



ALKALOIDS FROM TRUNK BARK OF *HERNANDIA NYMPHAEIFOLIA*

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(Received in revised form 18 December 1995)

Key Word Index—*Hernandia nymphaeifolia*; Hernandiaceae; bark; alkaloids; (+)-ovigeridimerine; 4-methoxyoxohernandaline; 7-formyldehydrohernangerine; 5,6-dimethoxy-*N*-methylphthalimide; 7-hydroxy-6-methoxy-1-methylisoquinoline; (+)-vateamine-2'- β -*N*-oxide; hernandial.

Abstract—Six new alkaloids, (+)-ovigeridimerine, 4-methoxyoxohernandaline, 7-formyldehydrohernangerine, 5,6-dimethoxy-*N*-methylphthalimide, 7-hydroxy-6-methoxy-1-methylisoquinoline and (+)-vateamine-2'- β -*N*-oxide, along with one new dialdehyde, hernandial, have been isolated and characterized from the trunk bark of *Hernandia nymphaeifolia*. The structures of these compounds were elucidated by spectral analyses.

INTRODUCTION

Hernandia nymphaeifolia [1–3], is a shore tree, distributed in tropics of the Old World. We have pointed out that this species was misnamed as *H. ovigera* or *H. sonora* in Taiwan and Japan for many years [4]. Many chemists have studied the alkaloids, lignans and other constituents from *H. nymphaeifolia* [5–27]; in previous papers, we have reported nine new alkaloids and ten known compounds, including several antiplatelet agents from the trunk bark [4, 28, 29]. Continuing our examination of the tertiary basic fraction of the trunk bark of this species has now resulted in the isolation of seven new minor compounds including three aporphines, (+)-ovigeridimerine (**1**), 4-methoxyoxohernandaline (**2**) and 7-formyldehydrohernangerine (**3**), one phthalimide, 5,6-dimethoxy-*N*-methylphthalimide (**4**), one isoquinoline, 7-hydroxy-6-methoxy-1-methylisoquinoline (**5**), one *bis*-benzylisoquinoline, (+)-vateamine-2'- β -*N*-oxide (**6**) and one dialdehyde, hernandial (**7**), as additional constituents. In this paper, we describe the isolation and structural elucidation of these new compounds.

RESULTS AND DISCUSSION

(+)-Ovigeridimerine (**1**) was isolated as light brownish prisms. The molecular formula was established as $C_{37}H_{28}O_9N_2$ by EI ($[M]^+$, m/z 644) and HR-mass spectrometry. The UV absorptions at 206, 229, 271, 313 nm were similar to those of ovigerine and were characteristic of a 1,2,10,11-oxygenated aporphine

skeleton [10]. The IR spectrum showed an amidocarbonyl absorption at 1640 cm^{-1} and that for a methylenedioxy group at 1060 and 930 cm^{-1} . The ^1H NMR spectrum of **1** showed three mutually coupling aliphatic protons at δ 2.58 (1H, *t*, $J = 13.1\text{ Hz}$, H-7), δ 3.05 (1H, *dd*, $J = 13.1, 3.6\text{ Hz}$, H-7) and δ 4.72 (1H, *dd*, $J = 13.1, 3.6\text{ Hz}$, H-6a); the signal for H-6a was moved downfield to δ 4.72 due to the anisotropic effect of the neighbouring carbonyl group. In addition, four mutually-coupling aliphatic protons at δ 2.80 (2H, *m*, H-4), δ 3.26 (1H, *m*, H-5) and δ 3.76 (1H, *m*, H-5) in ring B, and two methylenedioxy signals at δ 5.94, 5.96, 6.08, 6.09 (each 1H, *d*, $J = 1.4\text{ Hz}$) were observed. The aromatic region of the spectrum integrated for three protons; one at δ 6.62 (1H, *s*) was assigned to H-3, the other protons at δ 6.73 (2H, *s*) to H-8 and H-9. According to the above data and the significant fragments at m/z 336 [$M - C_{18}H_{14}O_4N$] $^+$, 308 [$M - C_{18}H_{14}O_4N - CO$] $^+$ in the EI-mass spectrum, **1** was elucidated as a dimer of ovigerine involving a carbonyl linkage to connect two nitrogen atoms. The structure of **1** was further confirmed by the ^1H – ^1H COSY and NOE difference experiments (Fig. 1). Its specific rotation is positive $[\alpha]_D^{22} +197^\circ$ (*c* 0.12, CHCl_3), so **1** possesses an *S*-configuration at C-6a and C-6'a [30–34].

