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2,3,5-Trichloro-4-methoxy-6-[2,3,5-trichloro-4-methoxy-6-(2,3,5,6-tetrachloro-4-methoxyphenoxy)phenoxy]phenol

Daisuke Hashizume,[a]* Hiroyuki Koshino,[a] In-Kyoung Lee[b] and Ick-Dong Yoo[b]

[a]Molecular Characterization Team, RIKEN, Hirosawa, Wako, Saitama 351-0198, Japan, and [b]National Research Laboratory of Antioxidants, Korea Research Institute of Bioscience and Biotechnology, 52 Oeundong, Yuseong ku, Daejeon 305-333, South Korea

Correspondence e-mail: hashi@riken.jp

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The title compound, $C_{21}H_{10}Cl_{10}O_6$, has been extracted from mushroom *Phellinus* sp. The molecule has a highly chlorinated diarylcatechol ether skeleton. The neighboring benzene rings are arranged approximately perpendicular to each other. There are intermolecular O—H···O hydrogen bonds and Cl···Cl/O short contacts.

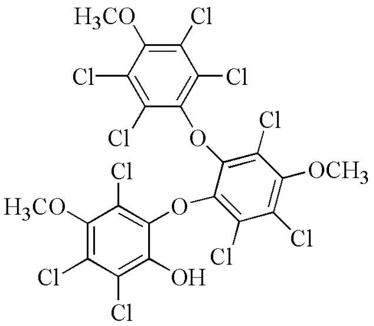
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.034
wR factor = 0.078
Data-to-parameter ratio = 18.1

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

Comment

Mushrooms produce various classes of secondary metabolites. Many of them exhibit significant antimicrobial, antitumor and antiviral activity. Hence, some species of mushrooms have been used in the Orient as traditional medicines. We have investigated biologically active and chemically novel compounds from basidiomycetes. As part of our ongoing efforts, a new polychlorinated compound, (I), has been isolated from the extract of Phellinus *sp.*



(I)

The title compound, (I), has a diarylcatechol ether skeleton (Fig. 1). The benzene rings, linked *via* O atoms, are arranged approximately perpendicular to each other (Table 1). The dihedral angle between the planes of ring *A* (atoms C1–C6) and ring *B* (atoms C8–C13) is 85.46 (6)°, and that between the planes of ring *B* and ring *C* (atoms C15–C20) is 88.12 (6)°. Such geometry is commonly observed in a series of diarylcatechol ether compounds, *e.g.* Cambridge Structural Database, Version 5.26 (Allen, 2002) refcodes DUZGOU (Burlinson *et al.*, 1986), PUVPUR, PUVQAY (Bryan *et al.*, 1998), QOBBOY (Öztürk *et al.*, 2000), RIRCUQ (Belostotskaya *et al.*, 1997) and ZEZBAH (Abd-El-Aziz *et al.*, 1995). The benzene rings are substituted by three or four Cl atoms and a methoxy group. Each methoxy group is directed perpendicular to the benzene ring to avoid steric repulsions from the neighboring Cl atoms. The hydroxy group O1/H1 is nearly coplanar with benzene ring *A*, forming an intramolecular hydrogen bond (Table 2) with atom Cl1. This is a bifurcated hydrogen bond, and there is also an intermolecular O1—H1···O2^{iv} hydrogen bond [symmetry code: (iv) $x - 1$, y,

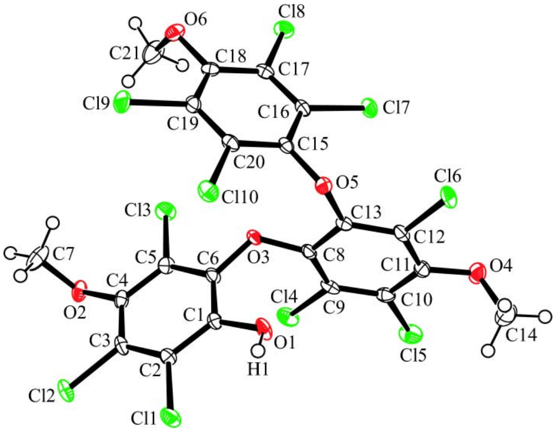


Figure 1
A view of the molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

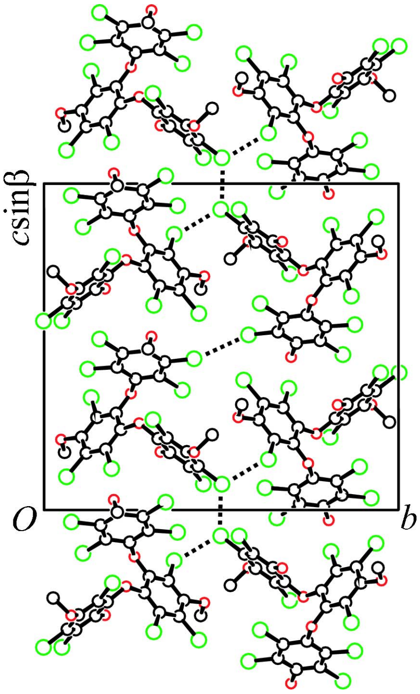


Figure 2
Crystal structure of (I), viewed along the *a* axis. Broken lines indicate intermolecular Cl···Cl contacts. H atoms have been omitted for clarity.

z], leading to the formation of a one-dimensional structure along the *a* axis.

