FRAGMENTATION OF NECIC ACIDS

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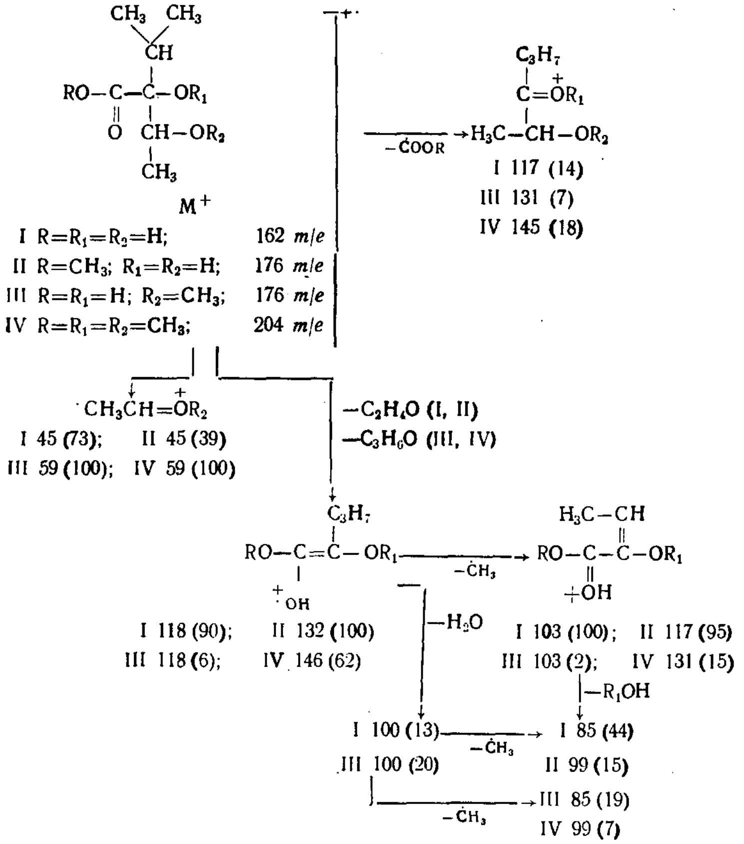
We have previously studied the mass spectra of some pyrrolizidine alkaloids and amino alcohols of the heliotridane series [1]. In the present communication we discuss the process of fragmentation of the necic acids obtained by the hydrolysis of the alkaloids, and also that of the methyl esters of these acids.



Scheme 1

The molecular ion is absent from the spectra of viridifloric acid (I) [2], its methyl ester (II), heliotric acid (III) [3], and methyl O,O'-dimethylviridiflorate (IV). The main directions of decomposition of compounds (I-IV) consist in the cleavage of the C−C diol bond (Scheme 1), which confirms the analogy with those fragments of the spectra of the alkaloids [1] that are formed when the charge is localized in the side chain. If the charge is present on the $-OR_2$ oxygen, strong ions with m/e 45 and 59 arise. The ejection of a C_2H_4O fragment (I, II) or a C_3H_6O fragment (III, IV) takes place, as is usually considered [1, 4, 5], through a six-membered state with migration of the hydrogen atom to the carbonyl oxygen. In compounds (III and IV) the hydrogen of the C-methyl group migrates. In the corresponding decomposition of the acid (I) and the ester (II) the hydrogen of the secondary OH group passes to the oxygen of the C=O group, as we have established by means of the spectrum of the OD analog of (II) where the ion with m/e 132 $(M-C_2H_4O)$

