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3,4-Dihydroxyphenyl 3,4,5-trimethoxybenzoate

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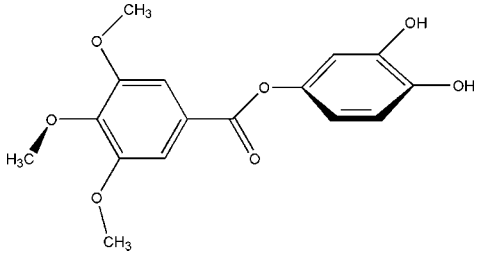
Key indicators: single-crystal X-ray study; T = 295 K; mean σ(C–C) = 0.003 Å; R factor = 0.050; wR factor = 0.126; data-to-parameter ratio = 15.7.

In the title compound, $C_{16}H_{16}O_7$, the dihedral angle between the two benzene rings is 82.02 (7)°. The crystal structure is stabilized by intermolecular O—H···O hydrogen bonds, which link the molecules into a two-dimensional network.

Related literature

For details of the general background of whitening agents, see: Nerya *et al.* (2003); Dawley *et al.* (1993); Maeda *et al.* (1991); Lee, *et al.* (2007).



Experimental

Crystal data

$C_{16}H_{16}O_7$
M_r = 320.29
Monoclinic, $P2_1/c$
a = 11.552 (2) Å
b = 12.817 (3) Å
c = 10.572 (2) Å
β = 105.57 (3)°
V = 1507.9 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 295 (2) K
0.2 × 0.2 × 0.16 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: none
4251 measured reflections
3444 independent reflections
2176 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
3 standard reflections
every 400 reflections
intensity decay: 2%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.126
S = 1.01
3444 reflections
219 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6O···O3^{i}	0.83 (3)	2.13 (4)	2.882 (2)	150 (3)
O7—H7O···O4^{ii}	0.84 (3)	2.02 (3)	2.855 (3)	179 (3)

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

X-ray data were collected at the Center for Research Facilities in Chungnam National University. This work was partially supported by the New Universities for Regional Innovation fund (05-Na-A-01) from the Ministry of Education and Human Resources Department, Republic of Korea.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LX2033).

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supporting information

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3,4-Dihydroxyphenyl 3,4,5-trimethoxybenzoate

Won Ki Hong, Ji Youn Heo, Byung Hee Han, Chang Keun Sung and Sung Kwon Kang

S1. Comment

A number of whitening agents (Nerya *et al.*, 2003; Dawley *et al.*, 1993; Maeda *et al.*, 1991) are containing hydroxyl (Lee *et al.*, 2007), aromatic, alkene, carbonyl and ether inside their structure and acting as a specific functional group to make the skin white by inhibiting the produce of melanin. In the course of our work on the development of new whitening agents, to complement the inadequacy of current whitening agents and maximize the inhibitory effects of melanin creation, we have synthesized the title compound. Herein we report the molecular and crystal structure of 3,4-dihydroxyphenyl 3,4,5-trimethoxybenzoate (Fig. 1).

The 3,4,5-trimethoxybenzoic acid moiety (except C15 methyl group) and a 3,4-dihydroxyphenyl ring are essentially planar, with a mean devation of 0.018 Å and 0.008 Å, respectively, from the least-squares plane defined by the ten and eght, respectively, constituent aoms. C15H_3 methyl group direct toward upside in the plane(Fig. 2), and the angle of C4—O2—C15 is 116.9 (2)°. The dihedral angle between two phenyl rings is 82.02(0.07)°. The intermolecular O—H···O hydrogen bonds link the molecules into a two-dimensional network (Table 1 & Fig.2).

S2. Experimental

The synthesis of the title compound started from sesamol (1 mmol) in THF and 3,4,5-trimethoxybenzoyl chloride (1.2 mmol) with NaH(1.5 mmol) as a catalyst by nucleophilic acyl substitution, then the deprotection of methylenedioxy group was accomplished by treatment of Pb(OAc)4 (1.5 mmol) in refluxing benzene, which generated the intermediate alkoxylated ester. Hydrolysis of alkoxylated ester in aqueous acetic acid gave a mixture as yellowish oil. The mixture was chromatographed on silica gel (30/1 = dichloromethane/ethyl acetate) to give the title compound as light yellow solid (61.8%, m.p. 408 K). Single crystals were obtained by slow evaporation from a solution of the title compound in ethyl acetate at room temperature.

