J' 9 Hz), *s* (1H) 7,42; MS: M^+ 398, principaux pics à *m/e* 223 et 69. *C isocaboxine-B*: $C_{22}H_{26}O_5N_2$ (M^+ 398); amorphe; $(\alpha)_D$ +53° ($CHCl_3$); UV λ_{max} 224, 244, 286 et 294 nm; IR *v*CO ester conjugué et lactame 1720 et 1620 cm^{-1}; RMN: *d* (3H) 1,21 (*J* 6 Hz), deux *s* (3H chacun) 3,62 et 3,80, *o.* (1H) 4,20 (*J o* Hz. *J'* 6 Hz), *d* (1H) 7,28 (*J* 9 Hz), *d* (1H) 6,48 (*J* 2 Hz), *q* (1H) 6,52 (*J* 2 Hz, *J'* 9 Hz), *s* (1H) 7,42; MS: M^+ 398, principaux pics à *m/e* 223 et 69. *F isocaboxine-A*: $C_{22}H_{26}O_5N_2$ (M^+ 398); F (130) 188°; $(\alpha)_D$ +31,7° ($CHCl_3$); UV λ_{max} 222, 244, 286 et 294 nm; IR *v*CO ester conjugué et lactame 1725–1640 cm^{-1}; RMN: *d* (3H) 1,25 (*J* 6 Hz), deux *s* (3H chacun) 3,43 et 3,80; *o.* (1H) 4,21 (*J* 3 Hz, *J'* 6 Hz), *d* (1H) 7,01 (*J* 9 Hz), *d* (1H) 6,55 (*J* 2 Hz), *q* (1H) 6,50 (*J* 2 Hz, *J'* 9 Hz), *s* (1H) 7,40; MS: M^+ 398, principaux pics à *m/e* 223 et 69. *I cabulatine*: $C_{22}H_{26}O_4N_2$ (M^+ 382); F 238–240°: $(\alpha)_D$ −68° ($CHCl_3$); UV λ_{max} 232 et 298 nm; IR *v*CO ester conjugué 1690 et 1630 cm^{-1}; RMN: *s* (1H) 1,28, *d* (3H) 1,38 (*J* 6 Hz), deux *s* (3H chacun) 3,76 et 380; *o.* (1H 4,48 (*J* 10 Hz, *J'* 6 Hz), *d* (1H) 7,30 (*J* 10 Hz), *d* (1H) 6,68 (*J* 2 Hz), *q* (1H) 6,72 (*J* 2 Hz, *J'* 10 Hz), *s* (1H) 7,56; MS: M^+ 382, principaux pics à *m/e*: 381, 367, 351, 323, 281, 253, 214, 200, 199, 186. *K monométhoxyoxindole*: $C_{22}H_{26}O_5N_2$ (M^+ 396); F 212 °; $(\alpha)_D$ +234 ($CHCl_3$); UV λ_{max} 230, 280 et 310 nm; IR *v*CO ester conjugué et lactame 1620 et 1700 cm^{-1}; RMN: *d* (3H) 1,12 (*J* 6 Hz) deux *s* (3H chacun) 3,70 et 3,78; *o.* (1H) 4,30 p.p.m. (*J* 3 Hz, *J'* 6 Hz), *d* (1H) 7,30 (*J* 9 Hz), *d* (1H) 6,98 (*J* 2 Hz), *q* (1H) 6,82 (*J* 2 Hz, *J'* 9 Hz), *s* (1H) 7,45; MS: M^+ 398, principaux pics à *m/e*: 223 et 69.

Tout comme dans le cas du *C. erythrocarpa*[1,2] l'alcaloïde majeur, contenu dans les tiges et racines est la cabucine (=méthoxy-10 ajmalicine) qui apparaît constituer l'alcaloïde le plus typique du genre *Cabucala*. Mais dans les feuilles, les alcaloïdes les plus abondants sont du type diméthoxyoxindole (carapanaubine et diméthoxy-10,11 isomitraphylline); les hétéroyohimbines correspondant aux deux diméthoxyoxindoles des feuilles ne semblent présents dans aucun organe de cette plante.

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ALKALOIDS OF *TABERNAEMONTANA DIVARICATA**

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Key Word Index—*Tabernaemontana divaricata*; *Apocynaceae*; varietal differences, coronaridine; voacangine; voaphylline; tabernaemontanine; lochnericine.

