plane.

Experimental

The plants were harvested in October 1994, in Dac Lac Province, Vietnam. Voucher specimens were deposited in the Herbarium of Hue University, Vietnam. The oil was prepared by steam distillation of fresh rhizome materials for 6 h using glass equipment (oil yield 3.1%). The essential oil was dissolved in both chloroform and ethanol. The chloroform solution was stored at 277–279 K, from which ethyl *p*-methoxycinnamate crystallized. It was recrystallized from ethanol giving colourless plate-shaped crystals (m.p. 322.5 K). The oils were investigated by capillary gas chromatography (GC) using a HP 5890 Series II gas chromatograph equipped

with an FID detector. Separation was performed on a HP-1 capillary column. The column was temperature programmed as follows: 2 min at 333 K, then the temperature was raised at a rate of 4 K min^{-1} to 493 K and held for 20 min. The injector and detector temperatures were 523 and 553 K, respectively. Samples (0.2 µl of the oil solution in hexane, ratio 1:500) were injected by the splitless technique into helium carrier gas. Peak areas and retention times were measured by electronic integration. The relative amounts of individual components are based on the peak areas obtained, without FID response-factor correction. Temperature-programmed retention indices of the compounds were determined relative to the retention times of a series of *n*-alkanes (Dung, Tho, Dan & Leclercq, 1989; Baruah & Leclercq, 1993). The gas chromatogram showed the rhizome oil to contain about 66% of ethyl *p*-methoxycinnamate.

Crystal data

$C_{12}H_{14}O_3$
M_r = 206.24
Monoclinic
$P2_1/a$
a = 21.640 (2) Å
b = 7.866 (1) Å
c = 6.72 (1) Å
β = 96.16 (1)°
V = 1137 (2) Å^3
Z = 4
D_x = 1.205 Mg m^{-3}
Cu $K\alpha$ radiation (Ni filtered)
λ = 1.5418 Å
Cell parameters from 190 reflections
θ = 20–35°
μ = 0.713 mm^{-1}
T = 293 K
Plate
0.50 × 0.35 × 0.25 mm
Clear

Data collection

Stoe four-circle MicroVAX-controlled diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2059 measured reflections
1883 independent reflections
1642 observed reflections [$F > 2\sigma(F)$]
R_{int} = 0.018
θ_{max} = 63.96°
$h = 0 \rightarrow 25$
$k = 0 \rightarrow 9$
$l = -7 \rightarrow 7$
3 standard reflections
frequency: 90 min
intensity decay: 3%

Refinement

Refinement on F
R = 0.039
wR = 0.034
S = 0.418
1829 reflections
193 parameters
All H-atom parameters refined
Unit weights applied
$(\Delta/\sigma)_{max}$ = 0.577
$\Delta\rho_{max}$ = 0.113 e Å^{-3}
$\Delta\rho_{min}$ = −0.103 e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 1545 (68)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
C1	0.72508 (9)	0.0651 (3)	0.1648 (3)	0.056 (1)
O1	0.66938 (7)	0.0660 (2)	0.0474 (2)	0.074 (1)
C2	0.7781 (1)	−0.0144 (3)	0.1137 (4)	0.063 (1)
C3	0.8322 (1)	−0.0037 (3)	0.2449 (4)	0.063 (1)
C4	0.83458 (9)	0.0841 (3)	0.4238 (3)	0.054 (1)
C5	0.7800 (1)	0.1606 (3)	0.4720 (3)	0.060 (1)
C6	0.7261 (1)	0.1518 (3)	0.3438 (4)	0.062 (1)
C7	0.8940 (1)	0.0968 (3)	0.5516 (3)	0.060 (1)
C8	0.9049 (1)	0.1751 (3)	0.7254 (4)	0.062 (1)
C9	0.9684 (1)	0.1830 (3)	0.8297 (3)	0.060 (1)
O91	1.01392 (7)	0.1264 (3)	0.7658 (3)	0.083 (1)
O92	0.96968 (7)	0.2647 (2)	1.0042 (2)	0.0657 (9)
C10	1.0311 (1)	0.2862 (4)	1.1135 (4)	0.072 (2)
C11	1.0227 (2)	0.3611 (6)	1.3106 (5)	0.088 (2)
C12	0.6657 (1)	−0.0139 (6)	−0.1431 (5)	0.086 (2)