4-Methoxyoxohernandaline (**2**) was obtained as orange-reddish prisms. The EI-mass spectrum afforded the molecular ion $[M]^+$ at m/z 531, implying a molecular formula of $C_{29}H_{25}O_9N$, which was confirmed by the HRFAB-mass spectrum. The UV absorptions at 208, 240, 270 sh, 315 sh, 327 and 461 nm suggested the presence of an oxoaporphine skeleton [35]. The IR spectrum revealed conjugated carbonyl absorption at 1650 cm^{-1} . The ^1H NMR spectrum of **2** showed the presence of six methoxyl groups at δ 3.82,

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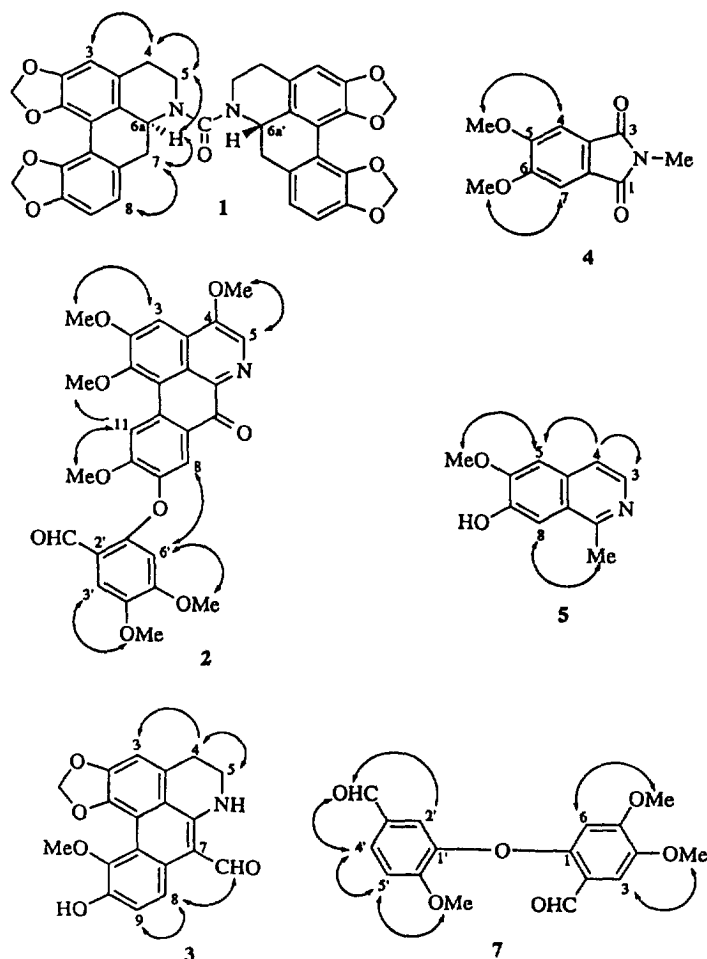


Fig. 1. NOE difference of compounds 1, 2, 3, 4, 5 and 7.

