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**.

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ALKALOIDS FROM *STRYCHNOS STAUDTII*

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

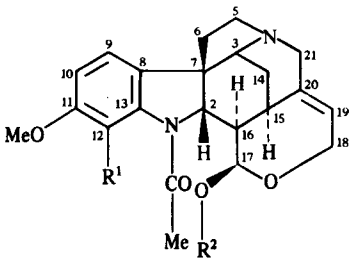
Abstract—Four alkaloids were found in the root bark, stem bark and leaves of *Strychnos staudtii*. They are 12-hydroxy-11-methoxyhenningsamine, 11-methoxyhenningsamine, 12-hydroxy-11-methoxydiaboline and 11-methoxydiaboline.

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%



1 R^1 = OH, R^2 = COMe
2 R^1 = H, R^2 = COMe
3 R^1 = OH, R^2 = H
4 R^1 = H, R^2 = H

of AM), 12-hydroxy-11-methoxydiaboline **3** (7% of AM) and 11-methoxydiaboline **4** (30% of AM). Among these, alkaloids **2**, **3** and **4** have been isolated from *S. henningsii* (**2**, [4]) and *S. spinosa* (**3**, **4**, [5]); alkaloid **1** is the 17-epimer of *O*-acetyl henningsoline from *S. henningsii* [4].

The mass spectra of compounds **1–4** showed the expected fragmentations for hexacyclic *Strychnos* alkaloids [4, 6]. The ^{1}H NMR spectra of compounds **1–4** were obtained at 300 MHz and interpreted by means of COSY and delayed COSY experiments. Alkaloids **1–3** were found to exist in $CDCl_3$ at room temperature as single rotamers with the oxygen carbonyl of the *N*-acyl group pointing towards C-12; on the contrary and as expected, 11-methoxydiaboline was, under the same conditions, a 2:1 mixture of rotamers.

Table 1 lists the chemical shifts of the protons of **1–4** and their coupling constants. Attributions of H-9 and H-10 in compounds **1** and **3** was based on the observation of a long range coupling between H-10 and the *ortho* methoxy group; this is the only discrepancy between our findings and those of Ohiri [5]. All these data and particularly the couplings between H-12, 16 and 17 show that **1–4** belong to the same series of alkaloids namely the isoretuline–diaboline–henningsamine series [7].

Table 2 gives ^{13}C NMR data for compounds **1–3** and for the two rotamers of **4**. The protonated carbons of **3** were assigned using heteronuclear ^{1}H–^{13}C correlations. All other assignments were performed after Wenkert [8] and Verpoorte [9]. The most unexpected shifts are those of C-15, C-16 and C-18; C-16 is deshielded with regard to C-15 because of the presence of three β heteroatoms. Acetylation of the C(17)-OH causes important deshieldings of C-15 and C-18, which can be explained in terms of downfield γ-effects; conformational changes may also rationalize this phenomenon but the coupling constants of the protons of the seven-membered oxepin ring rule out this hypothesis.

Although substitution of the aromatic ring of *Strychnos*

Table 1. ^{1}H NMR data for **1–4**. ($CDCl_3$, 300 MHz)

H	Multiplicity	1	2	3	4 (two rotamers)
2	*d*	4.3	4.3	4.25	4.2–4.8
3	*br s*	3.9	3.95	3.9	3.9
5	*dd*	3.38	3.36	3.4	3.4
5′	*ddd*	2.8	2.85	2.8	2.8–2.7
6	*dd*	1.95	1.97	1.9	1.9
6′	*dt*	1.7	1.65	1.8	1.8
9	*d*	6.55	6.96	6.6	6.95–7.1
10	*d*	6.70	6.62	6.75	6.6–6.6
12		–	7.67	–	7.6–6.7
14	*dt*	2.2	2.26	2.25	2.2
14′	*br d*	1.55	1.57	1.45	1.45
15	*br s*	2.7	2.7	3.4	3.4
16	*d*	1.9	1.88	1.6	1.6–1.65
17	*d*	5.8	5.84	5.3	5.3–4.8
18	*dd*	4.1	4.09	4.8	4.8–4.8
18′	*dd*	4.3	4.34	3.7	3.7–3.0
19	*br t*	5.9	5.89	5.9	5.9–5.7
21	*br d*	3.75	3.37	3.7	3.7
21°	*br d*	2.7	2.78	2.8	2.7
OH	*s*	10.6	–	10.15	—
OMe	*s*	3.85	3.81	3.85	3.85
NCOMe	*s*	2.45	2.38	2.45	2.4
OCOMe	*s*	2.08	2.08	–	–

Typical interproton coupling constants (Hz): $J_{9-10}=8.3$; $J_{10-12}=2.4$; $J_{18-19}=7$; $J_{18'-19}=3$; $J_{5-5'}=10$; $J_{6-6'}=12.6$; $J_{5-6'}=7.8$; $J_{5'-6}=6.3$; $J_{5'-6'}=12.5$; $J_{5',6'}=0$; $J_{21-21'}=15.1$; $J_{14-14'}=14.2$; $J_{3-14}=3.8$; $J_{14-15}=4$; $J_{16-2}=10.4$; $W_{1/2}$ H-17=2; $W_{1/2}$ H-19=10.

