Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1204). Services for accessing these data are described at the back of the journal.

References

Aggarwal, R. C., Singh, N. K. & Singh, R. P. (1981). *Inorg. Chem.* **20**, 2794–2798.

Dutta, R. L. & Das, B. R. (1985). *Indian J. Chem. Ser. A*, **24**, 493–497.

Dutta, R. L. & Hossain, M. M. (1985). *J. Sci. Ind. Res.* **44**, 635–674.

Dutta, R. L. & Sarkar, A. K. (1981). *J. Inorg. Nucl. Chem.* **43**, 57–67.

Siemens (1994). *XSCANS*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1995). *SHELXTL*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Acta Cryst. (1998). C**54**, 1929–1934

Investigation of Three Stilbene Derivatives by X-ray Crystallography and NMR Spectroscopy

ROLF STOMBERG,[a] SHIMING LI,[b] KNUT LUNDQUIST[b] AND BO ALBINSSON[c]

[a]*Department of Inorganic Chemistry, University of Gothenburg, S-412 96 Gothenburg, Sweden,* [b]*Department of Organic Chemistry, Chalmers University of Technology, S-412 96 Gothenburg, Sweden, and* [c]*Department of Physical Chemistry, Chalmers University of Technology, S-412 96 Gothenburg, Sweden. E-mail: rolf@inoc.chalmers.se*

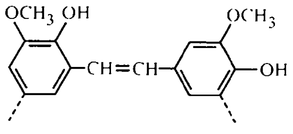
(*Received 6 March 1998; accepted 29 June 1998*)

Abstract

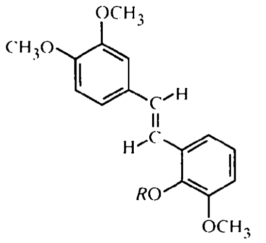
Crystal structure determinations demonstrate unambiguously the steric assignments of (*Z*)-2-hydroxy-3,3′,4′-trimethoxystilbene ($C_{17}H_{18}O_4$), (*E*)-2-hydroxy-3,3′,4′-trimethoxystilbene ($C_{17}H_{18}O_4$) and (*E*)-2-acetoxy-3,3′,4′-trimethoxystilbene ($C_{19}H_{20}O_5$). ^{13}C NMR data and UV data for the compounds are also reported. The steric assignments of structurally related compounds described in the literature are discussed on the basis of the crystallographic and spectral results.

Comment

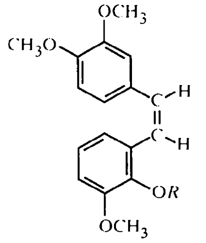
Stilbenes of type (1) have been detected in spent liquors from alkaline pulping (Gierer & Lindeberg, 1980; Niemelä, 1990; see also Miller & Schuerch, 1968). Experiments with lignin model compounds suggest that such stilbenes originate from structural elements in lignin of the phenylcoumaran type (Adler *et al.*, 1964; Yoon *et al.*, 1981). Conversion of such structural elements to stilbenes of type (1) also occurs under acid conditions (Li & Lundquist, 1998). Model experiments carried out by Lee *et al.* (1990) indicate that stilbenes of type (1) are formed on mechanical pulping. (*E*)-2-Hydroxy-3,3′,4′-trimethoxystilbene, (2*a*), and (*Z*)-2-hydroxy-3,3′,4′-trimethoxystilbene, (3*a*), are model compounds representative of lignin degradation products of type (1). To obtain unambiguous proof of the steric assignments of these stilbenes, crystal structure determinations of their acetate derivatives [*i.e.* compounds (2*b*) and (3*b*)] were carried out (Li *et al.*, 1996). The crystal structures of (2*b*) and the non-derivatized compounds [(2*a*) and (3*a*)] are described in this paper. The crystal structure determinations of (2*a*), (3*a*), (2*b*) and (3*b*) together with previously published NMR data (Li *et al.*, 1996; Li & Lundquist, 1998) and ^{13}C NMR and UV data reported in this paper provide a basis for the steric assignment of stilbenes of type (1). From the results of the studies of the stereochemistry of (2) and (3), it can be concluded that the *Z* form (3*b*) has incorrectly been assigned as the *E* form in two papers (Gierer *et al.*, 1974; Lee *et al.*, 1990).



