($CHCl_3$; *c* 1), (lit. +60° [6]). IR, UV, NMR and MS identical to lit. [6].

Ribalinine (**3**). Mp 232–234° (lit. 232° [5, 6]). $[\alpha]_D^{24}$ −78° ($CHCl_3$; *c* 1), (lit. 0° [5], −10° [6]). Other spectroscopic data identical to lit. cited in text.

Edulinine (**4**). Identified by spectroscopic data and also comparison with authentic sample (co-TLC).

Montrifoline (**5**). Mp 188–189° (lit. 189–190° [4]). Identified by NMR and MS data; identical with an authentic sample of montrifoline (mmp, co-TLC).

Skimmianine (**6**). Mp 168–170° (lit. 170–172° [12]), *flindersiamine* (**7**): mp 207–209° (lit. 207–208° [13]) and *maculine* (**8**): mp 197–199° (lit. 198° [14]) were identified based on their spectroscopic data which were in good agreement with the lit.

Acknowledgements—We are grateful to Prof. W. Steglich (Bonn University) for NMR and MS and Dr P. G. Waterman for the NOE study on nobiline. We also extend our thanks to Prof. Cavé (University of Paris) for an authentic sample of ribalinine, Prof. Okogun (Ibadan University) for montrifoline and Prof. Scheuer (University of Hawaii) for edulinine. This work was supported by a research grant from SAREC (Sweden).

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(+)-3′,4′-DIHYDROSTEPHASUBINE, A BISBENZYLISOQUINOLINE ALKALOID FROM *STEPHANIA HERNANDIFOLIA*

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Key Word Index—*Stephania hernandifolia*; Menispermaceae; bisbenzylisoquinoline alkaloid; 3′,4′-dihydrostephasubine; stephasubine; epistephanine.

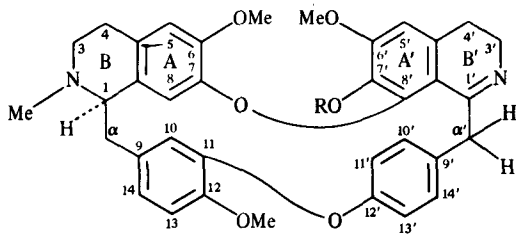
Abstract—A new bisbenzylisoquinoline alkaloid has been isolated from the stems of *Stephania hernandifolia* and its structure established as (+)-3′,4′-dihydrostephasubine. This is accompanied by the known alkaloid (+)-stephasubine (+)-Epistephanine has been found in the roots of the plant.

INTRODUCTION

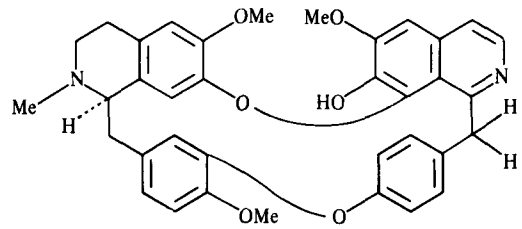
Recent phytochemical investigation on *Stephania suberosa* [1–3] prompted us to reinvestigate the alkaloid contents of *S. hernandifolia* Walp. We report here the isolation of a new bisbenzylisoquinoline alkaloid, the structure of which has been established as (+)-3′,4′-dihydrostephasubine (**1**), along with (+)-stephasubine (**2**) [1] from the stems of *S. hernandifolia*. (+)-Epistephanine (**3**) occurs in the roots of the same plant.

RESULTS AND DISCUSSION

Compound **1**, $C_{36}H_{36}N_2O_6$, exhibited a strong $[M]^+$ at *m/z* 592 (38%) with *m/z* 591 as the base peak. The fact



1 R = H
3 R = Me



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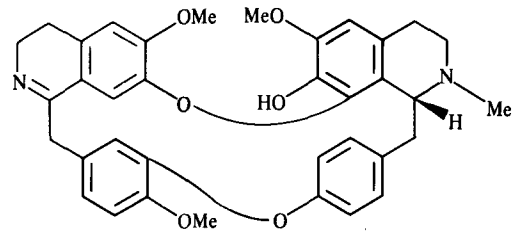

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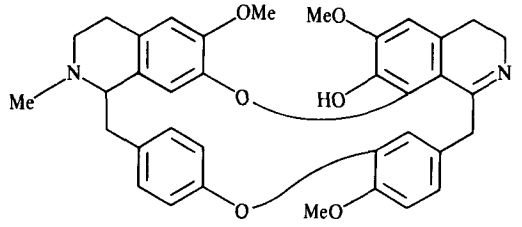

5

that the upper part of the dimer is not observed in the mass spectrum immediately suggested that an imine or aromatic ring B (or B′) was present. This suspicion was reinforced by IR absorption at 1460 cm^{-1} which showed the presence of the imine chromophore of a dihydroisoquinoline moiety and by UV absorption maxima (EtOH) at 283, 223 and 216 nm which were also characteristic of the congener epistephanine (**3**).