Table 2. ^{13}C NMR data for **1**–**4** ($CDCl_3$, 75 MHz)

C	1	2	3	4 (two rotamers)
2	65.5	64.5	66.8	65.4–65.1
3	58.8	58.7	58.7	58.8–59.1
5	51.6	51.4	51.4	51.4
6	37.7	38.3	38.0	38.4–38.6
7	53.1	53.2	52.9	52.9
8	128.1	126	128.3	127.3–127.7
9	111.9	121.7	112.1	121.8–123.0
10	109.7	110.0	110.1	110.7–108.8
11	–	159.9	150.1	159.7
12	137.8	105.2	137.7	106.0–105.6
13	–	142	129.8	142.6
14	25.3	25.5	25.0	25.1
15	33.3	33.4	28.5	28.5
16	44.2	45.0	45.7	46.7
17	101.9	102.4	93.5	93.6–97.3
18	64.3	64.1	54.9	55.1
19	125.5	125.2	126.8	126.7–126.0
20	141.7	144	142.4	143.1
21	53.6	53.6	53.1	53.2
O Me	56.4	55.6	56.4	55.5
N CO Me	23.6	24.2	22.8	23.3–24.4
O CO Me	20.9	21.0	—	—
N CO Me	172.7	170.5	172.6	170.0–169.7
O CO Me	168.7	168.9	—	—

alkaloids by hydroxy and methoxy groups on C-12 and C-11, respectively, is not rare [5, 10], to the best of our knowledge compound **1**, 12-hydroxy-11-methoxy-henningsamine is novel. Given the precedented natural *O*-acetylation of alkaloids of the diaboline series, it is not surprising to isolate compounds such as **1**.

EXPERIMENTAL

General. Plant material was collected by one of us (C.D.) in Cameroun on the left bank of the river Mungo near the bridge in Kumba-Loum; it has been identified by H. Breyne. A herbarium specimen is deposited in the Brussels National Gardens under No. HB 5105. ^1H and ^{13}C NMR were measured at 300 and 75 MHz, respectively.

Extraction and separation procedure. Finely ground root bark (30 g) was wetted with 20 ml of NH_4OH half dil. in H_2O and lixiviated overnight with 3 l of EtOAc. The organic soln was extracted with 2% H_2SO_4 (6 × 200 ml), the acid layer sepd, made alkaline with NH_4OH and extracted with $CHCl_3$ (4 × 200 ml). The $CHCl_3$ layer was washed with H_2O, dried (Na_2SO_4) and evapd *in vacuo*. This yielded 165 mg of crude alkaloid mixt. Similarly 15 g of stem bark yielded 45 mg of alkaloids and 11 g of leaves gave 11 mg of alkaloids. Part of the root bark alkaloid mixt (100 mg) was sepd by prep. TLC ($CHCl_3$–MeOH–NH_4OH; 91:8:1). The four major alkaloids had R_f values of 0.45, 0.39, 0.27 and 0.25, fluorescent bands at the top and bottom of the TLC plates corresponded to small quantities of material which were not investigated further.

12-*Hydroxy*-11-*methoxyhenningsamine* **1**. (CR grey-pink); $[\alpha]_D = -142$ ($CHCl_3$; *c*0.7); UV λ_{max}^{MeOH}: 227, 257, 292 (sh) nm; IR ν_{max}^{KBr} cm^{-1}: 3450, 2850, 2570, 1745, 1625, 1600, 1580, 1450, 1250, 1220, 1155, 800; MS *m/z* (rel. int.): 440 (30), 381(25), 380(100), 352(10), 338(25), 323(10), 190(30), 176(15), 162(25); NMR see Tables.

12-*Hydroxy*-11-*methoxydiaboline* **3**. (CR grey-pink); $[\alpha]_D = -147$ ($CHCl_3$, *c*1); UV λ_{max}^{MeOH}: 227, 255 nm; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3300, 1625, 1600, 1580, 1460, 1250, 1075, 750; NMR see Tables.

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