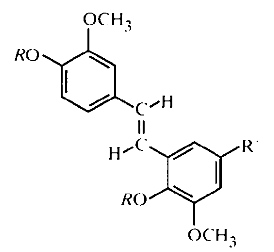
(1)



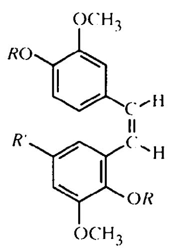
(2*a*) *R* = H
(2*b*) *R* = COCH$_3$



(3*a*) *R* = H
(3*b*) *R* = COCH$_3$



(4*a*) *R* = *R*′ = H
(4*b*) *R* = COCH$_3$, *R*′ = H
(6*a*) *R* = H, *R*′ = CH$_3$
(6*b*) *R* = COCH$_3$, *R*′ = CH$_3$
(8*a*) *R* = H, *R*′ = CH$_2$CH$_2$CH$_2$OH
(8*b*) *R* = COCH$_3$, *R*′ = CH$_2$CH$_2$CH$_2$OH



(5*a*) *R* = *R*′ = H
(5*b*) *R* = COCH$_3$, *R*′ = H
(7*a*) *R* = H, *R*′ = CH$_3$
(7*b*) *R* = COCH$_3$, *R*′ = CH$_3$

Both the *E* form (4*a*) and the *Z* form (5*a*) of a stilbene of type (1) have been detected in a kraft pulping liquor (Gierer & Lindeberg, 1980). The steric

Acta Crystallographica Section C
ISSN 0108-2701 © 1998

assignments of ($4a$) and ($5a$) are primarily based on the synthetic methods used for their preparation (Nelson & Wallis, 1973; Gierer *et al.*, 1974; Lonsky *et al.*, 1976). It is notable that the ^{1}H NMR signal from one of the methoxyl groups in the acetate derivative ($5b$) is located at comparatively high field (δ 3.45) (Gierer *et al.*, 1974). A methoxyl signal at high field (δ 3.56) is also found in the spectrum of ($3b$). Considerations based on the conformation of ($3b$) (Li *et al.*, 1996) suggest that the signal from one of the methoxyl groups is shifted upfield due to ring current effects. Deacetylated ($3b$), *i.e.* stilbene ($3a$), adopted a conformation [angle between the ring planes, 59.05 (6)°; torsion angles C2—C1—C7—C8 and C7—C8—C11—C16 −141.0 (2)° and 35.8 (3)°, respectively] that in certain respects resembled that of ($3b$) and exhibited a methoxyl signal at high field (δ 3.60) (Li & Lundquist, 1998). It seems that it is generally true that the signal from one of the methoxyl groups is shifted upfield in *Z* forms of stilbenes of type (1). Gierer & Lindeberg (1980) have reported the isolation of the *Z* isomer ($7a$) as the acetate derivative ($7b$) from a kraft pulping liquor. The methoxyl signals in the ^{1}H NMR spectrum of the obtained product are located at δ 3.82 and δ 3.85. Provided the structure of the isolated product is the correct one, this means that ($7b$) constitutes an exception in the respect that it does not exhibit a methoxyl signal at high field (*ca* δ 3.5). ^{13}C NMR data of ($4b$), ($5b$), ($6b$) and ($7b$) have been published by Mörck & Kringstad (1985). It seems that the steric assignments of ($6b$) and ($7b$) made by Mörck & Kringstad (1985) are based on comparisons with ($4b$) and ($5b$) and, to some extent, with ($8b$); the assignment of this latter compound is in turn based on UV and IR spectral comparisons of ($8a$) with other stilbenes (Falkehag *et al.*, 1966). The assignment of ($8a$) is further supported by UV spectral comparisons with ($2a$) and ($3a$) [UV data for ($2a$) and ($3a$) are given below]. Yoon *et al.* (1981) prepared the *E* form ($6a$) by alkaline cooking of a lignin model compound; their steric assignment is based on the analogous formation of ($8a$) on alkaline cooking of dihydrodehydrodiconiferyl alcohol (Adler *et al.*, 1964; Falkehag *et al.*, 1966). Further investigations of the stereochemistry of (4)–(8) based on spectral comparisons with (2) and (3) requires access to additional (or more precise) spectral data for (4)–(8).

The carbon skeletons of (*E*)-stilbenes are nearly planar provided they are lacking substituents in the

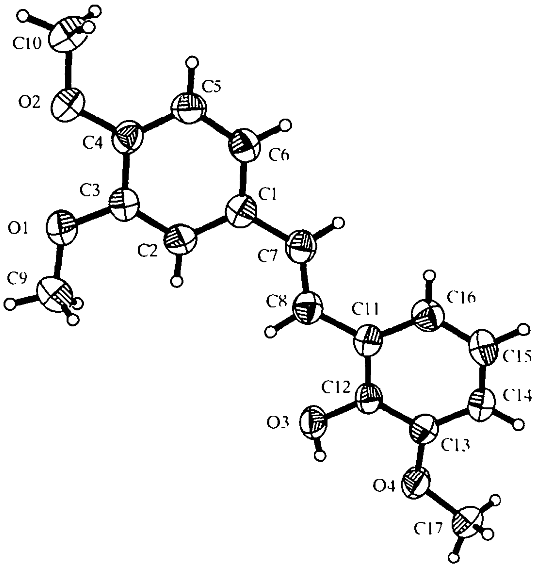


Fig. 1. A perspective drawing of ($2a$) showing the numbering of the non-H atoms. The displacement ellipsoids are given at the 50% probability level and the H atoms are shown as small spheres of arbitrary diameter.

