TRANSFORMATION OF SPECIOSINE INTO COLCHAMINE

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A minor alkaloid of Colchicum speciosum Stev. (showy autumn crocus) speciogine [1] is N-o-hydroxybenzylcolchamine [2]. Continuing a study of the properties of speciosine, we turned our attention to the fact that its mass spectrum (MKh-1303 instrument, temperature 200°C and ionizing voltage 35 V) in the region of high mass numbers practically coincides with the spectrum of colchamine (methyldeacetylcolchicine) [3]. In addition to this, the absence under the conditions given of the peak of a molecular ion with m/e 477 corresponding to speciosine apparently showed the decomposition of this alkaloid under the conditions of mass spectrometry and its conversion into colchamine. Furthermore, in agreement with the results of other authors [2], in the mass spectrum there is a triplet of ions with m/e 106-108 showing the appearance of the o-hydroxybenzyl residue of the speciosine molecule.

The results of mass spectrometry induced us to investigate how speciosine changes on heating. It was found that at a temperature of 210-212°C, with a holding time of 15 min, speciosine yields, in addition to by-products, colchamine, which was identified in the reaction mixture by chromatography (descending, "M" ["slow"] paper of the Volodarskii Leningrad Mill; solvent system butanol–water–acetic acid (4:5:1); spots revealed with modified Dragendorff's reagent).

This transformation also takes place on boiling in a high-boiling solvent (~200°C). For example, a solution of 0.20 g of speciosine in benzyl alcohol was boiled for 40 min. The solvent was distilled off in vacuum, and the residue was treated with 3 ml of 10% HCl and 10 ml of chloroform. The chloroform solution was extracted repeatedly with 2-3-ml portions of 10% HCl. To 16 ml of the combined acid solution was added 10% NaOH until weakly acid reaction to Congo Red was obtained, and the mixture was extracted with chloroform. The clarified mother solution was made alkaline with an excess of 10% NaOH. The light-colored amorphous precipitate that deposited was exhaustively extracted with chloroform. The residues from the extracts amounted to 0.08 g. On crystallization, the first of them gave unchanged speciosine (from ethanol), and the second gave colchamine mp 180-181°C (from acetone); a mixture with an authentic sample melted without depression; R_f 0.62. Authentic colchamine: mp 180-181°C, R_f 0.63. The IR spectra of the two samples coincided. For speciosine, R_f 0.81.

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