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SHORT COMMUNICATION

ALKALOIDS OF *SOPHORA TETRAPTERA SENSU* REICHE

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Abstract—*Sophora tetraptera sensu* Reiche seeds were examined for alkaloids. Cytisine, methylcytisine and matrine were isolated, and a fourth alkaloid was detected by TLC. The relative amounts of the three major alkaloids support the segregation of this Chilean species from *S. tetraptera* J. Mill. and *S. microphylla* Ait. of New Zealand.

INTRODUCTION

Briggs has shown[1] that the morphologically similar *Sophora tetraptera* J. Mill. and *S. microphylla* Ait. (Leguminosae) of New Zealand may readily be distinguished by their alkaloid contents. A tree growing on the Chilean mainland and neighbouring islands between 35°–44° South latitude, known by the names of pelú and pilo-pilo, has been ascribed by different authors[2,3] to one or the other of these combinations. Philippi[4] felt justified in distinguishing two forms of this plant, calling them *Edwardsia cassioides* and *E. macnabiana*. More recent work,[5] in using the name *S. tetraptera sensu* Reiche, points to the resemblance between one of the New Zealand species and the pilo-pilo, while keeping them apart as separate taxa. An examination of this plant for alkaloids was thus considered interesting as a possible contribution towards a firmer basis for classification.

RESULTS

Seeds collected near Valdivia, Chile, in the autumn of 1967 were extracted following a standard procedure, and the crude bases were fractionated by extraction with light petroleum, distillation,[1] crystallization and column chromatography on alumina.[6] Cytisine, *N*-methylcytisine and matrine were isolated and identified by their m.ps, i.r. spectra, chromatographic behaviour and derivatives. A fourth, relatively polar base, which appeared consistently as a weak Dragendorff-positive spot upon TLC of the crude alkaloids, was neither isolated nor otherwise investigated.

Although the methods employed do not allow trustworthy estimates of the percentages of the three major bases in the seeds, our data show that both cytisine and methylcytisine are

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[1] (a) L. H. Briggs and J. Ricketts, *J. Chem. Soc.* 1795 (1937); (b) L. H. Briggs and W. S. Taylor, *J. Chem. Soc.* 1206 (1938); (c) L. H. Briggs and J. L. Mangan, *J. Chem. Soc.* 1889 (1948).

[2] F. Fuentes, *Rev. Chilena Hist. Nat.* 20 (1918).

[3] W. R. Sykes and E. J. Godley, *Nature* **218**, 495 (1968).

[4] R. A. Philippi, *Botan. Z.* **47**, 737 (1873).

[5] (a) C. Muñoz Pizarro, *Mus. Nac. Hist. Nat. Not. mensual* **93**, (1964); (b) C. Muñoz Pizarro, *Flores Silvestres de Chile*, p. 191, Editorial Universitaria, Santiago de Chile (1966).

[6] F. Bohlmann, D. Rahtz and C. Arndt, *Ber.* **91**, 2189 (1958).

present in quantities which account for about 10% each of the total alkaloid content, while matrine accounts for at least 30%. Briggs was unable to isolate cytisine from *S. tetraptera*,[1(b)] and his work on *S. microphylla*[1(a)] yielded only 0·05% of this alkaloid. These results, when compared with our extremely facile isolation of relatively large amounts of cytisine, seem to indicate a significant difference between the synthetic capabilities of *S. tetraptera sensu* Reiche and the New Zealand species (Table 1).

TABLE 1. PERCENTAGES OF ALKALOIDS IN SOME *Sophora* SPP.