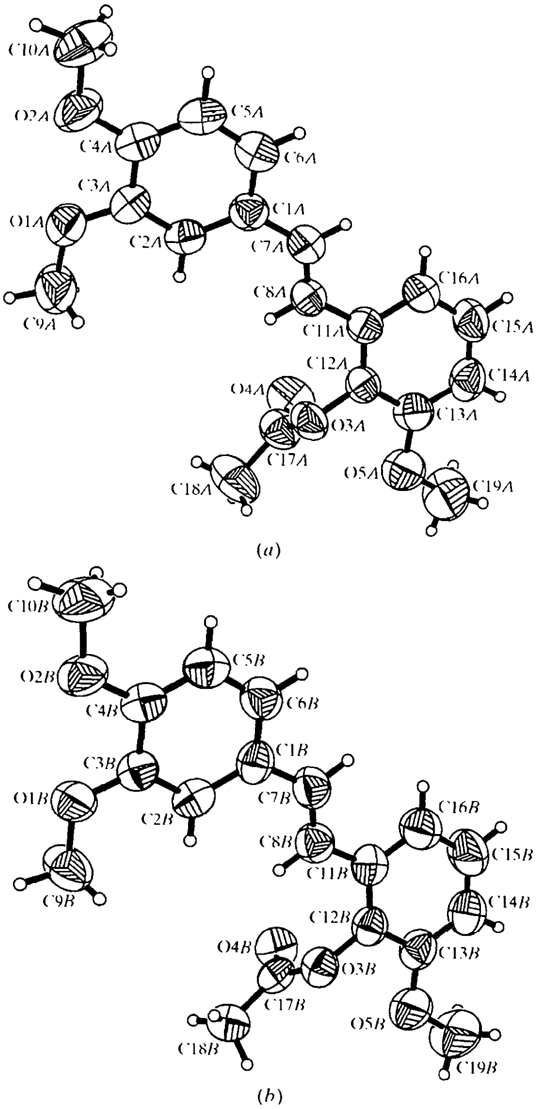


Fig. 2. Perspective drawings of (*a*) molecule *A* of $(2b)_{\text{tric}}$ and (*b*) molecule *B* of $(2b)_{\text{tric}}$ showing the numbering of the non-H atoms. The displacement ellipsoids are given at the 50% probability level and the H atoms are shown as small spheres of arbitrary diameter.

ring positions adjacent to the ethylenic group [*e.g.* (*E*)-stilbene (Ogawa *et al.*, 1992) and (*E*)-4,4′-dimethoxystilbene (Theocharis *et al.*, 1984)]. Disregarding some exceptions [*e.g.* the tetraacetate of chlorophorin (Krohn *et al.*, 1986)], (*E*)-stilbenes with substituents in the positions adjacent to the ethylenic group exhibit deviations from planarity (see, for example, Ogawa *et al.*, 1992). The (*E*)-stilbene (2*a*) adopts a conformation that deviates only slightly from planarity [angle between the ring planes 13.6 (1)°; torsion angles C2—C1—C7—C8 and C7—C8—C11—C16 −6.5 (4)° and 17.4 (3)°, respectively]. The acetate of this stilbene, (2*b*), exists in two crystalline modifications: a triclinic form melting at 374–375 K (from toluene) [$(2b)_{\rm tric}$] (Li *et al.*, 1996) and a monoclinic form melting at 389–390 K (from ethyl acetate) [$(2b)_{\rm mon}$]. In the asymmetric unit of the $(2b)_{\rm tric}$ crystals there are two molecules, *A* and *B*, with similar but different conformations. The carbon skeletons of both $(2b)_{{\rm tric},A}$ [angle between the ring planes 12.1 (1)°; torsion angles C2—C1—C7—C8 and C7—C8—C11—C16 2.2 (4)° and −13.5 (4)°, respectively] and $(2b)_{{\rm tric},B}$ [angle between the ring planes 10.82 (5)°; torsion angles C2—C1—C7—C8 and C7—C8—C11—C16 −2.3 (3)° and −8.3 (5)°, respectively] are nearly planar. The monoclinic form of the acetate [$(2b)_{\rm mon}$] adopts a non-planar conformation [angle between the ring planes 51.13 (8)°; torsion angles C2—C1—C7—C8 and C7—C8—C11—C16 22.6 (3)° and 27.2 (3)°, respectively].

