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ALKALOIDS OF RAUWOLFIA CANESCENS

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Rauwolfia canescens L. (Trinidad devilpepper) has been introduced by the Transcaucasian Zonal Experimental Station of the All-Union Scientific Research Institute for Medicinal Plants [1]. We have studied the roots and epigeal part of the plant grown in Kobuleti in 1963, 1964, and 1966. The total alkaloid contents were: in the roots 3.1–4.3% and in the epigeal part 1.9–2.4%. By thin-layer chromatography [silica gel with 15% of gypsum, in the chloroform—ethanol (9 : 1) system], 18 alkaloids have been found in the roots and 16 in the epigeal part.

The alkaloids were extracted from the roots with 5% acetic acid, the bases being precipitated with ammonia and extracted with chloroform. By chromatographing the ether-soluble part of the mixture of alkaloids on alumina by a known method [2], ajmalicine with mp 252° C (from aqueous methanol) and ajmaline with mp 205° C (from methanol) were isolated. The fraction of the polar bases was rechromatographed and chloroform containing 0.5% of ethanol eluted reserpine with a yield of 0.05%, having mp 256–257° C (from ethanol, decomp.). Sarpagine was obtained by Stoll and Hofmann's method [3], mp 304–306° C (from methanol, decomp.).

The alkaloids from the epigeal part of the plant were extracted in the same way as from the roots or were extracted in the form of the bases with benzene, xylene, or dichloroethane. They were then separated by the oxalate method [4]. From the fraction of ethanol-insoluble oxalates, we isolated α-yohimbine (0.4% of the raw material) with mp 230° C (from ethanol, decomp.). By chromatographing the bases from the fraction of ethanol-soluble oxalates we obtained aricine with mp 189–190° C (from ethanol) and reserpiline, the oxalate of which melted at 239–240° C (decomp.).

The ajmaline, ajmalicine, aricine, reserpiline, α-yohimbine, and sarpagine were identified by their melting points and UV and IR spectra [5], and reserpine by direct comparison with an authentic sample.

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ALKALOIDS OF SWERTIA MARGINATA, S. GRACILIFLORA, AND DIPSACUS AZUREUS

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We have studied the alkaloids of Swertia (Gentianaceae) and D. azureus (family Dipsacaceae) (table).

By chloroformic extraction from S. marginata, we obtain 0.30% of ethereal and 0.08% of chloroformic bases. When the combined ethereal bases were treated with acetone, gentiananine [1] was isolated. The mother liquor was passed through a column of alumina. Gentianine [2] was obtained from the ethereal eluates.

From the chloroformic alkaloids, treatment with acetone isolated a yellow base with mp 207–208° C (acetone), which proved to be identical with gentioflavine [3], given to us by S. Popov (Bulgaria) (mixed melting point and IR spectra).

By the method mentioned, from S. graciliflora we obtained gentiananine, gentianine, and gentioflavine.

From the roots of D. azureus by chloroform extraction we obtained 0.35% of benzene alkaloids and 0.07% of chloroform alkaloids, and from the epigeal parts 0.07% of benzene alkaloids and 0.06% of chloroform alkaloids. By separating the benzene fractions of the total alkaloids according to solubility and also on a column of alumina, we isolated gentianine [2].

Plant	Place and time of collection (year and date)	Plant organ	Vegetation period	Total alkaloids, % of weight of raw material
S. marginata	Eastern Alai, Karagai Tugai, KirgSSR, 5 July 10	Epigeal part	Budding	0.38
S. graciliflora	Darvazskii Range, R. Obinkhingau, TadzhSSR, 18 June 1966	»	Incipient budding	0.56
D. azureus	Malyi Chimgan, Tashkent region, UzSSR, 12 June 1966	» Root	» »	0.13 0.42

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THE STRUCTURE OF ERVINIDININE

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Ervinidinine $C_{21}H_{24}N_2O_3$ (M^+ 352), with mp 265–266° C (decomp., methanol) $[\alpha]_D^{26}$ −160.6° (methanol) contains a methoxy group and an active hydrogen [1]. Its IR spectrum: 3250, 1690, 1650, 1610, and 750 cm^{-1} (in KBr), and 3400, 1680, 1610 cm^{-1} (in chloroform). Consequently, it contains a secondary nitrogen atom, an ester carbonyl group conjugated with a double bond, and a 1,2-disubstituted benzene ring. The UV spectrum–λ_{max} (ethanol) 228, 298, 332 mμ (log ε 3.86, 3.84, 3.98)—is characteristic for α-methyleneinedoline alkaloids.

By the reduction of ervinidinine with zinc in methanolic sulfuric acid we obtain dihydroervinidinine $C_{21}H_{26}N_2O_3$ (M^+ 354) with mp 215–216° C (methanol). Its IR spectrum—λ_{max} (ethanol), 248, 308 mμ (log ε 3.40, 3.62)—is characteristic of indoline bases.

The NMR spectrum of ervinidinine exhibits the signals of an ethyl group (δ = 0.62 ppm), the methoxyl of an ester (δ = 3.69 ppm, singlet), four aromatic protons (δ = 6.9 ppm, multiplet), and NH (δ = 8.91 ppm, singlet).

The mass spectrum has peaks of ions with m/e 352 M^+ (58%), 320 $(M\text{-}CH_3OH)^+$ (7%), 214 $(M\text{-}138)^+$ (100%) and 138 (4%). The maximum peak with m/e 214 is a characterizing feature of α-methyleneindoline alkaloids of the type of aspidospermine and shows that the third oxygen atom in ervinidinine, like the oxygen atom in lochnericine and lochnerinine, is present in the piperidine ring of the molecule [2–4].

However, the IR spectrum of the base lacks a band in the 2700–2800 cm^{-1} region which shows a cis-oriented hydrogen with respect to the unshared pair of electrons of the N(b) nitrogen atom.

The information given permits a structure differing from that of lochnericine by the configuration of the hydrogen at C_{19} to be proposed.