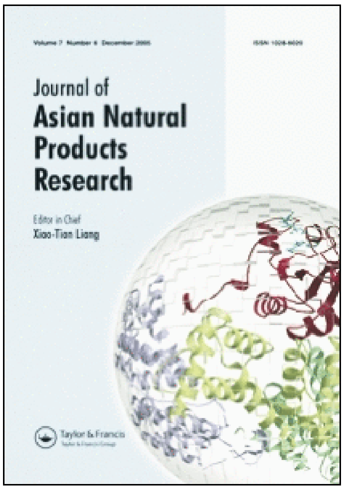

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One new benzyldihydrophenanthrene from *Arundina graminifolia*

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Note

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A novel benzyldihydrophenanthrene named arundinaol (**1**) has been isolated from the rhizoma of *Arundina graminifolia*. The structure of **1** has been elucidated as 7-hydroxy-1-(*p*-hydroxybenzyl)-2,4-dimethoxy-9,10-dihydrophenanthrene on the basis of physical and chemical evidence and spectral analysis.

Keywords: *Arundina graminifolia*; Benzyldihydrophenanthrene; Arundinaol

1. Introduction

Arundina graminifolia is a terrestrial plant belonging to the Orchidaceae, and is used as an antidote and demulcent [1] in China. Stilbenoids, sterols and triterpenes have been isolated from this genus [2–5]. We reported previously the isolation and characterization of a new stilbenoid named arundinan [6] from *Arundina graminifolia*. During further chemical investigation of medicinal plants, the ethanol extract of *Arundina graminifolia* was fractionated into light petroleum, ethyl acetate, acetone and methanol parts, and the ethyl acetate part was found to have an antitumor function *in vitro*. Further chemical investigation of the ethyl acetate part resulted in the isolation of a novel benzyldihydrophenanthrene, designated as arundinaol (**1**). Its structure has been established as 7-hydroxy-1-(*p*-hydroxybenzyl)-2,4-dimethoxy-9,10-dihydrophenanthrene from spectral and chemical evidence.

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2. Results and discussion

Arundinaol (**1**) was obtained as pink needle crystals, mp.218–219°C. The UV spectrum of **1** exhibited typical absorptions of the 9,10-dihydrophenanthrene chromophore at λ_{max} 212, 279 and 299(sh) nm (log ε 4.58, 3.15 and 3.03 respectively) [7,8]. Its IR spectrum reveals hydroxyl (3495, 3398 cm^{-1}), methylene (2943 cm^{-1}) and aromatic groups (1613, 1594, 1572, 1509 cm^{-1}). The phenolic nature of the compound was also indicated by its characteristic color reactions ($FeCl_3$: violet; phosphomolybdic acid: deep blue). A molecular formula of $C_{23}H_{22}O_4$ was determined on the basis of the molecular ion peak in its HR-EIMS, *m/z* 363.1610 $[M + H]^+$, 362.1542 $[M]^+$, and significant fragment ion peaks at *m/z* 242, 181, 134 and 107.

The ^1H NMR spectrum (table 1) of **1** shows signals for two phenolic hydroxyl protons at 9.24 and 9.05 and two doublets at δ 6.85 (2H, d, $J = 8.5$ Hz) and 6.61 (2H, d, $J = 8.5$ Hz) due to a pair of protons (H-2′, H-6′ and H-3′, H-5′) having an A_2B_2 system, which is characteristic of a *p*-substituted aromatic ring. In addition, the ^1H NMR spectrum exhibits a signal at δ 3.93 (2H, s), which is attributed to benzylic methylene. Furthermore, signals appear for a dihydrophenanthrene moiety, *i.e.* two multiplets at δ 2.46–2.50 (2H) and 2.51–2.54 (2H) due to H-9 and H-10, two doublets and a multiplet at δ 7.91 (1H, d, $J = 8.0$ Hz), 6.59 (1H, d, $J = 2.5$ Hz) and 6.60 (1H, m) assigned to H-5, H-8 and H-6, respectively, and a singlet at δ 6.67 (1H, s) due to H-3 of **1**. The ^1H NMR spectrum also showed that **1** contains two methoxyl groups, at δ 3.86 and 3.82 due to C-2 and C-4 as singlets, respectively. Its ^{13}C NMR spectrum (table 1) combined with DEPT spectra shows signals for three ethylenes, two methoxyls and 18 aromatic carbons (δ 95.0–157.0) of which eight aromatic carbons were protonated, the other ten were quaternary (δ 156.2, 155.4, 155.2, 155.0, 138.7, 138.6, 131.0, 123.7, 118.3, 116.1), and four are oxygen-bearing carbons (δ 156.2, 155.4, 155.2, 155.0). All signals were completely assigned with the assistance of the HMQC spectrum.

Table 1. ^1H and ^{13}C NMR data of **1** in CD_3COCD_3 (500 MHz for ^1H and 125 MHz for ^{13}C, δ in ppm, *J* in Hz).

