AZAFLUORENE AND APORPHINE ALKALOIDS FROM *POLYALTHIA LONGIFOLIA*

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Abstract— A novel azafluorene alkaloid , polylongine (5-hydroxy-6-methoxy-1-methyl-4-azafluoren-9-ol) (1) and three new aporphine N-oxide alkaloids named (+)-O-methylbulbocapnine-β-N-oxide (2) , (+)-O-methylbulbocapnine -α-N-oxide (3) and *(+)-N-methylnandigerine -β-N-oxide* (4) were isolated from the leaves of *Polyalthia longifolia* (Sonn.) Thwaites (Annonaceae).

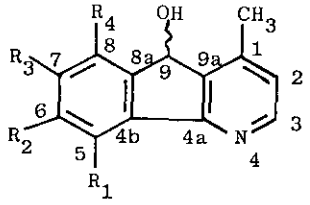
The Annonaceae is a large family comparising ca. 120 genera and more than 2000 species. Phytogeographically it is entirely tropical and subtropical, 120 species being presented in genus *Polyalthia*. Earlier work on the chemical examination from the plants of *Polyalthia* genus[1-13] has given carbohydrates, diterpenes, triterpenes, polyphenols, flavones, nitrogen heterocycles (zincpolyanemine),indolosesquiterpenes, zinc containing compound (anluosu), benzylisoquinolines, protoberberines, tetrahydroprotoberberines, bisbenzylisoquinolines, aporphines, dehydroaporphines, bisaporphines, oxoaporphines and morphinandienones. In the course of our study of the chemical constituents of the Formosan Annonaceous plants, we report the results of the investigation of the leaves from *P. longifolia* (Sonn.) Thwaites collected from the Taipei Botanical Garden of Taiwan Forestry Research Institute, in January, 1988.

RESULTS AND DISCUSSION

The methanolic extract of the leaves of *P. longifolia* was fractionated by solvent partitions. Chromatographic fractionation of the chloroform soluble bases over silica gel

afforded a novel azafluorenoid alkaloid, polylongine (5-hydroxy-6-methoxy-1-methyl-4-azafluoren-9-ol) (1) and three new aporphinoid alkaloids, they were named (+)-O-methylbulbocapnine-β-N-oxide (2), (+)-O-methylbulbocapnine-α- N-oxide (3) and (+)-N-methylnandigerine-β-N-oxide (4) as well as the known aporphinoid alkaloids, (-)-oliveroline-β-N-oxide (5), liriodenine (6), anonaine (7) and (+)-norlirioferine (8).

Polylongine (1) was obtained from chloroform as pale yellowish needles. Its molecular formula was established as $C_{14}H_{13}NO_3$ by high resolution ms (Found: 243.0865, Calcd 243.0894) and ^{13}Cnmr. The presence of a hydroxyl group instead of a carbonyl group at C-9 in the onychine series was indicated by the following evidence: i) no absorption band was seen at 1650-1750 cm^{-1} region and the ir spectrum showed a sharp peak at 3480 cm^{-1}, ii) there is not any signal near δ 190.0 (s) which appears in the onychine derivatives[14,15], but it showed a doublet signal at δ 72.9 in the ^{13}Cnmr spectrum, iii) a singlet singal seen at δ 5.59 in the ^{1}Hnmr spectrum can be assigned to the proton geminal to the alcoholic hydroxyl group. Its uv spectrum exhibited several absorption maxima in the same regions as dihydrodarienine[15]; these underwent bathochromic shifts on adding base, raising the possibility that polylongine might be a phenolic derivative of dihydroonychine. Proof of the phenolic character of polylongine was obtained with a preparation of O-methyl (1a) derivative. The ^{1}Hnmr spectrum of polylongine revealed the presence of a methyl group [δ 2.50 (3H, s)] bounded to an aromatic ring, one methoxyl group [δ 3.90 (3H, s)] and two AB-quartets (four aromatic protons). One of them at δ 6.90 and 8.23 (J=5.0 Hz) was assigned to H-2 and H-3 respectively, which is in agreement with the pyridine ring AB system[16,17], while the other at δ 6.82 and 7.08 (J=8.3 Hz) was attributed to two mutually ortho-located protons on the aromatic ring. This indicated that both substituents (hydroxy and methoxy groups) were located on the aromatic ring at positions allowing the protons to be ortho-distributed. The above data led us to propose that the structure of polylongine could be either 1, 1b, 1c or 1d. Confirmation of the substitution pattern of polylongine was sought in a nuclear Overhauser effect experiment. NOEDS of this compound which is presented around expression 1e showed reciprocal positive NOE's between the proton geminal to the alcoholic hydroxyl group (H-9) on the one hand and the C-methyl and the aromatic ring protons on the other. The NOE's between H-9 and the C-methyl protons can be taken as a demonstration that polylongine



