

ALKALOIDAL CONSTITUENTS OF
ERYTHRINA CRISTA-GALLI FLOWERS

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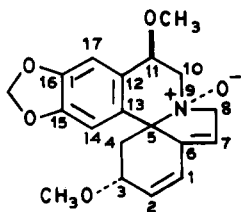
Erythrina crista-galli L. (Leguminosae) is the most common species of *Erythrina* in Argentina (1) and was introduced into Indian gardens as an ornamental plant (2). The seeds (1,3) and leaves (4,5) of this plant have already been studied. In this paper we report results of the studies of *E. crista-galli* flowers, which have not been investigated. This has led to the characterization of two new alkaloids, 11 β -methoxyerythraline-*N*-oxide [**1**] and 11-methoxyerythratine [**2**].

The dry, powdered flowers were exhaustively extracted with petroleum ether (60-80°), and the residue was extracted with MeOH and processed to afford a free alkaloid fraction and a liberated fraction; the latter was obtained by acidic hydrolysis of any alkaloid glycosides present after removal of the free alkaloids. Both the free and liberated alkaloid fractions were derivatized to form the trimethylsilyl ethers prior to gc and combined gc/ms.

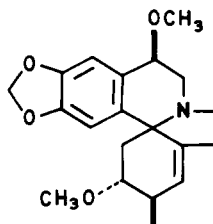
Gc and gc/ms examination of the petroleum ether fraction and the MeOH-soluble free alkaloid fraction showed the presence of 11 β -methoxyerythraline (44%), erythrinine (33%), erythraline (12%), 8-oxoerythrinine (5%), and 11-methoxyerythratine (4%) together with

traces of erysodine/erysovine. The liberated fraction indicated the presence of erysopine only. The petroleum ether fraction and MeOH-soluble free alkaloid fraction were identical in their tlc behavior. These were combined, and their chromatography over neutral alumina afforded 11 β -methoxyerythraline, erythraline, erythrinine, 8-oxoerythrinine, 11 β -methoxyerythraline-*N*-oxide [**1**], and 11-methoxyerythratine [**2**] on the basis of their spectral characteristics. The structural assignments were achieved by ¹H-nmr spectroscopy (360 MHz).

A number of features in the ¹H-nmr spectrum of 11 β -methoxyerythraline-*N*-oxide are worthy of comment. The 4-H_c resonance appears high field (δ 2.08), whereas the 4-H_a is shifted downfield (δ 3.09). The 8-H (δ 5.09, 4.71) and 10-H (δ 4.71, 3.91) resonances are about 0.7 to 1 ppm downfield as compared to the parent compound. The 11-H proton also resonates downfield (0.3 ppm). The eims of the base showed major peaks at *m/z* 343 (M⁺, 2%), 327 (M⁺-16, 44%), 312 (M⁺-31, 21%), 296 (M⁺-47, base peak), 295 (M⁺-48, 94%), 294 (M⁺-49, 68%), and 280 (46%). The presence of a (M⁺-16) peak



1



2

TABLE 1. ¹H-nmr Spectral Data of **1** and **2** (δ values; CDCl₃)

Compound	1-H	2-H	3-H	4-H _a	4-H _c	7-H	8-H	10-H _a	10-H _c	11-H	14-H or 17-H	OCH ₂ O	OCH ₃
11β-Methoxy-erythraline-N-oxide [1]	6.18 (d)	6.65 (dd)	4.19 (m)	3.09 (t)	2.08 (dd)	5.79 (br s)	5.09 (d) 4.71 (m)	4.71 (m)	3.91 (dd)	4.50 (d)	6.55, 6.86 (s) (s)	6.03, 5.97	3.63(s, 11-OCH ₃), 3.41(s, 3-OCH ₃)
11-Methoxy-erythratine [2]	5.75 (d)	4.31 (m)	3.59 (m)	1.77 (t)	2.19 (dd)		2.95 (m) 2.60 (m)			4.53 (t)	6.47, 6.64 (s) (s)	5.87, 5.84	3.40(s, 11-OCH ₃), 3.36(s, 3-OCH ₃)
	Coupling constants (Hz)												
1	1, 2 10.0	2, 3a 2.5	3a, 4a 11.5	3a, 4e 5.5	4a, 4e 11.5	7; 8α, 8β 2.0	8α, 8β 15.0	10a, 10e 14.0		10 a, 11e 4.6	10e, 11e 4.6		
2	2, 5		3a, 4a 11.5	3a, 4e 5.5	4a, 4e 11.5					4, 6	4, 6		

