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Preparation and Crystal Structure of (±)-1,2-Bis(3,4-dimethoxyphenyl)-1,2-ethanediol

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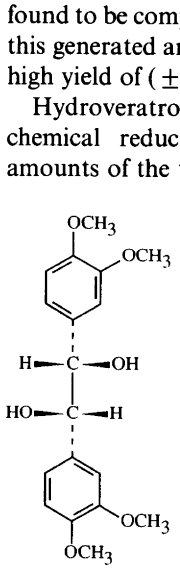
(±)-1,2-Bis(3,4-dimethoxyphenyl)-1,2-ethanediol has been prepared by reduction of veratraldehyde with low-valent titanium. Reduction with $TiCl_4$/Zn gave a mixture of the (±)-form (80%) and the *meso* form (20%) while only traces of the *meso* form could be detected when titanocene dichloride/Zn was used as the reducing agent. A combination of fractionation on the basis of solubility properties and ion-exchange chromatography on an anion exchanger using a borate solution as the eluent was used for the separation of the diastereomers. The crystal structure of (±)-1,2-bis(3,4-dimethoxyphenyl)-1,2-ethanediol was determined by single-crystal X-ray diffraction methods. The compound crystallizes as colourless, hexagonal prisms in the hexagonal space group $P6_5$ [as the (+)- or (−)-form] with $a = 12.309(5)$, $c = 9.665(2)$ Å, $V = 1268.1(9)$ Å^3 and $Z = 3$. A total of 1229 unique reflections was collected. Of these 893 were considered observed [$I > 3\sigma(I)$] leading to a final R-value of 0.033. The molecules are held together by van der Waals forces and moderately strong hydrogen bonds.

A previous paper[1] describes the preparation of the diastereomers of a series of hydrobenzoins (1,2-diaryl-1,2-ethanediols) by reduction of benzoins. The *meso* form is the major product from the reduction of benzoins with sodium tetrahydridoborate or borane–dimethyl sulfide complex. One of the hydrobenzoins prepared, 1,2-bis(3,4-dimethoxyphenyl)-1,2-ethanediol (hydroveratroin), has been found to be of interest in research related to lignin chemistry,[1–4] e.g., in studies of the oxidizing properties of enzymes of the ligninase type.[3,4] Owing to its solubility properties the racemic form [(±)-hydroveratroin, **1**] was found to be comparatively well suited to such studies[3] and this generated an interest in synthetic methods that give a high yield of (±)-hydroveratroin.

Hydroveratroin was originally prepared by electrochemical reduction of veratraldehyde.[5] About equal amounts of the two diastereomeric forms (**1** and **2**) were obtained. In connection with later electrochemical studies[6] steric assignments of the diastereomers were made on the basis of the fact that the racemic form (**1**) crystallizes from ethanol as separate (+)- and (−)-crystals. Parenthetically it could be mentioned that in this last work it was found that electrochemical reduction of phenolic aldehydes (e.g., vanillin) gave primarily the *meso* form of the corresponding hydrobenzoin. A synthesis of **1** proceeding via epoxidation of (*E*)-3,3′,4,4′-tetramethoxystilbene (**3**) has also been reported.[7] In the present paper the preparation of hydroveratroin by reduction of veratraldehyde with low-valent titanium is reported. Mukaiyama *et al.*[8] have described the reduction of carbonyl compounds using $TiCl_4$/Zn as the reducing agent. Reduction of veratraldehyde using this reducing agent gave hydroveratroin in about 80% yield [(*E*)-3,3′,4,4′-tetramethoxystilbene (**3**) and veratryl alcohol were present in the reaction mixture]. The product consisted of a 4:1 mixture of the (±)-form (**1**) and the *meso* form (**2**). Separation of the (±)-form was accomplished by fractionation on the basis of solubility properties in combination with ion-exchange chromatography on an anion exchanger using a borate solution as the eluent. Reduction experiments with veratraldehyde and titanocene dichloride/Zn gave a product consisting primarily of (±)-hydroveratroin (**1**) [the proportion of the *meso* form (**2**) in the product was estimated as 3%]. This is as expected from reduction experiments with benzaldehyde using the same reducing agent: (±)-hydrobenzoin is the predominant product but small amounts of the *meso* form are present in the reaction mixture.[9]