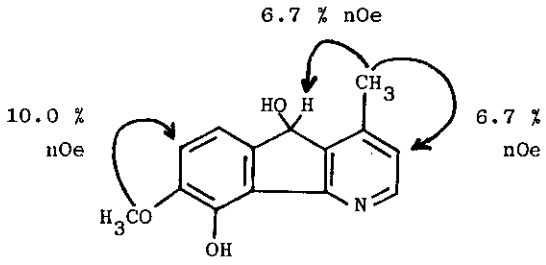
1 R_1=OH, R_2=OCH_3, R_3=R_4=H

1a R_1=R_2=OCH_3, R_3=R_4=H

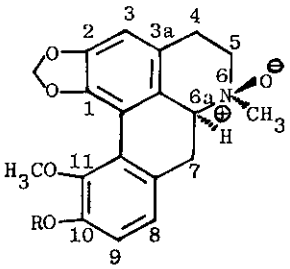
1b R_1=OCH_3, R_2=OH, R_3=R_4=H

1c R_1=R_2=H, R_3=OH, R_4=OCH_3

1d R_1=R_2=H, R_2=OCH_3, R_4=OH

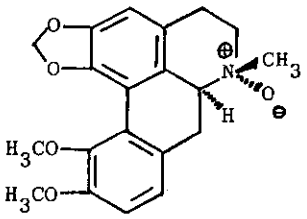


1e



2 R=CH_3

4 R=H



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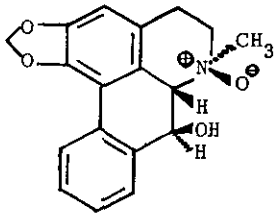

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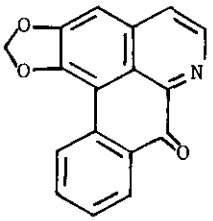

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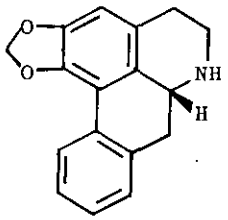

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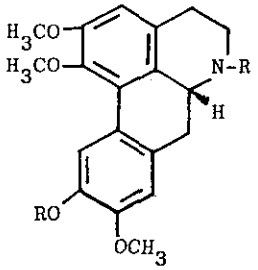