3.85, 3.99, 4.13 (each 3H, *s*) and 4.16 (6H, *s*) attributed to C-5', C-2, C-4', C-10, C-1 and C-4-OMe, respectively. Six aromatic protons at δ 6.58, 7.16, 7.32, 7.48, 8.32 and 9.30 (each 1H, *s*) were assigned to H-3, H-8, H-6', H-3', H-5 and H-11, respectively, and a formyl group at δ 10.31 (1H, *s*) assigned to the C-2' position. The above assignments were further confirmed by NOE-DIF experiments (Fig. 1). From the above observations, the structure of **2** was characterized as 4-methoxyoxohermandaline.

7-Formyldehydrohernangerine (**3**) was isolated as yellowish prisms. The molecular formula, $C_{19}H_{15}O_5N$, was determined by EI ($[M]^+$, m/z 337) and HRFAB-mass spectrometry. The presence of a 7-formyldehydroaporphine skeleton was characterized by the UV spectrum showing absorptions at 217, 265 and 429 nm, along with a conjugated carbonyl absorption band at 1620 cm^{-1} in the IR spectrum [28]. The presence of a phenolic hydroxyl group in the molecule was indicated by the IR absorption at 3250 cm^{-1} and a bathochromic shift of UV absorption in alkaline solution. The IR spectrum also showed the presence of a methylenedioxy group at 1060 and 930 cm^{-1} . The ^1H NMR spectrum of **3** showed four protons [δ 3.15

(2H, *t*, $J = 6.8\text{ Hz}$), δ 3.63 (2H, *dt*, $J = 6.8\text{ Hz}$, 2.8 Hz)] assignable to the two methylene units at C-4 and C-5, and a methylenedioxy (C-1, C-2) signal at δ 6.17 (2H, *s*). This spectrum also included a methoxyl signal at highfield δ 3.61 (3H, *s*), characteristic of OMe-11 [30–34], and a hydroxyl group at δ 5.95 (1H, *s*, disappeared with D_2O) due to OH-10 which was supported by a negative Gibbs test. The aromatic region of the spectrum showed three protons; one at δ 6.97 (1H, *s*) was assigned to H-3 and the other *ortho*-coupled protons at δ 7.21 and 7.82 (each 1H, *d*, $J = 9.0\text{ Hz}$) to H-9 and H-8. A downfield singlet at δ 10.46 was assigned to a formyl group at the C-7 position and a downfield broad singlet as an NH group at δ 10.97 (1H, *br s*, disappeared with D_2O) due to the formation of hydrogen bonding with the neighbouring carbonyl group. On the basis of the above data, the structure of **3** was elucidated as 7-formyldehydrohernangerine which was further confirmed by NOE difference experiments (Fig. 1).

5,6-Dimethoxy-*N*-methylphthalimide (**4**) was isolated as colourless prisms. The molecular formula was established at $C_{11}H_{11}O_4N$ by EI ($[M]^+$, m/z 221) and HR-mass spectrometry. The presence of a phthalimide skeleton in the molecule was easily deduced from the

UV spectrum (absorption maxima at 248 and 295 nm) which was similar to that of phthalimide, along with an amidocarbonyl group absorption band at 1705 cm^{-1} in the IR spectrum. Analysis of the ^1H NMR spectrum of **4** showed the presence of a sharp singlet at δ 3.15 (3H) due to an *N*-methyl group and a singlet integrating for six protons resonating at δ 4.0 indicated the presence of two methoxyl groups attached to the aromatic ring system. The *ortho*-disposition of these two methoxyl groups (C-5 and C-6) was supported by the presence of two aromatic protons (H-5 and H-8) which appeared as one singlet integrating for two protons at δ 7.31. The assignments for each proton in the ^1H NMR of **4** were substantiated by NOE-DIF experiments (Fig. 1). According to the above data, the structure of **4** was elucidated as 5,6-dimethoxy-*N*-methylphthalimide.

