and J_{ax} = 3–4 Hz, C-6a); 3.8 (s, 3H, C-9-OCH_3) and 3.6 (s, 3H, C-1-OCH_3) is in agreement with an 1,2,9,10-tetrasubstituted aporphine moiety. The positions of the phenolic protons were established by D_2O exchange. IR (KBr) gave a broad band between 3500 and 3300 cm^{-1} for both OH and NH groups.

The MS exhibited a fragmentation pattern characteristic of an 1,2,9,10-tetrasubstituted noraporphine [4], e.g. *m/e* 313 (M^+), 312 (100%) (**a**), 282 (**a**-30), 298 ($M^+ - CH_3$) (**b**), 269 (**b**-CH_2=NH), 284 (M^+-29) (**c**), 253 (**c**-31), etc.

The positions of the OH groups were established by preparing the *O,O,N* triacetate **2** of **1** by treatment with Ac_2O–Py at room temperature. The triacetate (M^+ 439), mp 103–105°, (IR(CCl_4) 1650 and 1765 cm^{-1} respectively for NAc and OAc) exhibited the following ^1H NMR peaks (CCl_4, 60 MHz) δ 8 (*s*, 1H, C-11), 6.85 (*s*, 1H, C-3), 6.78 (*s*, 1H, C-8) and 3 acetyl groups between 2.01 and 2.21 together with the other aliphatic protons between 2.8 and 3.6. The downfield shift of the C-11 and C-3 protons showed that the OH groups are at the C-2 and C-10 positions. Had it been a C-10, C-1 combination the C-11 proton would have been further upfield due to the diamagnetic anisotropy of the acetyl carbonyl group(s) [5]. The appearance of the C-3 proton at δ 6.85 in the acetylated product confirmed the position of the OH at C-2 [6].

The optical rotation of **1** was $(+)^{\frac{589}{105}\ \frac{578}{108}\ \frac{546}{122}}$ (c = 0.4 MeOH) which suggested an α (I. series) configuration for the C-6a proton [7].

Laetanine was therefore assigned structure **1** and no other permutation of phenolic OH or OMe group was in accord with the data obtained.

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ALCALOÏDES DE *PANDACA BOITEAUI* (APOCYNACEAE)

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Key Word Index—*Pandaca boiteaui*; Apocynaceae; monomeric and dimeric indole alkaloids derived from cleavamine; ervatamine type indole alkaloids.

Pandaca boiteaui Mgf. [1] est un arbuste de sous-bois à feuilles oblongues elliptiques que l'on rencontre au Sud-Est de Madagascar dans les forêts ombrophiles du quadrilatère: Vondrozo, Farafangana, Vangaindrano, Midongy-du-Sud.

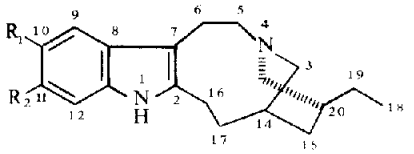
Les alcaloïdes totaux extraits de façon classique des feuilles (Rdt 2%), des écorces de tronc (Rdt 2%) et des écorces de racines (Rdt 4%) sont chromatographiés sur colonne d'alumine puis éventuellement ensuite sur couche épaisse de silice. Six alcaloïdes 'dimères' ont ainsi été isolés: trois sont connus, la voacamine **10** [2], la descarbométhoxyvoacamine **11** [3] et la capuvosidine **8** [4]; trois sont nouveaux, la (−)-20*R*-deshydroxycapuvosine **3**, la (−)-20*R*-isodeshydroxycapuvosine **4** et la 20*S*-dihydrocapuvosidine **9**.

Neuf alcaloïdes 'monomères' ont été séparés. Huit sont connus: la (+)-20*R*-dihydrocleavamine **1** [5], la (−)-20*S*-dihydrocleavamine **2** [5], la (+)-20*S*-Δ_1 ψ-aspidospermidine **5** [5], la (−)-20*S*-dihydro-1, 2 ψ-aspidospermidine **6** [5], la (+)-20*R*-dihydro-1,2 ψ-aspidospermidine **7** [5], la méthuénine **12** [6], la déhydro-19,20-ervatamine **13** [7] et la tubotaïwine [8].

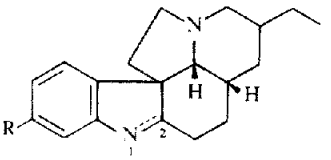
L'ervitsine **14** représente une structure d'un nouveau type.

L'étude structurale des alcaloïdes 'dimères' nouveaux [9] et de l'ervitsine [10] a fait l'objet de publications séparées.

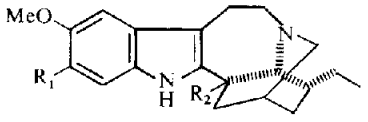
Il est à noter que *Capuronetta elegans* et *Pandaca*



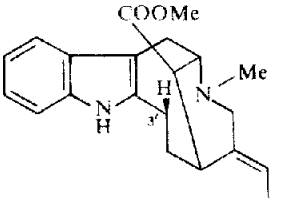
1 $R_1 = R_2 = H$: (+)-20*R*-dihydrocleavamine
2 $R_1 = R_2 = H$: (−)-20*S*-dihydrocleavamine
3 $R_1 = H, R_2$ = vobasinyl-3′: (−)-20*R*-deshydroxycapuvosine
4 R_1 = vobasinyl-3′, $R_2 = H$: (−)-20*R*-isodeshydroxycapuvosine



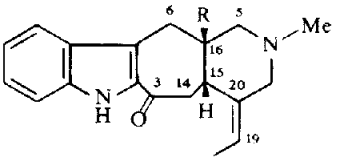
5 R = H: (+)-20*S*$\Delta_1\psi$-aspidospermidine
6 R = H: (−)-20*S*-dihydro-1,2 ψ-aspidospermidine
7 R = H: (+)-20*R*-dihydro-1,2 ψ-aspidospermidine
8 R = vobasinyl-3′,Δ_1: (−)-20*S*-capuvosidine
9 R = vobasinyl-3′: 20*S*-dihydro-capuvosidine



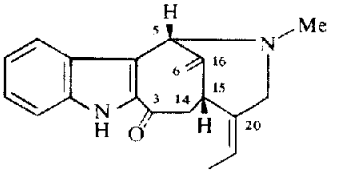
10 R_1 = vobasinyl; R_2 = COOMe: voacamine
11 R_1 = vobasinyl; R_2 = H: descarbométhoxyvoacamine



Vobasinyl-3′



12 R = H: méthuénine
13 R = COOMe: déhydro-19,20-ervatamine



14 Ervitsine

boiteaui sont les seules espèces de la tribu des Tabernaemontaneae, étudiées jusqu'ici, à contenir les nouveaux 'dimères' dérivés de la cleavamine. Par contre, *Pandaca boiteaui* s'apparente à d'autres espèces du même genre par la présence de 'monomères' dérivés de la cleavamine [5].

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