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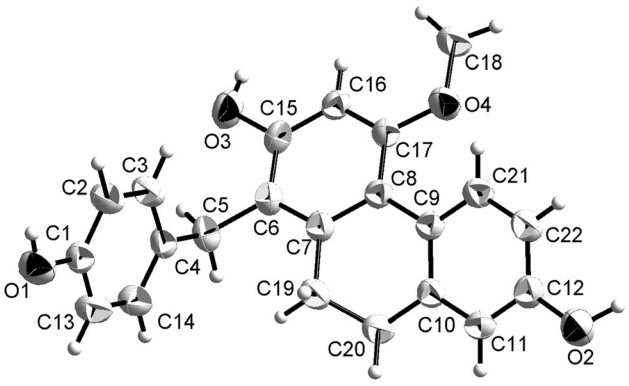
Crystal structure of 1-(4-hydroxybenzyl)-4-methoxy-9,10-dihydrophenanthrene-2,7-diol from Arundina graminifolia, $C_{22}H_{20}O_4$



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Abstract

$C_{22}H_{20}O_4$, orthorhombic, $P2_12_12_1$ (no. 19), a = 11.355(5) Å, b = 15.084(7) Å, c = 20.078(9) Å, V = 3439(3) Å^3, Z = 4, $R_{gt}(F)$ = 0.0382, $wR_{ref}(F^2)$ = 0.0994, T = 296(2) K.

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The molecular structure is shown in Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.28 × 0.26 × 0.22 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	0.09 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	27.4°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	38650, 7761, 0.0295
Criterion for I_{obs}, $N(hkl)_{gt}$:	I_{obs} > 2σ(I_{obs}), 6565
$N(param)_{refined}$:	487
Programs:	Bruker [1], SHELX [2, 3]

Source of material

Crush the dried rhizomes from the underground part of (300.0 g) *Arundina graminifolia* (D. Don) Hochr. It was extracted twice with ethanol (70%) under reflux. The extracts were combined and concentrated, and the samples were dry mixed and washed with petroleum ether, ethyl acetate, and methanol in sequence. The ethyl acetate fraction was eluted with gradient solvents of dichloromethane (DCM) and MeOH (100:1, 20:1, 5:1, 1:1, *v*/*v*) through a silica gel column to afford four fractions. The fraction three was purified by Octadecylsilyl (ODS), semi-preparative High Performance Liquid Chromatography (HPLC) and Sephadex LH-20 to obtain the title compound (10.5 mg).

Experimental details

All hydrogen atoms were identified in difference Fourier syntheses and included with U_{iso}(H) = 1.2U_{eq}(C). The methyl groups were idealized and refined using rigid groups allowed to rotate about the C–C bond (AFIX 137 option of the SHELXL program) [2, 3].

