

contents, showed an approximate ratio of berberine to muramine of about 4:1. This reversal of concentrations might be related to environmental factors or to a genetic nonhomogeneity of the subspecies. (See under *Materials*.)

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Alkaloids of the *Papaveraceae* VI.

Protopine and Allocryptopine from *Arctomecon californica*

By FRANK R. STERMITZ* and V. P. MURALIDHARAN

Protopine and allocryptopine (in approximately equal amounts) make up over 95 per cent of the alkaloidal content of *A. californica*.

THE GENUS *Arctomecon* consists of three species (*A. californica* Torr. et Fremont, *A. humilis* Coville, and *A. merriami* Coville) whose range is restricted to the extreme southwestern corner of Utah, southern Nevada, and the adjoining California desert (1). As part of the continuing investigation of the *Papaveraceae*, it was deemed advisable to investigate this relatively rare genus. Although extensive searches were conducted in 1962-1964 at locations where previous collections of each species had been made, only *A. californica* could be found.¹

From 700 Gm. of powdered stems and leaves, a total of 2.3 Gm. of crude alkaloid mixture was obtained after treating the powder with 1:1 butanol-benzene, extracting this solution with 1 *M* sulfuric acid, adjusting to pH 9, extracting with chloroform, and evaporating the chloroform layer to dryness. Thin-layer chromatography showed the presence of two alkaloids. A small portion of root material

treated in the same fashion showed similar results except with a slightly higher total alkaloid content.

The alkaloid mixture was treated with hot methanol, and protopine was precipitated from the cooled solution. Identification was made by NMR, U.V., and I.R. comparison with a known sample (2). Evaporation of the mother liquor, followed by crystallization of the residue from methanol, was accomplished three times with each crystallization yielding protopine. The fourth crystallization yielded a different alkaloid (m.p. 150°) which, after seven further recrystallizations, had m.p. 156° and was identical in all respects (NMR, I.R., U.V.) to α -allocryptopine, m.p. 160°.²

Thin-layer chromatographic analysis of the mother liquors again showed mainly protopine and allocryptopine. An additional two spots could be faintly seen, but sufficient material for further work was not available. Based on the isolated pure alkaloids and thin-layer chromatographic analysis of the mother liquors, protopine and allocryptopine occur in approximately equal amounts in *A. californica* and together represent probably 95% of the total alkaloid content.

General experimental procedures were as previously reported (3).

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- Previous paper: Stermitz, F. R., *J. Pharm. Sci.*, **56**, 760 (1967).
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- ¹ The authors are indebted to Nelson N. Williams, Department of Biology, University of Nevada (Southern), for this collection (made at Las Vegas, Nev.) and for his extensive attempts to locate other species of the genus *Arctomecon*.

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² The authors are indebted to Dr. R. H. Manske for supplying the authentic sample.