(University of New Orleans) for the sample of β-isosparteine, Dr. O. E. Edwards (Canadian National Research Council) for reference rhombifoline, and Dr. M. Wiewiorowski (Polish Academy of Sciences) for authentic angustifoline.

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ERYSOPINOPHORINE, A NEW QUATERNARY ALKALOID FROM PODS OF *ERYTHRINA ARBORESCENS*

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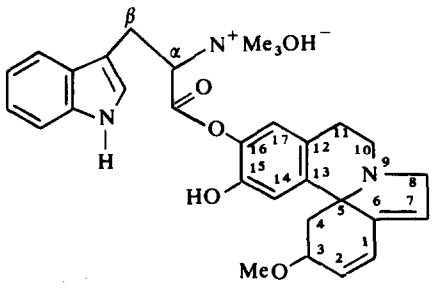
Key Word Index—*Erythrina arborescens*; Leguminosae; new quaternary alkaloid; erysopinophorine.

INTRODUCTION

Erythrina arborescens is distributed throughout the upper Gangetic plains, Assam and Manipur, extending west towards Nepal [1]. The seed of this plant has been reported to contain erysodine, erysovine, erysopine, hypaphorine, erythrascine, orientaline and erysophorine [2, 3], and the pod walls have been showed to contain erysodine, orientaline, hypaphorine and erysodinophorine [4]. In this paper we report the isolation of a new quaternary alkaloid **1**, provisionally named erysopinophorine, from the pod walls.



1

RESULTS AND DISCUSSION

The EtOH extract of pod walls of *E. arborescens* yielded a new alkaloid **1** besides other already reported alkaloids [4]. Hydrolysis of this alkaloid with EtOH–HCl afforded hypaphorine and erysopine. The molecular formula, $C_{31}H_{37}N_3O_5$, of **1** was established from elemental analysis, the integrals of the proton signals (33H in D_2O) and from the molecular formulae of the products of hydrolysis of erysopinophorine. Like erysophorine and erysodinophorine, **1** also did not respond to the Ehrlich test for α- and β-unsubstituted indoles, whereas the acid-hydrolysed product gave a positive test. The negative response by **1** was probably caused by the bulky ester function which blocks the free position of the indole ring [3, 4]. The UV spectrum of **1** is very similar to that of erysophorine and erysodinophorine, indicating its marked structural similarity [3, 4]. The compound showed major bands in the IR at 3400 (broad OH and NH), 1762 (phenolic ester group), 1618 (indole ring), 1590, 1498, 1262 and 1086 (spiro amine ring) cm^{-1}. The absence of a peak at 1442 cm^{-1} in the IR of **1** suggests the absence of a COO^- group, further supporting the fact that the two alkaloidal fragments are linked together by an ester group.

Since there are two OH groups at C-15 and C-16 in erysopine, in order to establish the position of esterification, **1** was methylated and hydrolysed with EtOH–HCl whereupon two alkaloids, hypaphorine and erysodine, were obtained indicating that hypaphorine is linked to C-16 of erysopine. **1** did not exhibit an M^+ peak in its MS but significant fragment ions appeared corresponding to the aromatic erythra-1,6-diene and hypaphorine [3, 4]. The ^1H NMR spectrum of the alkaloid in D_2O showed signals at δ 1.98 (1H, C-4a H), 2.45 (1H, C-4e H), 3.16 (9H, $N^+(Me)_3$), 3.42 (3H, C-3 OMe), 3.56 (4H, βCH_2 and C-8 CH_2), 3.94 (4H, C-10, C-11 CH_2), 4.02 (1H, C-3 H), 4.42 (1H, C-α H), 5.86 (1H, C-7 H), 6.06 (1H, C-1 H), 6.66 (1H, C-2 H) and 6.6–7.7 (7H, C-14 H, C-17 H and 5 protons of the indole ring).

The foregoing evidence is in conformity with the structure **1** for erysopinophorine.

EXPERIMENTAL

The powdered, air-dried and defatted pod walls (3 kg) of *E. arborescens* (supplied by United Chemical and Allied Pro-

ducts, Calcutta and identified by National Botanical Garden, Calcutta) were extracted exhaustively with EtOH. The EtOH extract was concd *in vacuo* and extracted successively with petrol and $CHCl_3$ which yielded erysodine and orientaline [4]. The conc EtOH extract left after $CHCl_3$ extraction was adsorbed onto a column of Si gel. On elution with $CHCl_3$–MeOH (1:1), it yielded hypaphorine and erysodinophorine [4]. Further elution of the column with $CHCl_3$–MeOH (1:4) yielded a brown syrupy alkaloid, 1 erysopinophorine, $C_{31}H_{37}N_3O_5$; λ_{max}^{EtOH} nm: 226, 282, 296; MS *m/e* 285 (22), 284 (38), 269 (40), 253 (18), 227 (9), 215 (3), 214 (6), 201 (3), 187 (15), 143 (45), 130 (95), 58 (100). (Found: C, 70.06; H, 6.72; N, 7.96. Calc. for $C_{31}H_{37}N_3O_5$: C, 70.18; H, 6.79; N, 7.92%).

Hydrolysis of **1**. Erysopinophorine (0.25 g) and 6 N HCl (15 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 a crystalline compound, $C_{17}H_{19}NO_3$, mp 242°, $[\alpha]_D^{26}$ +225° (morpholine), identified as erysopine by mmp, comparison of IR, ^1H NMR and MS [2, 5, 6] of the authentic sample isolated from the seed of *E. arborescens*. The alkaline aq. layer was again acidified with excess of HCl precipitating hypaphorine HCl (mp 232–234°) which was separated by filtration and purified by recrystallization (identified mmp) [4].

Methylation of **1** *and hydrolysis of methyl erysopinophorine.* Erysopinophorine (0.25 g), MeOH (15 ml), K_2CO_3 (1.5 g) and Me_2SO_4 (15 ml) were refluxed for 10 hr at 100°. After usual work-up, a syrupy base was isolated which was refluxed with 6 N HCl (15 ml) for 1 hr at 100°. The reaction mixture was cooled, made alkaline with NH_4OH and extracted with $CHCl_3$, which on evapn yielded erysodine, mp 204–206° (identified by mmp and IR comparison with authentic sample) [4]. The alkaline aq. layer on usual treatment yielded hypaphorine HCl, mp 232–234°.

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