

11-ALLYLCYTISINE AND OTHER MINOR ALKALOIDS FROM UNRIPE *SOPHORA SECUNDIFLORA* FRUITS

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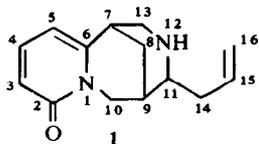
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Key Word Index—*Sophora secundiflora*; Leguminosae; quinolizidine alkaloids; 11-allylcytisine; β -isosparteine; lupanine; rhombifoline.

INTRODUCTION

Sophora secundiflora (Ort.) Lag. ex DC. (Leguminosae) is a shrub native to the drier areas of the southwestern portions of the United States. The mature seeds from this plant are referred to as mescal beans, red beans and big drunk beans, and have been cited in the ethnobotanical literature [1–3] as being hallucinogenic because of their past use in certain native American ceremonies. A recent lay publication [4] has indicated that the mature seeds are part of the modern drug scene. These reports stimulated extensive investigations [5, 6] of the mature seed material resulting in the isolation of 6 known quinolizidine alkaloids (anagyrine, cytisine, Δ^5 -dehydrolupanine, *epi*-lupanine, *N*-methylcytisine, and sparteine). The present report describes the isolation and structure elucidation of a new alkaloid, 11-allylcytisine **1**, from the green, unripe fruits of *S. secundiflora*. Rhombifoline, lupanine and β -isosparteine were also identified as being minor components in this material.



RESULTS AND DISCUSSION

PLC of an extract from unripe *S. secundiflora* fruits on Si gel with CHCl_3 -MeOH-18M NH_4OH (100:10:1) gave 3 bands of interest. One band was chromatographically homogeneous and proved to be identical (TLC, GLC, NMR, MS) with rhombifoline. Another band was a binary mixture consisting of sparteine and a trace of β -isosparteine (TLC, GLC, MS). The third band consisted of *N*-methylcytisine, previously undetected lupanine (TLC, GLC, MS), and the new alkaloid 11-allylcytisine **1**. PLC of this ternary mixture on Si gel with cyclohexane- CHCl_3 -MeOH-diethylamine (10:1:1:1) was used to isolate **1** in pure form.

Spectral evidence suggested the structure of the new base as being an allyl derivative of cytisine. The IR spectrum revealed absorption bands at 2700–2800 (*trans*-quinolizidine), 1645 (α -pyridone C=O) and 914 cm^{-1} ($-\text{CH}=\text{CH}_2$). The ^1H NMR spectrum (100 MHz, CDCl_3) was essentially the same as that of cytisine except for the signals at δ 5.12 (*bd*, 2H, $J = 12$ Hz) and 5.75 (*m*, 1H) indicating the presence of vinylic protons. The MS of the new alkaloid displayed a M^+ at m/e 230

together with the base peak at m/e 189 suggesting the loss of an allylic group from the parent ion. The remainder of the MS contained fragment peaks characteristic of cytisine.

Catalytic hydrogenation of the new alkaloid over PtO_2 gave a product which was identical (TLC, GLC, MS) with the reduction product of angustifoline. The observation that both alkaloids were reduced under the same conditions to give tetrahydrodeoxyangustifoline confirmed the identity of the new base as 11-allylcytisine **1**.

At the present time many of the postulated intermediates in quinolizidine alkaloid biosynthesis have been isolated from *S. secundiflora*. Based on biosynthetic precedents, 11-allylcytisine appears to be biosynthetically positioned between the tetracyclic anagyrine and the tricyclic cytisine. Likewise, rhombifoline may be an intermediate between anagyrine and *N*-methylcytisine and/or cytisine.

EXPERIMENTAL

Mps are uncorr. IR spectra were recorded neat. ^1H NMR spectra were determined on a 100 MHz instrument with TMS as int. standard. MS were measured at 70 eV on an instrument combined with GLC and interfaced with a data system.

