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SHORT COMMUNICATION

ERYTHRASCINE AND OTHER ALKALOIDS IN SEEDS OF *ERYTHRINA ARBORESCENS*

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Abstract—Isolation and characterization of a new erythrina alkaloid, erythrascine (I) and a tetrahydrobenzylisoquinoline alkaloid from the seeds of *Erythrina arborescens* Roxb. are reported. In addition, ten spiroamine erythrina alkaloids and hypaphorine, previously reported in other *Erythrina* species, have also been isolated from this species.

INTRODUCTION

THE INDIAN *Erythrina arborescens* Roxb. (Leguminosae: Lotoideae) is distributed[1] in the upper Gangetic plains, in Assam and Manipur extending westwards towards Nepal. Three eryso alkaloids, viz. erysodine, erysovine, and erysopine, were previously isolated[2] from the seeds of this species, collected elsewhere, by Folkers and Shavel. The present investigation, with the seed extracts of *E. arborescens* of Indian origin, revealed the presence of a complex mixture of alkaloids in their basic fractions. Isolation and characterization of these alkaloids constitute the subject of the present paper.

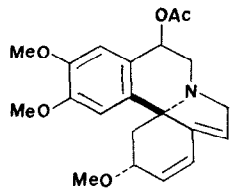
RESULTS AND DISCUSSION

Gradient-pH extraction and repeated preparative chromatography of the mixture of bases afforded a new erythrina alkaloid, erythrascine, and a tetrahydrobenzylisoquinoline alkaloid, together with ten previously known erythrina bases, viz. β-erythroidine, erythristemine, erythraline, erythramine, erysotrine, erythratine, erysovine, erysopine, erysodine, erythratidine, and the indole alkaloid, hypaphorine.

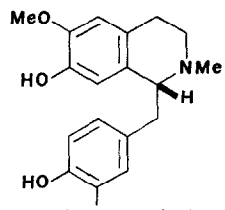
Erythrascine, $C_{21}H_{25}NO_5$ (molecular formula established by mass spectrometry and microanalysis), showed a strong band in its IR spectrum at ν_{max} (KBr) 1728 cm^{-1} (—COOR) but no band for hydroxyl or keto carbonyl function. The mass fragmentation pattern of the alkaloid was characteristic of an aromatic erythrina alkaloid having a 1,6-diene system[3] carrying an additional *O*-acetyl function in ring C. The NMR spectrum of erythrascine in $CDCl_3$ was also consistent with this conclusion. The two aromatic *para* proton signals of the alkaloid appeared at τ 2·95 (14-H) and 2·98 (17-H) and the *O*-acetyl protons appeared as a three-proton singlet at τ 7·88. Three methoxyl group singlets appeared at τ 6·52, 6·55 and 6·78. The 1-H, 2-H, and 7-H protons absorbed, respectively, at τ 4·08 (broad d, J 10·0 Hz),

[1] J. D. HOOKER, *Flora of British India* (Published under the authority of the Secretary of State for India in Council, London), Vol. II, 190 (1879).
[2] K. FOLKERS and J. SHAVEL, *J. Am. Chem. Soc.* **64**, 1892 (1942).
[3] R. B. BOAR and D. A. WIDDOWSON, *J. Chem. Soc.* **B**, 1591 (1970).

3·54 (broad dd, J 10·0, 2·5 Hz), and 4·32 (broad s). On the basis of the above results, the following structure (I) is assigned for erythrascine.



(I)



(II)

The tetrahydrobenzyl isoquinoline alkaloid was isolated as an oil, $C_{19}H_{23}NO_4$(M^+, 329). It gave a dimethyl ether, $C_{21}H_{27}NO_4$, which was found to be identical with (+)-laudanosine. The alkaloid showed major fragment-ion peaks in its mass spectrum at *m/e* 192, 177 and 137 indicating that the two methoxyl groups are distributed in the two aromatic rings. Out of the four possible dihydroxydimethoxytetrahydrobenzylisoquinoline bases, it was similar to orientaline (II) in its TLC behavior. Further characterization was not possible due to scarcity of material. Isolation of tetrahydrobenzylisoquinoline alkaloid from *E. arborescens* has special significance from the biogenetic point of view since aromatic erythrina alkaloids have recently been shown[4] to be elaborated via *N*-norprotosinomenine. In a previous communication, we have reported,[5] for the first time, the occurrence of this precursor (*N*-norprotosinomenine) in *E. lithosperma* Blume.

The natural occurrence of erythratidine and erythristemine has only been reported before in *E. falcata*[6] and *E. lysistemon*,[7] respectively. The number and content of the alkaloids in other parts of *Erythrina arborescens*, e.g. in root bark, stem bark, and in leaves, were found to be considerably less.

