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	"	"	0.13
		Root	"	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) $[\alpha]^{26}_{D}$ $-160.6°$ (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.

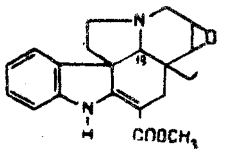
By the reduction of ervinidinine with zinc in methanolic sulfuric acid we obtain dihydroervinidinine $C_{21}H_{26}N_2O_3$ (M^+ 354) with mp 215–216° C (methanol). Its IR spectrum–λ_{max} (ethanol), 248, 308 mμ (log ε 3.40, 3.62)–is characteristic of indoline bases.

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 $(M-CH_3OH)^+$ (7%), 214 $(M-138)^+$ (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.



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MASS SPECTROMETRIC STUDY OF GENTIANADINE

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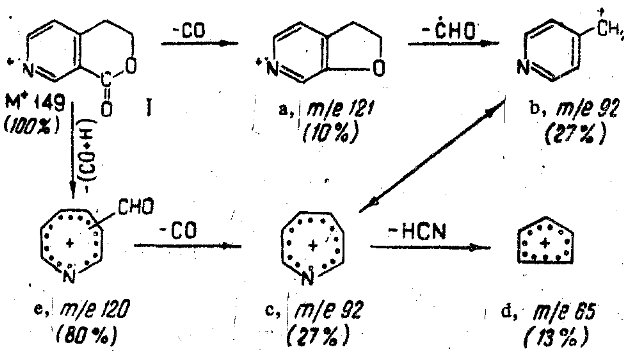
In the mass spectrum of gentianadine [1], the maximum peak corresponds to the molecular ion (M^+ 149). The main direction of fragmentation begins from the molecular ion by the expulsion from it of carbon monoxide, as a result of which fragment a with m/e 121 arises. The elimination of a formyl residue (CHO) from the ion-radical a leads to the formation of ion b with m/e 92. This is confirmed by the presence in the spectrum of a metastable peak with m/e 71 (calculated 69.1). The ion b possibly has the structure of the azotropylium cation c. The loss of a molecule of HCN by ion c gives rise to an ion with m/e 65. The presence of a metastable peak with m/e 46 (calculated 45.9) shows the m/e transition c → d.

A second intense peak corresponding to a fragment with m/e 120 is formed from the molecular ion by the splitting out of a CO group and also by the detachment of an atom of hydrogen and probably has the structure of an azotropylium aldehyde (ion e). The transition $M^+ \rightarrow$ e is shown by the presence in the spectrum of (I) of the metastable peak of an ion with m/e 96 (calculated 96.6).



Thus, the nature of the fragmentation of gentianadine resembles the course of the decomposition of alkylpyridinium bases [2].

We have studied the roots of Gentiana olivieri collected in the gorge of the Karatag R. TadzhSSR in the flowering period (0.7% of total alkaloids of the dry weight of the plants). Separation of the mixture of bases yielded gentianine, gentiananine, and gentianaine [1,3].