Table 2. *Selected geometric parameters (Å, °)*

C1—O1	1.368 (2)	C5—C6	1.377 (3)
C1—C2	1.381 (3)	C7—C8	1.319 (4)
C1—C6	1.381 (4)	C8—C9	1.475 (3)
O1—C12	1.420 (4)	C9—O91	1.201 (3)
C2—C3	1.391 (3)	C9—O92	1.335 (3)
C3—C4	1.382 (4)	O92—C10	1.458 (3)
C4—C5	1.394 (3)	C10—C11	1.479 (5)
C4—C7	1.471 (3)		
O1—C1—C2	124.2 (2)	C4—C5—C6	121.0 (2)
O1—C1—C6	115.5 (2)	C1—C6—C5	120.2 (2)
C2—C1—C6	120.3 (2)	C4—C7—C8	127.7 (2)
C1—O1—C12	118.5 (2)	C7—C8—C9	120.6 (2)
C1—C2—C3	118.7 (2)	C8—C9—O91	124.9 (2)
C2—C3—C4	122.1 (2)	C8—C9—O92	111.5 (2)
C3—C4—C5	117.7 (2)	O91—C9—O92	123.5 (2)
C3—C4—C7	119.3 (2)	C9—O92—C10	115.4 (2)
C5—C4—C7	122.9 (2)	O92—C10—C11	107.7 (2)

Data collection: Stoe software. Cell refinement: Stoe software. Data reduction: *Xtal*3.2 *ADDREF SORTRF* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *Xtal*3.2 *CRYLSQ*. Molecular graphics: *Xtal*3.2 *ORTEP* (Johnson, 1965) and *SCHAKAL*88 (Keller, 1988). Software used to prepare material for publication: *Xtal*3.2 *BONDLA CIFIO*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including inter- and intramolecular contact distances, have been deposited with the IUCr (Reference: KA1167). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-Hydroxyantipyrine

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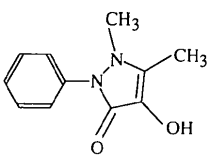
Abstract

The molecular structure of the title compound, 1,2-dihydro-4-hydroxy-1,5-dimethyl-2-phenyl-3*H*-pyrazol-3-one, $C_{11}H_{12}N_2O_2$, has been determined. Both rings are planar and make a dihedral angle of 42.5 (1)° with each other. In the crystal structure, the molecule is stabilized as a centrosymmetric hydrogen-bonded dimer. There is no conjugation between the phenyl and pyrazole rings.

Comment

The crystal and molecular structure of the title compound, (I), has been investigated in order to determine the conformation and crystal packing, and also to confirm its stereochemistry.



(I)

† Contribution No. 1356 of the Instituto de Química, UNAM.

A view of (I) with the numbering scheme is shown in Fig. 1. Bond lengths within the molecule correspond with the average C—C distance for a phenyl ring [1.378 (3) Å] and the angles are normal. The molecule consists of a phenyl (C1–C6) and a pyrazole ring (C7–C9, N1, N2), which are planar within 0.007 and 0.026 Å, respectively, and form an interplanar angle of 42.5 (1)°.

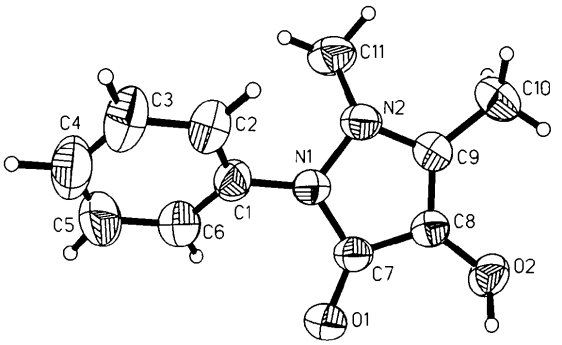


Fig. 1. The molecular structure of the title compound with the atom-labelling scheme and 50% probability displacement ellipsoids.

Fig. 2 shows a projection along the *c* axis. A hydrogen bond between the O2 hydroxy group and the carbonyl O1 atom of a neighbouring molecule constitutes the major intermolecular interaction and packing force. The two molecules are linked by a pair of O2—HO2···O1 hydrogen bonds across a crystallographic centre of inversion located at $(-x, -y, 1-z)$. The

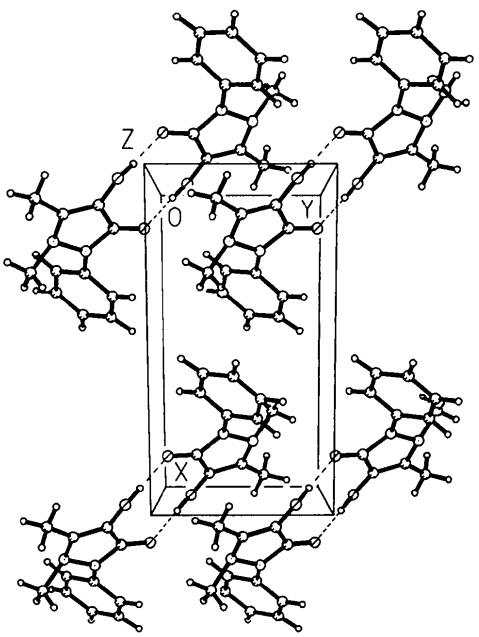


Fig. 2. A unit-cell drawing of the packing arrangement, with dashed lines indicating O—H···O intermolecular hydrogen-bonding interactions.