8 R=H

8a R=$COCH_3$

possesses the heterocyclic skeleton of onychine derivative proved by synthesis[18], and not the 4-methyl-1-azafluoren-9-one ring system proposed originally[19]. Irradiation at the resonance frequency (δ 2.50) of the C-methyl group also led to an enhancement of the pyridine β- proton (H-2) signal, while irradiation of the methoxyl signal at δ 3.90 also led to a 10.0% enhancement of the signal at δ 6.82, demonstrating that the methoxyl group is situated at C-6 (structure 1) or C-7 (structure 1d). Moreover, spin decoupling revealed that proton H-9 was coupled to the signals at δ 2.50 (C-methyl) and δ 7.08 [one of the ortho-coupled (J=8.3 Hz) protons]. This evidence demonstrated that both substituents, hydroxy and methoxy groups, were located at the C-5 and C-6, respectively. The uv-vis spectrum of polylongine(1), recorded in the presence of base exhibited a clear absorption maximum near 500 nm, supporting the assignment of the phenolic hydroxy group to C-5 in accordance with literature[17]. Furthermore, the ^{13}Cnmr spectrum of polylongine was also consistent with the proposed structure in accordance with those of onychine series [15,16,22]. Therefore, on the basis of the above results, the structure of polylongine should be represented as 1 (5-hydroxy-6-methoxy-1-methyl-4-azafluoren-9-ol). A further study on the stereochemistry of H-9 of polylongine is currently in progress. To the best of our knowledge, to date there are only eleven azafluorenone derivatives occurring in nature and they have all been isolated from the family Annonaceae[16]. e.g. *Cleistopholis patens*[14], *Guatteria dielisana*[20], *Onychopetalum amazonicum*[19], *Oxandra xylopioides*[15,21-23] and *Meiogyne virgata*[24]. This is the first report of the presence of azafluorenoid alkaloid in the genus *Polyalthia* and it is also the first time for polylongine(1), which possesses a unique 9-dihydroazafluorene skeleton[16], to be found in nature.

The three new aporphines are all N-oxides of the same configuration and are (+)-O-methylbulbocapnine-β-N-oxide (2), (+)-O-methylbulbocapnine-α-N-oxide (3) and(+)-N-methylnandigerine-β-N-oxide (4).

(+)-O-Methylbulbocapnine-β-N-oxide (2) was isolated as grayish-white needles from methanol. The mass spectrum of (+)-O-methylbulbocapnine-β-N-oxide (2) revealed the molecular ion m/z 355. Such an ion is characteristic of an N-oxide, inasmuch as facile loss of 16 a.m.u. results in formation of the correspoding ionized free base— in the present instance represented by the ion m/z 339. The m/z 339 ion can now lose a 43

a.m.u. to furnish base peak m/z 296. Such ready loss of CH_2NCH_3 is typical Retro-Diels-Alder fragmentation of aporphinoid alkaloids[25]. The uv spectrum showed maxima at 236, 274 and 308 nm. Except for the protons affected by the N-oxide function, the general features of the ^{1}Hnmr spectrum of (+)-O-methylbulbocapnine-β-N-oxide (2) paralleled those for (+)-O-methylbulbocapnine[26]. Two methoxyl singlets were present at δ 3.79 and 3.88, assignable to C-10 and C-11, in addition to one methylenedioxy group present at δ 5.87 and 6.08 (each 1H, d, J=1.3 Hz) which was located at C-1 and C-2. Three aromatic singlets were also in evidence, with the most upfield, at δ 6.67 due to H-3, while the other two at δ 6.87 and 7.03 (J=8.3 Hz) were attributed to two mutually ortho-located protons on the H-8 and H-9. The N-methyl signal was relatively downfield at δ 3.47, while H-6a appeared as a doublet of doublets at δ 4.14. NOEDS was used to settle the stereochemistry of the N-oxide center. Irradiation of the δ 3.47 N-methyl singlet led to a 7.8% enhancement of the δ 4.14 doublet of doublets (H-6a). Conversely, irradiation at δ 4.14 produced a 3.2% enhancement of the δ 3.47 singlet. It followed that the N-methyl group and H-6a must be *syn* to each other in accordance with literature[27].

(+)-O-Methylbulbocapnine-α-N-oxide (3) was isolated as a yellowish oily base. It displayed a pattern in the uv and ms spectra similar to those for (+)-O-methylbulbocapnine-β-N-oxide (2). *In the ^{1}Hnmr spectrum, except for the N-methyl singlet with* more upfield (at δ 3.05) than that of (+)-O-methylbulbocapnine-β-N-oxide (2) (at δ 3.47),the general features also paralleled those for (+)-O-methylbulbocapnine-β-N-oxide. In particlar, no NOE's were seen between the N-methyl and H-6a (δ 4.32) in the NOEDS. An *anti* arrangement must,therefore,exist between H-6a and the N-methyl group, which is different from that of (+)-O-methylbulbocapnine-β-N-oxide (2).

