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STRUCTURE, SYNTHESIS AND CYTOTOXICITY OF SPHENONE-A, A PHENANTHRENE-1,4-QUINONE FROM *SPHENOMERIS BIFLORA*

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Key Word Index - *Sphenomeris biflora*, Lindsaeaceae, phenanthrene-1,4-quinone, sphenone-A, cytotoxicity

Abstract—A new phenanthrene-1,4-quinone, sphenone-A was isolated from the whole herb of *Sphenomeris biflora*. The structure of sphenone-A was elucidated by spectral methods and synthesis Sphenone-A demonstrated potent cytotoxicity in the KB cell (ED_{50} = 2 7 mcg/ml) tissue culture assay

INTRODUCTION

The plants of the genus *Sphenomeris* are used in Taiwanese folk medicine for the treatment of diarrhoea and as an antipyretic agent [1] We have reported the isolation of a flavonoid, vitexin, from the whole herb of *Sphenomeris biflora* (Kaulf) Tagawa [2] As part of a continuing study of the constituents of this plant, we now describe the isolation, structural elucidation, synthesis and cytotoxicity of a new phenanthrene-1,4-quinone derivative, sphenone-A (**1**)

RESULTS AND DISCUSSION

Sphenone-A (**1**) gave a molecular ion peak at *m/z* 298. The UV absorption bands at 242 8, 278 8(sh), 298(sh), 319 6(sh) and 428 6 nm were consistent with a phenanthrene-1,4-quinone [3] The presence of a 1,4-quinone nucleus in the molecule was further confirmed by the IR spectrum in which characteristic absorption bands were observed at 1673 and 1639 cm^{-1}, together with the appearance of two carbonyl carbon signals at δ182 9 and 185 6 in the ^{13}C NMR spectrum In the ^1H NMR spectrum of **1**, two singlet aromatic signals appear at δ9 15 and 7 13, the lower field signal being characteristic of the C-5 proton in phenanthrene derivatives [4], indicating that the 6,7-positions of ring-A were substituted AB-type proton signals at δ7 95 and 8 11 (each 1H, *d*, *J* = 8.3 Hz) were attributed to mutually *ortho*-located protons on a tetrasubstituted aromatic ring The lower field signal could be assigned to H-10 which is deshielded by the 1-carbonyl moiety From the ^1H–^1H NOESY experiment, three sharp singlet signals at δ3 92, 4 05 and 4 11 (each 3H) were assigned to 2- or 3-OMe, 7-OMe, and 6-OMe, respectively In addition, a singlet olefinic proton signal at δ6 11 was assigned to H-2 or H-3 These spectral data are in excellent accord with the structure **1** or **2** for sphenone-A

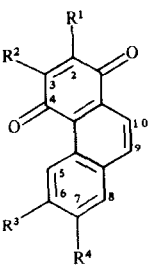
Final proof for the structure of sphenone-A was obtained by synthesis Condensation of 3,4-dimethoxystyrene with methoxy-*p*-benzoquinone in a sealed tube at 100°, as for annoquinone-A (**3**) [3], afforded orange needles which were identified as **1** by comparison of the spectral data. Sphenone-A showed significant cytotoxicity (ED_{50} = 2 7 mcg/ml) in the KB cell tissue culture assay [5]

EXPERIMENTAL

MPs are uncorr, ^1H NMR (100 MHz, 400 MHz) and ^{13}C NMR (100 MHz) $CDCl_3$, TMS as int standard, MS direct inlet

Plant material S biflora was collected at Orchid island, Taiwan and identified by Prof C -S Kuoh The voucher specimen is deposited in the Herbarium of Chia-Nan Junior College of Pharmacy, Tainan, Taiwan

Extraction and separation The dried whole herb (5 7 kg) of *S biflora* was extracted with EtOH under reflux The ethanolic extract was partitioned between $CHCl_3$ and H_2O The $CHCl_3$ layer was sepd, dried, and concd to give a brown syrup which was repartitioned between *n*-hexane and 90% MeOH The 90% MeOH layer was treated with CCl_4 The CCl_4 soluble fraction (10 g) was subjected to silica gel CC and eluted with $CHCl_3$ to afford 41 fractions The eighth fraction was rechromatographed by PLC with C_6H_6–Me_2CO (19 1) as eluant to give sphenone (**1**) (1 6 mg)



