(+)-*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).

Acknowledgements—The authors are grateful to the UGC, New Delhi, India for financial assistance under Faculty Improvement Programmes and also to the authority of Serampore College, Serampore, Hooghly, W.B. for granting study leave to T.K.M.

REFERENCES

1. Patra, A., Freyer, A. J., Guinaudeau, H., Shamma, M., Tantisewie, B. and Pharadai, K. (1986) *J. Nat. Prod.* **49**, 424.
2. Patra, A., Montgomery, C. T., Freyer, A. J., Guinaudeau, H., Shamma, M., Tantisewie, B. and Pharadai, K. (1987) *Phytochemistry* **26**, 547.
3. Patra, A. (1987) *Phytochemistry* **26**, 2391.
4. Lavault, M., Fournet, A., Guinaudeau, H. and Bruneton, J. (1986) *Chem. Pharm. Bull.* **34**, 1148.
5. Tackie, A. N., Dwuma-Badu, D., Knapp, J. E. and Schiff, Jr, P. L. (1973) *Phytochemistry* **12**, 203.

Phytochemistry, Vol. 27, No. 2, pp. 655–657, 1988.
Printed in Great Britain.

0031-9422/88 $3.00 + 0.00
Pergamon Journals Ltd.

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

PASCALE DUTÉ, MARIE-CHRISTINE CHALANDRE, PIERRE CABALION* and JEAN BRUNETON

C.E.P.M., U.F.R. dé Medecine et de Pharmacie, 16 Bd. Daviers, 49000 Angers, France; *O.R.S.T.O.M., Port Vila, BP 76, Vanuatu

(*Revised received* 4 *June* 1987)

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

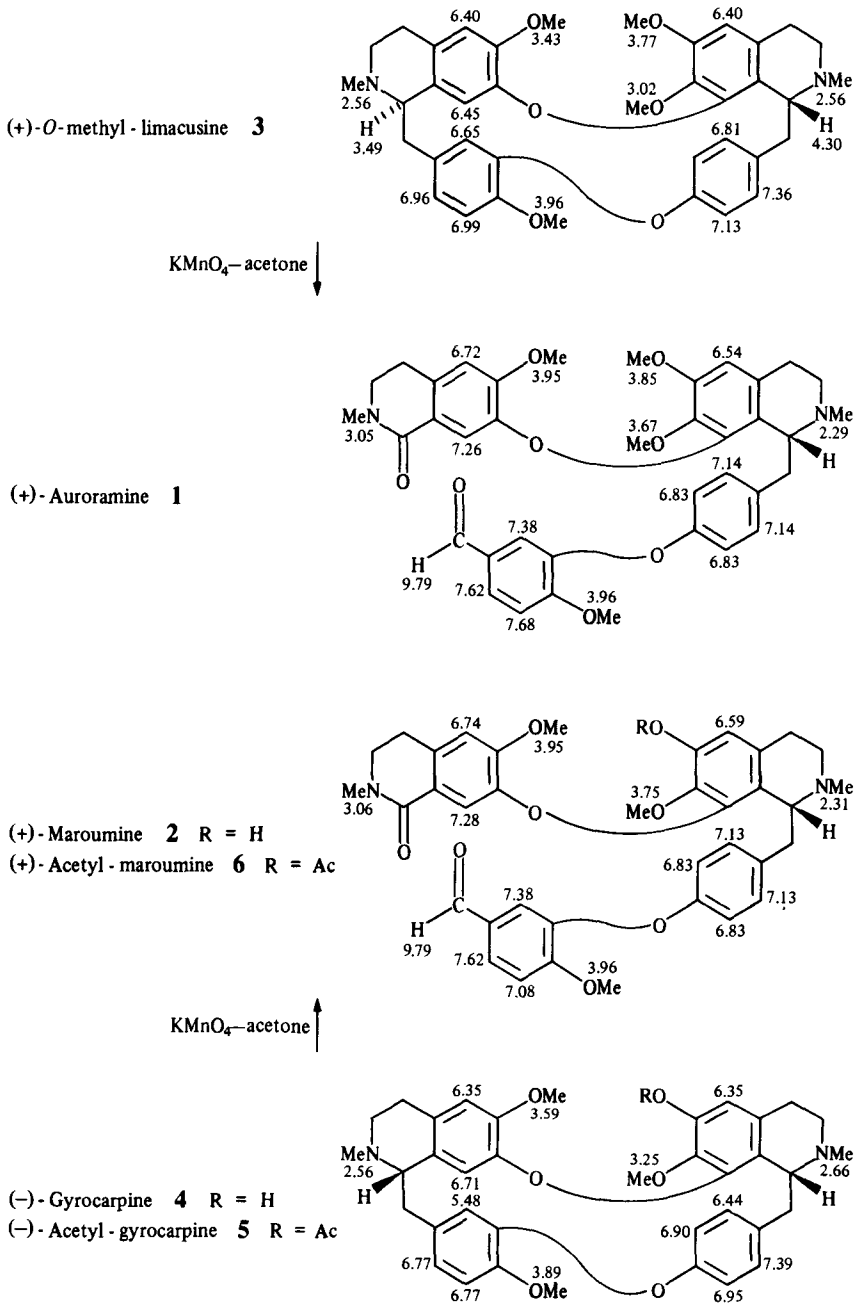
Abstract—Two new seco-*bis*-benzylisoquinoline alkaloids, (+)-auroramine and (+)-maroumine, have been isolated from the leaves of *Gyrocarpus americanus*. The structures of these new natural compounds have been established by spectroscopic means and by correlation with known products.