7-Hydroxy-6-methoxy-1-methylisoquinoline (**5**) was obtained as needles. Its HR-mass spectrum revealed a $[\text{M}]^+$ at m/z 189.0783 leading to the molecular formula $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}$ (calcd 189.0789). The UV absorption bands at 237, 270, 318 and 329 nm and the exhibition of a bathochromic shift on addition of aqueous potassium hydroxide suggested the presence of a phenolic bisbenzylisoquinoline skeleton [36]. The IR spectrum showed a broad band of OH absorption at 3340 cm^{-1} . The ^1H NMR spectrum showed a singlet at δ 2.88 (3H) for Me-1 and a singlet at δ 4.07 (3H) attributed to OMe-6. Two singlets at δ 7.08 and 7.51 (each 1H) were attributed to H-5 and H-8, respectively. Two doublets for two mutually coupled aromatic protons appeared at

δ 7.39 and 8.25 ($J = 5.8\text{ Hz}$) and were assigned to H-4 and H-3, respectively. The assignments for each proton in the ^1H NMR of **5** were substantiated by NOE-DIF experiments (Fig. 1). On the basis of the above spectroscopic studies, the structure of **5** was assigned as 7-hydroxy-6-methoxy-1-methylisoquinoline.

(+)-Vateamine-2'- β -*N*-oxide (**6**) was isolated as prisms. The FAB-mass spectrum afforded the positive ion at m/z 673 $[\text{M} + \text{H}]^+$, implying a molecular formula of $\text{C}_{38}\text{H}_{45}\text{O}_9\text{N}_2$. This was confirmed by the HRFAB-mass spectrum ($[\text{M} + \text{H}]^+$ found 673.3118, calcd 673.3125). The fragment peak at m/z 657 was due to the loss of an oxygen atom and suggested the presence of an *N*-oxide function; a dominating peak at m/z 192 suggested the presence of a tetrahydrobenzylisoquinoline dimer involving tail-to-tail coupling, as in the case of (+)-vanuatine and (+)-vateamine [23]. The UV absorption bands at 207, 230 sh and 284 nm and the observation of a bathochromic shift on addition of aqueous potassium hydroxide indicated the presence of a phenolic bisbenzylisoquinoline skeleton [23]. The IR spectrum showed absorptions due to a hydroxyl group (3300 cm^{-1}) and an aromatic ring (1600 , 1500 and 1435 cm^{-1}). The ^1H NMR spectrum of **6** (Fig. 2), especially those of the aromatic protons, including the relatively upfield aromatic singlets (H-8, H-8') at δ 5.06 and 5.90, were very similar to those observed for (+)-vateamine [23]. But the 2'-*N*-methyl group at δ 3.05 (3H, *s*) and H-1' at δ 4.17 (1H, *br d*) resonated