in the mass spectrum, characteristic of *N*-oxides (6), identified the base 11 β -methoxyerythraline-*N*-oxide. Its identity was confirmed by treating 11 β -methoxyerythraline with *m*-chloroperbenzoic acid. The resulting *N*-oxide was identical in all respects to the natural product. Earlier erysotrine-*N*-oxide and erythartine-*N*-oxide had been isolated from *Erythrina mulungu* flowers (7). These authors have also pointed out that these *N*-oxides are, in fact, the natural products and not artifacts.

The ^1H -nmr spectrum of 11-methoxyerythratine gave signals at δ 6.64 (s, 14-H or 17-H), 6.47 (s, 1H, 17-H or 14-H), 5.87 and 5.84 (2H, -OCH₂O), 5.75 (1H, 1-H), 4.53 (t, $J=4.6$ Hz, 1H, 11-H), 4.31 (1H, 2-H), 3.59 (m, 1H, 3-H), 3.40 (s, 3H, 11-OCH₃), 3.36 (s, 3H, 3-OCH₃), 2.95 (m, 1H, 8-H _{α}), 2.60 (m, 1H, 8-H _{β}), 2.19 (dd, $J=11.5, 5.5$ Hz, 1H, 4-H _{e}), and 1.77 (t, $J=11.5$ Hz, 1H, 4-H _{a}). The eims of the base (trimethylsilyl derivative) exhibited peaks at m/z 417 (M^+ , base peak), 329 ($M^+-88, 40\%$), 328 ($M^+-89, 52\%$), and 73 (94%). The molecular ion corresponds to a mono-hydroxylated alkaloid, molecular weight 345. The fragment ions at m/z 328 and 329 correspond to the loss of the trimethylsilyl ether moiety. These data identified the base as 11-methoxyerythratine [2].

EXPERIMENTAL

PLANT MATERIAL.—The flowers of *E. crista-galli* were collected from Chandigarh, India. The authenticity of the flowers was certified by the Curator, Department of Botany, Panjab University. The voucher specimen is deposited in the Herbarium, Department of Pharmaceutical Sciences, Panjab University, Chandigarh. The flowers were reduced to a moderately coarse powder.

ANALYSIS OF ALKALOIDS.—Alkaloids were extracted from a small sample of flowers (10 g) by

the same method as used previously (8), and ms were determined with a spectrometer coupled with a gc via a two-stage Watson-Biemann separator. The ion source was maintained at 220°, and the accelerating and ionizing voltages were set at 3 kV and 70 eV, respectively.

ISOLATION OF ALKALOIDS.—Preparative scale isolation of the petroleum ether-soluble alkaloid and MeOH-soluble free alkaloid fraction obtained from *E. crista-galli* flowers (8) on chromatography over neutral alumina yielded erythraline (0.011 g), 11 β -methoxyerythraline (0.064 g), erythrinine (0.18 g), and 8-oxoerythrinine (0.02 g). Two new alkaloid fractions obtained were characterized by their spectral data. These are as follows:

11 β -Methoxyerythraline-N-Oxide.—Compound 1 (0.005 g) Ir (Film) 1610 cm^{-1} (C=C); ^1H nmr (CDCl₃) complete assignments are shown in Table 1; ms m/z 343, 327, 312, 296, 295, 294, 280.

11-Methoxyerythratine.—Compound 2 (0.004 g), ^1H nmr (CDCl₃) assignments are shown in Table 1; ms (trimethylsilyl derivative) m/z 417, 329, 328, 73.

The liberated alkaloid fraction on chromatographic resolution over alumina yielded erythrinine (0.011 g) and erysopine (0.009 g).

The remaining aqueous layer afforded hypaphorine, betaine, and choline.

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