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



benzylic cleavage [3]. The difference of 14 mass units suggests that the phenolic function is either on the isoquinoline or on the isoquinolone moieties. Examination of NMR resonance values of the signals for the four methoxyls and the ABX and A_2B_2 aromatic systems indicates that (+)-auroramine is related to baluchistanamine [4]. The additional 3H signal at δ3.96 is strongly suggestive of the fact that **1** corresponds to (−)-*O*-methylbaluchistanamine (1*S*) or its 1*R* isomer. Indeed, a positive specific rotation confirms this last hypothesis. Final proof of structure derived from potassium permanganate in acetone oxidation of the *bis*-benzylisoquinoline (+)-*O*-methyllimacusine **3** which generated (+)-auroramine **1**.

In like fashion, analysis of the ^{1}H NMR spectrum of **2** shows that the phenolic function may be either at C-6 or C-7, while the positive specific rotation indicates the 1*R* configuration, as in **1**. (+)-Maroumine may result from cleavage of (−)-gyrocarpine **4**, or (+)-gyrocarpusine. Permanganate in acetone oxidation of (−)-*O*-acetylgyrocarpine **5** led to material identical in all respects with (+)-*O*-acetylmaroumine **6**, obtained by acetylation of (+)-maroumine **2**.

EXPERIMENTAL

Extraction. Dried leaves of *G. americanus* Jacq. (3.5 kg) were extd with $CHCl_3$, after the lipids had been removed with hexane. The crude alkaloids were purified by extn with 2% HCl and the alkaloidal exts (25 g) loaded on a column packed with 750 g of alumina (deactivated with 6% H_2O). Elution was with C_6H_6,

then with increasing proportions of $CHCl_3$ in C_6H_6. The third group of fractions, eluted with 5–10% $CHCl_3$ in C_6H_6, contained four alkaloids, (−)-phaeanthine, (+)-auroramine, (−)-limacine and (+)-pronucifĕrine and it was further purified by CC on silica gel and prep. TLC to yield 45 mg of (+)-auroramine. The sixth group of fractions (elution with $CHCl_3$) contained three alkaloids: (+)-maroumine, (−)-limacine, and (−)-gyrocarpine. Purification yielded 410 mg of (+)-maroumine.

(+)-*Auroramine* **1**. MS, *m/z* (%): 652 (0, 2), 651 (0, 3), 411 (100), 365 (8, 4), 241 (3), 206 (2, 1), 204 (4, 8). UV λ_{max}^{EtOH} nm: 220, 260, 270, 305. IR ν^{KBr} cm^{-1}: 2940, 2840, 1690, 1640, 1600, 1500, 1280, 1120.

(+)-*Maroumine* **2**. MS, *m/z* (%): 638 (0, 6), 637 (0, 6), 397 (100), 351 (14), 242 (8, 3), 207 (23), 164 (30). UV λ_{max}^{EtOH} nm 220, 270, 305. IR ν cm^{-1}: 2840, 1690, 1650, 1600.