Close contact between Cl atoms is expected in (I) because of the high degree of chlorination. Four intermolecular Cl···Cl contacts (Table 3) are observed, which are shorter than the sum of van der Waals radii of Cl atoms. Different directional preferences of Cl···Cl contacts are found, *viz.* head-to-head (type I) and head-to-side (type II), as classified by Pedireddi *et al.* (1994) [type I: Cl2···Cl2$^{\rm v}$ and Cl9···Cl9$^{\rm vi}$; type II: Cl2···Cl6$^{\rm vii}$; symmetry codes: (v) $1 - x, 1 - y, -z$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $-x, y + \frac{1}{2}, \frac{1}{2} - z$]. Short intermolecular Cl···O contacts of 3.1922 (17)–3.2518 (16) Å are also found (Table 2).

Experimental

The fruit body of *Phellinus* sp. (2 kg dry weight) was extracted twice with methanol. The methanol extract was evaporated to an aqueous concentrate and then partitioned between hexane and water. The organic layer was subject to silica gel column chromatography with chloroform–methanol (1:1). Final purification was achieved by reverse-phase HPLC (column, MAXSIL 5u C18 ϕ 21.2 × 250 mm; solvent, 90% aqueous acetonitrile; flow rate 6 ml min^{-1}) to give 12 mg of (I) at room temprtature in 48 min. Crystals of (I) were grown by slow evaporation of a methanol–chloroform solution at room temperature.

Crystal data

$C_{21}H_{10}Cl_{10}O_6$
$M_r = 712.79$
Monoclinic, $P2_1/c$
$a = 7.5031$ (13) Å
$b = 19.610$ (3) Å
$c = 18.401$ (4) Å
$\beta = 99.894$ (7)°
$V = 2667.2$ (8) Å^3
$Z = 4$

$D_x = 1.775$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 54 841 reflections
$\theta = 3.1$–27.6°
$\mu = 1.08$ mm^{-1}
$T = 100$ K
Block, pale yellow
0.43 × 0.35 × 0.25 mm

Data collection

Rigaku R-AXIS diffractometer
ω scans
Absorption correction: numerical (*NUMABS*; Higashi, 1999)
$T_{\rm min} = 0.712$, $T_{\rm max} = 0.782$
60 732 measured reflections
6109 independent reflections

5306 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.039$
$\theta_{\rm max} = 27.5°$
$h = -9 \rightarrow 9$
$k = -25 \rightarrow 25$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.078$
$S = 1.07$
6109 reflections
338 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 1.942P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.77$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.45$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl3$^{\rm i}$···O5$^{\rm ii}$	3.2518 (16)	Cl8$^{\rm i}$···O2$^{\rm iii}$	3.1922 (17)
C7—O2—C4—C3	91.8 (3)	C8—C13—O5—C15	−50.9 (3)
C1—C6—O3—C8	41.1 (3)	C13—O5—C15—C16	−61.5 (2)
C6—O3—C8—C9	60.1 (3)	C21—O6—C18—C17	83.1 (3)
C14—O4—C11—C10	−98.0 (2)		

Symmetry codes: (i) x, y, z; (ii) $x + 1, y, z$; (iii) $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···Cl1	0.84	2.55	3.007 (2)	115
O1—H1···O2$^{\rm iv}$	0.84	2.17	2.946 (2)	153

Symmetry codes: (iv) $x - 1, y, z$.

o1368 Hashizume *et al.* • $C_{21}H_{10}Cl_{10}O_6$ *Acta Cryst.* (2005). E**61**, o1367–o1369

Table 3
Geometry of intermolecular Cl···Cl contact (Å, °).

C—Cl···Cl—C	Cl···Cl	C—Cl···Cl	Cl···Cl—C
C3—Cl2···Cl2^{v}—C3^{v}	3.3973 (12)	128.92 (8)	128.92 (8)
C19—Cl9···Cl9^{vi}—C19^{vi}	3.3432 (12)	146.86 (9)	146.86 (9)
C3—Cl2···Cl6^{vii}—C12^{vii}	3.3982 (8)	101.51 (7)	141.27 (8)

Symmetry codes: (v) $1 - x, 1 - y, -z$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $-x, y + 1/2, 1/2 - z$.

H atoms were found in difference maps and were subsequently treated as riding atoms, with C—H = 0.98 Å and O—H = 0.84 Å, and with $U_{iso}(H) = 1.5U_{eq}(C)$ and $1.2U_{eq}(O)$.

Data collection: *R-AXIS Control Software* (Rigaku, 1996); cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Acta Cryst. (2005). E**61**, o1367–o1369 Hashizume *et al.* • $C_{21}H_{10}Cl_{10}O_6$ **o1369**