(+)-N-Methylnandigerine-β-N-oxide (4) was isolated as light grayish needles from methanol. It showed a pattern in the mass spectrum similar to those for both (+)-O-methylbulbocapnine-β-N-oxide (2) and (+)-O-methylbulbocapnine-α-Noxide (3). A molecular ion, m/z 341, was accompanied by free base peak at m/z 325 , due to loss of oxygen (16 a.m.u.). A strong base peak at m/z 282 was also present, accounted for by loss of CH_2NCH_3 (43 a.m.u.) from the free base in accordance with the Retro-Diels-Alder fragmentation. Except for the protons affected by the N-oxide function, the general features of the ^{1}Hnmr spectrum of(+)-N-methylnandigerine-β-N-oxide (4) also paralleled those for

(+)-N-methylnandigerine[26]. One methoxyl singlet was present at δ 3.56, assignable to C-11 in accord with the literature[26,28], in addition to the signals of a methylenedioxy group which was assigned to C-1 and C-2 appeared at δ 5.79 and 6.00 (each 1H, d, J=1.25 Hz). Three aromatic singlets were also in evidence, with the most upfield, at δ 6.59 due to H-3 while the other two at δ 6.77 and 6.86 (J=8.0 Hz) were attributed to two mutually ortho-located protons on the H-8 and H-9. The N-methyl signal was relatively downfield at δ 3.28, while H-6a showed as a doublet of doublets at δ 4.11. NOEDS was also used to settle the stereochemistry of the N-oxide center. Irradiation of the 3.28 N-methyl singlet led to a 10.0% enhancement of the δ 4.10 doublet of doublets (H-6a). Conversely, irradiation at δ 4.10 produced a 3.5% enhancement of the 3.28 singlet. It indicated that a *syn* arrangement also exists between the N-methyl group and H-6a which is similar to that of (+)-O-methylbulbocapnine-β-N-oxide (2). The remaining evidence that was gathered is in accord with the assignment of structure 4 to the alkaloid. There is no NOE enhancement observed during irradiation at the δ 3.56 methoxyl singlet in the NOEDS. Furthermore, the uv spectrum showed maxima at 226,274 and 312 nm, with a bathochromic shift in base due to the presence of a phenolic group at C-10.

Zinc in H_2SO_4 reduction of (+)-O-methylbulbocapnine-β-N-oxide (2), (+)-O-methylbulbocapnine-α-N-oxide (3) and (+)-N-methylnandigerine-β-N-oxide (4) provided (+)-O-methylbulbocapnine and (+)-N-methylnandigerine, respectively, while the product of 2 and 3 were the same. These were identified by comparision (ir, tlc and ^{1}Hnmr) with authentic samples available in our laboratory.

Because the three N-oxide alkaloids are all dextrorotary, they belong to the C-6a S absolute configuration as indicated in structures 2, 3 and 4[27,28].

(-)-Oliveroline-β-N-oxide (5) was obtained as a yellowish oily base. It displayed a pattern in the mass spectrum similar to that for (-)-ushinsunine-β-N-oxide[29]. A very small molecular ion, m/z 311, was accompanied by base peak m/z 295 due to loss of oxygen. A strong m/z 278 peak was also present, accounted for by loss of hydroxyl from the base peak. Particularly, the presence of the two one-proton doublets at δ 4.45 and 5.21 with J=12.0 Hz in the ^{1}Hnmr spectrum attested to the presence of an alcohol function at C-7 with a *trans* relationship between H-5a and H-7, whereas (-)-ushinsunine-β-N-oxide with a one-proton doublet at δ 5.41 (J=2.2 Hz) has H-7 to H-6a. Furthermore, a partial nmr

