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 δ185 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.

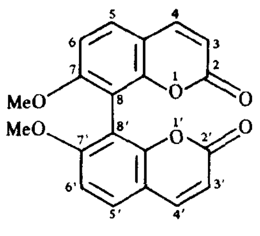
Abstract—A new dimeric coumarin, jayantinin has been isolated from *Boenninghausenia albiflora.* The structure of the compound has been elucidated from spectral analysis. Murralongin has also been isolated for the first time from this plant.

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 ^{1}H 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 ^{1}H 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 δ6 21/6.18 each as doublet ($J = 9.0$ Hz), C-4 (H) and C-4′ (H) also appeared in the expected regions at δ7.61/7.57 each as doublet ($J = 9.0$ Hz). Two aromatic methoxyl signals for C-7 and C-7′ (OMe) were observed at δ3.77 and 3 75 The remaining four protons appeared as two doublets at δ7.43 and δ6.93 (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 ^{1}H NMR spectrum these two rings must be symmetrically substituted. Considering these facts the possible structures for jayantinin



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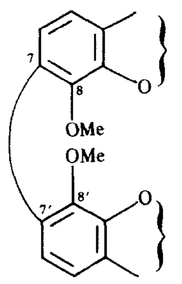

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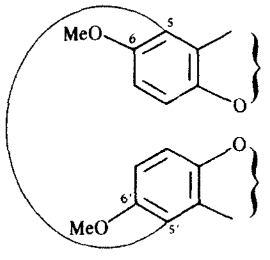

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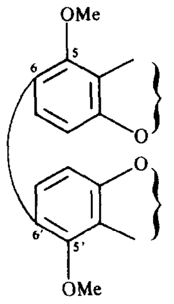
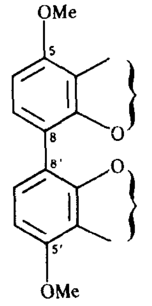
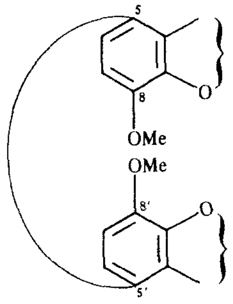


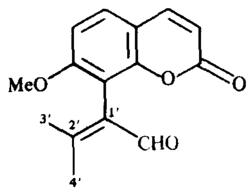
1c



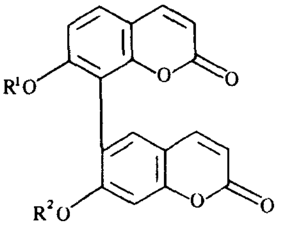
1d



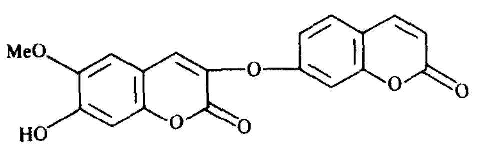
1e



2



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



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thus may be **1**, **1a**, **1b**, **1c**, **1d** or **1e**.

Since the dimeric compound bears 7 and 7′ alkoxy group and possesses one set of unsubstituted *ortho* positions in a symmetrical environment in each of the respective aromatic rings (B and B′) at C-5, C-6 and C-5′, C-6′, the only possibility for a C-C linkage between the two coumarin units would be C-8 and C-8′. ^{13}C NMR data supports this view [13] It is therefore concluded that jayantinin possesses the structure **1**

Interestingly, the spectral data of jayantinin bears a close resemblance to that of bhubaneswin (**3**) and matsukazelactone (**4**) However, in jayantinin the appearance of two pairs of *ortho* coupled protons at δ 7.43 and δ 6 93 (2H each $J = 9\ 0$ Hz) in addition to the coumarin protons at

C-3/C-3′ and C-4/C-4′, could fix the C–C linkage of the two coumarin units at C-8 and C-8′. The other known bis-coumarin isolated from this species is daphnoretin (**5**). In this compound the two coumarin units are linked by an oxygen bridge at C-3 and C-7′.