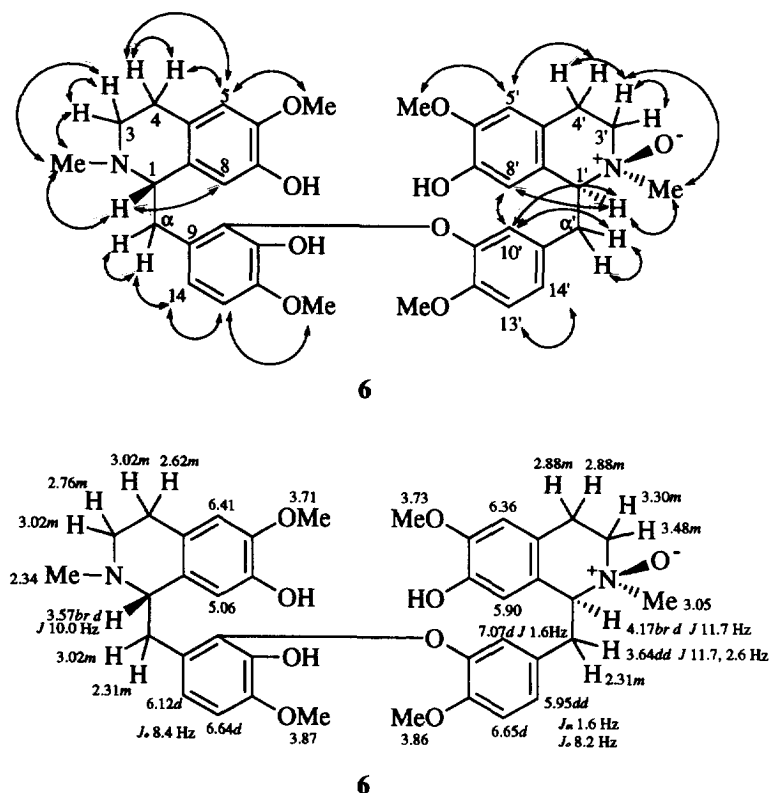


Fig. 2. NOESY and ^1H NMR chemical shifts (δ) of **6**.

further downfield than the corresponding protons in (+)-vateamine. Thus, **6** was reasonably proposed as vateamine-*N*-oxide. The downfield shifts of 0.53 ppm for the 2'-*N*-methyl singlet and of 0.36 ppm for the H-1' doublet, compared with the corresponding signals of (+)-vateamine, suggested that H-1' of **6** is on the side opposite to the *N*-oxide [37, 38]. The positive specific rotation indicated that **6** possessed the 1*S*, 1'*S*-configuration and, therefore, the *N*-oxide function had the β -orientation [37, 38]. The assignments of ¹H NMR spectrum of **6** were confirmed by NOESY experiments (Fig. 2). On the basis of the above results, structure **6** was assigned to (+)-vateamine-2'- β -*N*-oxide.

Hernandial (**7**) was obtained as pale yellowish prisms. The molecular formula, C₁₇H₁₆O₆, was determined by EI ([M]⁺, *m/z* 316) and HR-mass spectrometry. The UV absorption bands at 207, 239, 274 nm indicated that there was a benzenoid moiety in the molecule [39]. The IR spectrum revealed the presence of a carbonyl group (1685 cm⁻¹) and an aromatic nucleus (1600, 1505 and 1460 cm⁻¹). The ¹H NMR spectrum of **7** showed three sharp singlets at δ 3.81, 3.95 and 3.99 (each 3H) attributed to C-5, C-4 and C-6'-OMe, respectively. Three mutually coupling aromatic protons at δ 7.14 (*d*, *J* = 8.4 Hz), 7.39 (*d*, *J* = 1.9 Hz) and 7.68 (*dd*, *J* = 8.4, 1.9 Hz) were due to H-5', H-2' and H-4', respectively. Two singlet aromatic protons at δ 6.40 and 7.40 were assigned to H-6 and H-3, respectively. In addition, two singlet signals at δ 9.83 and 10.28 (each 1H) were assignable to two formyl groups at C-3' and C-2, respectively. From the above spectroscopic data, the structure of **7**, with two asymmetric benzenoid moieties joined by an ether linkage, was proposed as 4,5,6'-trimethoxyphenoxybenzene-2,3'-dialdehyde. The mass spectral fragments at *m/z* 181 [M - C₈H₇O₂]⁺, 135 [M - C₉H₉O₄]⁺ and *m/z* 165 [M - C₈H₇O₃]⁺, 151 [M - C₉H₉O₃]⁺ also supported the proposed structure. Finally, the structure of **7** was further confirmed by NOE difference experiments (Fig. 1). This is the first report of the occurrence of **7** from a natural source, although it has been synthesized by Kametani *et al.* [40]; its formation may be the result of oxidative cleavage of the dimeric alkaloid, 4-methoxyoxohernandaline (**2**), in the biogenetic process.

EXPERIMENTAL

Mp, are uncorr. ¹H NMR (200 and 400 MHz) was taken in CDCl₃. Chemical shifts are given in ppm (δ) with TMS as int. standard. MS were measured using a direct inlet system. Optical rotations were measured in CHCl₃. UV spectra were determined in EtOH and IR in KBr discs. Silica gel (60–230 mesh) (Merck) was used for CC and silica gel 60 F-254 for TLC.

