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8-OXO-ERYTHRALINE, A NATURALLY-OCCURRING PRINCIPAL ALKALOID FROM *ERYTHRINA CRISTA-GALLI*

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Key Word Index—*Erythrina crista-galli*; Leguminosae; alkaloids; 8-oxo-erythraline; crystamidine.

Abstract—The principal alkaloid of the leaves of a commercially available variety of *Erythrina crista-galli*, has been identified by mass and ^1H NMR spectroscopy as 8-oxo-erythraline.

INTRODUCTION

The South American legume *Erythrina crista-galli* L., in common with other *Erythrina* spp., produces several alkaloids, some as free bases and others as glycosides. The literature is fairly consistent concerning the particular free alkaloids of this species; erythraline (**1**) is usually the principal component with erythratine, erythratinone and erythramine as other significant compounds [1]. A more recently described minor component, designated crystamidine (**2**) (10,11dehydro-8-oxo-erythraline) was found occurring with **1** in leaves of *E. crista-galli* cv. Hosoba Deiko [2].

RESULTS AND DISCUSSION

In the expectation of the typical spectrum of alkaloids, plants were raised from seeds obtained from a commercial source (Thomas Butcher Ltd., Croydon, Surrey, U.K.) where they are marketed for the brilliant coral inflorescences characteristic of this species. It is thought that the seeds originated from Australia. Preliminary analysis of young plants revealed an alkaloid pattern which was very different from that expected. Leaf material was therefore collected at intervals over one year's continuous growth, initially in a glasshouse but later transferred to open ground where the typical inflorescences confirmed the identity of the plants.

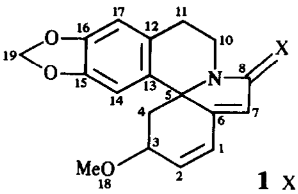
The principal alkaloid was consistently 8-oxo-erythraline (**3**), identified by mass and ^1H NMR spectroscopy and now reported as a new naturally-occurring substance. With the aid of double resonance experiments the ^1H NMR spectrum of **3** could be completely assigned and correlated with that of **2** (see Table 1). The 10,11 dehydro derivative of **3** (**2**), similarly identified by mass and ^1H NMR spectroscopy, is the only alkaloid found for which there is precedence in *E. crista-galli*. The relative abundance of **3** and **2** was in the ratio *ca* 6:1.

Several 8-oxo-derivatives of *Erythrina* alkaloids have been reported recently [4], for example 8-oxo-β-erythroidine is a minor component in the leaves of *E. berteroana* in which the principal alkaloid is β-erythroidine. The possibility that **3** is an artefact was initially entertained since autoxidation of β-erythroidine to the 8-oxo-derivative in chloroform over a few days has been reported [4], and **3** has been synthesized by oxidation of **1** [2]. However, the extraction procedure used in the present study was essentially that used previously [5] and at no stage in the growth of the plants was there any mass spectral evidence suggesting the macroscopic occurrence of **1** or erythratine in spite of systematic analysis of the whole range of extracted bases.

It is concluded that **3** is wholly a plant metabolite and that there is clearly variation in *E. crista-galli* with respect to the degree of oxidation of the erythraline molecule.

EXPERIMENTAL

Extraction of alkaloids (*typical example*). Leaves (250 g fr. wt) were homogenized and extracted in 0.025 M HCl (2 l.) overnight at room temp, basified with $NaHCO_3$ and the filtrate extracted with $CHCl_3$ (2 × 500 ml) which was taken to dryness *in vacuo*. The extract (280 mg) was chromatographed over silica gel (GF_{254}) layers (1 mm) using $CHCl_3$–Me_2CO (6:1). The principal alkaloid was evident (UV; 254 nm) at R_f ~ 0.7. This and other regions of the chromatogram were eluted with Me_2CO and the eluates resolved further by HPLC which used an Ultrasphere ODS (5 μ) column (25 × 1 cm) with $MeOH$–H_2O (4:1) as solvent



1 X=H_2
3 X=O

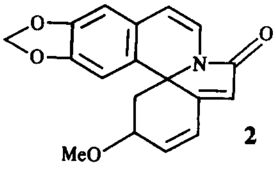


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Table 1. ^{1}H NMR spectral data of 8-oxo-erythraline and crystamidine (δ values in $CDCl_3$)

	1	2	3	4a	4e	7	10a	10e	11a	11e	14	17	18	19
8-Oxo-erythraline	6.30	6.87	3.78	1.67	2.80	6.0	3.87	3.62	3.10	2.96	6.74	6.72	3.33	5.91
	dd	*dd*	*ddd*	*ddd*	*ddd*	*s*	*ddd*	*ddd*	*ddd*	*ddd*	*s*	*s*	*s*	5.95
Crystamidine	6.30	6.92	3.65	1.6*	2.70	6.05		6.75		6.1	6.71	6.88	3.28	5.92
	dd	*dd*	*dd*		*ddd*	*s*		*d*		*d*	*s*	*s*	*s*	5.97