Methylation of limacusine. (+)-Limacusine (32 mg) was dissolved in MeOH and excess CH_2N_2 in Et_2O added. The contents were allowed to stand at 4° for 24 hr. Upon work-up, *O*-methyllimacusine **3** was obtained which was purified by prep. TLC.

Oxidation of (+)-*O-methyllimacusine* **3**. **3** (35 mg) was dissolved in 60 ml of Me_2CO and $KMnO_4$ (100 mg) in 65 ml of Me_2CO was added dropwise over 30 min with stirring. After 3.5 hr, the reaction mixt. was filtered, the solvent evapd and the residue purified by prep. TLC, to give 4 mg of amorphous (+)-seco-*O*-methyl-limacusine, identical with natural product **1**.

Acetylation of (−)-*gyrocarpine* **4**. **4** (75 mg) was dissolved in 1 ml of C_5H_5N and 1 ml of Ac_2O added. After standing for 24 hr, the solvent was evapd; work-up gave 70 mg of acetylgyrocarpine **5**.

Acetylation of (+)-*Maroumine* **2**. **2** (80 mg) was acetylated in the same way to afford **4**; 83 mg of acetylmaroumine **6** were obtained.

Oxidation of acetylgyrocarpine **5**. **5** (70 mg) was treated in the manner described above for **3**. (+)-Seco-acetyl-gyrocarpine (6 mg) was obtained, identical with product **6**.

REFERENCES

1. Chalandre, M.-C., Bruneton, J., Cabalion, P. and Guinaudeau H. (1986) *Can. J. Chem.* **64**, 123.
2. Nakanishi, K. (1962) *Infrared Absorption Spectroscopy*. Holden–Day, San Francisco.
3. Leet, J. E., Hussain, S. F., Minard, R. D. and Shamma, M. (1982) *Heterocycles* **19**, 2355.
4. Shamma, M. and Foy, J. E. (1975) *Tetrahedron Letters* 2249.
5. Shamma, M., Foy, J. E. and Miana, G. A. (1974) *J. Am. Chem. Soc.* **96**, 7809.

Phytochemistry, Vol. 27, No. 2, pp. 657–659, 1988.
Printed in Great Britain.

0031–9422/88 $3.00 + 0.00

ALKALOIDS FROM *STRYCHNOS STAUDTII*

PHILIPPE THEPENIER, MARIE-JOSÉ JACQUIER, GEORGES MASSIOT, LOUISETTE LE MEN-OLIVIER and CLEMENT DELAUDE*

Faculté de Pharmacie (U.A. au C.N.R.S. no. 492), 51 Rue Cognacq-Jay, 51096 Reims Cedex, France;* Université de Liège, Sart-Tilman, 4000, Liège, Belgium

(*Revised received* 6 *July* 1987)

Key Word Index—*Strychnos staudtii*; Loganiaceae; indole alkaloids; ^1H and ^{13}C NMR.

Abstract—Four alkaloids were found in the root bark, stem bark and leaves of *Strychnos staudtii*. They are 12-hydroxy-11-methoxyhenningsamine, 11-methoxyhenningsamine, 12-hydroxy-11-methoxydiaboline and 11-methoxydiaboline.

INTRODUCTION

Strychnos staudtii Gilg. is an erect tree from the rain forests of Cameroun and Gabon [1]. Despite the fact that preliminary screening by Phillipson and Bisset [2] showed it to contain alkaloids, the nature of these bases has never been elucidated. It is the purpose of this article to describe the isolation and structure elucidation of the four major alkaloids of the stem bark, root bark and leaves of *S. staudtii* collected in Cameroun.

RESULTS AND DISCUSSION

All extractions were conducted using published methods [3]; the alkaloid mixture (AM) obtained from the leaves, stem bark and root bark were similar by TLC. They were obtained with the following yields: 2.9 g/kg (stem) 5.4 g/kg (root) and 1 g/kg (leaves). Four alkaloids have been separated therefrom; they are in order of increasing polarity: 12-hydroxy-11-methoxyhenningsamine **1** (3% of AM), 11-methoxyhenningsamine **2** (13%