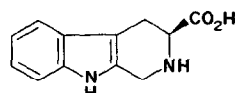


*work.* Fresh seeds (12 kg) were extracted with hot 95% MeOH, the extract concentrated and extracted with petrol and EtOAc. The H<sub>2</sub>O layer was further concentrated and passed through an Amberlite IR-120 (H<sup>+</sup> form) column, and the column washed with H<sub>2</sub>O. Elution was effected with 1N NH<sub>4</sub>OH, the eluate was concentrated, and the precipitated tyrosine was filtered off. The mother liquor was applied to an Amberlite CG-4B (AcO<sup>-</sup> form) column, and the H<sub>2</sub>O eluate (basic and neutral amino acids fraction) was concentrated to deposit a non-protein amino acids **1**, (53 mg pure) mp 297–299° (decomp.) (H<sub>2</sub>O),  $[\alpha]_D^{14} -59^\circ$  (c 0.44, 1N HCl-MeOH (1:1)),  $v_{\max}^{\text{KBr}}$  3255, 3000–2500, 1640, 1590, 1450 cm<sup>-1</sup>, PC (BAW 4:2:1) *R<sub>f</sub>* 0.51, yellow colour with ninhydrin. The UV spectrum shows maxima at 267 nm (log  $\epsilon$  3.87), 275 (3.86), 286 (3.74) (in H<sub>2</sub>O), and at 276 (3.88), 286 (3.80) (in 0.1 N NaOH), which are similar to those of tryptophan. The compound analysed for C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub> (Found: C, 65.53; H, 5.56; N, 12.75. Calc. for C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>·0.17 H<sub>2</sub>O: C, 65.73; H, 5.82; N, 12.77%) and this was confirmed by MS of its ethyl ester (*M*<sup>+</sup> 244) and *N*-acetyl methyl ester (*M*<sup>+</sup> 272). This molecular formula, the negative Ehrlich test, and the yellow colour with ninhydrin, suggest that **1** is a cyclic imino acid with an  $\alpha$ -substituted tryptophan skeleton. The NMR spectrum (CF<sub>3</sub>COOD) of **1** showed four aromatic protons as complex multiplet at  $\delta$  7.35–7.56 and AB part of the ABX system at  $\delta$  3.66 (*dd*, *J* 7 and 18 Hz) and 3.40 (*dd*, *J* 10 and 18 Hz). The X part was observed as a

double doublet at  $\delta$  4.65 partly overlapped with an uncoupled methylene signal at  $\delta$  4.85. Based on these data and the mass fragmentation of the ethyl ester (*m/e* 171 (68%), 169 (33), 144 (45), 143 (100), 115 (14)), the structure L-3-carboxyl-1,2,3,4-tetrahydro- $\beta$ -carboline was assigned to **1**, and this was confirmed by identification with synthetic material [3], by co-chromatography, mmp and comparisons of IR, UV, NMR and ORD spectra. This is the first time the compound has been isolated from natural sources.



(1)

*Other amino acids.* PC and automatic amino acid analyser showed the presence of following amino acids: lysine, histidine, arginine, aspartic acid, glutamic acid, glutamine, threonine, serine, proline, glycine, alanine, valine, isoleucine, leucine, tyrosine and phenylalanine. Tyrosine, aspartic acid, glutamine, arginine (flavinate), histidine and leucine were isolated as crystals and confirmed by mp and IR spectra.

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ALKALOIDS FROM *SOPHORA SECUNDIFLORA*

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**Key Word Index**—*Sophora secundiflora*; Leguminosae; mescal bean; quinolizidine alkaloids; cytisine; *N*-methyleytisine; sparteine.

*Plant.* *Sophora secundiflora* (Ort.) Lag. ex DC. Leguminosae. Voucher specimen deposited in the University of Texas herbarium (Austin, Texas).

*Source.* Austin, Texas area. Material collected in November, 1973. *Uses.* In the southwestern United States, the seeds of *S. secundiflora* (mescal

beans) have been used in Indian rituals because of their purported hallucinogenic effect [1-3]. This has led to their utilisation in the modern drug scene [4, 5]. *Previous work.* There is only one report concerning the actual isolation of an alkaloid (cytisine) from *S. secundiflora* (seeds) [6]. Another report deals with the absence of cytisine in the leaves [7].

*Present work.* Powdered seeds (1 kg) were extracted with EtOH in a large Waring blender. A crude alkaloid fraction was obtained by working up the extract in the usual fashion. The entire crude alkaloid fraction was subjected to PLC on Si gel with  $\text{CHCl}_3$ -MeOH-28%  $\text{NH}_4\text{OH}$  (100:10:1) to yield 3 major bands, A-C.

*Band A* was processed to yield 1.51 g (0.15%) of cytisine; perchlorate, mp  $294^\circ$  (lit. [8]  $296^\circ$ ) and picrate, mp  $276$ – $277^\circ$  (lit. [9]  $276$ – $279^\circ$ ). *Band B* was rechromatographed (PLC) on Si gel with EtOAc-MeOH-28%  $\text{NH}_4\text{OH}$  (17:2:1) to give 345 mg (0.03%) of sparteine; sulfate, mp  $263$ – $264^\circ$  (lit. [10]  $264$ – $265^\circ$ ) and methiodide, mp  $238$ – $239^\circ$  (lit. [10]  $237$ – $238^\circ$ ). *Band C* was rechromatographed (PLC) on Si gel with  $\text{CHCl}_3$ -MeOH (5:1) to give 459 mg (0.04%) of *N*-methylcytisine; perchlorate, mp  $281$ – $282^\circ$  (lit. [11]  $282^\circ$ ) and picrate, mp  $229$ – $230^\circ$  (lit. [12]  $230^\circ$ ). All three alkaloids were identified by comparing the IR and NMR spectra with those of authentic samples and co-chromatography (TLC 3 solvents) in addition

to mp. TLC of the crude alkaloid fractions from leaf and pod material revealed the presence of the same 3 major alkaloids that were isolated from the seeds.

*Significance.* The presence of cytisine in *S. secundiflora* seeds has often been cited as the basis for the past and present use of this psychotropic plant [1-4]. The present work verifies the presence of cytisine and suggests that 2 other major alkaloids in the seeds may contribute to the hallucinogenic activity.

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## NITRO COMPOUNDS IN *ASTRAGALUS* SPECIES

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**Key Word Index**—*Astragalus*; Leguminosae; nitro compounds; miserotoxin; cibarian; karakin; 3-nitro-1-propanol; 3-nitropropionic acid.

All numbered voucher specimens of *Astragalus* spp. described here are in the Intermountain Her-

barium, Utah State University, Logan, Utah, U.S.A. 84322. *Plant*, *A. canadensis* var. *brevidentis* (Gand.) Barneby, No. 138960; *source*, Custer Co., Idaho, U.S.A.; *part examined*, aerial portion. *Plant*, *A. convallarius* Greene, No. 138958; *source*, Oneida Co., Idaho, U.S.A.; *part examined*, aerial

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