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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.011 \text{ \AA}$
Disorder in main residue
R factor = 0.088
wR factor = 0.226
Data-to-parameter ratio = 12.3

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

Disorder in methyl 4-(3,5-dimethoxy-2-methylphenoxy)-2,6-dihydroxy-3-iodo-5-methylbenzoate

In the title compound, $\text{C}_{18}\text{H}_{19}\text{IO}_7$, the two aromatic rings are nearly perpendicular to each other with a dihedral angle of $83.0(4)^\circ$. One methoxy group is twisted out of the plane of its attached benzene ring, while another methoxy group and the carbomethoxy group are almost coplanar with their attached benzene rings. The hydroxyl groups are involved in intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds with the carbomethoxy O atoms. The crystal structure is stabilized by intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds and weak $\text{C}-\text{H}\cdots\text{O}$ interactions.

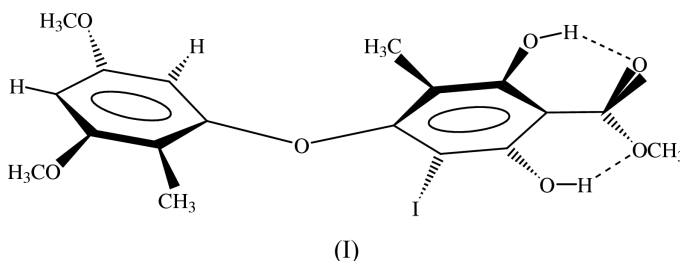
Received 8 October 2001

Accepted 9 October 2001

Online 13 October 2001

Comment

Diphenyl ethers can be prepared readily by the conversion of *p*-depsides which are produced from a wide variety of metabolites of lichen (Elix *et al.*, 1978) and by synthesis (Elix & Jenie, 1989; Chantrapromma *et al.*, 1998) via an intramolecular Smiles rearrangement (Elix *et al.*, 1984). Suitable reaction conditions for an intramolecular Smiles rearrangement of the prepared depsides have also been studied extensively (Elix & Jenie, 1989; Elix *et al.*, 1990). In previous work, we have reported the structure of diphenyl ethers obtained by intramolecular Smiles rearrangement of the prepared corresponding depsides (Chantrapromma *et al.*, 2000; Karalai *et al.*, 2001). Structure determinations were undertaken as part of our structural studies on diphenyl ether derivatives. The title compound, (I), was unexpectedly obtained upon treatment of methyl 4-(2-carboxy-3,5-dimethoxy-6-methylphenoxy)-2,6-dihydroxy-3-methylbenzoate with excess of methyl lithium (freshly prepared from methyl iodide and lithium), instead of the expected product, the 2-acetylphenoxy analog of the starting material. It is quite hard to obtain a good quality crystal of the title compound.



A displacement ellipsoid plot with the atomic numbering scheme of the title compound is shown in Fig. 1. The molecule is disordered over two conformations, one related to the other by 180° rotation of the 2,6-dihydroxy-3-iodo-5-methylbenzoate moiety about the $\text{O}-\text{C}$ central bond joining it to the phenoxy residue. The disorder is such that only the 3- and 5-positions of the phenyl ring are occupied alternately by the iodine and methyl group. The bond lengths and angles

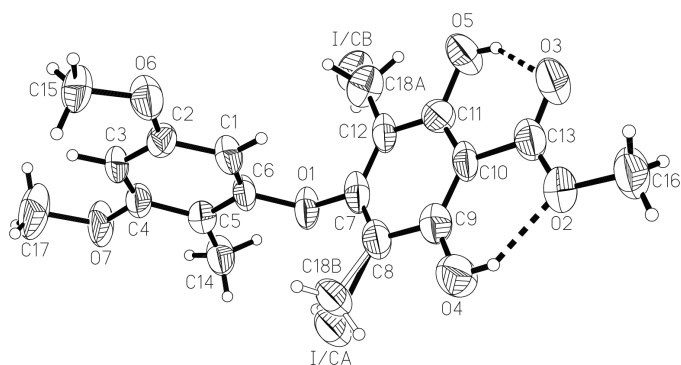


Figure 1

The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme. I/CA is the I atom for conformation A, whereas I/CB is the I atom for conformation B.

observed in the structure are normal and agree with reported values (Allen *et al.*, 1987; Chantrapromma *et al.*, 1998, 2000; Karalai *et al.*, 2001). The two benzene rings are nearly perpendicular to each other [dihedral angle $83.0(4)^\circ$]. One methoxy group is coplanar with the attached benzene ring [C17–O7–C4–C3 = $-0.5(13)^\circ$] but the other is twisted out of the benzene ring [C15–O6–C2–C3 = $16.6(12)^\circ$], while the carbomethoxy group is nearly coplanar with the attached benzene ring [C16–O2–C13–C10 = $174.2(3)^\circ$]. The hydroxyl groups in the molecule are involved in intramolecular O–H...O hydrogen bonds with the carbomethoxy O atoms (Table 2), whereas the O atom of one methoxy group is involved in a weak intramolecular C14–H14A...O7 interaction (H14A...O7 = 2.32 \AA and C14–H14A...O7 = 106°). The crystal structure is stabilized by these intramolecular O–H...O hydrogen bonds and weak C–H...O interactions. The molecules are stacked on top of one another along the *a* axis (Fig. 2).