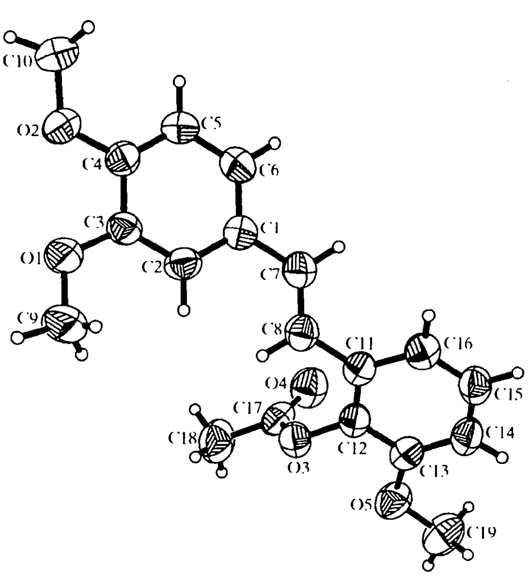


Fig. 3. A perspective drawing of $(2b)_{\rm mon}$ showing the numbering of the non-H atoms. The displacement ellipsoids are given at the 50% probability level and the H atoms are shown as small spheres of arbitrary diameter.

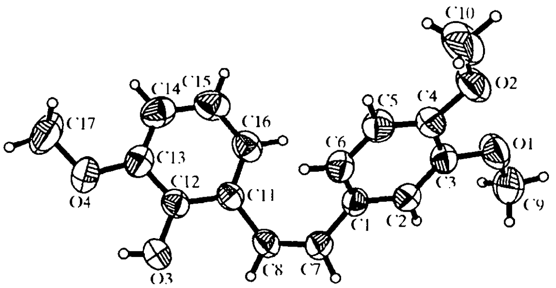


Fig. 4. A perspective drawing of (3*a*) showing the numbering of the non-H atoms. The displacement ellipsoids are given at the 50% probability level and the H atoms are shown as small spheres of arbitrary diameter.

In both (2*a*) and (3*a*) there is an intramolecular hydrogen bond between the hydroxy group and the adjacent methoxyl-O atom [O3···O4 is 2.648 (2) Å in (2*a*) and 2.665 (2) Å in (3*a*)]. In (2*a*) there is also a relatively weak intermolecular hydrogen bond [O3···O4 $(-x, y, \frac{1}{2}-z)$ 2.879 (2) Å].

Experimental

The acetate of stilbene (3*a*) [*i.e.* (3*b*)] was prepared by decarboxylation of (*E*)-3-(2-acetoxy-3-methoxyphenyl)-2-(3,4-dimethoxyphenyl)propenoic acid (2.5 g) using a modification (the reaction time was 15 instead of 30 min) of a previously described procedure (Li *et al.*, 1996). Work-up according to Li *et al.* (1996) gave a fraction of (3*b*) (1.1 g) contaminated with small amounts of the *E* isomer. Pure (3*b*) (m.p. 373–374 K) was obtained by recrystallization from ethanol. ^{13}C NMR (100.6 MHz, CDCl$_3$, 293 K, TMS): δ 20.5 (CH$_3$CO), 55.4 (OCH$_3$), 55.7 (OCH$_3$), 55.9 (OCH$_3$), 122.8 (vinyl C), 132.1 (vinyl C), additional signals in the range 110–152 (110.4, 110.7, 112.0, 121.9, 122.0, 126.0, 129.2, 132.6, 137.9, 148.1, 148.2, 151.5) (aromatic C), 168.8 (CO). The vinyl-C atom signals were assigned by HETCOR experiments. Compound (3*b*) (0.40 g) was deacetylated by treatment with LiAlH$_4$ in tetrahydrofuran. The crude product (0.34 g) was contaminated with small amounts of the *E* isomer. Pure (3*a*) (m.p. 373–374 K) was obtained by crystallizations from ethanol and ethyl acetate. ^{13}C NMR spectrum (100.6 MHz, CDCl$_3$, 293 K, TMS): δ 55.4 (OCH$_3$), 55.7 (OCH$_3$), 56.0 (OCH$_3$), 109–149 (109.3, 110.5, 111.5, 119.1, 122.0, 122.1, 123.0, 123.9, 129.8, 130.6, 143.2, 146.6, 148.08, 148.11) (aromatic and vinyl C).