NOE study clarified the configuration of the N-oxide function. Reciprocating nOe's were detected between the N-methyl signal (δ 3.34) and H-7 (δ 5.21), while no nOe's were seen between the N-methyl and H-6a (δ 4.45). An *anti* arrangement must, therefore, exist between H-6a and the N-methyl group. The negative specific rotation for (-)-oliveroline-β-N-oxide (5) testified to the *R* configuration at C-6a. Moreover, the ^{13}Cnmr spectrum of (-)-oliveroline-β-N-oxide was also assigned in accordance with literature[30]. (-)-Oliveroline-N-oxide was first isolated from *Polyalthia olivera* in 1977[31] and it was subsequently isolated from *Guatteria sagotiana* some ten years later[32]. However, the sterechemistry at the N-oxide center of this alkaloid had not been unequivocally determined. Now, it was also isolated from species *P. longifolia* and the stereochemistry of the N-oxide was settled as β form firstly.

The known alkaloids, liriodenine (6) and anonaine (7) were identified by direct comparison (mp, uv, ir, tlc and ^{1}Hnmr) with authentic samples, respectively. (+)-Norlirioferine (8) was readily identified by its spectra data (uv, ir and ^{1}Hnmr) with those in the literature[33,34]. Moreover, acetylation of (+)-norlirioferine with acetic anhydride and pyridine gave (+)-N,O-diacetylnorlirioferine (8a) which was identified by comparison (uv and ^{1}Hnmr) with literature data[33]. Liriodenine (6) and anonaine (7) are the most widely distributed aporphinoid alkaloids which have been thus far isolated from the families of Annonaceae, Magnoliaceae, Monimiaceae, Lauraceae, Nympheaceae, Papaveraceae, Rhamnaceae, Menispermaceae, Araceae, Eupomatiaceae and Rutaceae[16,28,30,35]. (+)-Norlirioferine (8) was firstly reported as a Zn-AcOH reduction product of O-acetyloxolirioferine in 1980[33] and it was subsequently isolated from the *Phoebe pittieri* (Lauraceae) in 1982[36] and 1985[34]. (+)-Norlirioferine is isolated for the first time from the family of Annonaceae.

EXPERIMENTAL

General

Melting points were determined on a Yanaco micro-melting point apparatus and are uncorrected. $[\alpha]_D$ was measured on a Jasco model Dip-181 Digital Polarimeter. Uv absorption spectra were obtained on a Beckman model 34 spectrophotometer. Ir spectra were taken on a Hitachi model 260-30 infrared spectrophotometer. The ^{1}Hnmr spectra were taken on

a Varian EM 360 L 60 MHz spectrometer, and a Jeol GX-400 spectrometer with TMS as internal and chemical shifts were recorded in δ units. Mass spectra were obtained on a Jeol JMS-D-100 mass spectrometer. E. M. Merck 9385 silica gel (230-400 mesh) was used for column chromatography and silica gel GF-254 was used for thin layer chromatography.

Extraction and isolation of alkaloids

The fresh leaves of *P.longifolia* (6.0 kg) was extracted 3 times with MeOH (10 l)at room temperature for 48 h, respectively. The combined methanol extracts were evaporated and partitioned to yield n-hexane, chloroform and aqueous extracts. The bases in the chloroform solution were extracted with 3% HCl. The HCl solution was basified with NH_4OH and extracted with $CHCl_3$. The $CHCl_3$ solution was dried (K_2CO_3) and evaporated to leave a brownish viscous residue (3.7 g). The residue was placed on a silical gel column and eluted with $CHCl_3$ gradually enriched with MeOH. The fractions (157 mg) eluting with $CHCl_3$ were further purified by neutral alumina column chromatography ($CHCl_3$) and preparative TLC ($CHCl_3$: MeOH = 20 : 1) provided liriodenine (6, 11 mg). Fractions (218 mg) eluting with $CHCl_3$-MeOH (50:1) were further separated and purified by sillica gel column chromatography ($CHCl_3$: MeOH = 25 : 1 and 15 : 1, respectively) and preparative TLC (silica gel, $CHCl_3$: MeOH = 15 : 1) gave anonaine (7, 8 mg), (+)-norlirioferine (8, 17 mg) and polylongine (1, 15 mg), respectively. Fractions (87 mg) eluting with $CHCl_3$-MeOH (20 : 1) were further purified by silica gel column chromatography ($CHCl_3$: MeOH = 10 : 1) and preparative TLC (silica gel, $CHCl_3$: MeOH = 10 : 1) yielded (-)-oliveroline-β-N-oxide (5, 9 mg). Fractions (418 mg) eluting with $CHCl_3$-MeOH(5 : 1) were further separated and purified by silical gel column chromatography ($CHCl_3$: MeOH = 8 : 1 and 3 : 1, respectively) and preparative TLC (silica gel, $CHCl_3$: MeOH = 5 : 1) afforded (+)-O-methylbulbocapnine-β-N-oxide(2, 16 mg), (+)-O-methylbulbocapnine-α-N-oxide (3, 4mg) and (+)-N-methylnandigerine -β-N-oxide (4, 11 mg), respectively.