Plant material. Trunk bark of *H. nymphaeifolia* (Presl) *Kubitzki* (*Biasoletia nymphaeifolia* Presl, *Hernandia peltata* Meissn.) was collected from Green Island, Taitung Hsien, Taiwan, in August 1992. A

voucher sample is deposited in the herbarium of the School of Pharmacy, Kaohsiung Medical College, Kaohsiung, Taiwan, Republic of China.

Extraction and isolation. The tert. phenolic bases (fr. A, 10.4 g) and non-phenolic bases (fr. B, 26.7 g) afforded from the MeOH extract of the trunk bark (7 kg) were described previously [28]. Fr. A (10.4 g) was rechromatographed on silica gel eluting with 10% MeOH-CHCl₃, gradually increasing the polarity with MeOH and 8 frs (A1–A8) were collected. Fr. A2 (134 mg) was purified by prep. TLC [CH₂Cl₂-MeOH (10:1)] to yield **3** (5.7 mg) (*R_f* 0.90) after recrystallization from CHCl₃-MeOH. Fr. A4 (1.603 g) was rechromatographed on silica gel using CHCl₃-MeOH (5:1) to give frs A4-1–A4-3. Fr. A4-2 (1.032 g) was sep'd by prep. TLC [CHCl₃-MeOH (9:1)] to give frs A4-2-a–A4-2-d. Fr. A4-2-b (123 mg) was further purified by prep. TLC [CHCl₃-MeOH (10:1)] to obtain **5** (2.7 mg) (*R_f* 0.48) after recrystallization from CHCl₃-MeOH. Fr. A5 (2.274 g) was rechromatographed on silica gel using EtOAc-MeOH (1:1) to give frs A5-1–A5-5. Fr. A5-4 (1.285 g) was further sep'd and purified by silica gel cc and prep. TLC [CHCl₃-MeOH (1:1)] to yield **6** (6.7 mg) (*R_f* 0.49) after recrystallization from MeOH. Fr. B (26.7 g) was washed with CHCl₃ to yield hernandonine (971 mg). The washings (25.3 g) were chromatographed over silica gel eluting with CHCl₃, gradually increasing the polarity with MeOH and 9 frs (B1–B9) were collected. Frs B1 and B2 (22 mg) was purified by prep. TLC [benzene-EtOAc (10:1)] to give **4** (2.3 mg) (*R_f* 0.44) after recrystallization from CHCl₃-MeOH. Fr. B3 (10.5 g) was rechromatographed on silica gel using CHCl₃ and gradually increasing the polarity with Me₂CO to obtain 15 frs (B3-1–B3-15). Fr. B3-4 (68.5 mg) was further purified by prep. TLC [*n*-hexane-EtOAc (1:1)] to give **1** (8.6 mg) (*R_f* 0.85) and **7** (2.6 mg) (*R_f* 0.50) after recrystallization from MeOH. Fr. B3-12 (1.5619 g) was rechromatographed on silica gel with CHCl₃-Me₂CO (10:1) to obtain frs B3-12-1–B3-12-5. Fr. B3-12-2 (116.7 mg) was further purified by prep. TLC [CHCl₃-Me₂CO (10:1)] to give **2** (2.8 mg) (*R_f* 0.44) after recrystallization from CHCl₃-MeOH.

