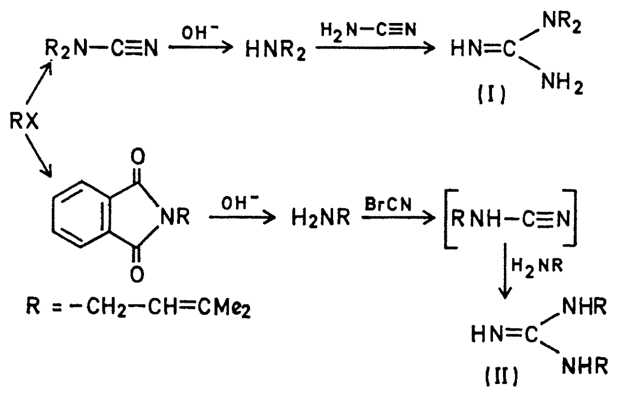
Synthesis of Pterogynine and Isolation of its Isomer Pterogynidine, a New Guanidine Alkaloid†

By RENÉE A. CORRAL,* ORFEO O. ORAZI, and MABEL F. de PETRUCCELLI

(*Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, Argentina*)

Summary The isolation, structure, and synthesis of a new guanidine alkaloid, pterogynidine (II), of *Pterogyne nitens* Tul. (Leguminosae) and the synthesis of pterogynine (I) are described.

RECENTLY we determined the structure of an *NN*-disubstituted-guanidine, pterogynine (I), isolated from *Pterogyne nitens* Tul. (Leguminosae).[1] Subsequently, other authors[2] obtained a guanidine alkaloid from an Euphorbiaceae species and allotted it the structure *N*-1,*N*-3-di-isopentenylguanidine (II). We believe that the compounds are identical because of the coincidence of the m.p.'s of the respective hydrochloride and picrate salts and the following results which led us to assign structure (II) to another natural guanidine.



SCHEME

Column chromatography on neutral alumina of the crude alkaloids from the bark of *Pterogyne nitens* Tul. gave a new guanidine alkaloid, pterogynidine (II), characterized as the picrate, $C_{17}H_{24}N_6O_7$, m.p. 105—106°.

The n.m.r. spectrum in $CDCl_3$ of the hydrochloride (prepared from the picrate with Dowex-2 chloride resin) indicates two 3,3-dimethylallyl substituents with peaks at δ 1·73 (12H), 3·88 (triplet, 4H), and 5·23 (triplet, 2H); further it shows two broad signals (both absent in D_2O solution) at 6·83 (2H) and 7·57 (triplet, 2H) assigned to one NH_2 and two equivalent NH groups respectively. This establishes structure (II) for pterogynidine. This structure was further proved by the synthesis (see Scheme) and identification (as picrates) of natural and synthetic samples by means of mixed m.p.'s and i.r. spectra.

We also report the synthesis (see Scheme) of pterogynine, thus providing a new proof for its structure (I); natural and synthetic specimens (as picrates m.p. 157—158°) were identified as before. Similarly, di-isopentylamine was converted into *N*-1,*N*-3-di-isopentylguanidine (picrate m.p. 164—165°) identical with tetrahydropterogynine.[1]

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† For previous part in the series see R. A. Corral, O. O. Orazi, and M. T. Pizzorno, *Anales Asoc. quím. Argentina*, in the press.

[1] R. A. Corral, O. O. Orazi, and M. F. de Petruccelli, *Experientia*, 1969, **25**, 1020.

[2] N. K. Hart, S. R. Johns, and J. A. Lamberton, *Chem. Comm.*, 1969, 1484.