powdered bark (5 kg) was carried out in the usual manner [9] and the crude alkaloids (5.440 g) were fractionated on a 500 g Si gel (Gebr. Herrmann/Köln) column, eluting with increasingly polar CH_2Cl_2/MeOH mixtures, into 9 fractions. The chromatographic separation was followed by LKB Uvicord, and the collected fractions were analysed by TLC, proving in every case to be mixtures of two or three main components, which were purified using PLC or column chromatography.

Frangulanine (102 mg), nummularine-B (69 mg) and mucronine-D (5 mg) were obtained and identified by spectroscopic methods and by chromatographic comparison with the authentic samples in several solvent systems.

Sativanine-A. 0.48 mg were obtained from fraction IV by repeated chromatography on Si gel using cyclohexane–Me_2CO–MeOH (35:15:1) and cyclohexane–EtOAc–MeOH (30:15:4) as solvent systems: mp 80° (uncorr.); UV (MeOH) strong end absorption and shoulders at 250 and 280 nm. Mol. wt. (MS) 520.3055; calcd. for $C_{30}H_{40}N_4O_4$, 520.3050.

Sativanine-B. 0.42 mg were obtained from fraction V using C_6H_6–Me_2CO–MeOH (25:30:4) and C_6H_6–EtOAc–MeOH (25:15:4) as solvent systems; mp: amorphous; UV (MeOH) strong end absorption with shoulder at 280 nm. Mol. wt. (MS) 518.2888; calcd. for $C_{30}H_{38}N_4O_4$, 518.2893.

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ALKALOIDS FROM PODS OF *ERYTHRINA ARBORESCENS*

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Key Word Index—*Erythrina arborescens*; Leguminosae; erysodine; orientaline; hypaphorine; a new quaternary alkaloid—erysodinophorine.

INTRODUCTION

Erythrina arborescens is distributed throughout the upper gangetic plains, Assam and Manipur, extending west towards Nepal [1, 2]. The seed of this plant has been reported to contain erysodine, erysovine, erysopine, hypaphorine, erythrascine, orientaline and erysophorine [2, 3]. The present investigation was carried out in order to determine the chemical constituents of the pod walls of *E. arborescens*.

RESULTS AND DISCUSSION

The EtOH extract of the pod walls of *E. arborescens* yielded erysodine, orientaline, hypaphorine (mmp, co-chromatography and spectral studies) and a new alkaloid provisionally named as erysodinophorine. Hydrolysis of erysodinophorine with EtOH–HCl afforded two alkaloids erysodine and hypaphorine. The molecular formula, $C_{32}H_{38}N_3O_5$, of erysodinophorine was established from elemental analysis, the integrals of the proton signals (37H in D_2O) and from the molecular formulae of the products of the hydrolysis of erysodinophorine. Like erysophorine, erysodinophorine also did not respond to the Ehrlich test for α and β unsubstituted indoles, whereas the acid hydrolysed product, on the other hand, gave a positive test. The negative response was presumably due to the attachment of the bulky ester function which blocks the free α position of the indole ring in erysodinophorine [3]. The UV spectrum of erysodinophorine is very similar to that of erysophorine indicating its marked structural similarity [3]. The compound showed major bands in the IR at 3400 (broad, —OH and >NH), 1754 (phenolic ester group), 1620 (indole ring), 1590, 1496, 1258, 1082 (spiroamine ring). The absence of a peak at 1442 cm^{-1} in the IR suggests

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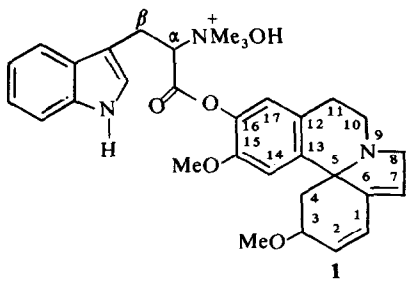
the absence of a —C—O⁻ group further supporting the fact that the two alkaloids are linked together by esterification. Erysodinophorine did not exhibit an M^+ peak in its MS but significant fragment ion peaks appeared, corresponding to the aromatic erythrine 1:6 diene and carboxylated indole 3 alkyl amine [3]. The PMR spectra of the alkaloid in D_2O showed the signals at δ 1.98 (1H, C_4aH), 2.46 (1H, C_4 eH), 3.15 (9H, $N^+(Me)_3$), 3.42 (3H, C_3-OMe), 3.57 (4H, βCH_2 and C_8CH_2), 3.82 (3H, C_{15}-OMe), 3.96 (4H, C_{10},C_{11}-CH_2), 4.08 (1H, C_3-H), 4.45 (1H, C_αH), 5.83 (1H, C_7-H), 6.12 (1H, C_1-H), 6.67 (1H, C_2-H), 6.7–7.8 (7H, C_{14}-H, C_{17}-H and five protons for the indole ring).