S3. Refinement

Atoms H6O and H7O of the OH group were found in a difference Fourier map and refined freely with an isotropic displacement parameter. The other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93 Å for aromatic H atoms and 0.96 Å for methyl H atoms, and with U_{iso}(H) = 1.2U_{eq}(C) for aromatic and 1.5U_{eq}(C) for methyl H atoms.

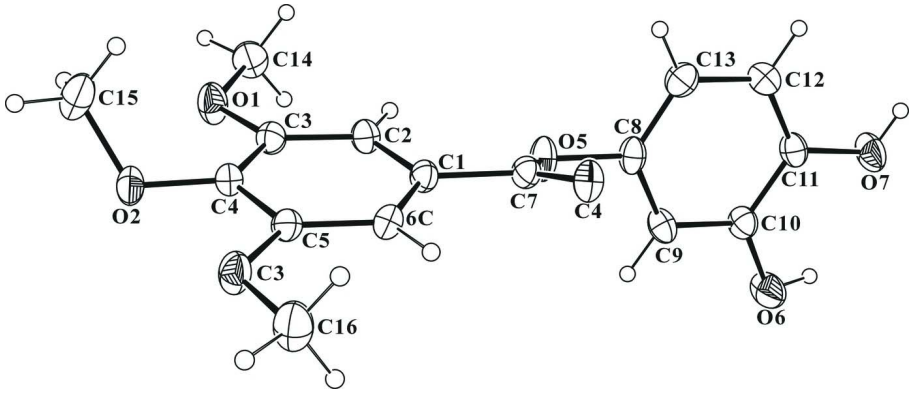

Figure 1

The molecular structure of the title compound, showing displacement ellipsoides drawn at the 30% probability level.

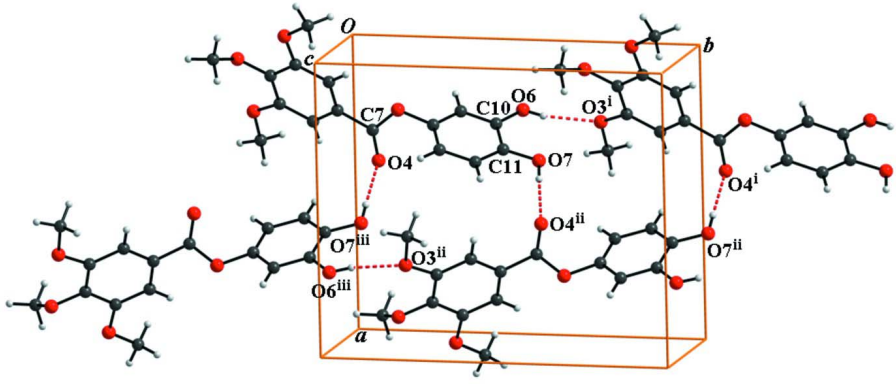

Figure 2

The O—H···O hydrogen bond interaction (dotted lines) in the title compound. [Symmetry codes: (i) *x*, *y* + 1, *z*; (ii) -*x* + 1, *y* + 1/2, -*z* + 1/2; (iii) -*x* + 1, *y* - 1/2, -*z* + 1/2.]

3,4-Dihydroxyphenyl 3,4,5-trimethoxybenzoate

Crystal data

$C_{16}H_{16}O_7$
M_r = 320.29
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 11.552 (2) Å
b = 12.817 (3) Å
c = 10.572 (2) Å
β = 105.57 (3)°
V = 1507.9 (6) Å^3
Z = 4
$F(000)$ = 672
D_x = 1.411 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 11.4–14.2°
μ = 0.11 mm^{-1}
T = 295 K
Block, colorless
0.2 × 0.2 × 0.16 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Non–profiled $\omega/2\theta$ scans
4251 measured reflections
3444 independent reflections
2176 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.4°$
$h = 0 \rightarrow 14$
$k = -16 \rightarrow 2$
$l = -13 \rightarrow 13$
3 standard reflections every 400 reflections
intensity decay: 2%

