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ISO-ERYSOPINOPHORINE, A NEW QUATERNARY ALKALOID FROM THE SEEDS OF *ERYTHRINA ARBORESCENS*

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

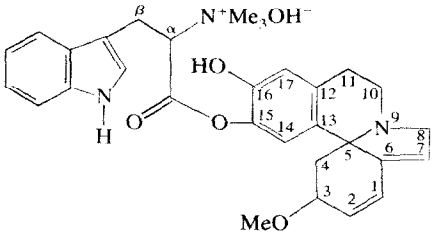
Abstract—The ethanolic extract of the seeds of *Erythrina arborescens* yielded a new quaternary alkaloid provisionally named as iso-erysopinophorine besides the other alkaloids reported previously. The new alkaloid was characterised by chemical and spectral studies.

Erythrina arborescens is distributed throughout the upper Gangetic plains, Assam and Manipur, extending west towards Nepal [1]. The pod wall of this plant has been reported to contain erysodine, orientaline, hypaphorine, erysodinophorine and erysopinophorine [2, 3] and the seeds erysodine, erysovine, erysopine, hypaphorine, erythrascine, orientaline and erysophorine [4, 5]. The re-examination of the alkaloidal constituents of the seeds of *E. arborescens* was carried out in order to isolate erysopine for direct comparison with the sample of erysopine obtained from the acid hydrolysate of erysopinophorine [3].

The EtOH extract of the seeds of *E. arborescens* yielded a new alkaloid provisionally named as iso-erysopinophorine besides other alkaloids reported previously [4, 5]. Hydrolysis of iso-erysopinophorine with EtOH/HCl afforded two alkaloids, hypaphorine and erysopine. The molecular formula, $C_{31}H_{37}N_3O_5$, of iso-erysopinophorine was established from elemental analysis, and integrals of the ^{1}H NMR proton signals (24 H in D_2O) and from the molecular formulae of the products of hydrolysis of iso-erysopinophorine. Like erysophorine, erysodinophorine and erysopinophorine, it 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 iso-erysopinophorine was also presumably due to the attachment of the bulky ester group which blocks the free position of the indole ring [2, 3, 5]. The UV spectrum of iso-erysopinophorine is very similar to that of erysopinophorine, erysodinophorine and erysophorine indicating its marked structural similarity [2, 3, 5]. The compound showed peaks in the IR at 3400 (broad, −OH and >NH), 1760 (phenolic ester group), 1618 (indole ring), 1952, 1500, 1285, 1090 cm^{-1} (spiro-amine ring). The absence of a peak at 1442 cm^{-1} in the IR of iso-erysopinophorine suggests the absence of a free COO^- group, which further supports the fact that the two alkaloidal fragments are linked together through an ester group.

Erysopine, one of the products of hydrolysis of iso-erysopinophorine, has two free OH groups at C-15 and C-16. In order to establish the position of esterification iso-erysopinophorine was methylated and hydrolysed with EtOH/HCl whereupon two alkaloids (hypaphorine and erysovine) were obtained indicating that hypaphorine is linked to C-15 of erysopine. Iso-erysopinophorine did not exhibit a M^+ peak in its MS but significant fragment ion peaks appeared corresponding to the aromatic erythra-1,6-diene and hypaphorine [2, 3, 5]. The ^{1}H NMR spectrum of the alkaloid in D_2O showed signals at δ 1.98 (1 H, C-4aH), 2.44 (1 H, C-4eH), 3.17 (9 H, $N^+(Me)_3$), 3.46 (3 H, C-3 OMe), 3.57 (4 H, βCH_2 and C-8CH_2), 3.94 (4 H, C-10, C-11CH_2), 4.04 (1 H, C-3H), 4.44 (1 H, Cα-H), 5.86 (1 H, C-7-H), 6.07 (1 H, C-1H), 6.66 (1 H, C-2H), 6.8–7.7 (7 H, C-14H, C-17H and 5 aromatic protons of indole ring).

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



1

EXPERIMENTAL

The powdered, air-dried and defatted seeds (8 kg) of *E. arborescens* (supplied by United Chemical & Allied Products, 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 the alkaloids reported previously [4, 5]. The conc EtOH extract left after extraction with $CHCl_3$ was adsorbed onto a column of Si gel. On elution with $CHCl_3$–MeOH (1 : 1), hypaphorine, two brown syrupy liquids erysophorine [5] and iso-erysopinophorine ($C_{31}H_{37}N_3O_5$, λ_{max}^{EtOH} nm: 226, 286, 294; MS *m/e* 285 (20), 284 (33), 269 (42), 253 (20), 215 (4), 214 (5), 201 (5), 187 (18), 143 (40), 130 (96), 50 (100); found: C, 70.08; H, 6.94; N, 7.97. calc. for $C_{31}H_{37}N_3O_5$: C, 70.05; H, 6.96; N, 7.90%) were obtained.

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Hydrolysis of isoerysopinophorine. Iso-erysopinophorine (150 mg) and 6 M HCl (5 ml) were refluxed for 1 hr at 100°. The reaction mixture was cooled, made alkaline with NH_4OH and extracted with $CHCl_3$ which on evapn yielded crysopine, $C_{17}H_{19}NO_3$, mp 242°, $[\alpha]_D^{26}+225°$ (morpholine), identified by mmp, comparison of IR, ^1H NMR and MS [4, 6, 7] with authentic erysopine. The alkaline aq. layer was again acidified with excess HCl whereupon hypaphorine HCl, mp 232–34° precipitated which was separated by filtration and purified by recrystallization (identified by mmp) [2, 3].

Methylation of iso-erysopinophorine and hydrolysis of Me iso-erysopinophorine (erysophorine). Iso-erysopinophorine (200 mg), MeOH (10 ml), K_2CO_3 (1 g) and Me_2SO_4 (15 ml) were refluxed for 8 hr at 100°. Work-up in the usual way gave a syrupy base which was refluxed with 6 M HCl (10 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 erysovine, mp 176°, identified by mmp, comparison of IR with authentic erysovine [5, 6]. The alkaline aq. layer on usual treatment yielded hypaphorine HCl, mp 232–34°.

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