(+)-**Ovigeridimerine** (**1**). Light-brownish prisms (MeOH), mp 207–210°. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 206 (4.81), 229 (4.84), 271 (4.55), 313 (4.26). IR ν_{max} cm⁻¹: 1640 (C=O), 1060, 930 (OCH₃O). EI-MS *m/z* (rel. int.): 664 [M]⁺ (60), 336 (17), 335 (52), 308 (45), 307 (57), 292 (40), 279 (78); HR-MS: C₃₇H₂₈O₉N₂, found: 644.1824, calcd: 644.1795. ¹H NMR (200 MHz): δ 2.58 (1H, *t*, *J* = 13.1 Hz, H-7), 2.80 (2H, *m*, H-4), 3.05 (1H, *dd*, *J* = 13.1, 3.6 Hz, H-7), 3.26 (1H, *m*, H-5), 3.76 (1H, *m*, H-5), 4.72 (1H, *dd*, *J* = 13.1, 3.6 Hz, H-6a), 5.94, 5.96, 6.08, 6.09 (each 1H, *d*, *J* = 1.4 Hz, OCH₂O \times 2), 6.62 (1H, *s*, H-3), 6.73 (2H, *s*, H-8,9). [α]_D²² +197° (c 0.12, CHCl₃).

4-Methoxyoxohernandaline (**2**). Orange-reddish prisms (CHCl₃-MeOH), mp 255–259°. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (log ϵ): 208 (4.53), 240 (4.63), 270 sh (4.35), 315 sh

(4.31), 327 (4.39), 461 (4.02). IR ν_{\max} cm^{-1} : 1650 (C=O). EI-MS m/z (rel. int.): 531 $[\text{M}]^+$ (10), 500 (2), 308 (1), 264 (2), 256 (3), 236 (2), 221 (2), 213 (2), 185 (3), 129 (8); HRFAB-MS: $\text{C}_{29}\text{H}_{26}\text{O}_9\text{N}$, found: 532.1657 $[\text{M} + \text{H}]^+$, calcd: 532.1608. ^1H NMR (200 MHz): δ 3.82 (3H, s, OMe-5'), 3.85 (3H, s, OMe-2), 3.99 (3H, s, OMe-4'), 4.13 (3H, s, OMe-10), 4.16 (6H, s, OMe-1,4), 6.58 (1H, s, H-3), 7.16 (1H, s, H-8), 7.32 (1H, s, H-6'), 7.48 (1H, s, H-3'), 8.32 (1H, s, H-5), 9.30 (1H, s, H-11), 10.31 (1H, s, CHO-2').

7-Formyldehydrohernangerine (3). Yellowish prisms (CHCl_3 -MeOH), mp 211–213°. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ϵ): 217 (4.52), 265 (4.54), 429 (3.99); UV $\lambda_{\max}^{\text{EtOH}+\text{KOH}}$ nm (log ϵ): 204 (4.63), 236 (4.46), 268 (4.52), 295 sh (4.24), 453 (3.80). IR ν_{\max} cm^{-1} : 3250 (br, OH), 1620 (C=O), 1060, 930 (OCH_2O). EI-MS m/z (rel. int.): 337 $[\text{M}]^+$ (100), 322 (12), 294 (23), 277 (4), 266 (8), 236 (21), 208 (8), 178 (9), 163 (9), 152 (25); HRFAB-MS: $\text{C}_{19}\text{H}_{15}\text{O}_5\text{N}$, found: 337.0949, calcd: 337.0950. ^1H NMR (200 MHz): δ 3.15 (2H, t, $J = 6.8$ Hz, H-4), 3.61 (3H, s, OMe-11), 3.63 (2H, dt, $J = 6.8, 2.8$ Hz, H-5), 5.95 (1H, s, OH-10, disappeared with D_2O), 6.17 (2H, s, OCH_2O), 6.97 (1H, s, H-3), 7.21 (1H, d, $J = 9.0$ Hz, H-9), 7.82 (1H, d, $J = 9.0$ Hz, H-8), 10.46 (1H, s, CHO-7), 10.97 (1H, br s, NH, disappeared with D_2O).

