Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(*Z*)-3-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-2-propenoic acid

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.034
wR factor = 0.101
Data-to-parameter ratio = 12.1

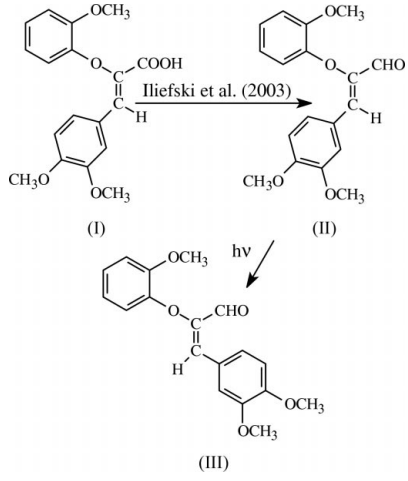
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 11 December 2003
Accepted 22 December 2003
Online 10 January 2004

In the crystal structure of the title compound, $C_{18}H_{18}O_6$, molecules are connected by strong O—H···O hydrogen bonds to form centrosymmetric dimers. The angle $C_{aryl}—C_{vinyl}—C_{vinyl}$ is considerably larger (130.2°) than could be expected (*ca* 120°). This is attributed to steric interactions. The structure of the title compound provides a basis for the assignment of the stereoisomers of 3-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-2-propenal.

Comment

A synthesis of the α-aryloxycinnamic acid, (I), has been described by Berndtsson & Lundquist (1977). It was shown by chemical means in a later study that (I) has the *Z* configuration (Brunow & Lundquist, 1984). The crystal structure of (I) reported in this paper constitutes final proof of the stereochemical assignment. The crystal structures of the *Z* forms of two related α-aryloxycinnamic acids have been reported (Lundquist *et al.*, 1987; Stomberg *et al.*, 1994).



A perspective drawing of (I) and the atomic numbering are shown in Fig. 1. The angles C2—C1—C7 [123.58 (17)°] and, in particular, C1—C7—C8 [130.22 (17)°] deviate from normal values (*ca* 120°). This can be attributed to steric interactions. Analogous deviations from normal bond angles were found in the crystal structures of (*Z*)-2-(2,6-dimethoxyphenoxy)-3-(3,4-dimethoxyphenyl)-2-propenoic acid (Lundquist *et al.*, 1987) and (*Z*)-3-(2-methoxyphenoxy)-3-(4-methoxyphenyl)-2-propenoic acid (Stomberg *et al.*, 1994). Aromatic ring C1–C6, the vinyl group and the carboxylic acid group are nearly coplanar [the r.m.s. deviation of fitted non-H atoms is 0.0538 Å and the largest deviation of 0.114 (1) Å is for O3]. The angle between this plane and the plane of the aromatic ring C11–C16 is

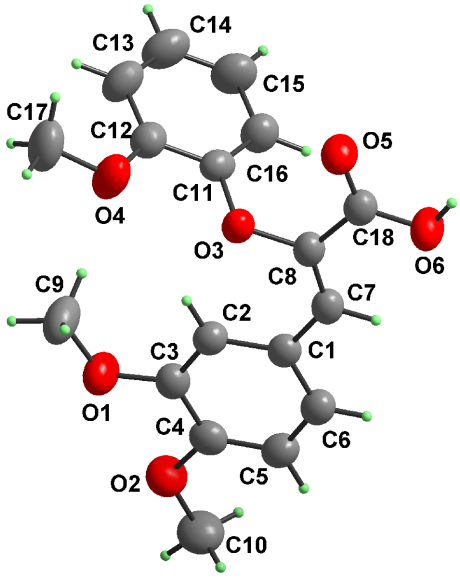


Figure 1
A perspective drawing of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

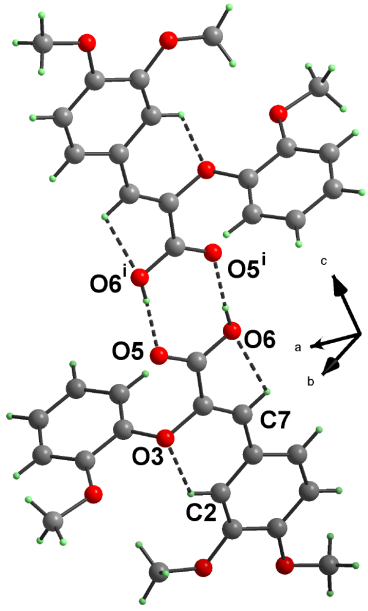


Figure 2
The hydrogen-bonding pattern of (I). A centrosymmetric dimer of the molecules is formed [symmetry code: (i) $-x, -y, 1-z$].

85.86 (6)°. The angle between the aromatic ring planes is 87.32 (7)°.