The structure of the alkaloid was established as **1** from the 270 MHz ^1H NMR spectrum ($CDCl_3$) and its comparison with those of the congeners stephasubine (**2**) and epistephanine (**3**). The spectrum indicated the presence of a highly functionalized bisbenzylisoquinoline system and displayed signals for the presence of one-NMe (δ2.51, 3H, *s*), three methoxyls (singlets at δ3.88, 3.91 and 3.95, 3H each) besides ten aromatic protons, three of which appeared as singlets at δ6.60 (H-5′), 6.51 (H-5) and 6.08 (H-8).

Homodecoupling experiments indicated that the resonance at δ6.84 (1H, *dd*, J = 8.3 and 1.0 Hz, H-14) was coupled with the resonances at δ6.73 (1H, *d*, J = 8.3 Hz, H-13) and 4.91 (1H, *br s*, H-10) which were thus part of an *ortho–para* trisubstituted benzene ring. The decoupling experiment also established that the signal at δ6.48 (1H, *dd*, J = 8.2 and 2.0 Hz, H-11′) was involved in large coupling with the resonance at δ7.36 (1H, *dd*, J = 8.2 and 2.0 Hz, H-10′) and a smaller coupling with δ6.77 (1H, *dd*, J = 8.2 and 2.0 Hz, H-13′) on one hand while on the other the δ6.77 (*dd*) signal was strongly coupled with the δ7.40 signal (1H, *dd*, J = 8.2 and 2.0 Hz, H-14′) and weakly coupled with the δ6.48 (*dd*) resonance in consonance with the presence of a *para* disubstituted benzene system.

The ^1H spectrum also displayed mutually coupled signals at δ4.52 and 4.08 (1H each, J = 14.0 Hz) which represented the two geminal protons of the methylene attached to the imine function. The presence of the H-1 broad singlet upfield at δ3.59 accompanied by the *N*-methyl signal at δ2.51, as found in stephasubine and epistephanine, argued convincingly in favour of placing the dihydropyridine system on the right hand side of the dimer. Furthermore the ^1H spectrum of **1** differed significantly from that of the recently isolated (+)-1,2-dehydro-2-norlimacusine (**4**) [4] and also from that of tiliafunimine (**5**) [5]. The structure of the alkaloid was further complemented by its *O*-methylation with diazomethane providing epistephanine (**3**).

EXPERIMENTAL

Plant material was purchased from a local supplier who identified the plant at the National Botanical Garden, Shibpur, Howrah 711103, India by comparison with a herbarium specimen.

Isolation. Air-dried and crushed stems of *S. hernandifolia* (500 g) were extracted with EtOH at room temp. The EtOH extract was concd under red. pres. and the residue subjected to CC over silica gel (BDH, mesh 60–120). Elution was carried out with petrol, benzene, $CHCl_3$ and $CHCl_3$–MeOH mixts, respectively. The $CHCl_3$–MeOH (3:1) eluates afforded a gummy mass which was further subjected to CC over silica gel. A crude mass was obtained from the $CHCl_3$–MeOH (4:1) eluate. Further sepn by prep. TLC on silica gel G furnished the compounds **1** (4 mg) and **2** (5 mg). Similar processing of the roots of the plant (600 g) yielded epistephanine **3** (9 mg).

(+)-3′,4′-*Dihydrostephasubine* (**1**). Amorphous: $[\alpha]_D^{25}$ +286°(MeOH); λ_{max} (EtOH) 283, 223, 216 nm; λ_{max} (EtOH + NaOH) 223 nm; λ_{max} (EtOH + H_3O^+) 338, 284, 216 nm; ν_{max} ($CHCl_3$) 1460, 1510, 1605, 3525, 3610, 3675 cm^{-1}.