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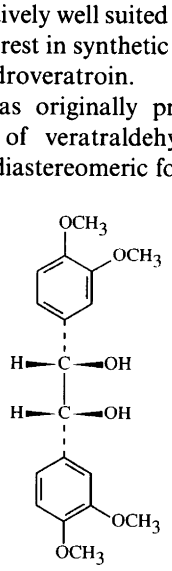

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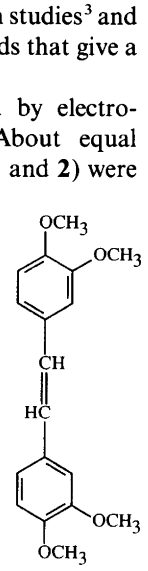

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Table 1. Atomic fractional coordinates and B_{eq} (B_{iso} for H) for (±)-1,2-bis(3,4-dimethoxyphenyl)-1,2-ethanediol (**1**), $C_{18}H_{22}O_6$, [(+)- or (−)-form].[a]

Atom	x	y	z	B_{eq}
C(1)	0.6336(2)	0.0321(2)	0.0379	2.10(7)
C(2)	0.6968(2)	0.1599(2)	0.0723(4)	2.15(8)
C(3)	0.7699(2)	0.2019(2)	0.1891(4)	2.18(8)
C(4)	0.7819(2)	0.1161(2)	0.2752(4)	2.24(8)
C(5)	0.7201(2)	−0.0089(2)	0.2415(4)	2.50(8)
C(6)	0.6464(2)	−0.0504(2)	0.1235(4)	2.57(9)
C(7)	0.8275(4)	0.4159(3)	0.1501(5)	4.0(1)
C(8)	0.8792(4)	0.0893(3)	0.4764(4)	3.9(1)
C(9)	0.5553(2)	−0.0121(2)	−0.0920(3)	2.27(8)
O(1)	0.8376(2)	0.3246(1)	0.2317(3)	2.98(6)
O(2)	0.8588(2)	0.1693(2)	0.3881(3)	2.80(6)
O(3)	0.6312(2)	0.0501(2)	−0.2102(3)	3.07(7)
H(C2)	0.692(2)	0.216(2)	0.009(3)	1.8(5)
H(C5)	0.731(2)	−0.064(2)	0.298(3)	2.4(5)
H(C6)	0.606(3)	−0.132(3)	0.105(3)	3.9(7)
H1(C7)	0.878(2)	0.498(3)	0.194(3)	3.2(6)
H2(C7)	0.853(3)	0.416(3)	0.065(4)	4.6(9)
H3(C7)	0.741(2)	0.395(2)	0.139(3)	3.9(7)
H1(C8)	0.806(3)	0.023(3)	0.514(4)	4.3(7)
H2(C8)	0.908(2)	0.050(3)	0.421(3)	3.1(6)
H3(C8)	0.937(3)	0.143(3)	0.548(4)	3.3(6)
H(C9)	0.482(2)	0.110(2)	−0.103(3)	2.0(5)
H(O3)	0.630(3)	0.001(3)	−0.266(3)	3.6(7)

[a] $T = -130\,^{\circ}C$. $B_{eq} = \frac{4}{3}\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i \cdot \mathbf{a}_j$.

It has been reported that (±)-hydroveratroin melts at 169–170 °C.[6] The products we prepared melted in the range 150–170 °C in spite of repeated purifications by recrystallization and column chromatography. According to X-ray crystallography, elemental analysis and ^{1}H NMR spectroscopy our crystalline products consist of (±)-hydroveratroin. Further investigations showed that observed melting points were influenced by thermal decomposition (dehydration) of the compound.

As a complement to the structural studies of hydrobenzoins previously presented[1] we determined the crystal structure of (±)-hydroveratroin by single-crystal X-ray crystallography (most of the results are summarized in Tables 1–3). (±)-Hydroveratroin crystallizes as a conglomerate and it is possible to pick out the individual stereoisomers. As expected from this a randomly selected crystal was found to crystallize in an acentric space group ($P6_2$ or $P6_4$) implying that only one of the enantiomers was present in the unit cell.