THE PLANTS of genus *Tabernaemontana* are fairly widely distributed constituting one of the most abundant groups of *Apocynaceae* and have extensively been examined for their alkaloidal constitutents.[1–3] T. *divaricata* R. Br. ex Roem and Schult is grown throughout India in gardens as an oranmental shrub. This species is represented by two varieties; one

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with petals in a single whirl (*var.* 1) and the other with petals in two whirls (*var.* 2). Although careful studies by Raghuvanshi and Chauhan[4] have indicated marked morphological differences between these two (*var.* 1 is diploid and *var.* 2 is triploid), no mention of any differences in their chemical constituents has been published. This, coupled with the reported anticancer activity in the crude extractives of this plant[5] prompted us to re-examine both varieties separately. The results were of considerable interest since the leaves of *var.* 1 afforded coronaridine, voacangine, voaphylline and tabernaemontanine whereas only voaphylline and lochnericine were obtained from the leaves of *var.*2.

With the isolation of tabernaemontanine, voacangine and voaphylline, the representative examples of *corynanthe*, *iboga* and *aspidosperma* skeletons respectively, T. *divaricata* becomes the seventh instance in the family *Apocynaceae*,[6] which produces all the three main types of the indole alkaloids and is, therefore, of considerable interest from the biogenetic viewpoint.

EXPERIMENTAL

The residue obtained after concentrating the EtOH extract of the fresh leaves (60 kg; single petal variety) was macerated with tartaric acid soln (4%, 8 × 1 l.). The acidic layer was defatted with hexane, and extracted at pH 4·3–4·5 with C_6H_6 (8 × 1 l.). The aq. fraction was brought finally to pH 7·3–8·0 and reextracted with $CHCl_3$ (6 × 2 l.). The C_6H_6 residue (25·5 g) on column chromatography over silica gel (1·5 kg) yielded coronaridine (20 mg), voacangine (9·0 g) and voaphylline (15 mg) from C_6H_6 eluate. The $CHCl_3$ residue (38 g) likewise afforded tabernaemontanine (60 mg) from neutral alumina column with 10% EtOAc–C_6H_6. In a similar way the double petal variety (35 kg; fresh leaves) yielded only voaphylline (500 mg) and lochnericine (30 mg) through silica gel column chromatography.

Tabernaemontanine, m.p. 215–217°, $[\alpha]_D^{25}$ −57° ($CHCl_3$), UV λ_{max}^{EtOH} 236 (log ε 4·21), 310 (4·26) nm MS. M^+ 354. *Voacangine*, m.p. 136–37°, $[\alpha]_D^{25}$ −28° ($CHCl_3$), UV λ_{max}^{EtOH} 224 (log ε 4·23), 285 (3·85), 299 (3·86) nm MS. M^+ 368. *Coronaridine*, amorphous solid, $[\alpha]_D^{25}$ −34° ($CHCl_3$). UV λ_{max}^{EtOH} 224 (log ε 4·55), 283 (3·72), 289 (3·80) nm MS. M^+ 338. *Voaphylline*, m.p. 170°, $[\alpha]_D^{24}$ +24° ($CHCl_3$), UV λ_{max}^{EtOH} 228 (log ε 4·51), 286 (3·76), 292 (3·70) nm NMR ($CDCl_3$, 60 MHz), δ 0·73 (*t*, *J* 7 Hz, 3H, $CH_2\underline{CH}_3$), 1·12 (*m*, *J* 7 Hz, 2H, $\underline{CH}_2Me$), 7·02 (*m*, 4H, Ar$\underline{H}$), 7·92 (NH, eliminated by D_2O). MS. M^+ 296. LAH reduction product ($C_{19}H_{26}N_2O$), m.p. 225° (d), $[\alpha]_D^{24}$ +150° (MeOH), MS. *m/e* 298 (M^+ 100%), 280 (5), 269 (13), 251 (45), 157 (50), 154 (54), 144 (46), 143 (54), 142 (52), 140 (42), 126 (46), 112 (10), 108 (18), LAD reduction product ($C_{19}H_{25}DN_2O$), MS. *m/e* 299 (M^+ 100%), 155 (33), 143 (33), 141 (39), 127 (47). *Lochnericine*, amorphous solid, $[\alpha]_D^{25}$ −360° ($CHCl_3$). UV λ_{max}^{EtOH} 225 (log ε 4·20), 297 (4·25), 328 (4·45) nm MS. M^+ 352.

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