Polylongine (1)—mp 148-151℃. $[\alpha]_D$-1.6° (c 0.1, $CHCl_3$). Ir ν_{max}^{Nujol} cm^{-1}:3480 (OH). Uv λ_{max}^{MeOH} nm (log ε): 222 (3.84) , 230 (3.81), 236sh (3.79), 265 (3.36), 302 (3.65) and 330sh (3.08); $\lambda_{max}^{MeOH+NaOH}$: 224 (3.88), 230sh (3.83), 250sh (3,38), 290 (3.57) and 360 (3.18). Ms m/z 243 (M^+,100), 226 (70), 214 (18), 172 (96). HRMS m/z M^+ 243.0865 (calcd for $C_{14}H_{13}NO_3$ 243.0894). ^{1}HNmr (400 MHz , $CDCl_3$): δ 2.50 (3H, s, C_1-CH_3), 3.90

(3H, s, C_6-OCH_3), 5.59 (1H, s, H-9), 6.82 (1H, d, J=8.3 Hz, H-7), 6.90 (1H, d, J=5.0 Hz, H-2), 7.08 (1H, d, J=8.3 Hz, H-8) and 8.23 (1H, d, J=5.0 Hz, H-3). ^{13}CNmr (25.0 MHz, $CDCl_3$): δ 124.0 (s, C-1), 123.2 (d, C-2), 148.4 (d, C-3), 159.6 (s, C-4a), 138.0 (s, C-4b or C-8a), 145.2 (s, C-5), 147.9 (s, C-6), 113.4 (d, C-7), 116.3 (d, C-8), 137.3(s, C-8a or C-4b), 72.9 (d, C-9),143.1 (s, C-9a), 17.7 (q, C_1-CH_3) and 56.4 (q, C_6-OCH_3).

O-Methylation of polylongine (1)— To a solution of polylongine (1) (5 mg), CH_2N_2 in ether (30 ml) was added and the mixture kept for four days at room temperature. After the mixture was acidified with 3% HOAc, the aqueous layer was basified with NH_4OH and extracted with $CHCl_3$. The $CHCl_3$ solution was dried (K_2CO_3) and evaporated to give a yellow oily base, O-methylpolylongine (1a)(3 mg), ^{1}Hnmr (400 MHz, $CDCl_3$): δ 2.51 (3H, s, C_1-CH_3), 3.92 (3H, s, C_6-OCH_3), 4.02 (3H, s, C_5-OCH_3), 5.57 (1H, s, H-9), 6.80 (1H, d, J=8.0 Hz, H-7), 6.91 (1H, d, J=5.1 Hz, H-2), 7.05 (1H, d, J=8.0 Hz, H-8) and 8.20 (1H, d, J=5.1 Hz, H-3).

