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SHORT COMMUNICATION

ORGANIC BASES FROM BRAZILIAN *PIPTADENIA* SPECIES

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Abstract—Basic compounds have been detected in five Brazilian *Piptadenia* species by means of electrophoresis. Bufotenine was detected in *P. contorta* Benth., and *P. moniliformis* Benth. The seeds of *P. leprostachya* Benth. contained theobromine, a new constituent in Leguminosae.

INTRODUCTION

Piptadenia species are common in South America and 31 species have been found in Brazil. Some Amazonian natives snuff the seed powder of *Piptadenia peregrina* Benth. (syn. *Adenanthera peregrina*)[1] for hallucinogenic purposes. Stromberg[2] isolated bufotenine from the seeds of *P. peregrina* whilst Horning *et al.*[3] studied the seeds and seed pods of *P. peregrina*, *P. macrocarpa* Benth. and *P. paniculata* Benth. and showed that the first two species contained bufotenine, bufotenine oxide and *N,N*-dimethyltryptamine oxide in the seeds and *N,N*-dimethyltryptamine in the seed pods. Ribeiro *et al.*[4] reported that bufotenine was found also in the seeds of *P. colubrina* Benth. Tschesche *et al.*[5] reported that *N*-methyltryptamine, 5-methoxy-*N*-methyltryptamine and 5-methoxy-*N,N*-dimethyltryptamine could be isolated from the bark of *P. peregrina* and Guillermo *et al.*[6] isolated 5-methoxy-*N*-methyltryptamine from the bark of *P. macrocarpa*. As can be seen, the indole bases of tryptamine type are widely distributed in the genus *Piptadenia*. The authors have attempted to detect the indole bases from five species of *Piptadenia*, which were collected by one of us (Y. H.) from Brazil in 1969. In order to investigate chemotaxonomical relationships, the following species have been used; *P. colubrina*, *P. contorta*, *P. leprostachya*, *P. moniliformis*, and *P. peregrina*. The authors are especially indebted to Professor Gerald Pint, Federal University of Bahia for taxonomical identifications.

RESULTS AND DISCUSSION

The paper electrophoretic behaviour of the alkaloid fraction from the seeds of *Piptadenia* species are shown in Table 1. The UV spectrum of the substance corresponding to II (5·0–5·5) showed λmax at 240 nm in acid solution. Substance III was identical to an authentic sample of bufotenine, giving an orange colouration with Dragendorff's reagent, a purple colouration with Ehrlich's reagent and a blue $FeCl_3$ test, respectively. The UV

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TABLE 1. PAPER ELECTROPHORESIS OF BASIC COMPONENTS IN *Piptadenia* spp.*

Piptadenia Benth.	Migration distance (cm)†					
	I	II	III	IV	V	VI
P. colubrina Benth.		5·5	14·0	15·4	17·3	
P. contorta Benth.		5·5	14·5	15·0		
P. leprostachya Benth.	0	5·0				29
P. moniliformis Benth.		5·5	14·1			
P. peregrina Benth.		5·5	14·0	15·4	17·3	

* For conditions see text. †(III) is bufotenine; (IV), *N,N*-Dimethyltryptamine; the others are unknown Dragendorff positive, compounds.

spectrum of the substance corresponding to III was as expected for the indole derivative. As mentioned above, *P. colubrina*, *P. macrocarpa* and *P. peregrina* were already known to contain bufotenine. In the present paper bufotenine was also detected in *P. contorta*, and *P. moniliformis*.

The substance corresponding to spot IV, separated from *P. contorta*, was analysed by NMR in deuterio dimethyl sulfoxide solution. The spectrum showed $N(CH_2)$ at δ 2·9 and methylene protons between δ 3·2–3·5. These signals were characteristic of protons in the side chain of N,N-dimethyltryptamine. The negative response to $FeCl_3$ indicated IV to be non-phenolic. Therefore, this compound appeared to be identical to *N,N*-dimethyltryptamine. The substance corresponding to spot V remains unidentified. The spot VI, isolated from *P. leprostachya*, gave an unknown picrate, m.p. 242°. Crystals, m.p. over 300° (yield, 0·03%) were also obtained from the alkaloid fraction of seeds in *P. leprostachya*. The UV spectrum of the substance indicated λmax at 273 nm in acid solution, and at 240 and 273 nm in alkaline solution, which are the same as those of an authentic sample of theobromine.[7] The identification of theobromine was also supported by the results of NMR, MS, and IR-spectra as well as elementary analysis.

It is noteworthy from a chemotaxonomic point of view that this is the first identification of theobromine in the Leguminosae. Previously it has been reported only from *Theobroma cacao* (Sterculiaceae) and as a minor component of caffeine bearing plants such as *Caffea* spp. (Rubiaceae) and *Ilex paraguayensis* (Aquifoliaceae).[8]

EXPERIMENTAL

Extraction. 100 g of each species was ground in a Wiley mill and the powder was extracted with MeOH for 7 hr at 60°. The extracted solution was evaporated to dryness and dissolved in 1 N HCl. The acid solution was made basic with NH_4OH. This was extracted repeatedly with $CHCl_3$ until a negative reaction for Meyer's reagent was obtained. The dried extract of $CHCl_3$ layer was dissolved in MeOH and chromatographed on neutral alumina column, eluting with MeOH:$CHCl_3$ = 1:1.

Microelectrophoresis. The alkaloid fraction obtained was separated on filter paper (40 cm, Toyo-Roshi No. 52) with 800V, 0·3mA/cm applied for 2·5 hrs using 5N acetic acid as electrolyte. The alkaloids were detected with Dragendorff's reagent,[9] Ehrlich's reagent and $FeCl_3$ solution: the latter were prepared according to the *Japanese Pharmacopeia*, 8th Ed.

Theobromine from P. leprostachya. The methanolic extract was evaporated to yield monoclinic needles (30 mg. yield 0·03%), m.p. over 300° (Calcd. for $C_7H_8N_4$: C, 46·44; H, 4·48; N, 31·10. Found; C. 46·47;

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H, 4·71; N, 30·69%) NMR bands ($CDCl_3$) δ 3·62, 4·11, 8·2; mass spectra at *m/e* 180 (parent ion), 137, 109, 82, 67 (base peak); ν_{max} 1690, 1670, 1549, 1488, 1457 and 1277 $cm.^{-1}$

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Key Word Index—Piptadenia; Leguminosae; alkaloids; bufotenine; N_1N-dimethyltryptamine; theobromine.