(+)-*Stephasubine* (**2**). Amorphous; $[\alpha]_D^{25}$ +340° (MeOH); λ_{max} (MeOH) 337, 287, 240 nm; λ_{max} (MeOH + H_3O^+) 374, 368, 321, 290 sh, 264, 235 nm; 270 MHz ^1H NMR ($CDCl_3$) δ2.51 (3H, *s*, *N*-Me), 3.60 (1H, *m*, H-1), 3.86 (3H, *s*, MeO-12), 4.05 (6H, *s*, MeO-6 and MeO-6′), 4.49 (1H, *d*, J = 14.0 Hz, H-α′), 4.84 (1H, *br s*, H-10), 5.36 (1H, *d*, J = 14.0 Hz, H-α′), 5.95 (1H, *s*, H-8), 6.49 (1H, *dd*, J = 8.4 and 2.0 Hz, H-13′), 6.54 (1H, *s*, H-5), 6.65 (1H, *dd*, J = 8.3 and 2.0 Hz, H-11′). 6.71 (2H, *br s*, H-13 and H-14), 7.00 (1H, *s*, H-5′), 7.03 (1H, *dd*, J = 8.3 and 2.0 Hz, H-10′), 7.43 (1H, *dd*, J = 8.4 and 2.0 Hz, H-14′), 7.47 (1H, *d*, J = 5.6 Hz, H-4′) and 8.45 (1H, *d*, J = 5.6 Hz, H-3′).

(+)-*Epistephanine* (**3**). Amorphous; $[\alpha]_D^{25}+220°$ ($CHCl_3$); λ_{max} (EtOH) 282, 214 nm; λ_{max} (EtOH + NaOH) 281, 218 nm; λ_{max} (EtOH + H_3O^+) 335, 288, 212 nm; ν_{max} ($CHCl_3$) 1462 cm^{-1}; 270 MHz ^1H NMR ($CDCl_3$) δ2.53 (3H, *s*, N-Me), 3.36 (3H, *s*, MeO-7′) 3.86 (6H, *s*, MeO-6 and MeO-6′), 3.90 (3H, *s*, MeO-12), 4.02 (1H, *d*, J = 13.8 Hz, H-α′), 4.42 (1H, *d*, J = 13.8 Hz, H-α′), 4.92 (1H, *br s*, H-10), 6.11 (1H, *s*, H-8), 6.46 (2H, *m*, H-5 and H-11′), 6.57 (1H, *s*, H-5′), 6.72 (1H, *d*, J = 8.1 Hz, H-13), 6.76 (1H, *dd*, J = 8.3 and 2.3 Hz, H-13′), 6.86 (1H, *dd*, J = 8.1 and 1.2 Hz, H-14), 7.33 (1H, *dd*, J = 8.2 and 2.0 Hz, H-10′), 7.40 (1H, *dd*, J = 8.3 and 2.0 Hz, H-14′).

O-*Methylation of dihydrostephasubine* (**1**). Compound **1** (2 mg) dissolved in Et_2O (2 ml) was treated with CH_2N_2–Et_2O and then kept at −5° for 2 days. Work-up and TLC purification afforded epistephanine (**3**) (^1H NMR and TLC).

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(+)-AURORAMINE AND (+)-MAROUMINE, NEW SECO-*BIS*-BENZYLISOQUINOLINE DIMERS FROM *GYROCARPUS AMERICANUS*

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Key Word Index—*Gyrocarpus americanus*; Hernandiaceae; leaves; seco-*bis*-benzylisoquinoline alkaloids; auroramine; maroumine.

Abstract—Two new seco-*bis*-benzylisoquinoline alkaloids, (+)-auroramine and (+)-maroumine, have been isolated from the leaves of *Gyrocarpus americanus*. The structures of these new natural compounds have been established by spectroscopic means and by correlation with known products.

INTRODUCTION

Nine *bis*-benzylisoquinolines from the stems of *Gyrocarpus americanus* have been described [1]. We have now found that most of these are also present in the leaves, where they are accompanied by the new isoquinolone-benzylisoquinoline dimers (+)-auroramine (**1**) and (+)-maroumine (**2**). These two seco-*bis*-benzylisoquinolines are most probably catabolic products formed by oxidative cleavage of the less hindered benzylic bond of the main dimers of this species, namely (+)-O-methyllimacusine (**3**) or (−)-gyrolidine for species **1**, and (−)-gyrocarpine (**4**) or (+)-gyrocarpusine for (**2**).

RESULTS AND DISCUSSION

(+)-Auroramine **1**, $C_{38}H_{40}O_8N_2$ ($[M]^+$ *m/z* 652) and (+)-maroumine **2**, $C_{37}H_{38}O_8N_2$ ($[M]^+$ *m/z* 638) are characterised by IR bands at 1600, 1640, and 1690 cm^{-1}, typical of a tertiary δ-lactam linkage and conjugated aldehyde carbonyl of seco-dimers [2]. The presence of the aldehyde function is confirmed by the existence of very deshielded signals in the ^1H NMR spectra of **1** and **2**. The 'seco' character of these dimers is corroborated by mass spectral fragmentation which generates ions *m/z* 411 ($C_{23}H_{27}O_5N_2$) for **1** and *m/z* 397 ($C_{22}H_{25}O_5N_2$) for **2**. These are the base peaks and result from the usual