(+)-O-Methylbulbocapnine-β-N-oxide (2)— mp 115-117℃. $[\alpha]_D$ +158° (c 0.1, MeOH). Ir ν_{max}^{KBr} cm^{-1}: 1046 and 948 (-OCH_2O-). Uv λ_{max}^{MeOH} nm (log ε): 236 (4.21), 274 (3.94) and 308 (3.65). Ms m/z 355 (M^+, 30), 339 (15), 338 (11), 325 (10) and 296 (100). ^{1}HNmr (400 MHz, $CDCl_3$): δ 3.47 (3H, s, N-CH_3), 3,79 and 3.88 (each 3H, s, C_{10} and C_{11}-OCH_3), 4.14 (1H, dd, J=3.4, 3.4 Hz, H-6a), 5.87 and 6.08 (each 1H, d, J=1.3 Hz, -OCH_2O-), 6.67 (1H, s, H-3), 6.87 and 7.03 (each 1H, d, J=8.3 Hz, H-8 and H-9).

(+)-O-Methylbulbocapnine-α-N-oxide (3)— Yellowish oily base with $[\alpha]_D$ +153° (c 0.1, $CHCl_3$). Ir ν_{max}^{Nujol} cm^{-1}: 1042 and 945 (-OCH_2O-). Uv λ_{max}^{MeOH} nm (log ε): 235 (4.20), 275 (3.95) and 310 (3.64). Ms m/z 355 (M^+, 7), 339 (100), 338 (51), 325 (81) and 296 (68). ^{1}HNmr (400 MHz, $CDCl_3$) : δ 3.05 (3H, s, N-CH_3), 3.75 and 3.87 (each 3H, s, C_{10}-OCH_3 and C_{11}-OCH_3), 4.32 (1H, dd, J=3.3, 3.3 Hz, H-6a), 5.94 and 6.12 (each 1H, d, J=1.0 Hz, -OCH_2O-), 6.63 (1H, s, H-3), 6.87 and 7.06 (each 1H, d, J=8.5 Hz, H-8 and H-9).

(+)-N-Methylnandigerine-β-N-oxide (4)— mp 218-220℃. $[\alpha]_D$ +252° (c 0.1, MeOH). Ir ν_{max}^{KBr} cm^{-1}: 1043 and 946 (-OCH_2O-), 3295 (OH). Uv λ_{max}^{MeOH} nm (log ε): 226 (4.20), 274 (4.11) and 312 (3.35); $\lambda_{max}^{MeOH+NaOH}$: 217 (4.53), 251 (4.21), 286 (4.08) and 336 (3.51). Ms m/z 341 (M^+, 18), 325 (20), 324 (11), 282 (100) and 266 (30). ^{1}HNmr (400 MHz, $CDCl_3$): δ 3.28 (3H, s, N-CH_3), 3.56 (3H, s, C_{11}-OCH_3), 4.10 (1H, dd,

J=4.5, 4.5 Hz, H-6a), 5.79 and 6.00 (each 1H, d, J=1.3 Hz, $-OCH_2O-$), 6.59 (1H, s, H-3), 6.77 and 6.86 (each 1H, d, J=8.0 Hz, H-8 and H-9).

Reduction of (+)-O-methylbulbocapnine-β-N-oxide (2), (+)-O-methylbulbocapnine-α-N-oxide (3) and (+)-N-methylnandigerine-β-N-oxide (4)— In a 10 ml flask equipped with a magnetic stirrer, 2 (3 mg), 3 (3 mg), and 4 (3 mg) were admixed with zinc (3 mg), $CHCl_3$ (3 ml) and H_2SO_4 (2 ml), respectively. The mixture were stirred and gently heated over a steam-bath for 2 h and then treated in the usual manner to give (+)-O-methylbulbocapnine and (+)-N-methylnandigerine, respectively. Identification was done by direct comparison with authentic samples (tlc, ir and ^{1}Hnmr), available in our laboratory, respectively.