No.	^1H	^{13}C	*HMBC* (^1H to ^{13}C)
1		118.3	
2		155.4	
3	6.67 (H, s)	95.1	C-1,2,4,4a
4		156.2	
5	7.91 (H, d, $J = 8.0$)	128.9	C-6,7,4a,8a
6	6.60 (H, m)	112.6	C-7,8,5a
7		155.2	
8	6.59 (H, d, $J = 2.5$)	113.7	C-6,7,9,5a
9	2.47 (2H, m)	29.2	C-8,10,1a,5a
10	2.53 (2H, m)	25.8	C-1,9,4a,1a
1a		138.7	
4a		116.1	
5a		123.7	
8a		138.6	
α	3.93 (2H, s)	29.5	C-1,2,1a,1′,2′,6′
1′		131.0	
2′(6′)	6.85 (2H, d, $J = 8.5$)	128.6	C-α, 6′(2′),3′(5′),4′,1′
3′(5′)	6.61 (2H, d, $J = 8.5$)	114.9	C-1′,5′(3′),4′,2′(6′)
4′		155.0	
2-OCH_3	3.86 (3H, s)	55.6	C-2
4-OCH_3	3.82 (3H, s)	55.7	C-4
7-OH	9.24 (H, s)		C-6,7,8
4′-OH	9.05 (H, s)		C-4′,3′,5′

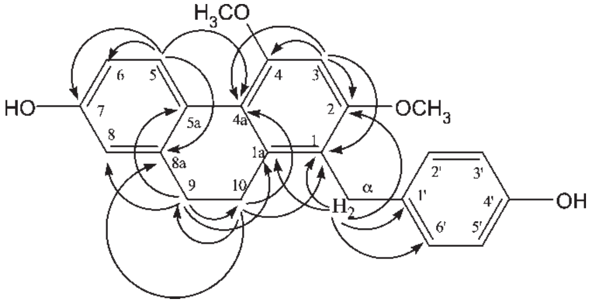

Figure 1. Important HMBC correlations for **1**.

The structure of **1** was further confirmed by its HMBC spectrum. Cross peaks were observed: δ 7.91 (H-5)/112.6(C-6), 116.1 (C-4a), 138.6 (C-8a) and 155.2 (C-7); δ 6.67 (H-3)/116.1 (C-4a), 118.3 (C-1), 155.4 (C-2) and 156.2 (C-4); δ 6.59 (H-8)/29.2(C-9), 112.6 (C-6), 123.7 (C-5a) and 155.2 (C-7); δ 6.60 (H-6)/113.7 (C-8), 123.7 (C-5a) and 155.2 (C-7); δ 6.85 (H-2′, 6′)/29.5 (C-a), 114.9 (C-3′, C-5′), 128.6 (C-2′, 6′), 131.0(C-1′) and 155.0 (C-4′); δ 6.61 (H-3′, 5′)/128.6 (C-2′, 6′), 131.0 (C-1′) and 155.0 (C-4′); δ 2.48 (H-9)/25.8 (C-10), 113.7 (C-8), 123.7 (C-5a) and 138.7 (C-1a); δ 2.53 (H-10)/29.2 (C-9), 116.1 (C-4a), 118.3 (C-1) and 138.7 (C-1a); δ 3.86 (H-a)/118.3 (C-1), 128.6 (C-2′, 6′), 131.0(C-1′), 138.7 (C-1a) and 155.4 (C-2); δ 9.24 (7-OH)/155.2 (C-7), 112.6 (C-6) and 113.7 (C-8); δ 9.05 (4′-OH)/114.9 (C-3′ and C-5′) and 155.0 (C-4′); δ 3.86 (2-OCH_3)/155.4 (C-2); δ 3.83 (4-OCH_3)/156.2 (C-4) (figure 1). On the basis of the above spectral evidence, the structure of **1** was established as 7-hydroxy-1-(*p*-hydroxybenzyl)-2,4-dimethoxy-9,10-dihydrophenanthrene.

3. Experimental

3.1 General experimental procedures

Melting points were determined on an X-4 micro melting point apparatus and are uncorrected. UV spectra were measured on TU-1800PC spectrophotometer. IR spectra were recorded in KBr on a Perkin-Elmer GX-FTIR spectrophotometer. HR-FABMS were obtained on an APEXII mass spectrometer. NMR spectra were determined on a Bruker AM500 instrument, using TMS as internal standard. Column chromatography was performed on silica gel (Qingdao Haiyang Chemical Group Co., Qingdao, China); TLC was conducted on silica gel 60 F_{254} (Merck Co., Germany) and monitored at 254 nm. Sephadex LH-20 was purchased from the Beijing Jinouya Technology and Development Co.

3.2 Plant material

Rhizoma of *Arundina graminifolia* were collected from Yunnan Province in April 2002 and were identified by Professor Yang Chong-ren of the Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen (02041) of the plant has been deposited in Laboratory of Pharmacy and Pharmacology, Department of Biological Science and Biotechnology, Tsinghua University.

3.3 Extraction and isolation

Air-dried powder of the rhizoma of *Arundina graminifolia* (4 kg) was refluxed with 95% EtOH (3 ×).The EtOH extract was then concentrated under reduced pressure to 200 ml and mixed with silica gel (1 kg), followed by elution with light petroleum, ethyl acetate, acetone and methanol sequentially. The ethyl acetate extract (70 g) was fractioned on a silica gel column eluted with gradients of ethyl acetate in light petroleum to give 340 fractions. Fr64-66 (2 g) was subjected to Sephadex LH-20 column chromatography eluted with MeOH–H_2O (4:1) to give arundinaol (**1**).

3.4 Characterization of the new vompound

7-hydroxy-1-(*p*-hydroxybenzyl)-2,4-dimethoxy-9,10-dihydrophenanthrene (**1**): pink needle crystals (MeOH). Mp 218–219°C; UV λ_{max} (nm): 212, 279 and 299(sh) (log ε 4.58, 3.15 and 3.03). IR ν(cm^{-1}): 3495, 3398, 2934, 1613, 1594, 1572, 1509. For ^{1}H and ^{13}C NMR data see table 1. For HR-EIMS *m*/*z* 362.1542 $[M]^+$ (calcd. for $C_{23}H_{22}O_4$, 362.1518); negative-FAB-MS *m*/*z*(rel. int): 361 $[M - H]^-$.

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