Experimental

A solution of 0.98 M methyl lithium (1.10 ml, 0.99 mmol), which was freshly prepared from methyl iodide and lithium, was added to a cool solution of methyl 4-(2-carboxy-3,5-methoxy-6-methylphenoxy)-2,6-dihydroxy-3-methylbenzoate (39 mg, 0.01 mmol) in dry tetrahydrofuran (5 ml) under a nitrogen atmosphere. The reaction mixture was stirred at 273 K for 3 h and for an additional 6 h at room temperature. Saturated ammonium chloride (30 ml) was then added to the solution. The resulting mixture was extracted with ether. After extraction, the solvent was removed *in vacuo* and the crude product was purified by preparative thin-layer chromatography with 20% hexane/chloroform as eluent to give a brown solid which was recrystallized from chloroform.

Crystal data

$C_{18}H_{19}IO_7$	$Z = 2$
$M_r = 474.23$	$D_x = 1.688 \text{ Mg m}^{-3}$
Triclinic, $P1$	Mo $K\alpha$ radiation
$a = 8.8878(3) \text{ \AA}$	Cell parameters from 3302 reflections
$b = 10.6008(2) \text{ \AA}$	$\theta = 2.0\text{--}25.0^\circ$
$c = 11.2792(3) \text{ \AA}$	$\mu = 1.75 \text{ mm}^{-1}$
$\alpha = 62.253(1)^\circ$	$T = 293(2) \text{ K}$
$\beta = 87.872(1)^\circ$	Block, brown
$\gamma = 82.953(1)^\circ$	$0.36 \times 0.24 \times 0.18 \text{ mm}$
$V = 933.16(4) \text{ \AA}^3$	

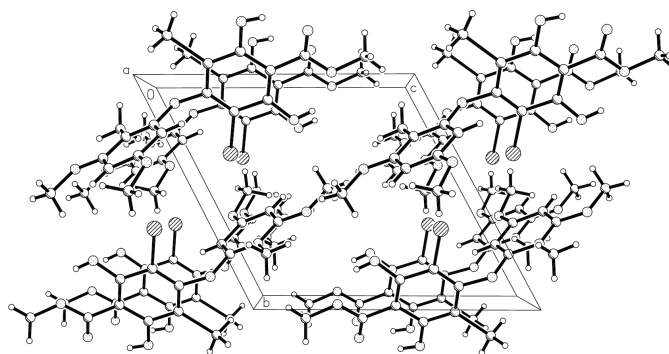


Figure 2

Packing diagram of the title compound viewed down the *a* axis. To avoid confusion only conformation A is shown.

Data collection

Siemens SMART CCD area-detector diffractometer	3302 independent reflections
ω scans	2039 reflections with $I > 2\sigma(I)$
Absorption correction: empirical (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.081$
$T_{\text{min}} = 0.571$, $T_{\text{max}} = 0.743$	$\theta_{\text{max}} = 25.0^\circ$
5044 measured reflections	$h = -7 \rightarrow 10$
	$k = -10 \rightarrow 12$
	$l = -10 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1141P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.088$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.226$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.98$	$\Delta\rho_{\text{max}} = 1.46 \text{ e \AA}^{-3}$
3078 reflections	$\Delta\rho_{\text{min}} = -0.65 \text{ e \AA}^{-3}$
250 parameters	Extinction correction: SHELXTL (Sheldrick, 1997)
H-atom parameters constrained	Extinction coefficient: 0.098 (11)

Table 1

Selected geometric parameters (\AA , $^\circ$).

I/CA–C8	1.995 (6)	I/CB–C12	1.958 (6)
C18A–C12	1.452 (9)	C18B–C8	1.468 (10)
C6–O1–C7	117.7 (5)		
C15–O6–C2–C3	16.6 (12)	C8–C7–C12–C18A	178.7 (13)
C6–C1–C2–O6	$-177.3(6)$	C8–C7–C12–I/CB	$-179.3(6)$
C14–C5–C6–C1	$-177.2(8)$	C16–O2–C13–C10	174.2 (7)
I/CA–C8–C9–C10	$-178.6(6)$		

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
O4–H4A...O2	0.82	1.90	2.600 (9)	143
O5–H5A...O3	0.82	1.80	2.538 (9)	148

After checking their presence in a difference map, all H atoms were geometrically fixed and allowed to ride on the atoms to which they are attached, with $U_{\text{iso}} = 1.2U_{\text{eq}}$ for aromatic parent atoms and $1.5U_{\text{eq}}$ for methyl C atoms and hydroxyl O atoms; C–H = 0.96 \AA and O–H = 0.82 \AA . Due to a large fraction of weak data at higher angles, the 2θ maximum was limited to 50° . Even with this limitation, the

coverage of the unit set is only 93.2% complete because the crystal is not very strongly diffracting and there is disorder in the structure.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

The authors would like to thank the Prince of Songkla University for a research grant. KC and NS would like to thank the Golden Jubilee PhD program and the Thailand Research Fund for financial support. The authors also would like to thank the Malaysian Government and Universiti Sains Malaysia for research grant R&D No. 305/PFIZIK/610961.

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