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MASS-SPECTROMETRIC STUDY OF PRANGOSINE

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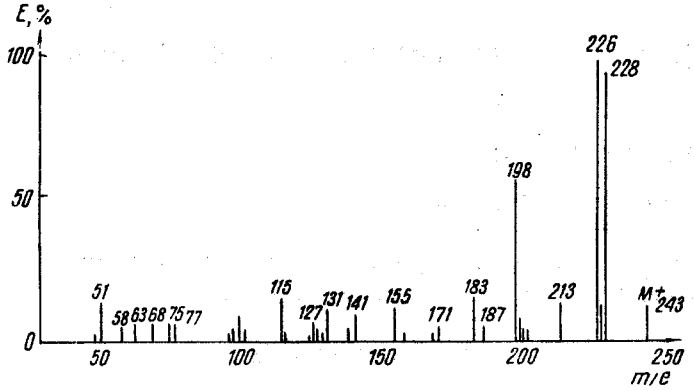
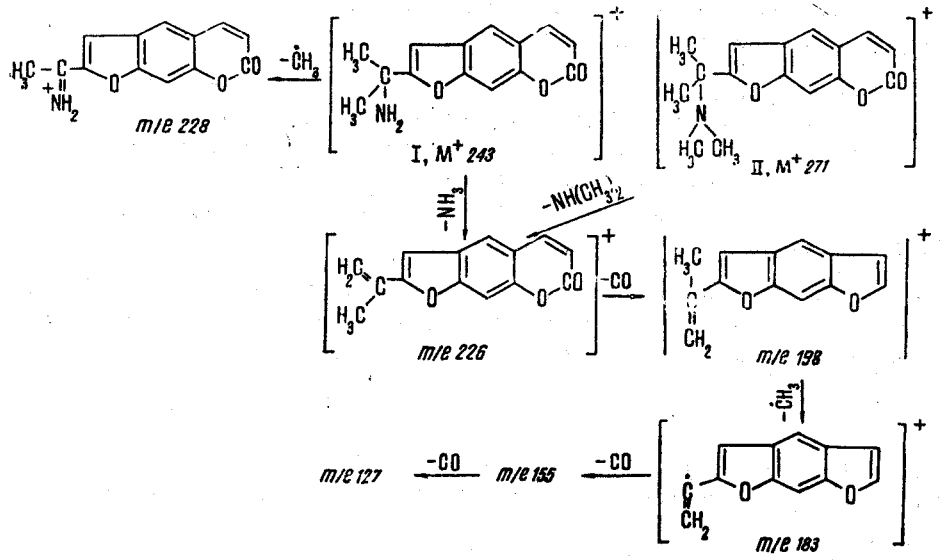
A structural formula has been proposed previously for the alkaloid prangosine isolated from the seeds of Prangos pabularia Lindl. [1].

The mass spectrum of prangosine (figure) is characterized by a low-intensity molecular peak (M^+) with m/e 243 (14%), while in the spectrum of N-dimethylprangosine (II), the peak of the molecular ion with m/e 271 amounts to only 2%. Repeated elimination of CO (with m/e 28) in the mass spectra of both prangosine and its N-dimethyl derivative, be-



ginning from the fragment with m/e 226, which is probably formed by the loss of NH_3 and $NH(CH_3)_2$ groups, respectively, is characteristic for furocoumarins [2]. Although the spectra have a fairly intense peak with m/e 228, its appearance is not due to the main direction of fragmentation.

The ion with m/e 226 is converted by loss of a CO group into a fragment with m/e 198. The existence of a metastable peak with m/e 174 (calculated, 173.5) characterizes the transition m/e 226 → 198. Then the ion with m/e 198 loses a methyl group, being converted into a fragment with m/e 183. The transition 198 → 183 is confirmed by the presence in the mass spectra of (I) and (II) of a metastable peak with m/e 169 (calculated 169.3). Subsequently, peaks with m/e 155 and 127, corresponding to the loss of one and two CO groups from the fragment with m/e 183, are formed.



Thus, the fragmentation of prangosine is similar to that of the furocoumarins; it confirms the structure proposed for prangosine.

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SOLID-PHASE SYNTHESIS OF A TETRADEPSIPEPTIDE CONTAINING THREE HYDROXY ACIDS

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Continuing our investigations on the solid-phase synthesis of depsipepsides, we have carried out a model synthesis of a tetradepsipeptide (I) containing three hydroxy acids and one amino acid:

L-Val-Glyc-L-HyTV-L-PhLac (1)

C-Terminal unprotected L-phenyllactic acid was added to 8 g of chloromethylated polymer containing 7% of chlorine in absolute alcohol in the presence of triethylamine under the conditions usually used for the solid-phase synthesis of peptides [1]. The amount of L-phenyllactic acid adding (1.16 g) was determined from the amount of triethylamine hydrochloride liberated. The subsequent addition of the O-tert-butyl ether of L-hydroxyisovaleric acid was carried out by the acylation of the hydroxy group of the L-phenyllactic acid in absolute pyridine at −10° C with a 50% excess of the mixed anhydride obtained by the interaction of the O-tert-butyl ether of L-hydroxyisovaleric acid with benzenesulfonyl chloride in absolute pyridine [2]. After being allowed to stand for 30 min at −10° C and for 24 hr at 20° C, the solution was filtered and the reaction resin was washed successively with dioxane, ethanol, ether, and petroleum ether, the washing with each solvent being carried out three times.

The subsequent splitting off of the O-tert-butyl group was effected by treating the polymer with 98% CF_3COOH at 20° C for 1 hr. The addition of the dicyclohexylammonium salt of the O-tert-butyl ether of glycolic acid [3] and of BOC-L-valine [4] was carried out under analogous conditions, but in the case of the O-tert-butyl ether of glycolic acid, the condensation was carried out in methylene chloride.

To complete the growth of the depsipeptide chain, the polymer was washed as described above and was carefully dried in vacuum. Then it was treated with 100% CF_3COOH and with a current of dry HBr for 15 min. After the CF_3COOH had been distilled off in vacuum, the hydrobromide of the tetradepsipeptide (I) that had been formed was extracted by carefully washing the polymer with methanol. The methanolic solution was evaporated to dryness in vacuum. The yield of the depsipeptide hydrobromide $C_{21}H_{30}NO_8Br$ (I) was 2.8 g (39%), mp 62° C (from absolute isopropanol), $[\alpha]_D^{20}$ −26 ± 2° C (c 2.0; methanol).

The substance gave one spot on chromatography in a thin layer of hydrated silica containing 13% of gypsum in the 1-butanol–acetic acid–water (4:1:1) system, R_f 0.71; and in the 1-butanol–pyridine–acetic acid–water (15:10:3:6) system, R_f 0.79. The spot was revealed with ninhydrin and Bromothymol Blue.

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