Stilbene (2*a*) was prepared by acidolysis of *erythro*-1-(3,4-dimethoxyphenyl)-2-(2-hydroxy-3-methoxyphenyl)-1,3-propanediol (Li & Lundquist 1998). M.p. 438 K (from ethyl acetate); Nelson & Wallis (1973) report m.p. 437–438 K. ^{13}C NMR spectrum of the acetate derivative (2*b*) (m.p. 389–390 K, from ethyl acetate) (100.6 MHz, CDCl$_3$, 293 K, TMS): δ 20.3 (CH$_3$CO), 55.6 (OCH$_3$), 55.68 (OCH$_3$), 55.73 (OCH$_3$), 108–152 (109.0, 110.5, 111.0, 117.5, 119.6, 119.7, 126.1, 130.0, 130.9, 131.1, 137.2, 148.8, 148.9, 151.2) (aromatic and vinyl C), 168.6 (CO).

UV spectra of (2*a*) and (3*a*) in ethanol: the (*E*)-stilbene (2*a*) had a weakly structured lowest absorption band at $\lambda = 324$ nm ($\varepsilon = 26500$ M^{-1}cm^{-1}) and the (*Z*)-stilbene (3*a*) had a broad unstructured band at $\lambda = 290$ nm ($\varepsilon = 13200$ M^{-1}cm^{-1}).

Compound (2*a*)

Crystal data

$C_{17}H_{18}O_4$	Mo *Kα* radiation
$M_r = 286.31$	$\lambda = 0.71073$ Å

Orthorhombic
Pbcn
$a = 23.5530\,(5)$ Å
$b = 5.3933\,(1)$ Å
$c = 22.9996\,(3)$ Å
$V = 2921.61\,(7)$ Å^3
$Z = 8$
$D_x = 1.302$ Mg m^{-3}
D_m not measured

Cell parameters from 8192 reflections
$\theta = 1.73–25.13°$
$\mu = 0.092$ mm^{-1}
$T = 293\,(2)$ K
Rod
0.55 × 0.15 × 0.12 mm
Colourless

Data collection

Siemens SMART CCD diffractometer
ω oscillation 0.30°, 30 s frames
Absorption correction: none
17825 measured reflections
2451 independent reflections

2058 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.079$
$\theta_{\rm max} = 25.13°$
$h = -26 \rightarrow 26$
$k = -6 \rightarrow 6$
$l = -26 \rightarrow 25$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.121$
$S = 1.075$
2450 reflections
195 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0589P)^2 + 0.8513P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.159$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.188$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0038 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (2a)*

C1—C7	1.463 (2)	C9—O1	1.419 (2)
C3—O1	1.375 (2)	C10—O2	1.421 (2)
C4—O2	1.369 (2)	C12—O3	1.369 (2)
C7—C8	1.323 (2)	C13—O4	1.371 (2)
C8—C11	1.469 (2)	C17—O4	1.427 (2)
C2—C1—C7	123.2 (2)	C7—C8—C11	125.8 (2)
O1—C3—C2	125.3 (2)	O3—C12—C11	118.46 (14)
O2—C4—C5	124.8 (2)	O4—C13—C14	125.40 (15)
C8—C7—C1	128.4 (2)		
C2—C1—C7—C8	−6.4 (3)	C7—C8—C11—C16	17.4 (3)
C1—C7—C8—C11	−175.0 (2)		

Compound $(2b)_{\rm tric}$

Crystal data

$C_{19}H_{20}O_5$
$M_r = 328.35$
Triclinic
$P\overline{1}$
$a = 12.4168\,(7)$ Å
$b = 12.9562\,(7)$ Å
$c = 12.2833\,(7)$ Å
$\alpha = 97.641\,(7)°$
$\beta = 113.547\,(7)°$
$\gamma = 77.483\,(7)°$
$V = 1766.1\,(3)$ Å^3
$Z = 4$
$D_x = 1.235$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 20 reflections
$\theta = 21.8–23.5°$
$\mu = 0.734$ mm^{-1}
$T = 293\,(2)$ K
Fragment of prism
0.68 × 0.43 × 0.25 mm
Colourless

Data collection

Syntex $P2_1$ diffractometer
$\omega–2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min} = 0.607$, $T_{\rm max} = 0.832$
6924 measured reflections
5635 independent reflections
3632 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.047$
$\theta_{\rm max} = 62.55°$
$h = 0 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 12$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.153$
$S = 1.033$
5633 reflections
421 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.061P)^2 + 0.4466P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.043$
$\Delta\rho_{\rm max} = 0.315$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.143$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0102 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for $(2b)_{\rm tric}$*

