Moreover the compounds were either unchanged upon acid hydrolysis or yielded the expected C-6, C-8 pair of C-glycosyl isomers. Finally, the compounds were identical by paper co-chromatography (in two solvent systems) with authentic samples.* Thus, the mature leaves and stems of L. usitatissimum contain orientin, isoorientin, vitexin, isovitexin, lucenin-1, -2, vicenin-1 and -2.

EXPERIMENTAL

Most of the genetic lines of *L. usitatissimum* were provided by F. Plonka, Institut National de la Recherche Agronomique, Versailles, France; others were obtained from the plant collection available in the senior author's Research Station. All of the two-dimensional paper chromatographic, hydrolytic and UV spectral analyses were carried out by standard procedures.⁵

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* Samples of several of the C-glycosylflavonoids were available from the flavonoid collection of T.J.M.; however, all the compounds were available in chromatographic quantities from Mark Bierner who had previously identified them in various species of *Helenium* (Compositae). The latter work is unpublished.

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MALPIGHIACEAE

ALKALOIDS OF THE LEAVES OF BANISTEREOPSIS ARGENTEA

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Plant. Banistereopsis argentea Spring ex Juss.

Occurrence. The species is now being grown in Indian Botanic Gardens, Howrah.¹

Uses. Members of the genus *Banistereopsis* are used in the preparation of narcotic and/or hallucinogenic decoctions by certain Colombian and Peruvian Indian tribes.²

Previous work. A preliminary report based on this work has recently been presented.³ *Leaves.* Total alkaloids, 0.02%.

Defatted (petroleum 60–80°) plant material (1.8 kg) hot extracted with EtOH. EtOHextract concentrated under reduced pressure, the residue taken up in AcOH (4%, 200 ml), clarified acidic solution extracted with CHCl₃ at two pH levels (4 and 9), H₂O-soluble bases isolated through their reineckates.⁴

¹ The plant material was obtained through the kind courtesy of Mr. R. Biswas, Indian Botanic Gardens, Howrah.

2840

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⁴ S. GHOSAL, P. K. BANERJEE and S. K. BANERJEE, Phytochem. 9, 429 (1970).

(+)- N_b -Methyltetrahydroharman. Weakly basic gum from pH level 4, chromatographed (Al_2O_3) , first CHCl₃ eluates afforded homogeneous gum (37 mg), sublimed *in vacuo*, crystallized from xylene as flakes (m.p., mixed m.p., co-TLC, $[a]_D$, UV, IR, m/e 200 (M⁺), 199, 197). Methiodide (m.p., mixed m.p. superimposable IR).

N,N-Dimethyltryptamine. Brown oil (48 mg) from middle CHCl₃ eluates (co-TLC, UV). Yellow picrate from MeOH (m.p., mixed m.p.); methiodide (m.p., mixed m.p., IR).

N,N-Dimethyltryptamine- N_b -oxide. Hygroscopic solid (26 mg) from MeOH eluates (co-TLC, UV). Reduced with Zn and AcOH to N,N-dimethyltryptamine.

Harmine. Basic gum from pH level 9, chromatographed, homogeneous gum (0.11 g) from CHCl₃ eluates, sublimed *in vacuo*, colourless needles (m.p., mixed m.p., UV, m/e). Base hydrochloride from AcMe-MeOH (m.p., mixed m.p.).

(+)-Tetrahydroharmine. Amorphous solid (96 mg) from $CHCl_3$ -MeOH (99:1) eluates, crystallized from xylene-ether as needles (m.p., mixed m.p., co-TLC, UV, IR, m/e).

Harmaline. Snuff coloured solid (21 mg) from MeOH eluates (m.p., mixed m.p., co-TLC, UV, superimposable IR, m/e).

Choline. Reineckate salt precipitated at pH ~ 8, passed over De-Acidite FF, regenerated base obtained as hygroscopic solid (0.17 g) (co-TLC, pharmacological properties). Yellow picrate (m.p., mixed m.p.).

Betaine. Regenerated from the reineckate salt, precipitated at pH ~ 1, as hygroscopic solid (82 mg) (co-TLC). Orange picrate (m.p., mixed m.p.).

New compound. (+)-5-Methoxytetrahydroharman. Pale brown gum from xylene-ether mother liquor, after separation of tetrahydroharmine, $C_{13}H_{16}N_2O$, m/e 216 (M⁺), significant peaks at m/e 215, 213, 201, 187, 170, 169, $[a]_D^{25} + 34^\circ$ (CHCl₃), λ_{max} 217, 266–270, 290 (sh)nm. Dehydrogenation with Pd-C gave 5-methoxyharman (m.p., mixed m.p., UV, m/e 212 (M⁺), 197, 169, metastable peak at m/e 145, 197 \rightarrow 169 transition requires m^{*} at m/e 145). Methosulphate of 5-methoxyharman (m.p., mixed m.p., UV, violet fluorescence under UV light on papers).

Uncharacterized indolic bases. EtOH mother liquor, after separation of betaine picrate, was again passed over DeAcidite FF, the regenerated base (12 mg) showed two Dragendorffand van Urk-positive spots, $R_f 0.09$ (major), 0.12, $pK_a \sim 10.5$, $\lambda_{max} 224$, 272, 294, 305-310 nm. Further characterization of these compounds is in progress.

This is the first report of occurrences of a 5-methoxy tetrahydro- β -carboline alkaloid in nature and of (+)-N_b-methyltetrahydroharman in the Malpighiaceae. Although harman type alkaloids have been isolated from many plant families, N_b-methyltetrahydroharman appears to have been reported only in the Leguminosae^{5.6} and Chenopodiaceae.⁷

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