THE PYROLYSIS OF THE ACONITUM ALKALOIDS

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A characteristic feature of the aconitum alkaloids with an acetoxy group at C_8 is the unusual ease of elimination of a molecule of acetic acid [1-3]. We have reported previously that this process accompanies the mass-spectrometric decomposition of these compounds and that the presence of intense peaks of M−AcOH and M−AcOH−OCH_3 or M−OCH_3−AcOH can serve as a reliable proof of the presence of an acetoxy group at C_8 [4].

We have considered the mass spectra of aconitine (I), acetylbenzoyltalatisamine (II), diacetyltalatisamine (III), and dehydroacetyltalatisamine (IV). The thermal instability of these compounds on mass spectrometry appears in the fact that at a temperature of 100°C and above acetic acid is split off, and its molecular ion can be recorded at m/e 60. (During the process, the vacuum in the ionization chamber deteriorates.) Furthermore, the occurrence of pyrolysis is confirmed by the fact that when a sample remains in the inlet system for a long time (20-30 min), the peaks of the ions M and M−OCH_3 decrease relatively, and the peaks M−AcOH and M−AcOH− OCH_3 increase. At lower temperatures (70-80°C), no pyrolytic decomposition takes place: the inlet is fairly stable. The formation of the ions M−AcOH under the given conditions is apparently due to electron impact (scheme a). A process connected with the detachment of an acetoxy radical competes successfully with this direction of fragmentation (scheme b). The peak of the ion M−AcO is the strongest in the spectrum of (IV) (Table 1), and this fact can apparently be used to explain the cause of the above-mentioned ease of the elimination of acetic acid. Ring E in the aconitum alkaloids has the distorted chair form in solutions [5, 6], while in the crystalline state, according to Birnbaum [7], it has the form of a strongly distorted boat. In both cases (in the chair form, the substituents at C_8, C_{10}, and C_{15} have the axial orientation), when the substituents in ring E are voluminous, their mutual repulsion favors the ejection of acetic acid. Consequently, the ease of pyrolysis must rise in the sequence (I) ≈ (II) ≥ (III) > (IV) (see Table 1). The relative ease of pyrolysis can be followed by comparing the intensities of the M−AcOH and M−AcO peaks. The elimination of acetic acid takes place most readily in (I) and (II) and considerably less readily in (IV), while (III) occupies an intermediate position.

a

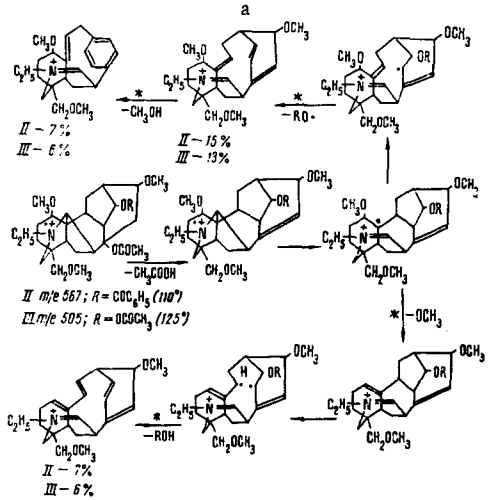

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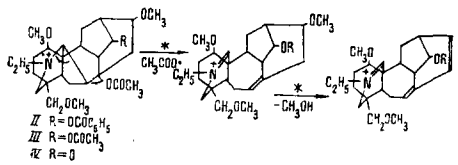
TABLE 1

Ions	Relative intensity, %					
	I (125°)	II (110°)	III (125°)	III (70°)	IV (105°)	IV (75°)
M	—	0,1	2	3,5	3,5	6
M−OCH_3	—	0,3	100	100	100	100
M−AcOH	6	40	22	7	6	5
M−AcOH−OCH_3 / M OCH_3−AcOH / M−AcO−CH_3OH	100	100	33	19	22	14
M−AcO	1	6	14	10	16	16

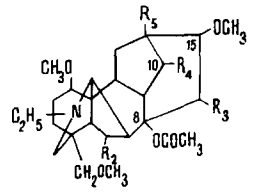
b



II R=$OCOC_6H_5$
III R=$OCOCH_3$
IV R=O

In diacetyltalatisamine (III) at 125°C, fragmentation by scheme a is the main process; with a reduction in the temperature, scheme b becomes the main one. In dehydroacetyltalatisamine at 105 and 75°C, decomposition by scheme b predominates, but here its dependence on the temperature is considerably less. The increase in the ease of pyrolysis from (IV) to (I) is also shown in a reduction in the intensity of the peak of molecular ions in the same direction. In acetylbenzoyltalatisamine it is extremely low (0.1%), and in aconitine it is absent. The factor mentioned above apparently also explains the mobility of the methoxy groups in the C_8 and C_{15} positions, which favors the ejection of a molecule of methanol [4, 8].

The decrease in the ease of pyrolysis from (I) to (IV) also takes place when the reaction is performed under the usual conditions [6]. While 5 min is necessary for the complete elimination of acetic acid in the case of (I-III), 15 min is required for (IV). In the latter case, the process was followed chromatographically (see Experimental).



I $R_1=R_5=R_3=OH$; $R_2=OCH_3$; $R_4=OCOC_6H_5$

IV $R_1=R_2=R_3=R_5=H$; $R_4=O$

EXPERIMENTAL

The mass spectra were taken on an MKh-1303 instrument fitted with a system for the direct introduction of the sample into the ion source at an ionizing voltage of 40 eV. The molecular weights were determined mass spectrometrically.

Dehydrotalatisamine. With cooling, a solution of 0.2 g of talatisamine in 30 ml of acetone was added to 0.2 g of chromium trioxide in 10 ml of acetone. The mixture was left at 25°C for two days. The acetone was evaporated off, and the residue was dissolved in 5% sulfuric acid, and the solution was made alkaline with sodium carbonate. The precipitate was filtered off, and the aqueous mother solution was shaken with ether. Distillation of the solvent from the extract gave a crystalline substance with mp 127-131°C (ether). Mol. wt. 419. IR spectrum: 1750 cm^{-1} (KBr).

Acetyldehydrotalatisamine (IV). A mixture of 0.2 g of dehydrotalatisamine and 3 ml of acetyl chloride was left at 25°C for 7 days. Then the reaction mixture was evaporated, the residue was dissolved in 5 ml of cooled 5% sulfuric acid, the solution was washed with ether, and, after it had been made alkaline, the reaction product was extracted with ether. This gave an amorphous, chromatographically homogeneous substance with mol. wt. 461.

Pyrolysis of Acetyldehydrotalatisamine. Compound (IV) (0.1 g) was heated in vacuum at 185-195°C for 6 min. On a chromatogram, product A showed two spots with R_f 0.8 and 0.9. This product was again subjected to pyrolysis for 5 and 10 min. As a result of 15-min pyrolysis, the chromatogram showed a single spot with R_f 0.9. To confirm the assumption that the second spot (R_f 0.8) corresponded to the starting material [the initial (IV) has R_f 0.8], we saponified product A in 10% methanolic caustic potash. A chromatogram showed two spots with R_f 0.9 and 0.5, the latter being identical with the R_f value of dehydrotalatisamine.

SUMMARY

It has been shown that with a decrease in the number of substituents in ring E the ease of pyrolysis of the aconitum alkaloids falls.

The directions of the fragmentation of these alkaloids during mass spectrometry as a function of the temperature and the functional groups present have been determined.

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