5,6-Dimethoxy-N-methylphthalimide (4). Prisms (CHCl_3 -MeOH), mp 149–151°. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ϵ): 248 (4.50), 295 (3.13). IR ν_{\max} cm^{-1} : 1705 (C=O). EI-MS m/z (rel. int.): 221 $[\text{M}]^+$ (12), 178 (8), 177 (12), 162 (3), 149 (5), 136 (9), 121 (25), 93 (33); HR-MS: $\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$, found: 221.0697, calcd: 221.0688. ^1H NMR (200 MHz): δ 3.15 (3H, s, N-Me), 4.00 (6H, s, OMe-5,6), 7.31 (2H, s, H-4,7).

7-Hydroxy-6-methoxy-1-methylisoquinoline (5). Needles (CHCl_3 -MeOH), mp 121–123°. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ϵ): 237 (4.55), 270 (4.53), 318 (3.35), 329 (3.39); UV $\lambda_{\max}^{\text{EtOH}+\text{KOH}}$ nm (log ϵ): 257 (4.43), 291 (3.69), 355 (3.51), IR ν_{\max} cm^{-1} : 3340 (OH). EI-MS m/z (rel. int.): 189 $[\text{M}]^+$ (100), 174 (26), 163 (5), 149 (13), 146 (59), 117 (12), 105 (12); HR-MS: $\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}$, found: 189.0783, calcd: 189.0789. ^1H NMR (200 MHz): δ 2.88 (3H, s, Me-1), 4.07 (3H, s, OMe-6), 7.08 (1H, s, H-5), 7.39 (1H, d, $J = 5.8$ Hz, H-4), 7.51 (1H, s, H-8), 8.25 (1H, d, $J = 5.8$ Hz, H-3).

(+)-Vateamine-2'- β -N-oxide (6). Needles (MeOH), mp 133–135°. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ϵ): 207 (4.94), 230 sh (4.51), 284 (4.07); UV $\lambda_{\max}^{\text{EtOH}+\text{KOH}}$ nm (log ϵ): 208 (4.97), 289 (4.06). IR ν_{\max} cm^{-1} : 3300 (br, OH), 1600, 1500, 1435 (aromatic ring C=C stretch). FAB-MS m/z (rel. int.): 673 $[\text{M} + \text{H}]^+$ (100), 657 $[\text{M} + \text{H} - \text{O}]^+$ (21); HRFAB-MS: $\text{C}_{38}\text{H}_{45}\text{O}_9\text{N}_2$, found: 673.3118 $[\text{M} + \text{H}]^+$, calcd: 673.3125. ^1H NMR (400 MHz): see Fig. 2. $[\alpha]_{\text{D}}^{24} + 341^\circ$ (c 0.11, CHCl_3).

Hernandial (7). Pale yellowish prisms (MeOH), mp 137–139°. UV $\lambda_{\max}^{\text{EtOH}}$ nm (log ϵ): 207 (4.22), 239 (4.28), 274 (4.26). IR ν_{\max} cm^{-1} : 1685 (C=O), 1600, 1505, 1460 (aromatic ring C=C stretch). EI-MS m/z (rel. int.): 316 $[\text{M}]^+$ (49), 307 (6), 285 (7), 279 (10), 181 (17), 180 (100), 165 (34), 151 (9), 149 (24), 137

(30), 135 (19); HR-MS: $\text{C}_{17}\text{H}_{16}\text{O}_6$, found: 316.0962, calcd: 316.0947. ^1H NMR (400 MHz): δ 3.81 (3H, s, OMe-5), 3.95 (3H, s, OMe-4), 3.99 (3H, s, OMe-6'), 6.40 (1H, s, H-6), 7.14 (1H, d, $J = 8.4$ Hz, H-5'), 7.39 (1H, d, $J = 1.9$ Hz, H-2'), 7.40 (1H, s, H-3), 7.68 (1H, dd, $J = 8.4, 1.9$ Hz, H-4'), 9.83 (1H, s, CHO-3'), 10.28 (1H, s, CHO-2).

Acknowledgement—This work was kindly supported by a grant (NSC 82-0420-B-037-007-M13) from the National Science Council of the Republic of China.

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