Comment

A. graminifolia (Orchidaceae), which is a perennial herb, is mainly distributed in tropical and subtropical regions in

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	0.40577 (17)	−0.17274 (13)	−0.25213 (9)	0.0584 (5)
H1	0.386 (3)	−0.220 (3)	−0.2354 (17)	0.088*
O2	1.01661 (15)	0.14306 (17)	0.12358 (10)	0.0704 (6)
H2	1.039 (4)	0.146 (3)	0.169 (2)	0.106*
O3	0.17125 (14)	0.08737 (13)	0.03049 (9)	0.0558 (4)
H3	0.124 (3)	0.100 (2)	0.0669 (17)	0.084*
O4	0.48402 (14)	0.09327 (14)	0.19175 (8)	0.0568 (5)
C1	0.3873 (2)	−0.10470 (16)	−0.20717 (11)	0.0463 (5)
C2	0.3430 (3)	−0.11996 (18)	−0.14437 (12)	0.0582 (7)
H2A	0.326111	−0.177369	−0.130451	0.070*
C3	0.3241 (3)	−0.04899 (17)	−0.10233 (12)	0.0575 (6)
H3A	0.293799	−0.059541	−0.060036	0.069*
C4	0.3487 (2)	0.03719 (15)	−0.12097 (11)	0.0445 (5)
C5	0.3236 (2)	0.11445 (16)	−0.07587 (11)	0.0497 (5)
H5A	0.239109	0.123586	−0.074473	0.060*
H5B	0.358524	0.167114	−0.095351	0.060*
C6	0.36795 (19)	0.10560 (15)	−0.00521 (11)	0.0426 (5)
C7	0.48753 (19)	0.11021 (15)	0.01109 (10)	0.0420 (5)
C8	0.52844 (18)	0.10278 (14)	0.07706 (10)	0.0387 (4)
C9	0.65658 (18)	0.10683 (14)	0.09052 (10)	0.0389 (4)
C10	0.72821 (18)	0.15196 (15)	0.04475 (10)	0.0409 (5)
C11	0.84772 (19)	0.16173 (17)	0.05690 (11)	0.0468 (5)
H11	0.894570	0.191468	0.026164	0.056*
C12	0.89760 (19)	0.12807 (17)	0.11368 (12)	0.0490 (5)
C13	0.4111 (2)	−0.01979 (17)	−0.22744 (13)	0.0552 (6)
H13	0.439508	−0.009214	−0.270154	0.066*
C14	0.3928 (2)	0.04988 (17)	−0.18420 (12)	0.0534 (6)
H14	0.410718	0.107120	−0.198112	0.064*
C15	0.28825 (18)	0.09443 (15)	0.04651 (11)	0.0439 (5)
C16	0.32462 (19)	0.09094 (15)	0.11242 (11)	0.0443 (5)
H16	0.269235	0.085923	0.146328	0.053*
C17	0.44313 (19)	0.09493 (15)	0.12765 (10)	0.0417 (5)
C18	0.4035 (2)	0.0831 (2)	0.24468 (12)	0.0626 (7)
H18A	0.351962	0.133509	0.246255	0.094*
H18B	0.445756	0.078495	0.285933	0.094*
H18C	0.357806	0.030274	0.237873	0.094*
C19	0.5792 (2)	0.12626 (18)	−0.04231 (11)	0.0504 (6)
H19A	0.615456	0.070480	−0.054845	0.060*
H19B	0.541925	0.151277	−0.081509	0.060*
C20	0.6723 (2)	0.18928 (18)	−0.01663 (11)	0.0507 (6)
H20A	0.731794	0.198422	−0.050595	0.061*
H20B	0.636707	0.246172	−0.006491	0.061*
C21	0.7107 (2)	0.06927 (16)	0.14615 (11)	0.0441 (5)
H21	0.665548	0.036707	0.176076	0.053*
C22	0.8298 (2)	0.07942 (18)	0.15772 (12)	0.0506 (5)
H22	0.864375	0.053634	0.194991	0.061*
O5	0.5799 (2)	1.15015 (13)	0.46744 (10)	0.0713 (5)
H5	0.598310	1.195147	0.447037	0.107*
O6	−0.01697 (14)	0.82947 (15)	0.10381 (9)	0.0612 (5)
H6	−0.035 (3)	0.844 (3)	0.0607 (19)	0.092*
O7	0.52609 (14)	0.83749 (15)	0.04515 (7)	0.0593 (5)
O8	0.82875 (14)	0.84154 (12)	0.21153 (9)	0.0510 (4)
H8	0.876 (3)	0.848 (2)	0.1719 (16)	0.076*
C23	0.5999 (2)	1.07626 (16)	0.42751 (12)	0.0512 (5)
C24	0.5396 (2)	1.00031 (18)	0.44225 (13)	0.0584 (6)
H24	0.484884	1.000044	0.476705	0.070*
C25	0.5599 (2)	0.92404 (17)	0.40606 (12)	0.0529 (6)
H25	0.518460	0.872837	0.416847	0.064*
C26	0.63977 (19)	0.92150 (16)	0.35439 (10)	0.0432 (5)
C27	0.6656 (2)	0.83601 (16)	0.31712 (10)	0.0463 (5)
H27A	0.749676	0.824848	0.318910	0.056*
H27B	0.626536	0.787533	0.339914	0.056*
C28	0.62709 (18)	0.83590 (15)	0.24480 (10)	0.0408 (4)
C29	0.50811 (18)	0.83106 (14)	0.22620 (10)	0.0398 (4)
C30	0.4129 (2)	0.81940 (17)	0.27779 (11)	0.0477 (5)
H30A	0.382028	0.877044	0.290143	0.057*
H30B	0.446434	0.792434	0.317346	0.057*
C31	0.3134 (2)	0.76184 (17)	0.25213 (11)	0.0493 (5)
H31A	0.342118	0.702110	0.244618	0.059*
H31B	0.251294	0.759047	0.285231	0.059*
C32	0.2651 (2)	0.79861 (15)	0.18846 (11)	0.0420 (5)
C33	0.1453 (2)	0.79668 (16)	0.17405 (11)	0.0459 (5)
H33	0.093189	0.771285	0.204260	0.055*
C34	0.10315 (18)	0.83204 (16)	0.11546 (12)	0.0465 (5)
C35	0.6803 (3)	1.07618 (18)	0.37588 (12)	0.0562 (6)
H35	0.721451	1.127567	0.365238	0.067*
C36	0.6991 (2)	0.99931 (18)	0.34022 (12)	0.0543 (6)
H36	0.753357	0.999836	0.305540	0.065*
C37	0.47251 (18)	0.83501 (15)	0.15905 (10)	0.0391 (4)
C38	0.34520 (18)	0.83474 (15)	0.14239 (11)	0.0399 (4)
C39	0.1793 (2)	0.87017 (17)	0.07072 (12)	0.0505 (5)
H39	0.150750	0.894910	0.031501	0.061*
C40	0.2989 (2)	0.87164 (15)	0.08424 (11)	0.0471 (5)
H40	0.349749	0.897916	0.053765	0.057*
C41	0.56128 (19)	0.83946 (15)	0.11026 (10)	0.0417 (5)
C42	0.6077 (3)	0.8620 (2)	−0.00488 (12)	0.0695 (8)
H42A	0.643640	0.917481	0.006723	0.104*
H42B	0.567532	0.867874	−0.046705	0.104*
H42C	0.667406	0.817150	−0.008578	0.104*
C43	0.67897 (18)	0.84183 (16)	0.12762 (11)	0.0434 (5)
H43	0.736667	0.844169	0.094792	0.052*
C44	0.71043 (18)	0.84069 (15)	0.19430 (11)	0.0414 (5)