There are hydrogen bonds of the O—H···O and C—H···O types in the crystal structure of (I) (Table 1). The hydrogen-bonding pattern is presented in Fig. 2. On the first-level graph-set, following Bernstein *et al.* (1995) and Grell *et al.* (1999), very strong hydrogen bonds of the O—H···O type form an $R_2^2(8)$ ring, implying that (I) exists as dimers in which the molecules are attached to each other by strong hydrogen bonds. The dimers are centrosymmetric. The intramolecular hydrogen bonds C2—H2···O3 and C7—H7···O6 are described as $S(6)$ and $S(5)$, respectively. The assignments of graph-set descriptors were performed using *PLUTO* as described by Motherwell *et al.* (1999).

A conversion of (I) into (*Z*)-3-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-2-propenal, (II), has recently been reported by Iliefski *et al.* (2003). This aldehyde is a model compound representative of certain structural elements present in lignins from various plants deficient in cinnamyl alcohol dehydrogenase (Iliefski *et al.*, 2003; Kim *et al.*, 2003). The conversion of (I) into (II) is supposed to proceed without stereochemical changes, implying that the stereochemical assignment of (II) relies on the correctness of the assignment of (I). (*E*)-3-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-2-propenal, (III), could be prepared by irradiation of (II) in chloroform solution. The signal from the formyl group in the ^{1}H NMR spectrum of (III) is located at lower field (δ 9.78) than the corresponding signal from (II) (δ 9.46). This is what can be expected from comparisons with stereoisomers of other cinnamaldehydes, *e.g.* 3-(3,4-dimethoxyphenyl)-2-propenal (Li & Lundquist, 1995).

Experimental

The synthesis of (*Z*)-3-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-2-propenoic acid, (I), is described by Berndtsson & Lundquist (1977). The conversion of (I) into (*Z*)-3-(3,4-dimethoxyphenyl)-2-(2-methoxyphenoxy)-2-propenal (II) is described by Iliefski *et al.* (2003). (*E*)-3-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)-2-propenal, (III), was prepared by irradiation (wavelength range 290–320 nm) of a chloroform solution of (II) in a photochemical reactor (Corona Mini, Esshå Sweden) for 6 h. A mixture of (II) and (III) (ratio 80:20) was obtained. The *E* form (III) was separated from the mixture by column chromatography (SiO_2, eluant hexane–acetone, 5:1). Compound (III) was eluted before (II). ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 295 K) spectrum of (III): δ 3.87 (3H, *s*, OCH_3), 3.88 (3H, *s*, OCH_3), 3.92 (3H, *s*, OCH_3), 6.81 (1H, *d*, J = 1.7 Hz, Ar—H), 6.87 (1H, *d*, J = 8.3 Hz, Ar—H), 6.88–7.05 (5H, *m*, vinyl H and Ar—H) [the vinyl proton signal (*s*) was located at δ *ca* 6.90], 7.14 (1H, *ddd*, J = 1.7, 7.3 and 8.3 Hz, Ar—H), 9.78 (1H, *s*, CHO).

Crystal data

$C_{18}H_{18}O_6$
M_r = 330.32
Monoclinic, $P2_1/c$
a = 8.920 (7) Å
b = 12.053 (6) Å
c = 15.658 (6) Å
β = 101.70 (4)°
V = 1648.4 (16) Å^3
Z = 4
D_x = 1.331 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 18.6–23.1°
μ = 0.10 mm^{-1}
T = 296 (2) K
Prism, light yellow
0.60 × 0.50 × 0.30 mm

Data collection

Rigaku AFC-6 diffractometer
2θ-ω scans
Absorption correction: none
3100 measured reflections
2901 independent reflections
1919 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 25.0°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 14$
$l = -18 \rightarrow 18$
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0335P)^2 + 0.3604P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.101$	$\Delta\rho_{max} = 0.21$ e Å^{-3}
$S = 1.04$	$\Delta\rho_{min} = -0.13$ e Å^{-3}
2901 reflections	Extinction correction: *SHELXTL*
240 parameters	Extinction coefficient: 0.0178 (15)
H-atom parameters constrained	

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6A···O5^{i}	0.82	1.79	2.607 (2)	173
C2—H2···O3	0.93	2.31	2.941 (2)	125
C7—H7···O6	0.93	2.42	2.787 (2)	103

Symmetry code: (i) $-x, -y, 1-z$.

H atoms were refined isotropically and were constrained to an ideal geometry using an appropriate riding model. For the OH group, the O—H distance (0.82 Å) and C—O—H angle (109.5°) were fixed, while the torsion angle was allowed to refine, with the starting position based on a circular Fourier synthesis. For methyl groups, the C—H distances (0.96 Å) and C—C—H angles (109.5°) were kept fixed, while the torsion angles were allowed to refine, with the starting position based on a threefold averaged circular Fourier synthesis. For aromatic H atoms, the C—H distance was fixed at 0.93 Å. U_{iso} values were not restrained and were refined freely.

Data collection: *TEXSAN–TEXRAY* (Molecular Structure Corporation, 1985); cell refinement: *TEXSAN–TEXRAY*; data reduction: *TEXSAN–TEXRAY*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2000); software used to prepare material for publication: *SHELXTL*.

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