Structure of Erythrinine, a New Alkaloid from *Erythrina indica* Lam.

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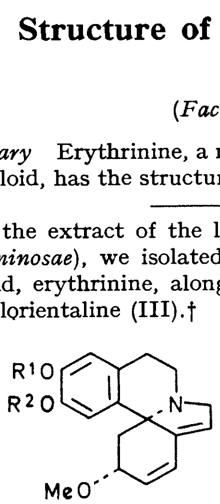
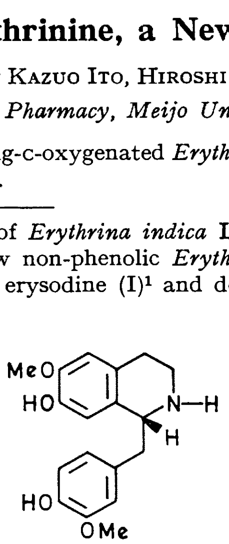
Summary Erythrinine, a new ring-C-oxygenated *Erythrina* alkaloid, has the structure (IV).

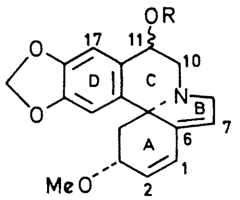
FROM the extract of the leaves of *Erythrina indica* Lam. (*Leguminosae*), we isolated a new non-phenolic *Erythrina* alkaloid, erythrinine, along with erysodine (I)[1] and de-*N*-methylorientaline (III).†



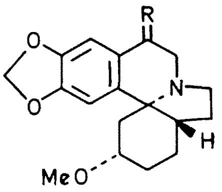
(I) $R^1 = H, R^2 = Me$
(II) $R^1, R^2 = CH_2$



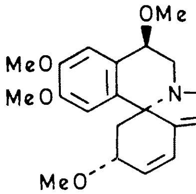
(III)



(IV) R = H
(V) R = Ac



(VI) R = H,OH
(VII) $R = H_2$
(VIII) R = O



(IX)

The structure (IV) is assigned to erythrinine on the basis of following chemical and spectral studies.

Erythrinine (IV)‡: m.p. 197—200° (decomp.), $[\alpha]_D$ +204° ($CHCl_3$), $C_{18}H_{19}O_4N$ (M^+ *m/e* 313), λ_{max} (log ϵ): 209(4·35), 230(4·26), and 289 nm (3·70); ν_{max} 3560 cm^{-1} (OH), and n.m.r. signals at δ 3·32 (3H, singlet, OCH_3), 5·94 (2H, multiplet, $\cdot OCH_2\cdot O\cdot$), 6·82, 7·00 (2H, two singlets, *para*-aromatic protons), 4·73 (1H, triplet, *J* 4·5 Hz, HO·C*H*), 3·62, 2·95 (2H, a pair of quartets, *J* 13·5, 4·5 Hz, 10-H), 5·75 (1H, broad singlet, 7-H), 6·00 (1H, broad doublet, *J* 10·0 Hz, 1-H), and 6·60 (1H, broad double doublet, *J* 10·0, 2·5 Hz, 2-H). The presence of an alcohol group was shown by the formation of an *O*-acetyl derivative (V), having n.m.r. signals at δ 2·10 (3H, singlet CH_3CO_2), 3·35 (3H, singlet, CH_3O), 5·93 (2H, multiplet, $\cdot O\cdot CH_2\cdot O\cdot$), and 6·75 and 6·85 (2H, two singlets, aromatic protons); ν_{max} 1730^{-1} cm (acetate C=O). Catalytic hydrogenation of erythrinine (IV) with PtO_2–AcOH gave tetrahydroerythrinine (VI), n.m.r. signals at δ 3·23 (3H, singlet, OCH_3), 5·91 (2H, singlet, $\cdot O\cdot CH_2\cdot O\cdot$), 4·45 (1H, broad quartet, *J* 2·5 Hz, HO·C*H*), and 6·80 and 6·91 (2H, two singlets, aromatic protons). Hydrogenolysis of tetrahydroerythrinine (VI) with platinum black in aqueous hydrobromic acid afforded a colourless oil, showing n.m.r. signals at δ 3·28 (3H, singlet, OCH_3), 5·86 (2H, singlet, $\cdot O\cdot CH_2\cdot O\cdot$), and 6·55 and 6·75 (2H, two singlets, aromatic protons). Its picrate, m.p. 162—163°, was identical with an authentic sample of tetrahydroerythraline (VII) picrate§ by mixed m.p. and the comparison of i.r. spectra (Nujol).

The location of the hydroxy-group at C-11 was suggested by easy catalytic hydrogenolysis of (VI) and confirmed by the following evidence. In the n.m.r. spectrum of erythrinine (IV), the one-proton triplet (*J* 4·5 Hz.) at δ 4·73 as the X part of a ABX system was assigned to a proton attached to a carbon bearing both hydroxy and aryl groups, and the AB part of this system was observed as a pair of quartets centred at δ 3·62 and 2·95 (*J* 13·5, 4·5 Hz). Oxidation of tetrahydroerythrinine (VI) with activated MnO_2 in chloroform solution afforded the corresponding basic keto-compound (VIII), the i.r. spectrum of which had a conjugated carbonyl absorption band at 1680 cm^{-1}; its n.m.r. spectrum revealed a broad singlet at δ 3·62 attributable to two protons

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† The isolation of this alkaloid (III) from natural sources has not previously been reported, although it has been synthesized by Tomita *et al.*[3] The isolation and characterization of this alkaloid will be reported elsewhere.

‡ The homogeneity of erythrinine and all of its derivatives was evaluated by t.l.c. and by n.m.r. spectroscopy.

§ This compound was prepared from the sample of erythraline hydrobromide supplied by Professor V. Prelog.

at C-10, and the low-field shift of the aromatic proton at C-17 was observed (δ 6·78 and 7·42).

The presence of a 1,6-diene system in the molecule of erythrinine (IV) was indicated by the fact that its u.v. spectrum was almost identical with that of erythraline (II) and the mass spectrum of erythrinine (IV) indicated significant ions at m/e 313 (M^+), 298, 283, 282, and 280 The fragmentation pattern of erythrinine (IV) was also consistent with that of erythraline (II).¶

Hence, erythrinine is represented by the stereostructure (IV) (except for the configuration at C-11).

Recently, Barton *et al.*[2] reported the isolation and structure determination of erythristemine (IX), which has a methoxy-group at C-11. Erythrinine (IV) is the second example of a ring-c-oxygenated aromatic *Erythrina* alkaloid.

We thank Professor V. Prelog (ETH, Zürich) for the authentic sample of erythraline hydrobromide, and Mr. S. Yamada (Nagashima Botanical Garden of Tropical Plants, Mie Prefecture) for a supply of the plant material.

(*Received, June 9th,* 1970; *Com.* 892.)

¶ The mass spectrum of erythraline (II) showed significant peaks at m/e 297 (M^+), 282, 267, 266, 264.

[1] D. H. R. Barton, R. James, G. W. Kirby, D. W. Turner, and D. A. Widdowson, *J. Chem. Soc.* (*C*), 1968, 1529.
[2] D. H. R. Barton, P. N. Jenkins, R. Letcher, E. Hough, and D. Rogers, *Chem. Comm.*, 1970, 391.
[3] M. Tomita and J. Kunitomo, *J. Pharm. Soc. Japan*, 1960, **80**, 1238.