Coupling constants (J, Hz)

	1,2	2,3	1,3	3a,4a	3a,4e	4a,4e	10a,10e	10a,11a	10a,11e	10e,11a	10e,11e	11a,11e	10,11
8-Oxo-erythraline	10.10	2.60	2.25	10.10	5.25	11.60	15.75	9.0	7.10	7.10	4.10	5.75	—
Crystamidine	10.0	2.50	2.50	10.30	5.0	11.25	—	—	—	—	—	—	7.20

*Position and coupling uncertain due to contamination in sample.

(2 ml/min) and UV detection (A_{270}). R_ts for **3** (total yield 7.3 mg) and **2** (total yield 1.2 mg) were 8 min and 9 min, respectively.

MS analysis. EI spectra (including HRMS) showed the following important ions for the alkaloids isolated. *8-oxo-erythraline m/z* (rel. int.): 311 $[M]^+$ (100), 296 $[M-15]^+$ (50), 280 $[M-31]^+$ (65), 279 (33), 278 (76), 268 (15), 266 (15), 250 (30). HRMS $[M]^+$ 311.1163, $C_{18}H_{17}NO_4$ (calc. 311.1157). *Crystamidine m/z* (rel. int.). 309 $[M]^+$ (85), 294 $[M-15]^+$ (28); 278 $[M-31]^+$ (60), 277 (65), 276 (100), 266 (35), 250 (20). HRMS $[M]^+$ 309.0997, $C_{18}H_{15}NO_4$ (calc. 309.1000).

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THREE PRENYLATED FLAVANOIDS FROM *HELICHRYSUM ATHRIXIIFOLIUM*

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Key Word Index—*Helichrysum athrixiifolium*; Compositae; flavanones, chalcones; prenylated flavanoids.

Abstract—*Helichrysum athrixiifolium* afforded in addition to known ones three new prenylated flavanoids, one chalcone and two flavanones.

In continuation of our chemical investigation of the genus *Helichrysum* [1] we now have studied the constituents of *H. athrixiifolium* (Kuntze) Moeser. The aerial parts afforded the flavanoids **1**, **2**, **3** [2], **4** [3], **5** [4] and **6**. The structure of **1**, molecular formula $C_{20}H_{20}O_4$, followed from the ^{1}H NMR spectrum (Table 1) especially when compared with those of similar prenylated compounds. The presence of an *O*-prenyl derivative could be deduced from the mass spectrum, which showed a strong fragment formed by loss of isoprene, and from the typical broadened doublet at δ 4.52 in the ^{1}H NMR spectrum of **1**. The position of the free hydroxyl group followed from the low field singlet at δ 10.26 and from the IR spectrum, which showed the presence of a hydrogen bonded aromatic ketone (3500–2700, 1650 cm^{-1}). Since a *meta*-coupling was visible, the second oxygen function could be assigned to C-7. The ^{1}H NMR spectrum of **2** (Table 1) was close to that of **1** However, an additional hydroxyl group at C-4′ was indicated by the typical doublets of H-2′, H-3′, H-5′ and H-6′. If the chemical shifts of the aromatic protons were compared with those of similar flavanones, the relative positions of the free hydroxyl groups again were clear. This was supported further by the observed fragments in the mass spectrum of **2**.

The molecular formula of **6** was the same as that of **2**. However, the ^{1}H NMR spectrum (Table 1) clearly showed that a chalcone was present. Accordingly, the spectral data were close to those of the known compound **5**. Again the presence of a free *para* hydroxyl group followed from the chemical shifts of the corresponding aromatic signals.

The roots afforded **1** and **5** only. The chemistry of this species is similar to that of a group of *Helichrysum* species, which also contains prenylated flavanoids [1, 4, 5]. However, some prenylated flavanones also have been isolated from Compositae belonging to *Marshallia* [2, 6], *Flourensia* [7] and *Wyethia* [8].

EXPERIMENTAL

The air dried plant material (collected in February 1981 in Transvaal, voucher 81/98, deposited in the Botanic Research Institute, Pretoria) was extracted with Et_2O–petrol, 1:2, and the resulting extracts were separated first by CC (silica gel) and further by TLC (silica gel PF 254, detection by UV light). The CC fraction (Et_2O–petrol, 1 1) of the roots (20 g) gave by TLC (silica gel, solvent Et_2O–petrol, 1·1) 7 mg **1** (R_f 0.43) and 4 mg **5** (R_f 0.38). The CC fractions (Et_2O–petrol, 1:1 and Et_2O) of the aerial parts (180 g) were combined and separated by repeated