The foregoing evidence is in good agreement with the structure 1 for erysodinophorine.



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EXPERIMENTAL

The powdered, air-dried and defatted pod walls (3 kg) of *E. arborescens* Roxb. (supplied by United Chemical and Allied Products, Calcutta) was extracted exhaustively with EtOH. The EtOH extract was concd under red. pres. and extracted with petrol to remove fats and chlorophyll. The defatted EtOH extract was then extracted with $CHCl_3$. The $CHCl_3$ extract on passing through a column of Si gel yielded erysodine (0.302 g) as a crystalline solid, $C_{18}H_{21}NO_3$, mp 204–206°; $[\alpha]_D^{27}$ +248° (EtOH); R_f 0.62 (Si gel, $CHCl_3$–MeOH 1:1); λ_{max}^{EtOH} 235, 285 nm; ν_{max}^{Nujol} 3435, 2940, 2873, 1592, 1510, 1468, 1385, 1330, 1295, 1260, 1180, 1160, 1100, 992, 870 and 796 cm^{-1}; PMR ($CDCl_3$) δ 1.98 (1H, C_4aH), 2.49 (1H, C_4eH), 3.4 (3H, C_3-OMe), 3.85 (3H, C_{15}-OMe) 4.06 (1H, C_3H), 5.84 (1H, C_7-H), 6.1 (1H, C-1H), 6.8 (1H, C_{17}H), 6.94 (1H, C_{14}H); MS *m/e* 299 (M^+), 284, 268, 266, 241, 228, 215 and orientaline, an oily alkaloid (86 mg), $C_{19}H_{23}NO_4$; R_f 0.32 (BuOH–HOAc–H_2O, 4:1:2); λ_{max}^{EtOH} 220–222, 283–285 nm; MS *m/e* 329 (M^+) 329 (12), 192 (100), 177 (46), 137 (50), 134 (32). Orientaline on treatment with CH_2N_2 gave laudanosine, $C_{21}H_{27}NO_4$, mp 86°, MS *m/e* 357 (M^+).

The conc EtOH extract left after the extraction with $CHCl_3$ was adsorbed onto a column of Si gel. On elution with $CHCl_3$–MeOH (1:1) it yielded (i) a white crystalline alkaloid, hypaphorine (0.65 g), $C_{14}H_{18}N_2O_2$, mp 252–254°; $[\alpha]_D^{27}$ +113.5 (H_2O); λ_{max}^{EtOH} 224, 275, 294 nm; ν_{max}^{KBr} 3030, 2833, 2353, 1642, 1504, 1462, 1418, 1381, 1359, 1307, 1244, 1133, 1111, 1073, 1015, 978, 968, 913, 893, 829, 755, 684 cm^{-1}; PMR (D_2O) δ 2.85 (9H, N-Me_3), 2.97 (2H, CH_2), 3.61 (1H, CH), 6.98–7.53 (5H, aromatic ring), which gave trimethylamine (picrate, mp 212–4°) and indole, mp 50–52° on Zn dust distillation and heating with KOH [4] and (ii) a brown syrupy alkaloid, erysodinophorine, $C_{32}H_{38}N_3O_5$; λ_{max}^{EtOH} 220, 280, 288 nm; MS *m/e* 298 (30), 285 (6), 283 (8), 267 (40), 240 (18), 227 (5), 215 (6), 214 (3), 187 (12), 170 (18), 143 (40), 130 (100).

Hydrolysis of erysodinophorine. Erysodinophorine (0.5 g) and 6 N HCl (25 ml) were refluxed for 1 hr at 100°. The reaction mixture was cooled, made alkaline with NH_4OH and extracted with $CHCl_3$. The $CHCl_3$ extract on evapn yielded crystalline needles, mp 204–206°, identified as erysodine (mmp and IR). The alkaline aq. layer was again acidified with excess of HCl whereupon hypahorine hydrochloride, mp 232–234° precipitated which was separated by filtration and purified by recrystallization.

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