1 R^1 = H, R^2 = R^3 = R^4 = OMe
2 R^2 = H, R^1 = R^3 = R^4 = OMe
3 R^1 = R^3 = R^4 = H, R^2 = OMe

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Sphenone-A (**1**) Orange granules ($CHCl_3$), mp 235–238°. UV λ_{max}^{MeOH} nm. 242.8, 278.8(sh), 298(sh), 319 6(sh) and 423.6, IR ν_{max}^{KBr} cm^{-1}: 1673, 1639, 1622, 1567, 1510, 1491, 1467, 1450 and 1440; MS *m/z*: 298 $[M]^+$ (100%), 283, 268, 255, 253, 227, 199; ^{13}C NMR δ 185 6(*s*), 182.9(*s*), 160 8(*s*), 153.4(*s*), 151.1(*s*), 133 6(*d* + *s*), 131.0(*s*), 126.7(*s*), 124.2(*s*), 120 8(*d*), 107.4(*d*), 106 7(*d*), 106 0(*d*), 56 5(*q*), 56 1(*q*), 55 9(*q*)

Synthesis of sphenone-A (**1**) 3,4-Dimethoxystyrene (500 mg) and methoxy-*p*-benzoquinone (850 mg) in 10 ml C_6H_6 in a sealed tube were heated at 100° for 12 hr, and then evapd to dryness. The residue was chromatographed on a silica gel column and eluted with $CHCl_3$ to afford **1** (300 mg). Compound **1** was recrystallized from Me_2CO to give orange needles, mp 257–259°. Calcd for $C_{17}H_{14}O_5$: C, 68 45, H, 4.73% Found: C, 68 40, H, 4.78% This compound was identical with natural sphenone-A by comparison of spectral data and TLC.

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JAYANTININ, A DIMERIC COUMARIN FROM *BOENNINGHAUSENIA ALBIFLORA*

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Key Word Index—*Boenninghausenia albiflora* Rutaceae, dimeric coumarin, jayantinin, murralongin.

Abstract—A new dimeric coumarin, jayantinin has been isolated from *Boenninghausenia albiflora*. The structure of the compound has been elucidated from spectral analysis. Murralongin has also been isolated for the first time from this plant.

INTRODUCTION

The plant *Boenninghausenia albiflora* Reichb & Meissner is a slender, erect, perennial herb found mostly at a temperate climate in the Himalayan ranges between 1000 and 2800 m above sea level. Previous work on this plant resulted in the isolation of several coumarins [1–8] and acridone alkaloids [9, 10]. Reinvestigation of the plant has now resulted in the isolation of a new dimeric coumarin designated as jayantinin (**1**) along with the known compound murralongin (**2**).

RESULTS AND DISCUSSION

Jayantinin (**1**), $C_{20}H_{14}O_6$, mp 255–256° showed the UV absorption [λ_{max}^{EtOH} 324, 256(sh), and 209 nm], characteristic of a 7-alkoxy coumarin [11], being very similar to that of matsukazelactone (**4**) and bhubaneswin (**3**), the two other dimeric coumarins isolated from this plant [7, 8, 12]. The presence of a lactone carbonyl (1715 cm^{-1}) and an aromatic nucleus (1605 and 1590 cm^{-1}) could be recognised also from its IR spectrum As expected the ^1H NMR spectrum (300 MHz) of **1** was in conformity with that of a 3,4-unsubstituted coumarin nucleus Mass spectral analysis of jayantinin, $C_{20}H_{14}O_6$, showed a $[M]^+$ at *m/z* 350 (100%) and other fragments (see Experimental) established the structure as a dimeric coumarin. From analysis of the ^1H NMR signals of jayantinin two monomeric units could be identified and characterized The coumarinic protons C-3(H) and C-3′(H) in the respective units A and A′ resonated at δ 6 21/6.18 each as doublet (J = 9.0 Hz), C-4 (H) and C-4′ (H) also appeared in the expected regions at δ 7.61/7.57 each as doublet (J = 9.0 Hz). Two aromatic methoxyl signals for C-7 and C-7′ (OMe) were observed at δ 3.77 and 3 75 The remaining four protons appeared as two doublets at δ 7.43 and δ 6.93 (2H each, J = 9 0 Hz) As two pairs of *ortho* coupled protons in the respective aromatic rings B and B′ are discernible in the same regions of the ^1H NMR spectrum these two rings must be symmetrically substituted. Considering these facts the possible structures for jayantinin