C1A—C7A	1.464 (4)	C1B—C7B	1.465 (3)
C3A—O1A	1.365 (3)	C3B—O1B	1.364 (3)
C4A—O2A	1.367 (3)	C4B—O2B	1.368 (3)
C7A—C8A	1.310 (4)	C7B—C8B	1.300 (4)
C8A—C11A	1.480 (3)	C8B C11B	1.491 (4)
C9A—O1A	1.414 (3)	C9B—O1B	1.422 (3)
C10A—O2A	1.420 (3)	C10B—O2B	1.427 (4)
C12A—O3A	1.398 (3)	C12B—O3B	1.396 (3)
C13A—O5A	1.369 (3)	C13B—O5B	1.358 (3)
C17A—O4A	1.180 (3)	C17B—O4B	1.189 (3)
C17A—O3A	1.378 (3)	C17B—O3B	1.349 (3)
C17A—C18A	1.472 (5)	C17B—C18B	1.488 (4)
C19A—O5A	1.396 (4)	C19B—O5B	1.419 (4)
C2A—C1A—C7A	122.9 (2)	C2B—C1B—C7B	122.88 (12)
O1A—C3A—C2A	125.4 (2)	O1B—C3B—C2B	125.7 (2)
C5A—C4A—O2A	124.7 (2)	C5B—C4B—O2B	124.5 (2)
C8A—C7A—C1A	129.1 (2)	C8B—C7B—C1B	127.2 (2)
C7A—C8A—C11A	126.0 (2)	C7B—C8B—C11B	126.0 (3)
C12A—C11A—C8A	120.4 (2)	C12B—C11B—C8B	118.8 (2)
C11A—C12A—O3A	120.7 (2)	C11B—C12B—O3B	119.4 (2)
O5A—C13A—C14A	126.2 (2)	O5B—C13B—C14B	126.2 (3)
O4A—C17A—O3A	122.3 (2)	O4B—C17B—O3B	123.4 (2)
O4A—C17A—C18A	127.1 (3)	O4B—C17B—C18B	126.8 (3)
O3A—C17A—C18A	110.5 (3)	O3B—C17B—C18B	109.9 (2)
C2A—C1A—C7A—C8A	2.2 (4)		
C1A—C7A—C8A—C11A	178.7 (2)		
C7A—C8A—C11A—C16A	−13.5 (4)		
C11A—C12A—O3A—C17A	112.0 (3)		
C2B—C1B—C7B—C8B	−2.3 (3)		
C1B—C7B—C8B—C11B	−179.2 (2)		
C7B—C8B—C11B—C16B	−8.3 (5)		
C11B—C12B—O3B—C17B	102.2 (3)		

Compound $(2b)_{\rm mon}$

Crystal data

$C_{19}H_{20}O_5$
$M_r = 328.35$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Monoclinic
$P2_1/c$
$a = 12.8655$ (2) Å
$b = 12.0107$ (2) Å
$c = 12.4608$ (1) Å
$\beta = 117.031$ (1)°
$V = 1715.15$ (4) Å^3
$Z = 4$
$D_x = 1.272$ Mg m^{-3}
D_m not measured

Cell parameters from 4713 reflections
$\theta = 1.78$–25.13°
$\mu = 0.092$ mm^{-1}
$T = 293$ (2) K
Plate
0.40 × 0.22 × 0.09 mm
Colourless

Data collection

Siemens SMART CCD diffractometer
ω oscillation 0.30°, 15 s frames
Absorption correction: none
11226 measured reflections
2844 independent reflections

2005 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.036$
$\theta_{\rm max} = 25.13°$
$h = -15 \rightarrow 14$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.118$
$S = 1.124$
2842 reflections
222 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0399P)^2 + 0.5648P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.004$
$\Delta\rho_{\rm max} = 0.191$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.133$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.019 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for* $(2b)_{mon}$

