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ALKALOIDS FROM THE FLOWERS OF *ERYTHRINA AMERICANA*

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Key Word Index—*Erythrina americana*; Leguminosae; flowers; α-erythroidine; β-erythroidine; alkaloids; hypnotic effects; NMR spectra.

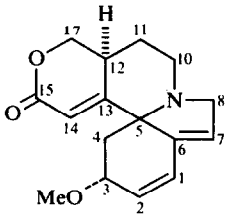
Abstract—The two alkaloids, α- and β-erythroidine have been identified in 0.034 and 0.11 % yield in flowers of *Erythrina americana* and could be responsible for the hypnotic activity of flower extracts.

INTRODUCTION

The alkaloids of *Erythrina* have been widely studied [1–3], principally because of the paralysing activity of their seed extracts. With the exception of *E. variegata* [4], however, the flowers of various *Erythrina* species have not been examined for their alkaloid content until recently. In some regions of Mexico where the flowers of *E. americana* are used in cooking, they are thought to act as weak hypnotics. Since it is known that the seeds of *E. americana* are highly toxic when taken orally, we have attempted to isolate the active principle(s) in the flowers of the Mexican colorin (*E. americana* Miller) which were gathered in Cuernavaca, Morelos, Mexico.

RESULTS AND DISCUSSION

The red flowers (2.5 kg) were air-dried, defatted and extracted with MeOH, yielding 418 g of crude extract which was purified as indicated in the Experimental. Following TLC, the free alkaloid fraction (0.4 %) showed three spots; two of the components with similar polarity were positive for alkaloids. The mixture decomposed readily, and was converted to stable hydrodides. A portion of the hydrodide mixture (2 spots) was treated with $NaHCO_3$ and the free alkaloids were chromatographed. Attempts to separate them by Si gel TLC or GLC using 3 % OV-17 on Chromosorb W columns failed. Column chromatography on neutral alumina–C_6H_6 gave two compounds which were further characterized as α-erythroidine (**1**) and β-erythroidine (**2**). No hypaphorine, erysodine or other alkaloids reported to be present in the seeds [5] were found in this material. Compounds **1** (0.034 %) and **2** (0.11 %) were characterized by their spectral (UV, IR, NMR and MS) properties, optical activity, formation of ammonium quaternary salts, and conversion of α-erythroidine into the β-isomer by treatment with base.



1

2

Particular attention was given to the NMR and MS spectra, as the former had not been reported for either compound. The structure was assigned on the basis of the NMR spectra. The more polar compound on TLC (**1**) has a vinylic signal corresponding to C-14, and two ABX systems at δ 4.46 and 4.03, respectively, corresponding to protons at C-17 (equatorial and axial). These signals are lacking in the spectrum of the less polar alkaloid (**2**).

Since the α- and β-erythroidines are presumably the only active compounds in the flowers, we suggest that the hypnotic activity attributed to them is probably due to the muscle-relaxing effect of the erythroidines, which are present in very small amounts (0.11 % β-erythroidine in the flowers as compared with *ca* 2 % of both erythroidines in the seeds). It is worth noting that erythroidines are present not only in the fresh material but also in the cooked flowers and cooking water.

EXPERIMENTAL

Air-dried flowers (2.5 kg) (calyx, corolla, stamen, pistil) of *E. americana* were milled, defatted with heptane (23.3 g of fats), and extracted for 48 hr with MeOH. The acidic soln was extracted with $CHCl_3$, adjusted to pH 9 with $NaHCO_3$ and extracted with $CHCl_3$. This 'free alkaloid' extract gave three spots on TLC, two of them were positive for alkaloids (Dragendorff). The crude extract (9.6 g) was converted to the hydrodides [6] and crystallized from EtOH–$CHCl_3$ (9.05 g), mp 227°. A small amount of this material (300 mg in 5 ml H_2O) was adjusted with $NaHCO_3$ to pH 8 and extracted with $CHCl_3$. The $CHCl_3$ soln was evapd and the resulting extract was column chromatographed on neutral alumina (Brockmann II–III) using C_6H_6 to elute the first fractions (30 × 150 ml) and C_6H_6–EtOAc (19:1), the later ones. Two products were separated.