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.126$
$S = 1.02$
3444 reflections
219 parameters
0 restraints
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 0.3432P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	−0.00088 (14)	−0.18103 (12)	0.14141 (16)	0.0519 (4)
O2	0.09341 (15)	−0.33144 (11)	0.01850 (15)	0.0509 (4)
O3	0.27941 (14)	−0.29798 (11)	−0.07081 (15)	0.0463 (4)
O4	0.41661 (13)	0.07744 (11)	0.09149 (15)	0.0434 (4)
O5	0.24027 (13)	0.13828 (11)	0.11272 (16)	0.0482 (4)
O6	0.24533 (18)	0.48003 (14)	−0.05695 (17)	0.0619 (5)
H6O	0.261 (3)	0.541 (3)	−0.030 (3)	0.107 (12)*
O7	0.39231 (17)	0.54885 (12)	0.17566 (19)	0.0554 (5)
H7O	0.448 (3)	0.556 (2)	0.244 (3)	0.083 (11)*
C1	0.25245 (18)	−0.04039 (15)	0.07245 (19)	0.0339 (5)
C2	0.15217 (18)	−0.05794 (16)	0.1181 (2)	0.0374 (5)
H2	0.1214	−0.0047	0.1594	0.045*
C3	0.09822 (18)	−0.15538 (17)	0.1017 (2)	0.0384 (5)
C4	0.14486 (19)	−0.23470 (15)	0.0401 (2)	0.0369 (5)
C5	0.24393 (19)	−0.21565 (15)	−0.00864 (19)	0.0348 (5)
C6	0.29865 (18)	−0.11831 (15)	0.0089 (2)	0.0350 (5)
H6	0.3657	−0.1054	−0.0216	0.042*
C7	0.31335 (19)	0.06225 (15)	0.09277 (19)	0.0353 (5)
C8	0.28605 (19)	0.24148 (15)	0.1316 (2)	0.0388 (5)
C9	0.2473 (2)	0.31040 (16)	0.0299 (2)	0.0421 (5)
H9	0.1966	0.2881	−0.0495	0.05*
C10	0.28413 (19)	0.41347 (16)	0.0461 (2)	0.0402 (5)
C11	0.35900 (18)	0.44546 (15)	0.1663 (2)	0.0383 (5)

C12	0.3939 (2)	0.37553 (18)	0.2672 (2)	0.0441 (5)
H12	0.4424	0.3978	0.3478	0.053*
C13	0.3579 (2)	0.27155 (17)	0.2510 (2)	0.0444 (5)
H13	0.382	0.224	0.3194	0.053*
C14	−0.0468 (2)	−0.1053 (2)	0.2138 (2)	0.0520 (6)
H14A	0.0153	−0.0851	0.2901	0.078*
H14B	−0.1131	−0.1346	0.2405	0.078*
H14C	−0.0737	−0.0452	0.1596	0.078*
C15	0.0859 (2)	−0.38926 (18)	0.1315 (3)	0.0591 (7)
H15A	0.1518	−0.3706	0.2048	0.089*
H15B	0.0893	−0.4626	0.1141	0.089*
H15C	0.0115	−0.3735	0.1514	0.089*
C16	0.3815 (2)	−0.28499 (19)	−0.1210 (3)	0.0572 (7)
H16A	0.3659	−0.2304	−0.1855	0.086*
H16B	0.3971	−0.349	−0.1606	0.086*
H16C	0.4502	−0.2668	−0.0505	0.086*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0493 (9)	0.0470 (9)	0.0685 (11)	−0.0157 (8)	0.0314 (8)	−0.0152 (8)
O2	0.0682 (11)	0.0364 (8)	0.0530 (9)	−0.0229 (8)	0.0249 (8)	−0.0078 (7)
O3	0.0567 (10)	0.0310 (8)	0.0592 (9)	−0.0067 (7)	0.0293 (8)	−0.0079 (7)
O4	0.0393 (9)	0.0319 (8)	0.0603 (10)	−0.0038 (7)	0.0155 (7)	−0.0008 (7)
O5	0.0411 (8)	0.0249 (7)	0.0802 (12)	−0.0018 (7)	0.0189 (8)	−0.0017 (7)
O6	0.0868 (14)	0.0336 (9)	0.0539 (11)	−0.0055 (9)	−0.0011 (9)	0.0021 (8)
O7	0.0614 (11)	0.0327 (9)	0.0638 (11)	−0.0104 (8)	0.0026 (9)	−0.0078 (8)
C1	0.0359 (11)	0.0267 (10)	0.0374 (11)	−0.0018 (9)	0.0069 (9)	0.0021 (9)
C2	0.0389 (11)	0.0303 (10)	0.0433 (12)	−0.0017 (9)	0.0112 (9)	−0.0036 (9)
C3	0.0375 (11)	0.0394 (12)	0.0395 (12)	−0.0068 (9)	0.0123 (10)	−0.0023 (10)
C4	0.0434 (12)	0.0304 (11)	0.0357 (11)	−0.0090 (9)	0.0086 (9)	−0.0013 (9)
C5	0.0426 (12)	0.0277 (10)	0.0345 (11)	−0.0003 (9)	0.0110 (9)	0.0001 (9)
C6	0.0350 (11)	0.0305 (10)	0.0408 (12)	−0.0022 (9)	0.0124 (9)	0.0043 (9)
C7	0.0381 (12)	0.0283 (10)	0.0379 (11)	−0.0007 (9)	0.0075 (9)	0.0026 (9)
C8	0.0370 (11)	0.0251 (10)	0.0575 (14)	−0.0007 (9)	0.0182 (10)	−0.0037 (10)
C9	0.0418 (12)	0.0322 (11)	0.0489 (13)	−0.0027 (10)	0.0066 (10)	−0.0087 (10)
C10	0.0445 (12)	0.0290 (11)	0.0457 (13)	0.0012 (9)	0.0096 (10)	−0.0008 (10)
C11	0.0381 (11)	0.0278 (10)	0.0494 (13)	−0.0009 (9)	0.0124 (10)	−0.0085 (10)
C12	0.0439 (12)	0.0441 (13)	0.0420 (12)	−0.0013 (10)	0.0074 (10)	−0.0054 (10)
C13	0.0477 (13)	0.0381 (12)	0.0487 (13)	0.0031 (10)	0.0150 (11)	0.0049 (10)
C14	0.0499 (13)	0.0566 (15)	0.0554 (15)	−0.0032 (12)	0.0241 (12)	−0.0083 (12)
C15	0.0704 (17)	0.0391 (13)	0.0760 (18)	−0.0060 (12)	0.0340 (15)	0.0078 (13)
C16	0.0606 (16)	0.0463 (14)	0.0754 (17)	−0.0061 (12)	0.0369 (14)	−0.0136 (13)