C1—C7	1.466 (3)	C12—O3	1.408 (2)
C3—O1	1.368 (2)	C13—O5	1.374 (3)
C4—O2	1.365 (2)	C17—O4	1.195 (3)
C7—C8	1.325 (3)	C17—O3	1.359 (3)
C8—C11	1.466 (3)	C17—C18	1.491 (3)
C9—O1	1.424 (3)	C19—O5	1.428 (3)
C10—O2	1.426 (3)		
C2—C1—C7	121.0 (2)	C11—C12—O3	118.9 (2)
O1—C3—C2	124.9 (2)	O5—C13—C14	125.2 (2)
O2—C4—C5	125.9 (2)	O4—C17—O3	122.6 (2)
C8—C7—C1	126.5 (2)	O4—C17—C18	126.3 (2)
C7—C8—C11	125.9 (2)	O3—C17—C18	111.1 (2)
C12—C11—C8	120.9 (2)		
C2—C1—C7—C8	22.6 (3)	C7—C8—C11—C16	27.2 (3)
C1—C7—C8—C11	−178.0 (2)	C11—C12—O3—C17	98.8 (2)

Compound (3*a*)

Crystal data

$C_{17}H_{18}O_4$
$M_r = 286.31$
Monoclinic
Cc
$a = 21.2854$ (1) Å
$b = 7.8608$ (1) Å
$c = 9.3555$ (2) Å
$\beta = 100.229$ (1)°
$V = 1540.48$ (4) Å^3
$Z = 4$
$D_x = 1.235$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 4489 reflections
$\theta = 1.94$–25.19°
$\mu = 0.087$ mm^{-1}
$T = 293$ (2) K
Prism
0.51 × 0.43 × 0.37 mm
Colourless

Data collection

Siemens SMART CCD diffractometer
ω oscillation 0.30°, 10 s frames
Absorption correction: none
5099 measured reflections
2403 independent reflections

2323 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\rm max} = 25.19°$
$h = -24 \rightarrow 25$
$k = -9 \rightarrow 9$
$l = -11 \rightarrow 11$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.074$
$S = 1.048$
2403 reflections
195 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0385P)^2 + 0.267P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.089$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.099$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.013 (1)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 4. *Selected geometric parameters (Å, °) for (3a)*

C1—C7	1.474 (2)	C9—O1	1.411 (3)
C3—O1	1.373 (2)	C10—O2	1.427 (3)
C4—O2	1.368 (2)	C12—O3	1.361 (2)
C7—C8	1.334 (2)	C13—O4	1.368 (2)
C8—C11	1.471 (2)	C17—O4	1.414 (3)
C2—C1—C7	118.81 (13)	C7—C8—C11	128.52 (15)
O1—C3—C2	124.56 (14)	C12—C11—C8	119.13 (14)
O2—C4—C5	125.76 (15)	O3—C12—C11	118.54 (13)
C8—C7—C1	129.46 (14)	O4—C13—C14	125.7 (2)
C2—C1—C7—C8	−141.0 (2)	C7—C8—C11—C16	35.8 (3)
C1—C7—C8—C11	8.4 (3)		

For (2*a*), $(2b)_{\rm mon}$ and (3*a*), data collection: *SMART* (Siemens, 1994*a*); cell refinement: *SAINT* (Siemens, 1994*b*); data reduction: *SAINT*, *XPREP* (Siemens, 1996); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*93; molecular graphics: *XP* (Siemens, 1994*c*); software used to prepare material for publication: *SHELXL*93. For $(2b)_{\rm tric}$, data collection: *TEXSAN* (Molecular Structure Corporation, 1995); cell refinement: *TEXSAN*; data reduction: *TEXSAN*; program(s) used to solve structure: *SHELXS*86; program(s) used to refine structure: *SHELXL*93; molecular graphics: *XP*; software used to prepare material for publication: *SHELXL*93.

We are grateful to Dr Vratislav Langer for valuable technical help.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1025). Services for accessing these data are described at the back of the journal.

References

Adler, E., Marton, J. & Falkehag, I. (1964). *Acta Chem. Scand.* **18**, 1311–1312.

Falkehag, I., Marton, J. & Adler, E. (1966). *Adv. Chem. Ser.* **59**, 75–89.

Gierer, J., Lenic, J., Norén, I. & Szabo-Lin, I. (1974). *Acta Chem. Scand. Ser. B*, **28**, 717–729.