	Cytisine	Methylcytisine	Matrine	Sophochrysine
S. microphylla Ait.	0·05	20	27	trace
S. microphylla var. *fulvida* Allan[7]	4	40	1·5	—
S. tetraptera J. Mill.	—	3	45	1
S. tetraptera sensu Reiche	10	10	30	—

While *S. microphylla* var *fulvida*[7] contains larger quantities of cytisine,[1(c)] its matrine content is extremely low and its methylcytisine content is higher than that of the other *Sophora* species and varieties studied by Briggs; it thus differs from our material no less than *S. tetraptera* and *S. microphylla* do. It seems safe to consider our results as evidence in favour of the proposed[5] segregation of the Chilean and New Zealand species of *Sophora*. However, an exhaustive quantitative study of seasonal and regional variations of alkaloid contents of these plants is still needed and work in this direction is in progress.

EXPERIMENTAL

The dry seeds were ground and extracted (Soxhlet) with light petroleum (60–70°); only traces of alkaloid were detected in this extract. The defatted plant material was extracted with methanol (Soxhlet), and the solution was concentrated under reduced pressure, filtered to eliminate a yellowish precipitate, and evaporated to dryness. The residue was taken up with 2 N HCl and extracted with $CHCl_3$; the aqueous solution was made alkaline with concentrated NH_4OH and extracted continuously with $CHCl_3$, and the $CHCl_3$ solution, dried over Na_2SO_4, was evaporated under reduced pressure yielding 1·35 to 1·95% of crude alkaloids as a viscous pale-yellow oil which crystallized on standing. The mixture of bases was examined by TLC on Al_2O_3 dried overnight at room temp., with $CHCl_3$ (2% EtOH, v/v)–cyclohexane, 1:1. The spray was a modified Dragendorff reagent.[8] Three intense Dragendorff-positive spots with R_f 0·12, 0·43, and 0·70 were observed, corresponding to cytisine, *N*-methylcytisine and matrine respectively; a weak spot with R_f 0·06 was also observed.

Cytisine. 6·4 g of crude alkaloids were washed several times with 5-ml portions of light petroleum (<40°) The residue was then taken up with a small vol. of CCl_4 and filtered, yielding 575 mg of cytisine (chromatographically pure) which, after recrystallization from petroleum (80–100°), had m.p. 151·5–153°, $[\alpha]_D$ − 104° (c = 1·0, H_2O), i.r. spectrum identical with reference spectra, picrate m.p. 280° (decomp.).

Matrine. The CCl_4 mother liquors were evaporated to dryness on Kieselguhr and the residue was extracted (Soxhlet) with light petroleum (<40°). The solution was evaporated yielding 1·73 g of matrine which crystallized upon seeding; this material contained a trace of methylcytisine (TLC). After recrystallization from petroleum (80–100°) it had m.p. 75–77°, i.r. spectrum identical with reference spectra. The exhausted Kieselguhr–alkaloid mixture was re-extracted (Soxhlet) with petroleum (80–100°) yielding a solution from which 0·29 g of cytisine crystallized; the cytisine mother liquors were evaporated to dryness and chromatographed on Al_2O_3 with C_6H_6–Et_2O, 95:5 and 9:1, yielding 0·16 g matrine, a mixture of matrine and methylcytisine, and finally a small amount of methylcytisine

N-*methylcytisine.* 19 g of crude alkaloids were extracted with petroleum (80–100°) and the extract was distilled collecting the fraction passing over between 180°–200° at 5 Torr. The pale-yellow oil crystallized in part upon keeping at 5° for 48 hr, and the long prisms were filtered off: 1·2 g of methylcytisine which after

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[7] H. H. ALLAN, *Flora of New Zealand*, Vol. 1, p. 370, R. E. Owen, Wellington, New Zealand (1961).

[8] R. MUNIER and M. MACHEBOEUF, *Bull. Soc. Chim. Biol.* **38**, 864 (1951).

recrystallization from petroleum (80–100°) had m.p. 136·5°, $[\alpha]_D$ − 233° ($c = 1{\cdot}0$, H_2O), i.r. spectrum identical with reference spectra. The original mother liquors, chromatographed on Al_2O_3 with C_6H_6, yielded a small amount of pure matrine. Picrate m.p. 229°, methiodide m.p. 248°.

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