Geometric parameters (Å, º)

O1—C3	1.361 (2)	C5—C6	1.388 (3)
O1—C14	1.424 (3)	C6—H6	0.93

O2—C4	1.367 (2)	C8—C13	1.366 (3)
O2—C15	1.428 (3)	C8—C9	1.371 (3)
O3—C5	1.363 (2)	C9—C10	1.384 (3)
O3—C16	1.427 (3)	C9—H9	0.93
O4—C7	1.212 (2)	C10—C11	1.393 (3)
O5—C7	1.343 (2)	C11—C12	1.369 (3)
O5—C8	1.419 (2)	C12—C13	1.393 (3)
O6—C10	1.362 (3)	C12—H12	0.93
O6—H6O	0.83 (3)	C13—H13	0.93
O7—C11	1.376 (2)	C14—H14A	0.96
O7—H7O	0.84 (3)	C14—H14B	0.96
C1—C2	1.388 (3)	C14—H14C	0.96
C1—C6	1.388 (3)	C15—H15A	0.96
C1—C7	1.480 (3)	C15—H15B	0.96
C2—C3	1.386 (3)	C15—H15C	0.96
C2—H2	0.93	C16—H16A	0.96
C3—C4	1.391 (3)	C16—H16B	0.96
C4—C5	1.397 (3)	C16—H16C	0.96

