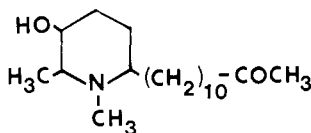


ISOLATION OF N-METHYLCASSINE FROM SPECIES OF THE GENUS *PROSOPIS*

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Previous phytochemical studies of the genus *Prosopis* (Leguminosae) have demonstrated that several species contain a number of known flavonoids (1-3) as well as alkaloids (4-10). In this paper we wish to report the isolation and structural determination of *N*-methylcassine (1) from the bark of *Prosopis nigra* (Griseb.) Hieron., *P. ruscifolia* Griseb. and *P. vinalillo* Stuck. This is the first report of the isolation of this compound from a natural source, although it has been previously synthesized from cassine by Highet (11).



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The crude alkaloid extracts obtained from all the species, when purified by preparative tlc, yielded *N*-methylcassine. The mass spectrum showed the molecular ion at m/e 311 (0.79%) ($C_{19}H_{37}NO_2$) and the base peak at 128 (100%) due to the loss of the aliphatic side chain. Other identified peaks indicated the elimination of the $COCH_3$ moiety and a number of signals, separated 14 m.u. each, corresponding to the degradation of the side chain. This pattern of fragmentation is coincident with that previously reported for this type of alkaloid (8).

The nmr spectrum was almost identical with that of cassine, except for a singlet at δ 2.28 (3H) attributed to the methyl attached to the nitrogen.

The identification of (1) was confirmed by comparison of the physical properties with those of the authentic compound which was prepared from cassine according to the literature (11). A portion of *N*-methylcassine was converted in the hydrochloric derivative by treatment with 5% methanolic-hydrochloric acid solution, evaporated to dryness and recrystallized from absolute ethanol. The mp observed was 109-110° (lit. (11): 110.5-111.5°).

EXPERIMENTAL¹

PLANT MATERIAL.—*P. nigra* (Griseb.) Hieron. and *P. ruscifolia* Griseb. were identified by Prof. Ing. Agr. A. T. Huntziker. Voucher specimens are on deposit in Museo Botánico, Univ. Nac. de Córdoba. *P. vinalillo* Stuck. was identified by Dra. Beatriz Soraru; a voucher specimen is on deposit in the Herbarium of the Departamento de Farmacognosia y Fitoquímica Fac. de Farmacia y Bioquímica, Univ. Nacional de Buenos Aires. Plant material was collected in Santiago del Estero (República Argentina). The bark was air dried and powdered.

EXTRACTION AND PURIFICATION.—The extraction method was identical for all the three species. Powdered bark (400 g) was extracted with methanol for 48 h at room temperature. After elimination of the solvent at reduced pressure, the total residue was suspended in 200 ml of 5% hydrochloric acid, stirred mechanically and filtered. The acidic extract containing the alkaloids was adjusted to pH 8 with ammonia and extracted with petroleum ether in a liquid-liquid extractor until no Dragendorff reaction was observed in the aqueous layer.

¹Nmr spectra were carried out on a Varian T-60 instrument in DCC13 with tms as internal standard; ms spectra in a Varian MAT CH 7 at 70 eV; ir spectra in a Beckman IR 8 instrument in KBr disc. The melting points were determined in a Koffler apparatus and are uncorrected. Silica gel G was used for tlc. The solvent systems and Rf were, respectively: A) *n*-butanol-acetic acid-water (4:1:2) (0.58) and chloroform-methanol-ammonia (93:7:0.1) (0.10).

The organic solvent was then removed *in vacuo*. The alkaloid residue showed several spots on tlc. The spot at Rf 0.10 (Syst. B) corresponded to *N*-methylecassine. The alkaloid was obtained pure by preparative tlc (Syst. B); the zone at Rf 0.10 was removed from the tlc plate and eluted with methanol, and the solvent was then removed *in vacuo*. This was repeated several times to obtain pure material. *N*-methylecassine thus obtained showed identical chromatographic properties with those of the synthetic alkaloid prepared from cassine (11). Both ir spectra were superimposable.

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