ELEMENTARY COMPOSITION OF SOME IONS IN THE MASS SPECTRA OF STROPHANTHIDIN AND PERIPLOGENIN

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The results of a comparison of the mass spectra of a series of cardenolides with an oxygen function at C_{19} have permitted the conclusion that the most probable composition for the ion with m/e 160 is $C_{12}H_{16}$ [1]. This ion has a high intensity in the spectra of strophanthidin, its 3β-monoacetate, 16-hydroxystrophanthidin, and strophanthidol. Shortly before the publication of the paper referred to [1] a communication appeared from Brown et al. [2] in which the ion with m/e 160 in the spectrum of strophanthidin was ascribed the composition $C_{11}H_{12}O$. The mechanism for the formation of this ion by the cleavage of the C_9-C_{11} and C_8-C_{14} bonds with the subsequent ejection of two molecules of water and the retention of the aldehyde group at C_{10} proposed by these authors raised doubts. A study of metastable transitions has shown that the fragmentation of the cardenolide skeleton begins, as a rule, after the elimination of all or almost all the oxygen-containing substituents of rings A/B of strophanthidin and its near analogs. For a check, the elementary composition of the ion with m/e 160 has been measured on an MS-902 instrument (M. I. Gorfinkel', Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR). In the interval corresponding to the mass number 160, no peaks were found other than that corresponding to the composition $C_{12}H_{16}$.

The elementary compositions of a number of ions in the spectrum of periplogenin have been determined on an MS-3301 Soviet high-resolution mass spectrometer. It must be considered of the greatest interest to have established the composition of the maximum ion with m/e 318 – $C_{19}H_{26}O_4$ –, which confirms its formation in two stages by the ejection from M^+ of a molecule of water and a molecule of butadiene. The compositions of the ions with m/e 262 ($C_{17}H_{26}O_2$) and 219 ($C_{15}H_{23}O$) show that they are analogs of the ions c (M−18−110) and α of the digitoxigenin spectrum [1-4].

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