Identification of α-*erythroidine* (**1**). R_f 0.48 (0.041 g); UV λ_{max}^{EtOH} 226 nm (log ε 4.18); $[\alpha]_D^{20}$ +123.85° (*c* 2.39, H_2O); IR ν_{max}^{film} cm^{-1}: 2840, 1730, 1090, 890, 650; ^1H NMR (60 MHz, $CDCl_3$): δ 6.43 (1 H, *q*, $J_{2,1}$ = 11 Hz, $J_{2,3}$ = 2 Hz, C-2), 5.91 (1 H, *d*, $J_{1,2}$ = 11 Hz, C-1), 5.8 (1 H, *s*, C-14), 5.76 (1 H, *m*, C-7) 4.46 (1 H, A from ABX, *q*, $J_{A,B}$ = 11 Hz, $J_{A,X}$ = 6 Hz, C-$17_{ax\,or\,eq}$), 4.03 (1 H, B from ABX, *q*, $J_{B,A}$ = 11 Hz, $J_{B,X}$ = 8 Hz, C-$17_{eq\,or\,ax}$), 3.5–3.96

(1 H, *m*, C-3), 3.65 (2 H, *s*, C-8), 3.4 (3 H, *s*, –OMe), 2.33–3.23 (5 H, *m*, C-10, 11, 12), 1.66–1.93 (2 H, *m*, C-4).

Identification of β-erythroidine (**2**). R_f 0.35 (0.133 g), mp 100° [7]; MS (*m/z*): 273.1359 M^+; UV λ_{max}^{EtOH} 235 nm (log ε 4.15); IR ν_{max}^{KBr} cm^{-1}: 2810, 1720, 1090, 810, 645; ^{1}H NMR (60 MHz, $CDCl_3$): δ 6.43 (1 H, *q*, $J_{2,1}$ = 10 Hz, $J_{2,3}$ = 2 Hz, C-2), 5.85 (1 H, *q*, $J_{1,2}$ = 10 Hz, C-1), 5.71 (1 H, *m*, C-7), 4.63 (2 H, *s*, C-17), 4.1 (1 H, *m*, C-3), 3.58 (2 H, *m*, C-8), 3.38 (3 H, *s*, –OMe), 2.35–3.23 (6 H, *m*, C-14, 10, 11), 1.58–1.96 (2 H, *m*, C-4). The methiodide of β-erythroidine which we prepared [8] had the following constants: mp 219–220°, IR ν_{max}^{KBr} cm^{-1}: 2820, 1740, 1110, 840, 810. As it was not possible to obtain α-erythroidine in a pure crystalline form, it was converted to the β-isomer [9] and compared with an authentic sample.

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1-HYDROXYCANTHIN-6-ONE, AN ALKALOID FROM *AILANTHUS GIRALDII*

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Key Word Index—*Ailanthus giraldii*; Simaroubaceae; 1-hydroxycanthin-6-one; alkaloid.

Abstract—A new alkaloid has been isolated from the heartwood of *Ailanthus giraldii* and its structure determined as 1-hydroxycanthin-6-one.

The reported presence of 4-methoxy-1-methyl-3(3,3-dimethyl-allyl)-2(1 H)quinone [1], alkaloids [2,3] and quassinoids [4] in simaroubaceous plants and the anti-cancer activity associated with several of these compounds [5,6] prompted this investigation. The MeOH extract of the heartwood of *Ailanthus giraldii* on work-up yielded a yellow solid (**1a**), mp 220°. Positive reactions towards both Dragendorff's and Mayer's reagents as well as its acid solubility revealed the alkaloid nature of **1a**, making it possible to assign the band appearing in its IR spectrum at 1655 cm^{-1} to a lactam function. Absorptions characteristic of its aromatic and hydroxylic nature were also discernible in the spectrum (3350, 1585, 1545, 770 and 720 cm^{-1}). The UV spectrum of **1a** (263, 287.8, 336, 364, 370 and 385 nm) was entirely compatible with those reported for canthinones [7]. The mass spectral fragmentation pattern also resembled that reported for canthinones, the M^+ appearing at *m/z* 236 ($C_{14}H_8O_2N_2$) and a metastable ion at *m/z* 183.32 corresponding to the loss of CO from the M^+ (236–208). **1a** is thus a hydroxycanthinone. The ^{1}H NMR of **1a**, signals of which integrated for the correct number of protons by the appearance of a pair of doublets at δ 6.89 and 8.09 (1 H each, J = 10 Hz), indicated that ring D was unsubstituted. Evidence for the location of the OH function on either C-1 or C-2 could also be obtained from the ^{1}H NMR by the absence of the *ortho*-coupled doublets characteristic of H-1 and H-2, in place of which appeared a singlet at 8.48.

1a was acetylated to yield a monoacetate (**1b**), mp 205°.