The crystals of (+)- and (−)-hydroveratroin consist of molecules held together by van der Waals forces and moderately strong hydrogen bonds (see Table 2). The shortest intermolecular contact distance (except for hydrogen bonds, Table 2) is 2.52(4) Å [between H1(C7) and H(O3)]. The (±)-hydroveratroin molecule has C_2 symmetry (this follows from space group symmetry); the twofold axis bisects the bond between the benzylic carbon atoms [C(9)–C(9)′]. All bond distances and bond angles are normal (see Table 2). They compare well with those obtained for *meso*-hydroveratroin.[1] The torsion angle between the hydroxy groups is 180° in *meso*-hydroveratroin and 66.3° in (±)-hydroveratroin. The difference in hydroxy-group orientation may have some connection with the fact that (±)-hydroveratroin forms a stronger borate complex than does the *meso*-form.[1]

Table 2. Bond distances (Å) and angles (°) in (±)-1,2-bis(3,4-dimethoxyphenyl)-1,2-ethanediol (**1**), $C_{18}H_{22}O_6$, [(+)- or (−)-form].

Bond distances

C(1)–C(2)	1.402(3)	C(3)–C(4)	1.408(3)	C(5)–C(6)	1.386(4)
C(1)–C(6)	1.379(3)	C(3)–O(1)	1.374(3)	C(7)–O(1)	1.427(4)
C(1)–C(9)	1.509(3)	C(4)–C(5)	1.372(3)	C(8)–O(2)	1.418(3)
C(2)–C(3)	1.374(3)	C(4)–O(2)	1.376(3)	C(9)–C(9)′	1.531(5)
				C(9)–O(3)	1.431(3)

Bond angles

C(2)–C(1)–C(6)	118.7(2)	C(4)–C(3)–O(1)	114.5(2)	C(1)–C(9)–C(9)′	113.6(1)
C(2)–C(1)–C(9)	119.8(2)	C(3)–C(4)–C(5)	119.6(2)	C(1)–C(9)–O(3)	110.1(2)
C(6)–C(1)–C(9)	121.4(2)	C(3)–C(4)–O(2)	114.6(2)	C(9)′–C(9)–O(3)	107.6(2)
C(1)–C(2)–C(3)	120.6(2)	C(5)–C(4)–O(2)	125.8(2)	C(3)–O(1)–C(7)	117.2(2)
C(2)–C(3)–C(4)	119.9(2)	C(4)–C(5)–C(6)	120.1(2)	C(4)–O(2)–C(8)	117.8(2)
C(2)–C(3)–O(1)	125.7(2)	C(1)–C(6)–C(5)	121.1(2)		

Hydrogen bonds

O···H–O	O···O	O···H	∧O···H–O
O(1)···H(O3)–O(3) $(1+y, 1-x+y, \frac{2}{3}+z)$	3.143(3)	2.43(3)	151(2)
O(2)···H(O3)–O(3) $(1+y, 1-x+y, \frac{2}{3}+z)$	2.862(3)	2.22(3)	138(2)

Selected torsion angles

C(2)–C(1)–C(9)–C(9)′	−62.4(3)	O(3)–C(9)–C(9)′–O(3)′	66.3(3)
C(2)–C(1)–C(9)–O(3)	58.3(3)	C(2)–C(3)–O(1)–C(7)	2.4(4)
C(1)–C(9)–C(9)′–C(1)′	−49.6(3)	C(5)–C(4)–O(2)–C(8)	1.7(4)
C(1)–C(9)–C(9)′–O(3)′	−171.7(2)		

Table 3. Crystal and experimental data for (±)-1,2-bis(3,4-dimethoxyphenyl)-1,2-ethanediol (**1**), $C_{18}H_{22}O_6$, [(+)- or (−)-form].

Crystal data	
Formula weight	334.37
Crystal colour; habit	Colourless; hexagonal prism
Crystal dimensions/mm	0.26 × 0.36 × 0.44
Crystal system	Hexagonal
No. of reflections used for unit cell determination (2θ range/°)	25 (37.8–44.4)
Lattice parameters[a]	$a = 12.309(5)$ Å [12.343(1) Å] $c = 9.665(2)$ Å [9.719(2) Å] $V = 1268.1(9)$ Å^3 [1282.4(3) Å^3]
Space group	$P6_2$ (No. 171)
Z	3
D_{calc}/g cm^{-3}	1.313
$F(000)$	534
μ(Mo Kα) (cm^{-1}); no correction	0.92
Intensity measurements	
Diffractometer	Rigaku AFC6R
Radiation	Mo Kα (λ = 0.71069 Å)
T/°C	−130
Scan type	ω–2θ
Scan rate/° min^{-1}	4.0 (maximum of 2 rescans)
Scan width/°	1.26 + 0.30 tan θ
2θ range/°	3.5–60.0
No. of unique reflections measured	1229
Corrections	Lorentz polarization
Structure solution and refinement	
Structure solution	Direct methods. Electron density difference maps
Refinement	Full-matrix least-squares
Hydrogen atom treatment	Refined
Function minimized	$\Sigma w(\|F_o\| - \|F_c\|)^2$
Least-squares weights	$w = 1/\sigma^2(F_o)$
Anomalous dispersion	All non-hydrogen atoms
No. of observed independent reflections [$I > 3.00\sigma(I)$]	893
No. of variables	152
Reflection/parameter ratio	5.88
Residuals: R; R_w	0.033; 0.034
Goodness-of-fit indicator	1.65
Maximum shift/error in final cycle	0.01
Maximum peak in final diff. map (e$^-$ Å^{-3})	0.18
Minimum peak in final diff. map (e$^-$ Å^{-3})	−0.12