(-)-Oliveroline-β-N-oxide (5)— Yellowish oily base with $[\alpha]_D$ -54.7° (c 0.06, $CHCl_3$). Uv λ_{max}^{MeOH} nm (log ε): 235 (4.14), 276 (4.03) and 314 (3.58). Ms m/z 311 (M^+, 6), 295 (100), 294 (72), 278 (46), 277 (24), 252 (87) and 236 (30). ^{1}HNmr (400 MHz, $CDCl_3$): δ 3.34 (3H, s, $N-CH_3$), 4.45 (1H, d, J=12.0 Hz, H-6a), 5.21 (1H, d, J=12.0 Hz, H-7), 6.01 and 6.18 (each 1H, J=1.8 Hz, $-OCH_2O-$), 6.60 (1H, s, H-3), 7.34-7.46 (2H, m, H-8,9), 7.87 (1H, m, H-10) and 8.05 (1H, m, H-11). ^{13}CNmr (25.0 MHz, $CDCl_3$): δ 143.9 (s, C-1), 116.2 (s, C-1a), 119.6 (s, C-1b), 148.9 (s, C-2), 107.2 (d, C-3), 123.0 (s, C-3a), 27.3 (t, C-4), 67.2 (t, C-5), 76.4 (d, C-6a), 68.8 (d, C-7), 137.2 (s, C-7a), 124.7 (d, C-8), 127.6 (d, C-9), 128.8 (d, C-10), 126.3 (d, C-11), 127.3 (s, C-11a), 101.6 (t, $-O\underline{C}H_2O-$) and 48.9 (q, $N-\underline{C}H_3$).

Liriodenine (6)— mp 280-282℃, $[\alpha]_D$ ±0° (c 0.1, $CHCl_3$) and ^{1}Hnmr as in reference[28,37]. The alkaloid was identified by comparison with an authentic sample available in our laboratory (mp, ir, tlc and ^{1}Hnmr).

Anonaine (7)— Colorless oily base with $[\alpha]_D$-48° (c 0.1, $CHCl_3$) and ^{1}Hnmr as inreference[28,37]. The alkaloid was identified by comparison with an authentic sample available in our laboratory (uv, ir, tlc and ^{1}Hnmr).

(+)-Norlirioferine (8)— Amorphous with $[\alpha]_D$ +58° (c 0.1, MeOH), uv λ_{max}^{MeOH} nm(log ε): 222 (4.35), 280 (3.85), 305 (3.92) and 310sh (3.86); $\lambda_{max}^{MeOH+NaOH}$: 280sh (3.82), 312sh (3.96), 318 (4.00) and 332sh (3.93). ^{1}HNmr (60 MHz, $CDCl_3$): δ 3.68 (3H, s, C_1-OCH_3), 3.89 (6H, s, C_2 and C_9-OCH_3), 6.58 (1H, s, H-3), 6.74 (1H, s, H-8) and 8.06 (1H, s, H-11). Comparison of uv and ^{1}Hnmr with those of literature data of norlirioferine[33,35]

proved them to be identical.

Acetylation of (+)-norlirioferine (8)— (+)-Norlirioferine (10 mg) was acetylated with acetic anhydride (2 ml) and pyridine (0.5 ml) at room temperature for 20 h. The solvent was evaporated in vacuo to give a dark brownish oily residue. The residue was treated with preparative TLC (silical gel, $CHCl_3$: MeOH = 7 : 1). When the base of Rf=0.76 obtained by preparative TLC was purified by silica gel column chromatography ($CHCl_3$: MeOH = 10 : 1), a colorless oily base, (+)-N,O-diacetylnorlirioferine (8a), was afforded, ^{1}Hnmr (60 MHz, $CDCl_3$): δ 2.20 and 2.32 (each 3H, s, N-$COCH_3$), and O-$COCH_3$), 3.69 (3H, s, C_1-OCH_3), 3.88 and 3.90 (each 3H, s, C_2 and C_9-OCH_3), 6.68 (1H, s, H-3), 6.96 (1H, s, H-8) and 8.26 (1H, s, H-11). Comparison of uv and ^{1}Hnmr with those of literature of N,O-diacetylnorlirioferine[33] showed them to be identical.

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