558 (22), 545 (36), 515 (22), 501 (26), 485 (54), 469 (30), 453 (50), 439 (29), 393 (36), 341 (58), 327 (100), 297 (54), 219 (14), 218 (26), 187 (>100).

MS von Saponarin-Permethyläther, hergestellt nach Brimacombe [10], ST 210°, PT 200°, 70 eV, *R* 1000/4 KV, *m/e* (rel. Int.); 734 M^+ (<1), 703 (31), 656 (25), 614 (16), 611 (11), 571 (15), 559 (18), 558 (17), 454 (22), 515 (21), 501 (29), 485 (62), 469 (26), 453 (50), 439 (32), 393 (42), 341 (75), 327 (100), 297 (65), 219 (10), 218 (47), 187 (96), 101 (>100).

Isovitexin-2″-O-rhamnosid = Glykosid **4**. Smp. = 225–230° [9].

DC: LM I 0.72; LM II 0.70; LM III 0.60; LM IV 0.45.

MS (Permethyläther, hergestellt nach Brimacombe [10], ST 220°, PT 200°, 70 eV, *R* 1000/4 KV, *m/e* (rel. Int.)): 704 M^+ (<1), 545 (9), 515 (24), 501 (37), 499 (50), 485 (12), 467 (5), 453 (10), 421 (15), 367 (21), 341 (73), 327 (100), 325 (27), 323 (25), 311 (50), 298 (18), 268 (8), 203 (9), 189 (10), 143 (66), 101 (75).

Darstellung der Isopropyliden-(IP) Derivate. 2 mg Substanz wurden in 10 ml Aceton abs. gelöst, mit wenig frisch geschmolzener *p*-Toluolosulfonsäure versetzt und mehrere Stdn. am Magnetrührer gerührt. Die Umsetzung wurde chromatographisch kontrolliert (LM III). Das Reaktionsgemisch wurde anschließend mit wässrigem Ammoniak neutralisiert, zur Trockene einrotiert und mit Äthanol abs. nachgetrocknet. Die Verbindungen wurden zur Auffindung des Molekülpeaks im MS nach Brimacombe [10] permethyliert.

3″-*O*-Glucosyl-Isovitexin-7-*O*-galactosid: M^+ 974 entsprechend einer 4,6-*O*-IP- bzw. 3,4-*O*-IP-Galactose-PMÄ- und zwei 4,6-*O*-IP-Glucose-PMÄ-Einheiten.

3″-*O*-Rhamnosyl-Isovitexin-7-*O*-galactosid: M^+ 944, entsprechend 4,6-*O*-IP- bzw. 3,4-*O*-IP-Galactose-PMÄ-, 4,6-*O*-IP-Glucose-PMÄ-und 2,3-*O*-IP-Rhamnose-PMÄ.

Isovitexin-7-*O*-glucosid (Saponarin): M^+ 758, entsprechend zwei 4,6-*O*-IP-Glucose-PMÄ-Einheiten.

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LAETANINE, A NEW NORAPORPHINE ALKALOID FROM *LITSEA LAETA*

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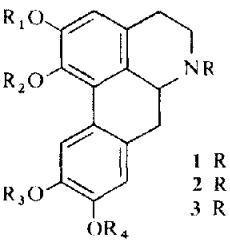
Key Word Index—*Litsea laeta*; Lauraceae; new noraporphine alkaloid; laetanine; 2, 10-dihydroxy-1,9-dimethoxy noraporphine.

Ground defatted bark of *Litsea laeta* Benth and HK f. collected from the western part of Sibsagar district (Assam) was exhaustively extracted with MeOH. After removal of solvent, the residue was extracted with 2% HCl, made alkaline with NH_4OH and extracted with MeOH–$CHCl_3$ (3:97). Repeated column chromatography over acidic Al_2O_3 with MeOH–EtOAc (1:9) led to the isolation of a new compound as light amber coloured crystals (EtOAc–MeOH) mp 226 228°. We propose the structure **1** for this new noraphorphine alkaloid which we name as laetanine (2,10-dihydroxy-1,9-dimethoxy noraporphine) on the basis of the following spectroscopic and chemical evidence. It should be noted here that the formula **1** was proposed by Clezy for laurelliptine [1] but afterwards he revised it to **3** [2].



1 R = H; R_1 = R_3 = H; R_2 = R_4 = Me
2 R = R_1 = R_3 = Ac; R_2 = R_4 = Me
3 R = H; R_1 = R_3 = Me; R_2 = R_4 = H

Compound **1**, which gave positive Meyer's and Dragendorff's tests, showed a M^+ (92%) at *m/e* 313.1303 for $C_{18}H_{19}NO_4$ (calcd 313.1313). The UV λ_{max}^{EtOH} (ε) 284 (11 842) and 304 (12 463) nm suggested a 1,2,9,10-tetra-substituted aporphine skeleton [3]. The phenolic nature of the compound was established from the positive $FeCl_3$ test and a bathochromic UV shift of 32 nm in alkaline solution. The ^1H NMR spectrum (DMSO-d_6, 270 MHz) δ 9.47 (*s*, 1H, OH), 9.36 (*s*, 1H, OH), 7.91 (*s*, 1H, C-11), 6.77 (*s*, 1H, C-8), 6.65 (*s*, 1H, C-3), 4.15 (*dd*, 1H, J_{aa} – 1.2 Hz

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*