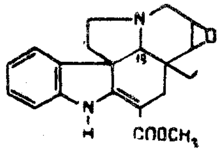

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MASS SPECTROMETRIC STUDY OF GENTIANADINE

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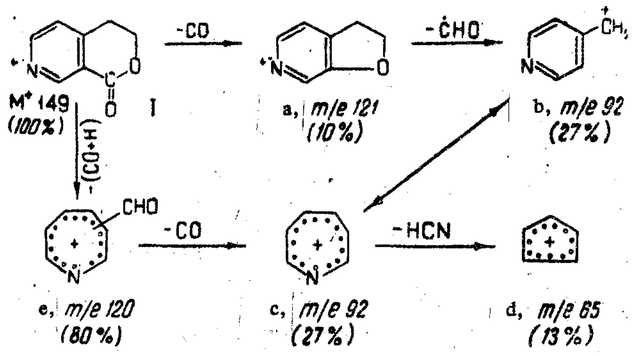
In the mass spectrum of gentianadine [1], the maximum peak corresponds to the molecular ion (M^+ 149). The main direction of fragmentation begins from the molecular ion by the expulsion from it of carbon monoxide, as a result of which fragment a with m/e 121 arises. The elimination of a formyl residue (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 <u>Gentiana olivieri</u> 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].

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STACHYDRINE FROM *CAPPARIS SPINOSA*

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The roots and leaves of *C. spinosa* gathered in the Farish region of the Syr-Dar'ya region were extracted with water. The aqueous extract was evaporated in vacuum to dryness, and the resulting dark brown mass was treated by a published method [1]. This gave 1.2 and 1.5%, respectively (on the weight of the dry raw material) of total alkaloids in the form of a light yellow noncrystalline mass. The action of an ethanolic solution of hydrogen chloride on the combined bases yielded optically inactive white acicular crystals with mp 228–229° C (decomp., ethanol–acetone) and the composition $C_7H_{14}O_2NCl$. On a paper chromatogram in the butanol (saturated with water)–hydrochloric acid (5 : 1) system, the base isolated had R_f 0.5 (revealed by Dragendorff's reagent). The addition of a saturated ethanolic solution of oxalic acid to a concentrated solution of the hydrochloride of the base formed an oxalate with mp 104–105° C. A picrate with mp 194–195° C was obtained analogously. When an aqueous solution of the hydrochloride was shaken with silver hydroxide, the free base precipitated with mp 103–105° C; after drying in vacuum (100° C), mp 225–226° C. From the properties described, this base is stachydrine [1–4]. Thin-layer chromatography showed that the mother liquors from the total alkaloids contained another base, with R_f 0.1.

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CONIDENDRIN FROM *PICEA OBOVATA*

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By steeping wood chips from *Picea obovata* in acetone, we obtained 1.0% of extractive substances. On concentration, the acetone extract formed two layers: an upper oily layer and a lower aqueous-acetonic layer. Thin-layer chromatography on alumina and silica gel using diazotized sulfanilic acid as revealing agent showed the presence in both layers of several components of a hydroxyaromatic nature. By repeatedly treating the upper layer of the extract with petroleum ether, the separation of the petroleum-insoluble hydroxyaromatic substances was achieved.

Preparative chromatography on silica gel with gradient elution by means of mixtures of benzene and isopropanol (96 : 4 → 90 : 10) of the total hydroxyaromatic substances yielded conidendrin with mp 212–219° C (ethanol–acetone) $[\alpha]_D^{20}$ $-51.3°$ (c 2.3; acetone). UV spectrum: λ_{max} 283, 287 (shoulder), mμ (log ε 3.97, 3.95). The IR spectrum contained characteristic absorption bands: 1515, 1584, and 1616 cm^{-1} (C_6H_5—), 1758 cm^{-1} (lactone carbonyl), 3415 cm^{-1}