EXPERIMENTAL

Plant material was collected from the Chaubattia area of Ranikhet, District Almora, U.P. India, during Oct. and identified by R. N. Tewari, A.R.O. and S. C. Pant, R. A. (Botany) of the Amalgamated Units, CCRAS, Tarikhet, Ranikhet. A voucher specimen has been deposited at the Department of Pure Chemistry, University of Calcutta, India. Mps are uncorr. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) were recorded in $CDCl_3$ with TMS as int. std. MS were obtained at 70 eV. Silica gel (BDH, 60–120 mesh) and silica gel G (Merck, 350 mesh) were used for CC and TLC, respectively. Analytical samples were dried *in vacuo* over P_2O_5 for 24 hr.

Isolation of murralongin. Air-dried powdered plant material (whole plant, 7 kg) was Soxhlet extracted with petrol (60–80°) for 24 hr. After removal of solvent, the crude residue was chromatographed over silica gel and elution was performed by repeated chromatography with hexane–EtOAc with increasing proportions of EtOAc. In 3–4 from hexane–EtOAc (1:1) a solid (30 mg) was obtained, mp 128–130° (Et_2O–petrol); R_f 0.35 [C_6H_6–EtOAc (3:7)], 0.48 [EtOAc]; $\lambda_{\max}^{\text{EtOH}}$ 323, 237, 225 nm (log ε 4.17, 4.16 and 4.14), $\nu_{\max}^{\text{KBr}}$ 1725 (unsaturated lactone carbonyl), 1665 (conjugated carbonyl), 1565 and 1495 cm^{-1} (aromatic moiety), ^{1}H NMR (300 MHz, $CDCl_3$), δ 6.90 (1H, *d*, *J* = 9.0 Hz, H-3), 7.65 (1H, *d*, *J* = 9.0 Hz, H-4), 7.42 (1H, *d*, *J* = 9.0 Hz, H-5), 6.2 (1H, *d*, *J* = 9.0 Hz, H-6), 3.82 (OMe), 1.78 and 2.42 (3H, *s*, each 2′–Me), 10.20 (1H, *s*, –CHO), ^{13}C NMR ($CDCl_3$ ppm*), 160.9 (C-2), 113.1 (C-3), 143.5 (C-4), 112.9 (C-4a), 128.5 (C-5), 107.5 (C-6), 159.4 (C-7), 113.0 (C-8), 160.0 (C-8a), 56.1 (C-7 –OMe), 152.5 (C-1′), 188.6 (C-1′–CHO), 129.1 (C-2′), 24.7 and 19.7 (C-2′, 2 × CH_3). The identity of the compound was finally confirmed from mp, co-TLC and co-IR with an authentic sample.

Isolation of jayantinin. Fractions 7–13 in the same eluent [hexane–EtOAc (1:1)] afforded another solid. Rechromatography of this solid followed by fractional crystallization afforded jayantinin (**1**) as a greenish powder (25 mg), mp 255–256° (Et_2O) R_f 0.17 [hexane–EtOAc (1:1)], 0.53 [EtOAc], $\lambda_{\max}^{\text{EtOH}}$ 324, 256, 209 nm (log ε 4.41, 4.11 and 4.63), $\nu_{\max}^{\text{KBr}}$ 1715 (lactone carbonyl), 1605 and 1590 (aromatic nucleus) cm^{-1}, ^{1}H NMR (300 MHz), $CDCl_3$ δ 6.21/δ 6.18, (1H, *d*, *J* = 9.0 Hz each, H-3/H-3′), δ 7.61/δ 7.57, (1H, *d*, *J* = 9.0 Hz each, H-4/H-4′), δ 7.43/δ 6.93, (2H, *d*, *J* = 9.0 Hz each, H-5 and H-5′ and H-6 and H-6′, respectively); ^{13}C NMR ($CDCl_3$ ppm) 161.0 (C-2, C-2′), 113.0 (C-3, C-3′), 143.1/143.1 (C-4/C-4′), 112.7 (C-4a, C-4a′), 130.4/130.5 (C-5/C-5′), 107.3 (C-6, C-6′), 159.5 (C-7, C-7′), 99.2 (C-8, C-8′) [13], 153.0/153.1 (C-8a/C-8a′), 55.8/55.9 (C-7 –OMe/C-7′ –OMe), MS: *m/z* (rel. int.) 350 ([M$^+$], 100%), 335 (8.7), 320 (7.9), 319 (34.3), 305 (11.3), 291 (11.8), 279 (9.4), 276 (8.4) and 248 (8.5).

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*^{13}C NMR ($CDCl_3$) data on naturally occurring murralongin is being reported for the first time.