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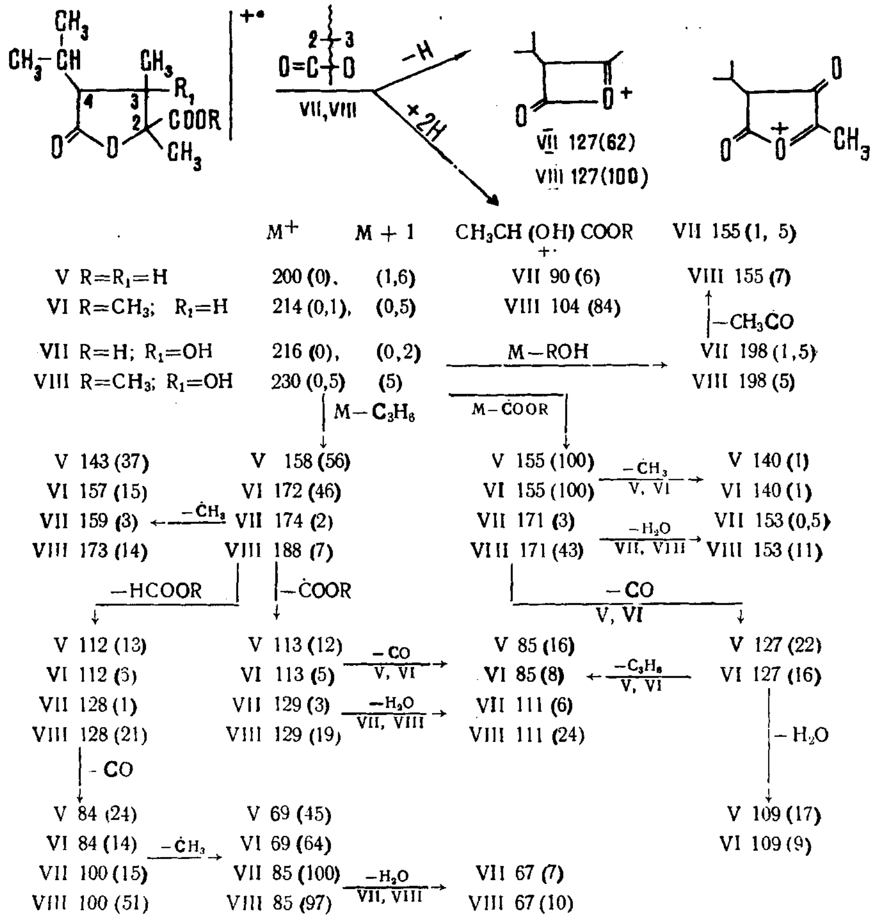
is displaced by two m.u. The subsequent fragmentation of this ion consists in the alternative elimination of $\dot{C}H_3$ from the isopropyl group and a molecule of H_2O. A comparison of the spectra of the isomers (II) and (III) shows that the ions M − 45 and M − 59 are formed by the splitting off of a $\dot{C}OOR$ radical, since the ion M − 45 is absent from the spectrum of (II) and the ion M − 59 is absent from the spectrum of (III). The intensity of the ions M − COOR (where R is a pyrrolizidine nucleus) is also high in the spectra of the N-oxides of some alkaloids, which can be explained by a decrease in the proportion of ions with localized charges in the pyrrolizidine nucleus.



Scheme 2

The mass spectra of the lactone acids obtained on the hydrolysis of the macrocyclic pyrrolizidine alkaloids have been characterized in their broad outlines by A. Klásek [6] and S. Kohlmünzer [7]. We have investigated fragmentation of incanic acid (V) [8] and of trichodesmic acid (VII) [9] and their methyl esters (VI and VIII). The presence of a larger $(M+1)^+$ peak than of the M^+ peak is characteristic of all the spectra studied and also of the spectrum of tetrahydroclivoneic acid [6]. The fragmentary ions (V-VIII) are formed by the elimination of molecules of propylene (according to McLafferty [10]), HCOOR, CO, and H_2O, and the radicals $\dot{C}OOR$ and $\dot{C}H_3$ (Scheme 2).

The presence of an OH group in the molecules of (VII) and (VIII) makes some directions of decomposition that are characteristic for (V) and (VI) insignificant and causes the appearance of new ions. Thus, the cleavage of the C_2-C_3 and OC−O bonds leads to the appearance of fragments with m/e 127 and 90 (VII) and 104 (VIII). The deuteration of (VI) and (VIII) with heavy water showed that about 50% of the ions with m/e 127 are formed with the transfer of the hydrogen of the OH group to the neutral fragment. On the other hand, 100% of the ions with m/e 90 and 104 include this hydrogen. In the spectra of (VII) and (VIII), the ions M − ROH do not contain the isotopic label. This means that the water from the M^+ ion of (VII) separates out in the form of D_2O and the methanol from the M^+ ion of (VIII) in the form of CH_3OD. This characteristic of the fragmentation process explains the appearance of an ion with m/e 155 in the spectra of (VII) and (VIII).

SUMMARY

1. The main direction of fragmentation of the monobasic necic acids of the viridifloric type is due to the cleavage of the diol C—C bond.

2. The processes of fragmentation of the lactone acids incanic and trichodesmic acids differ considerably because of the presence of an OH group at C_3 in the molecule of the latter.

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