C3—O1—C14	117.83 (17)	C10—C9—H9	120.2
C4—O2—C15	116.87 (18)	O6—C10—C9	118.3 (2)
C5—O3—C16	118.32 (16)	O6—C10—C11	122.40 (19)
C7—O5—C8	118.20 (16)	C9—C10—C11	119.3 (2)
C10—O6—H6O	109 (2)	C12—C11—O7	123.8 (2)
C11—O7—H7O	108 (2)	C12—C11—C10	119.94 (19)
C2—C1—C6	121.14 (18)	O7—C11—C10	116.3 (2)
C2—C1—C7	120.15 (18)	C11—C12—C13	121.0 (2)
C6—C1—C7	118.70 (18)	C11—C12—H12	119.5
C3—C2—C1	119.46 (19)	C13—C12—H12	119.5
C3—C2—H2	120.3	C8—C13—C12	118.1 (2)
C1—C2—H2	120.3	C8—C13—H13	120.9
O1—C3—C2	124.49 (19)	C12—C13—H13	120.9
O1—C3—C4	115.54 (18)	O1—C14—H14A	109.5
C2—C3—C4	119.97 (19)	O1—C14—H14B	109.5
O2—C4—C3	122.36 (19)	H14A—C14—H14B	109.5
O2—C4—C5	117.33 (19)	O1—C14—H14C	109.5
C3—C4—C5	120.22 (18)	H14A—C14—H14C	109.5
O3—C5—C6	125.10 (18)	H14B—C14—H14C	109.5
O3—C5—C4	115.13 (17)	O2—C15—H15A	109.5
C6—C5—C4	119.77 (18)	O2—C15—H15B	109.5
C1—C6—C5	119.39 (19)	H15A—C15—H15B	109.5
C1—C6—H6	120.3	O2—C15—H15C	109.5
C5—C6—H6	120.3	H15A—C15—H15C	109.5
O4—C7—O5	123.18 (18)	H15B—C15—H15C	109.5
O4—C7—C1	124.89 (19)	O3—C16—H16A	109.5
O5—C7—C1	111.93 (17)	O3—C16—H16B	109.5
C13—C8—C9	122.2 (2)	H16A—C16—H16B	109.5
C13—C8—O5	120.3 (2)	O3—C16—H16C	109.5

C9—C8—O5	117.3 (2)	H16A—C16—H16C	109.5
C8—C9—C10	119.5 (2)	H16B—C16—H16C	109.5
C8—C9—H9	120.2		

C6—C1—C2—C3	0.9 (3)	C8—O5—C7—O4	0.8 (3)
C7—C1—C2—C3	−178.15 (18)	C8—O5—C7—C1	−179.03 (18)
C14—O1—C3—C2	−5.1 (3)	C2—C1—C7—O4	158.2 (2)
C14—O1—C3—C4	175.30 (19)	C6—C1—C7—O4	−21.0 (3)
C1—C2—C3—O1	−179.38 (19)	C2—C1—C7—O5	−22.1 (3)
C1—C2—C3—C4	0.2 (3)	C6—C1—C7—O5	158.83 (18)
C15—O2—C4—C3	−60.4 (3)	C7—O5—C8—C13	−79.4 (3)
C15—O2—C4—C5	123.0 (2)	C7—O5—C8—C9	105.9 (2)
O1—C3—C4—O2	1.2 (3)	C13—C8—C9—C10	1.8 (3)
C2—C3—C4—O2	−178.35 (19)	O5—C8—C9—C10	176.44 (19)
O1—C3—C4—C5	177.74 (18)	C8—C9—C10—O6	179.3 (2)
C2—C3—C4—C5	−1.9 (3)	C8—C9—C10—C11	−0.7 (3)
C16—O3—C5—C6	0.8 (3)	O6—C10—C11—C12	179.1 (2)
C16—O3—C5—C4	−178.79 (19)	C9—C10—C11—C12	−0.9 (3)
O2—C4—C5—O3	−1.2 (3)	O6—C10—C11—O7	−0.1 (3)
C3—C4—C5—O3	−177.91 (18)	C9—C10—C11—O7	179.9 (2)
O2—C4—C5—C6	179.11 (19)	O7—C11—C12—C13	−179.4 (2)
C3—C4—C5—C6	2.4 (3)	C10—C11—C12—C13	1.5 (3)
C2—C1—C6—C5	−0.3 (3)	C9—C8—C13—C12	−1.3 (3)
C7—C1—C6—C5	178.76 (18)	O5—C8—C13—C12	−175.74 (19)
O3—C5—C6—C1	179.05 (18)	C11—C12—C13—C8	−0.4 (3)
C4—C5—C6—C1	−1.3 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6*O*···O3^{i}	0.83 (3)	2.13 (4)	2.882 (2)	150 (3)
O7—H7*O*···O4^{ii}	0.84 (3)	2.02 (3)	2.855 (3)	179 (3)

Symmetry codes: (i) *x*, *y*+1, *z*; (ii) −*x*+1, *y*+1/2, −*z*+1/2.