[a] Room temperature data, collected with a Syntex $P2_1$ X-ray diffractometer (Cu Kα radiation) are given within square brackets.

Within the limits of experimental error, the benzene ring carbon atoms are coplanar (to within less than 0.3σ) in (±)-hydroveratroin. The methoxy oxygen and carbon atoms are almost coplanar with the benzene ring plane; the maximum deviation is shown by C(8) [0.071(2) Å]. The benzylic carbon atom [C(9)] is also almost coplanar with the aromatic ring plane [the deviation is 0.023(3) Å].

Experimental

Tetrahydrofuran was purified by distillation over Na.

^1H NMR spectra were recorded at 400 MHz with a Varian VXR-5000 instrument at 300 K. Deuteriochloroform was used as a solvent (internal reference, Me_4Si).

Thin layer chromatography (TLC) was performed on silica gel plates (Merck, Kieselgel 60 F_{254}) with toluene–dioxane–acetic acid (90:25:4) as the eluent (R_f values: **1**, 0.14; **2**, 0.14; veratryl alcohol, 0.26; **3**, 0.46). Spots were made visible by UV light and by spraying with formalin–H_2SO_4 (1:9) and subsequent heating.

(E)-*3,3',4,4'-Tetramethoxystilbene* (**3**) was prepared by refluxing 1,2-bis(3,4-dimethoxyphenyl)-1,3-propanediol with 0.2 M methanesulfonic acid in dioxane–water (9:1) for 4 h (cf. Ref. 10). Recrystallization from ethanol gave a product melting at 157 °C (lit.[11] 153–154 °C). Regarding the steric assignment, see Ref. 11. ^1H NMR: δ 3.88 (6 H, s, OCH_3), 3.93 (6 H, s, OCH_3), 6.84 (2 H, d, $J = 8.2$ Hz, aromatic protons), 6.91 (2 H, s, vinyl protons), 7.02 (2 H, dd, $J = 1.6$ and 8.2 Hz, aromatic protons), 7.05 (2 H, d, $J = 1.6$ Hz, aromatic protons).

Preparation of (±)-hydroveratroin (**1**) *by reduction of veratraldehyde with $TiCl_4$/Zn.* Veratraldehyde (1.00 g, 6.0 mmol) was dissolved in tetrahydrofuran (40 ml) in a 100 ml three-necked flask. The flask was equipped with an inlet and an outlet for argon, septum for injection of reagents and a solid addition tube containing Zn (1.01 g, 15 mmol). The solution was cooled using an NaCl–ice mixture. $TiCl_4$ (1.4 ml, 13 mmol) was slowly injected into the flask (argon atmosphere, magnetic stirring). The Zn was added to the reaction mixture in portions. An additional amount of tetrahydrofuran (20 ml) was injected into the flask. The ice-bath was removed and the reaction mixture allowed to reach room temperature (magnetic stirring). After 3 h the reaction was quenched by addition of 10% K_2CO_3 solution and the reaction mixture transferred to a separatory funnel using 10% K_2CO_3 solution (the total amount of K_2CO_3 solution added was 50 ml) and chloroform (100 ml). The layers were separated and the aqueous layer extracted with chloroform (100 ml + 50 ml). The combined organic layers were dried (Na_2SO_4) and solvents removed by film evaporation. The residue weighed 1.03 g after drying over P_2O_5 and KOH. From an ^{1}H NMR examination of the crude product the total yield of *meso*-hydroveratroin and (±)-hydroveratroin was estimated as ≈80% (for NMR data, see Ref. 1). The *meso*-hydroveratroin/(±)-hydroveratroin ratio was determined to be 1:4 (^{1}H NMR, cf. Ref. 1). The presence of traces of veratryl alcohol in the crude product was detected by TLC and ^{1}H NMR spectroscopy [signal at δ 5.04 (CH_2) in the acetylated product]. Stilbene **3** was also present in the crude product according to TLC and ^{1}H NMR spectroscopy; measurements on the basis of the ^{1}H NMR signals at δ 6.91, δ 7.02 and δ 7.05 suggest a small percentage yield of stilbene **3**.