China. It is a species of Arundina Blume, a genus in the family Orchidaceae Juss [4]. It is a kind of national medicine that is widely used for clearing heat, detoxicating, and dissipating blood stasis by Dai people [5–7]. Previous studies of this phytochemistry have shown the presence of bibenzyl [8], phenanthrene [9], stilbenoids [10], and other phenolic compounds [11]. In the previous study, we also obtained a single crystal named *orchinol* from the plant [12]. Motivating to find biologically active compounds from this plant, further chemical research was carried out.

As a result, the title compound was obtained from the ethyl acetate part in the ethanol extract, and its crystal structure was analyzed. The single crystal structure verifies

that all bond lengths and angles are within the normal range. The two crystallographically independent molecules (see the figure) are connected by O–H···O hydrogen bonds to form a complex network.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Bruker. SAINT, APEX2 and SADABS; Bruker AXS Inc.: Madison, Wisconsin, USA, 2009.
2. Sheldrick G. M. A short history of *SHELX*. *Acta Crystallogr.* 2008, *A64*, 112–122.
3. Sheldrick G. M. *SHELXTL* – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
4. Hong D. Y., Lian Y. S., Shen L. D. Orchidaceae, in flora of China. *Chin. Sci.* 1983, *73*, 320–321.
5. Chinese Pharmacopoeia Commission. *Pharmacopoeia of the People's Republic of China*, Edition 2010; Beijing Chemical Industry Press: Beijing, 2010.
6. Zhang L. X., Zhang Z. L., Li T. H., Niu Y. F., Guan Y. H., Ma X. J. Investigation, collation and research of traditional Dai medicine of China. *China J. Chin. Mater. Med.* 2016, *41*, 3107–3112.
7. Yu L., Lin Y. Dai medicine "Yajie" (antidotes) clinical application. *J. Med. Pharm. Chin. Minor* 2008, *7*, 25–29.
8. Liu M. F., Han Y., Xing D. M., Shi Y., Xu L. Z., Du L. J., Ding Y. A new stilbenoid from Arundina graminifolia. *J. Asian Nat. Prod. Res.* 2004, *6*, 229–232.
9. Hu Q. F., Zhou B., Ye Y. Q., Jiang Z. Y., Huang X. Z., Li Y. K., Du G., Yang G. Y., Gao X. M. Cytotoxic deoxybenzoins and diphenylethylenes from Arundina graminifolia. *J. Nat. Prod.* 2013, *76*, 1854–1859.
10. Liu Q. Q., Wang H. T., Lin F. K., Dai R. J., Yu D. L., Lv F. Study on the structures and anti-hepatic fibrosis activity of stilbenoids from Arundina graminifolia (D. Don) Hochr. *Mater. Sci. Eng.* 2017, *274*, 12024–12031.
11. Auberon F., Olatunji O., Krisa S., Antheaume C., Herbette G., Bonté F., Mérillon J., Lobstein A. Two new stilbenoids from the aerial parts of *Arundina graminifolia* (Orchidaceae). *Molecules* 2016, *21*, 1430–1439.
12. Zhang X. Y., Chen W. C., Liu M. F. Crystal structure of 7-hydroxy-2,4-dimethoxy-9,10-dihydrophenanthrene from *Arundina graminifolia*, $C_{16}H_{16}O_3$. *Z. Kristallogr. NCS* 2021, *236*, 729–730.