Gierer, J. & Lindeberg, O. (1980). *Acta Chem. Scand. Ser. B*, **34**, 161–170.
Gierer, J., Pettersson, I. & Szabo-Lin, I. (1974). *Acta Chem. Scand. Ser. B*, **28**, 1129–1135.
Krohn, K., Müller, H., Adiwidjaja, G., Jarchow, O. H., Schmalle, H. W., Hausen, B. M. & Schulz, K.-H. (1986). *Z. Kristallogr.* **174**, 283–290.
Lee, D.-Y., Matsuoka, M. & Sumimoto, M. (1990). *Holzforschung*, **44**, 415–418.
Li, S. & Lundquist, K. (1998). *Holzforschung*. In the press.
Li, S., Lundquist, K. & Stomberg, R. (1996). *Acta Cryst.* C**52**, 3118–3121.
Lonsky, L., Lonsky, W., Kratzl, K. & Falkehag, I. (1976). *Monatsh. Chem.* **107**, 685–695.
Miller, J. G. & Schuerch, C. (1968). *Tappi*, **51**(6), 273–277.
Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Mörck, R. & Kringstad, K. P. (1985). *Holzforschung*, **39**, 109–119.
Nelson, P. J. & Wallis, A. F. A. (1973). *Tappi*, **56**(8), 132–137.
Niemelä, K. (1990). *Ann. Acad. Sci. Fenn. Ser. A2*, Monogr. 229.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Ogawa, K., Sano, T., Yoshimura, S., Takeuchi, Y. & Toriumi, K. (1992). *J. Am. Chem. Soc.* **114**, 1041–1051.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for Refinement of Crystal Structures*. University of Göttingen, Germany.
Siemens (1994*a*). *SMART*. Version 4.021. *Data Collection Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994*b*). *SAINT*. Version 4.021. *Data Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1994*c*). *XP. Molecular Graphics Program*. Version 5.03. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996). *XPREP* in *SHELXLTL. Program for Data Preparation and Reciprocal Space Exploration*. Version 5.05. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Theocharis, C. R., Jones, W. & Rao, C. N. R. (1984). *J. Chem. Soc. Chem. Commun.* pp. 1291–1293.
Yoon, B.-H., Terashima, N. & Yasuda, S. (1981). *Mokuzai Gakkaishi*, **27**, 311–317.

Acta Cryst. (1998). C**54**, 1934–1936

An Unexpected Product of an Indium-Mediated Carbon–Carbon Coupling: 2-(1-Phenyl-1,3-butadien-2-yl)benzoic Acid

JOEL T. MAGUE, XIAO-GANG HUA AND CHAO-JUN LI

Department of Chemistry, Tulane University, New Orleans, LA 70118, USA. E-mail: joelt@mailhost.tcs.tulane.edu

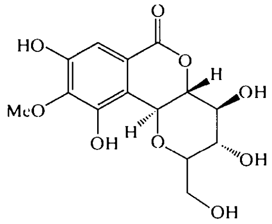
(*Received 14 May 1998; accepted 24 July 1998*)

Abstract

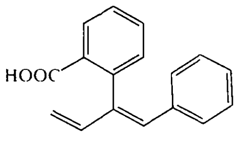
The title compound, 2-(1-phenyl-1,3-butadien-2-yl)benzoic acid, $C_6H_5CH{=}C(C_6H_4COOH)CH{=}CH_2$ (or $C_{17}H_{14}O_2$), has been obtained as the major product from an indium-mediated coupling of benzaldehyde with methyl *o*-(3-bromo-1-propynyl)benzoate. The compound crystallizes as centrosymmetric hydrogen-bonded dimers. The diene portion is in the *s-trans* conformation, with the aromatic groups *cis* to one another.

Comment

Recent developments in Barbier–Grignard-type C—C bond-formation reactions in aqueous media (Li, 1993; Li & Chan, 1997; Lubineau *et al.*, 1994) present opportunities for the synthesis of heavily oxygenated compounds of biological significance. The success of a synthesis of (+)-goniofufurone *via* a highly regio- and diastereoselective indium-mediated allenylation of carbonyl compounds in an aqueous medium (Yi *et al.*, 1998) led us to consider similar chemistry in a synthesis of bergenin (*A*). To model the initial step of the proposed synthesis, which was expected to generate a δ-lactone, the indium-mediated coupling of aldehydes with methyl *o*-(3-bromo-1-propynyl)benzoate in aqueous DMF was studied (Hua *et al.*, 1998). Under these conditions, several linear aldehydes, for example hexaldehyde, gave the desired δ-lactone but, in the case of benzaldehyde, it was evident from spectroscopic data that the major product obtained (55% yield) was not the expected δ-lactone, although these data did not enable an unequivocal determination of its structure to be made. Because this last reaction took a course different from that expected, it was of interest to determine the structure of the product, although, even with this in hand, the mechanism by which it is formed is still unclear.



(*A*)



(1)

2-(1-Phenyl-1,3-butadien-2-yl)benzoic acid, (1), exists in the solid as hydrogen-bonded dimers disposed about centers of symmetry [*e.g.* $(1,1,\frac{1}{2})$]. There is disorder in the carboxyl group, as evidenced both by a difference map, which showed somewhat elongated regions of electron density close to both O atoms, and also by the

Acta Crystallographica Section C
ISSN 0108-2701 © 1998