EXPERIMENTAL

Isolation of alkaloids from the seeds of Erythrina arborescens. Dry and finely ground seeds (4·8 kg) were continuously extracted with light petroleum (60–80°), this extract triturated with aqueous citric acid (12%), liberated bases ('weak' base fraction) from the clarified acidic solution purified by repeated extractions with 2 N HCl to remove fatty matters, re-basification, and column chromatography (over Brockmann neutral alumina) and TLC (silica gel G) of the mixture of bases. Defatted plant material was continuously extracted with EtOH, EtOH-extract processed in the above way, and the mixture of bases extracted at two pH-levels (4 and 9), marked 'moderately strong' and 'strong' base fractions, were purified by chromatography. Water-soluble bases were isolated through the reineckate salts.[8]

'Weak' base fraction. β-Erythroidine (55 mg, m.p., Lapiére colour test, UV, *m/e*). *Erythristemine* (26 mg, m.p., $[\alpha]_D$, UV, IR, *m/e*).[7] *Erythraline* (0·21 g, m.p., m.m.p., co-TLC, *m/e*); base-HCl (m.p., m.m.p.). *Erythramine* (32 mg, m.p., $[\alpha]_D$, UV, *m/e*). *Erysotrine* (18 mg, co-TLC, IR, *m/e*);[9] Picrate (m.p., m.m.p.).

'Moderately strong' base fraction. Erythratine (82 mg, m.p., $[\alpha]_D$, *m/e*), base-HBr (m.p., m.m.p.). *Erysovine* (37 mg, m.p., *m/e*); Picrate of methyl ether (m.p., m.m.p.).

New compound. Dihydroxydimethoxytetrahydrobenzylisoquinoline, brown oil (16 mg); λ_{max} (EtOH)

[4] D. H. R. BARTON, R. JAMES, G. W. KIRBY, D. W. TURNER and D. A. WIDDOWSON, *J. Chem. Soc.* 1529 (1968).
[5] S. GHOSAL, S. K. MAJUMDER and A. CHAKRABORTI, *Austral. J. Chem.* **24**, 2733 (1971).
[6] V. DELOFEU, *Chem. Ber.* **85**, 620 (1952).
[7] D. H. R. BARTON, P. N. JENKINS, R. LETCHER, D. A. WIDDOWSON, E. HOUGH and D. ROGERS, *Chem. Commun.* **391** (1970).
[8] S. GHOSAL, P. K. BANERJEE and S. K. BANERJEE, *Phytochem.* **9**, 429 (1970).
[9] S. GHOSAL, D. K. GHOSH and S. K. DUTTA, *Phytochem.* **9**, 2397 (1970).

220–222 (inflec.) (log ϵ, 4·24), 283–85 nm (log ϵ, 3·81); λ_{min} 255–257 nm (log ϵ, 2·95); R_f 0·32 (*n*-BuOH–AcOH–H_2O, 4:1:2); co-TLC with (±)-orientaline showed a single spot at R_f 0·32; *m/e* 329 (M^+, 2%), 192 (100), 177 (48), 137 (52), 134 (26). Treatment of the alkaloid with ethereal CH_2N_2 gave a dimethyl ether which crystallized from light petroleum–Me_2CO as micro-needles, m.p. and m.m.p. with (+)-laudanosine, 85–87°; co-TLC showed a single spot at R_f 0·88. ($C_{21}H_{27}NO_4$ requires: N, 3·92; M^+, 357. Found: N, 3·63; M^+, 357.)

'*Strong*' *base fraction. Erythratidine*[6] (0·11 g, m.p., UV, $[\alpha]_D$, *m/e*, NMR). Further crops of *Erysovine* (66 mg) and *Erythratine* (28 mg). *Erysopine* (1·8 g, m.p., m.m.p., co-TLC, *m/e*). *Erysodine* (0·92 g, m.p., m.m.p., co-TLC, *m/e*).

New compound. Erythrascine (I), cream coloured needles from EtOH–Me_2CO (38 mg), m.p. 138–140°; $[\alpha]_D^{25}$ +152° (*c* 0·51, $CHCl_3$); λ_{max} 210–212 (log ϵ, 4·88), 233–235 (log ϵ, 4·36), 284–288 nm (log ϵ, 3·34); *m/e* 371 (M^+, 42%), 356 (22), 340 (100), 339 (27), 329 (31), 313 (24), 311 (17). ($C_{21}H_{25}NO_5$ requires: N, 3·77. Found: N, 3·54%.)

Water-soluble bases. Hypaphorine (0·52 g, m.p., m.m.p., co-TLC); base-HCl (m.p., m.m.p.). Three uncharacterized bases from the base reineckate; *Choline* (co-TLC, pharmacological properties); Picrate (m.p., m.m.p.).

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Key Word Index—Erythrina arborescens; Leguminosae; erythrascine; tetrahydrobenzylisoquinoline alkoloid; hypaphorine; spiroamine erythrina alkaloids.