The bulk of the crude product (0.97 g) was heated with 40 ml ethanol and the mixture was allowed to cool to room temperature. Solids (0.56 g) were filtered off and washed with 10 ml ethanol. Leaching of the solids with ethanol (35 ml) gave a crystalline residue (0.164 g, m.p. 195–200 °C) identified as *meso*-hydroveratroin (**2**) (^{1}H NMR). Removal of ethanol (film evaporation) from the combined filtrates yielded a residual product weighing 0.84 g. (±)-Hydroveratroin (**1**) present in this fraction was separated by ion-exchange chromatography on an anion exchanger [QAE-Sephadex A-25 (100 g), column dimensions 4.2 × 42 cm] using 0.06 M $K_2B_4O_7$ in acetone–water (1:4) as the eluent (cf. Ref. 1). *meso*-Hydroveratroin is only slightly soluble in the eluent and a small amount of this compound (16 mg) precipitated during the application of the fraction to the column. The separation procedure gave *meso*-hydroveratroin (40 mg), (±)-hydroveratroin (0.45 g) and a mixture of *meso*-hydroveratroin and (±)-hydroveratroin (0.22 g). Application of the mixture to the anion exchange column gave 0.20 g (±)-hydroveratroin. A total of 0.65 g (±)-hydroveratroin was obtained (yield, 69%); the product was pure according to TLC and ^{1}H NMR spectroscopy. Recrystallization from ethanol gave 0.45 g of a product with a melting range (150–170 °C); the crystals were examined by X-ray crystallography (see below). Most of our crystalline samples of **1** melted in the range 150–170 °C but in some instances the m.p. 166–168 °C (lit.[6] 169–170 °C) was observed. We could trace the anomalies to thermal decomposition (dehydration) of the compound.

Preparation of (±)-hydroveratroin by reduction of veratraldehyde with titanocene dichloride/Zn. Veratraldehyde (1.00 g) was treated with titanocene dichloride/Zn essentially according to a procedure described by Handa and Inanaga[9] for the preparation of (±)-hydrobenzoin from benzaldehyde. Work-up procedures were largely the same as those used in the preceding synthesis. Examination of the crude product (1.01 g) as the acetate derivative by ^{1}H NMR spectroscopy (cf. Ref. 1) showed that (±)-hydroveratroin was the major constituent (the proportion of the *meso*-form was determined as 3%). The major part of the *meso*-form could be released by crystallization from ethanol. Recrystallization gave 0.47 g product containing less than 1% of the *meso*-form (^{1}H NMR). Repeated recrystallization gave 0.31 g pure (±)-hydroveratroin (signals from the *meso*-form could not be detected in the acetate derivative of the product).

X-Ray work. Crystal data and conditions for the data collection are given in Table 3. Symmetry and approximate cell dimensions were derived from rotation and Weissenberg photographs (Cu Kα radiation) of the X-ray diffraction patterns. Intensity data were recorded with a Rigaku AFC6R X-ray diffractometer with graphite-monochromated Mo Kα radiation from an RU200 rotating anode source operated at 9 kW (50 kV; 180 mA). The weak reflections [$I < 10.0\sigma(I)$] were rescanned and the counts were accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 40 cm. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout the data collection indicating crystal and electronic stability (no decay correction was applied). Azimuthal scans of several reflections indicated no need for an absorption correction. The intensities were corrected for Lorentz and polarization effects. The unit cell dimensions were determined from a least-squares fit of refined diffractometer setting angles for 25 reflections.