Frozen green, unripe fruits (440 g) of *S. secundiflora* collected on the Amistad Recreation Area near Del Rio, Texas on 3 April, 1977, were homogenized with EtOH and processed as described in [6] to give a crude alkaloid extract. PLC of the crude extract on Si gel (1 mm) with CHCl_3 -MeOH-18M NH_4OH (100:10:1) gave bands containing β -isosparteine, lupanine, and rhombifoline. These known alkaloids were identified as being present in the band extracts by spectral and chromatographic comparisons with reference standards. Rechromatography of one band extract on Si gel layers (1 mm) with cyclohexane- CHCl_3 -MeOH-diethylamine (10:1:1:1) resulted in the isolation of **1** as a thick brown oil. IR $\nu_{\text{max}}^{\text{neat}} \text{cm}^{-1}$: 2700–2800 (*trans*-quinolizidine), 1645 (α -pyridone C=O) and 914 ($-\text{CH}=\text{CH}_2$). ^1H NMR (CDCl_3): δ 1.26–3.32 (8H, *m*), 4.01 (2H, *m*, C-10 CH_2), 5.12 (2H, *bd*, $J = 12$ Hz, C-16 $\text{CH}_2=\text{C}$), 5.75 (1H, *m*, C-15 $\text{CH}=\text{C}$), 6.01 (1H, *dd*, $J = 7, 1.5$ Hz, C-5H), 6.42 (1H, *dd*, $J = 9, 1.5$ Hz, C-3H), 7.3 (1H, *dd*, $J = 9, 7$ Hz, C-4H). MS (70 eV): m/e 230 (M^+), 189 (100), 160, 147, 146, 117, 93, 84. After recording these spectral data, the base was treated with 70% HClO_4 to give 30 mg of white needles (EtOH-Et₂O), mp 183–184°; $[\alpha]_D^{26} - 215^\circ$ (MeOH, c 0.006). The perchlorate salt of the new alkaloid (5 mg) dissolved in 5 ml 15% HCl was hydrogenated over PtO_2 at room temp. The reduction product was chromatographically (TLC, GLC) and spectrally (MS) identical with tetrahydrodeoxyangustifoline. Reference tetrahydrodeoxyangustifoline was obtained by reducing authentic angustifoline as described above.

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ERYSOPINOPHORINE, A NEW QUATERNARY ALKALOID FROM PODS OF *ERYTHRINA ARBORESCENS*

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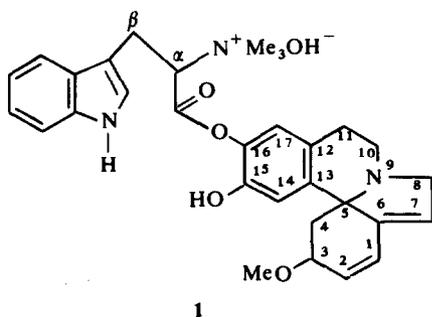
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Key Word Index—*Erythrina arborescens*; Leguminosae; new quaternary alkaloid; erysopinophorine.

INTRODUCTION

Erythrina arborescens is distributed throughout the upper Gangetic plains, Assam and Manipur, extending west towards Nepal [1]. The seed of this plant has been reported to contain erysodine, erysovine, erysopine, hypaphorine, erythrasine, orientaline and erysophorine [2, 3], and the pod walls have been showed to contain erysodine, orientaline, hypaphorine and erysodinophorine [4]. In this paper we report the isolation of a new quaternary alkaloid 1, provisionally named erysopinophorine, from the pod walls.



RESULTS AND DISCUSSION

The EtOH extract of pod walls of *E. arborescens* yielded a new alkaloid 1 besides other already reported alkaloids [4]. Hydrolysis of this alkaloid with EtOH-HCl afforded hypaphorine and erysopine. The molecular formula, $C_{31}H_{37}N_3O_5$, of 1 was established from elemental analysis, the integrals of the proton signals (33H in D_2O) and from the molecular formulae of the products of hydrolysis of erysopinophorine. Like erysophorine and

erysodinophorine, 1 also did not respond to the Ehrlich test for α - and β -unsubstituted indoles, whereas the acid-hydrolysed product gave a positive test. The negative response by 1 was probably caused by the bulky ester function which blocks the free position of the indole ring [3, 4]. The UV spectrum of 1 is very similar to that of erysophorine and erysodinophorine, indicating its marked structural similarity [3, 4]. The compound showed major bands in the IR at 3400 (broad OH and NH), 1762 (phenolic ester group), 1618 (indole ring), 1590, 1498, 1262 and 1086 (spiro amine ring) cm^{-1} . The absence of a peak at 1442 cm^{-1} in the IR of 1 suggests the absence of a COO⁻ group, further supporting the fact that the two alkaloidal fragments are linked together by an ester group.

Since there are two OH groups at C-15 and C-16 in erysopine, in order to establish the position of esterification, 1 was methylated and hydrolysed with EtOH-HCl whereupon two alkaloids, hypaphorine and erysodine, were obtained indicating that hypaphorine is linked to C-16 of erysopine. 1 did not exhibit an M⁺ peak in its MS but significant fragment ions appeared corresponding to the aromatic erythra-1,6-diene and hypaphorine [3, 4]. The ¹H NMR spectrum of the alkaloid in D_2O showed signals at δ 1.98 (1H, C-4a H), 2.45 (1H, C-4e H), 3.16 (9H, N⁺(Me)₃), 3.42 (3H, C-3 OMe), 3.56 (4H, β CH₂ and C-8 CH₂), 3.94 (4H, C-10, C-11 CH₂), 4.02 (1H, C-3 H), 4.42 (1H, C- α H), 5.86 (1H, C-7 H), 6.06 (1H, C-1 H), 6.66 (1H, C-2 H) and 6.6-7.7 (7H, C-14 H, C-17 H and 5 protons of the indole ring).

The foregoing evidence is in conformity with the structure 1 for erysopinophorine.

EXPERIMENTAL

The powdered, air-dried and defatted pod walls (3 kg) of *E. arborescens* (supplied by United Chemical and Allied Pro-