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Harmane derivatives in Marcgravia williamsii (MacBr). VII Hallucinogens from South American plants

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SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica. — *Harmane derivatives in Marcgravia williamsii (MacBr). VII Hallucinogens from South American plants.* Nota di NANCY LOZANO REYES (*) e GIULIANO DELLE MONACHE (**), presentata (***) dal Corrisp. G. B. MARINI-BETTÒLO.

RIASSUNTO. — In *Marcgravia williamsii* (Marcgraviaceae) pianta usata in Perù nella medicina popolare con il nome di Murcu Huasca sono stati isolati l'armina, la tetraidroarmina e in minore quantità l'armalina, l'armolo e l'armano. È la prima volta che questo gruppo di alcaloidi viene riscontrato in Marcgraviaceae.

In the study of the chemistry of South American plants we have previously reported on hallucinogens isolated either from plants [1, 4, 5] or from particular preparations made by the natives—e.g. yopo, epenà, paricà [1, 2,3].

We have found alkaloids belonging to the indole derivatives: tryptamines and harmanes, as well as one alkaloid of the tropane group: scopolamine [4].

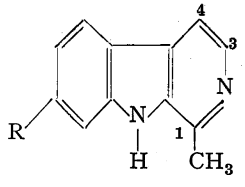
Other hallucinogenic substances from Latin America flora belong to the phenylethylamine (*Anhalonium williamsii* or peyotl) and lysergic acid (*Rivea corymbosa* or ololiuqui) groups, and have been widely used in Mexico since pre-Columbian times [6].

We have now examined a Peruvian plant, *Marcgravia williamsii*, MacBr., Marcgraviaceae, known by the common name of *Murcu huasca*. Leaves, trunk and trunk-bark of the plant were extracted with 5 % acetic acid.

Basification with ammonia and extraction with EtOAc gave in all cases a mixture of alkaloids, in a rather low percent from the leaves (1 ‰) and higher from the trunk and trunk-bark (2 %); tlc examination showed the overall alkaloid composition to be identical in the different parts of the plant.

The alkaloids were purified by extraction with 2N HCl, precipitation with NaOH and reextraction with EtOAc. The residue was fractionated on Silica-gel with $CHCl_3$-MeOH mixtures and on Al_2O_3 with EtOAc-MeOH mixtures.

Five alkaloids were identified.



I R = H
II R = OCH_3
III R = OCH_3; 3, 4 dihydro
IV R = OCH_3; 1, 2, 3, 4 tetrahydro
V R = OH

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(***) Nella seduta del 10 marzo 1979.

Harmine (II): $C_{13}H_{12}N_2O$, mp 261–2° (MeOH), lit [7] 262°; 75 % of the alkaloid content, PMR (60 MHz, $CDCl_3$): δ 2.82 (3 H, s, CH_3), 3.82 (3H, s, OCH_3), 6.84 (1 H, q, J = 8 and 2 Hz, H–6), 6.92 (1 H, d, J = 2 Hz, H–8), 7.40 (1 H, d, J = 6 Hz, H–4), 7.72 (1 H, d, J = 8 Hz, H–5), 7.87 (1 H, d, J = 6 Hz, H–3); 10.65 (1 H, large, NH); UV λ_{max}^{MeOH} nm: 242, 301, 326 sh, 336 sh; identification was confirmed by direct comparison with an authentic sample.

Tetrahydroharmine (IV): $C_{13}H_{16}N_2O$, mp 198–199° (MeOH), lit [7] 200°, $[\alpha]_D^{27} = +34°$ ($CHCl_3$, p.17), 15–20 % of the alkaloid mixture; PMR (60 MHz, CD_3COCD_3): δ 1.38 (3 H, d, J = 6.5 Hz, CH_3), 2.4–3.0 (4 H, complex, CH_2—CH_2), 3.1 (1 H, m, J = 6.5 Hz, CH), 3.70 (3 H, s, OCH_3), 6.58 (1 H, q, J = 8.5 and 2 Hz, H–6), 6.78 (1 H, large, NH); UV λ_{max}^{MeOH} nm: 240–271–297; identification was confirmed by direct comparison with an authentic sample.

Harmaline (II) and *harmol* (V): minor components (2–3 %); compared to authentic specimens they exhibited the same Rf in three different tlc systems, identical colour reactions and superimposable UV spectra.

Harmane (I) is present only in traces and was identified by tlc comparison with an authentic specimen.

The presence of these alkaloids in *Murcu huasca* accounts for the use of the plant in folk medicine. This is also the first time that harmane derivatives are reported in the family of *Marcgraviaceae*, which is related to the families of *Guttiferae* and *Theaceae* (order Guttiferales). In the table the distribution of harmane derivatives in different plant families and preparations is reported [1].

It gives an interesting account both for chemotaxonomy in order to establish similar biogenetic patterns and for ethnopharmacology for the use in folk medicine.

Besides alkaloids, a mixture of sugars, constituting about 1.5 % of the plant material, was obtained by percolation with MeOH of the extracted trunk. Fructose (~ 90 %) and glucose (~ 10 %) were identified by paper chromatography (Whatmann 1, eluting with acetone, butanol, H_2O 7 : 2 : 1).

(1) Minute amounts of harmane derivatives have been isolated from a *Virola* species (Myristicaceae) [9].

Distribution of Harmane derivatives in plants [7, 8]

FAMILY	GENUS	Species or preparation	HARMANE aribine loturine passiflorine	HARMINE banisterine yageine telepathine	TETRAHYDRO-HARMINE leptaflorine	HARMALINE harmidine	HARMOL O-demethyl harmine
Malpighiaceae	*Banisteria*	*caapi*	—	+	+	+	—
	Banisteriopsis	*inebrians*	—	+	—	+	—
	Cabi	*paraensis*	—	+	—	—	—
		" epenà " [10]	—	+	+	—	—
		" paricà " [1]	—	+	+	—	—
		" natem " [11]	—	+	—	—	—
Passifloraceae	*Passiflora*	*incarnata*	+	+	—	+	+
		actinea, alata, alba, bryonoides, edulis eichleriana, ruberosa quadrangularis	+	—	—	—	—
Zygophyllaceae	*Zygophyllum*	*fabago*	+	+	—	—	—
	Peganum	*harmala*	—	+	+	+	+
Rubiaceae	*Arariba*	*rubra*	+	+	—	—	—
	Ophiorrhiza		+	—	—	—	—
	Leptactinia	*densiflora*	—	—	+	—	—
Calycantaceae	*Calycanthus*		—	+	—	—	—
Elaeagnaceae	*Elaeagnus*		—	—	+	—	—
Polygonaceae	*Calligonum*	*minimum*	+	—	—	—	—
Symplocarpaceae	*Symolocos*		+	—	—	—	—
Bignoniaceae	*Newbouldia*		+	+	—	—	—
Cyperaceae	*Carex*		+	—	—	—	—
Marcgraviaceae	*Marcgravia*	williamsii	+	+	+	+	+

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