Structure determination. The structure was solved by direct methods using the program SHELXS[12] and by electron-density calculations. The SHELXS solution gave the positions of all non-hydrogen atoms. A full-matrix least-squares refinement of positional and anisotropic thermal parameters for these atoms was performed. All hydrogen atoms were located in the subsequent electron-density

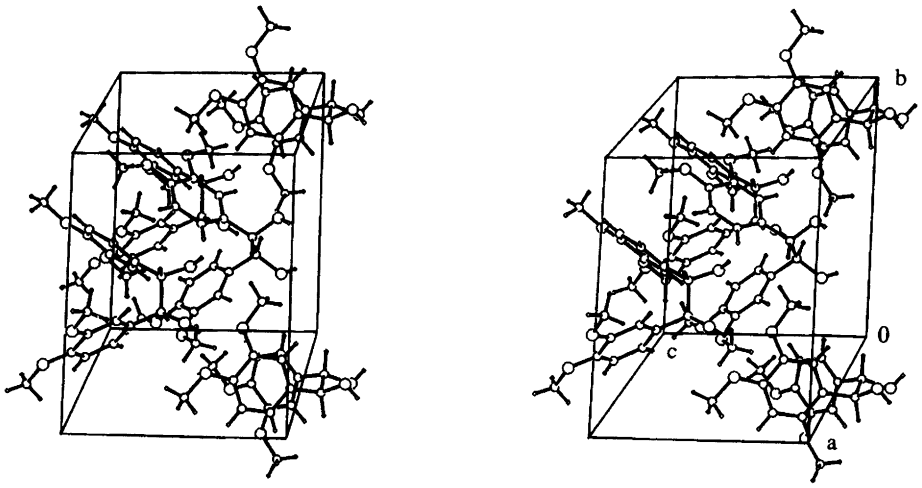

Fig. 1. Stereoscopic view[18] of the unit cell of a crystal from a sample of (±)-hydroveratroin. The molecules in the unit cell shown in the figure have the *S,S*-configuration which, according to Ref. 7, corresponds to the (−)-form.

difference map. Inclusion of positional and isotropic thermal parameters for the hydrogen atoms in the refinement reduced R to 0.033 ($R = \Sigma \, ||F_o| - |F_c|| / \Sigma \, |F_o|$). The weighting scheme (see Table 3) was based on counting statistics. Plots of $\Sigma w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $\sin\theta/\lambda$ and various classes of indices showed no anomalous trends.

Further details concerning the refinement of the structure are given in Table 3. Neutral atomic scattering factors for the non-hydrogen atoms were taken from Ref. 13. Anomalous dispersion effects were included in F_c;[14] the values for $\Delta f'$ and $\Delta f''$ were those given by Cromer.[15] Scattering factors for the hydrogen atoms were taken from Ref. 16. Calculations were carried out on a VAX computer using the TEXSAN crystallographic software package of the Molecular Structure Corporation.[17]

Atomic fractional coordinates and equivalent isotropic thermal parameters are given in Table 1. Table 2 lists bond distances, bond angles and selected torsion angles. Fig. 1 shows a stereoscopic view of the unit cell. The molecule and the atomic numbering is shown in Fig. 2. Average bond distances (RMS deviations are given in parentheses) are: $C(sp^2)$–$C(sp^2)$ (aromatic) 1.387(14) Å, $C(sp^2)$–$C(sp^3)$ 1.509(3) Å, $C(sp^3)$–$C(sp^3)$ 1.531(5) Å, $C(sp^2)_{aromatic}$–O 1.375(3) Å and $C(sp^3)$–O 1.425(5) Å.

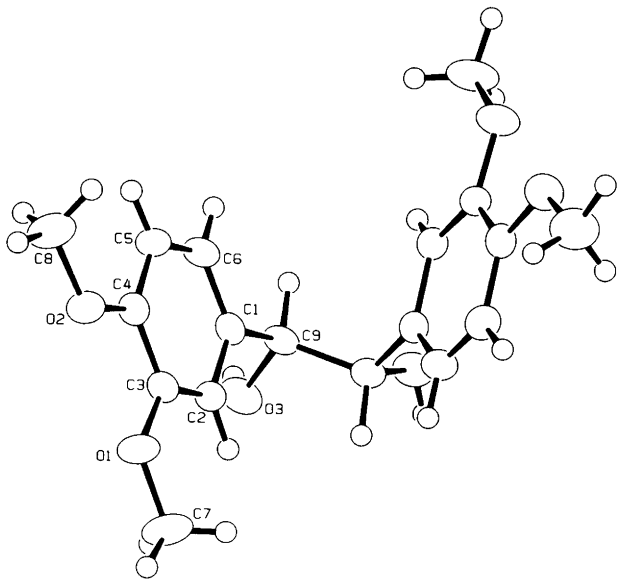

Fig. 2. A perspective drawing of a molecule in a crystal from a sample of (±)-hydroveratroin; the atomic numbering is shown. The particular molecule shown in the figure has the *S,S*-configuration which, according to Ref. 7, corresponds to the (−)-form.

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