Mass Spectra of Some Branched-Chain Aliphatic Lactones

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The mass spectra of some branched-chain γ- and δ-lactones have been determined. The spectra differ markedly from the spectra of the corresponding straight-chain lactones. The typical cleavage of these branched-chain lactones is the loss of carbon dioxide from the molecular ion. In both series the lactones having a methyl group in different position are recognizable on the basis of their different peak intensity ratios. Distinguishing between the geometrical isomers is, however, very difficult. Only small differences were found in the mass spectra of *cis*- and *trans*-4-methyl-5-hydroxyhexanoic acid lactones.

Gas chromatographic retention times in two different columns for the γ- and δ-lactones investigated are given.

For the present only one publication [10] appears in the literature concerning the mass spectra of some methyl-substituted δ-lactones. Since none of these spectra resembles the mass spectrum of a new branched-chain lactone compound recently isolated from milk in this laboratory [1] another series of methyl-substituted γ- and δ-lactones, namely 2-, 3- and 4-methyl-4-hydroxypentanoic and 4-methyl-4-hydroxyhexanoic acid lactones, and in addition 2-, 3-, 4- and 5-methyl-5-hydroxyhexanoic acid lactones, were synthesized for mass spectrometric identification. The mass spectra were determined in a gas chromatograph-mass spectrometer unit using a molecular separator made from Teflon tubing. The spectra are seen in Figs. 1—8. The peaks $m/e=28$, 32, 40, and 44 originating from N_2, O_2, Ar, and CO_2, respectively, have been removed from the spectra.

As can be seen, these branched-chain lactones do not give such characteristic peaks obtained in the case of straight-chain γ- and δ-lactones,[2,3] which give the intense peaks at $m/e=85$ and 99, for γ- and δ-lactones, respectively, arising from the rupture of the bond between the side chain and the ring. The typical cleavage in all compounds investigated is the loss of carbon dioxide from the molecular ion forming the peaks at $m/e=70$ and 84 for C_6 and C_7 compounds, respectively. Only with 5-methyl-5-hydroxyhexanoic

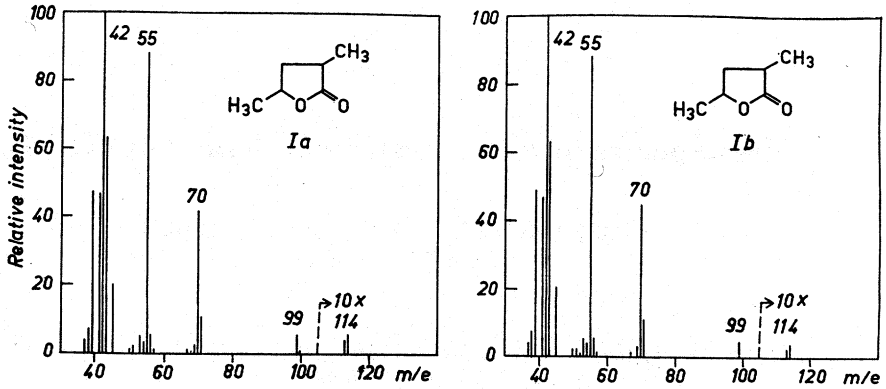

Fig. 1. Mass spectra of 2-methyl-4-hydroxypentanoic acid lactones; a. faster moving compound, b. slower moving compound.

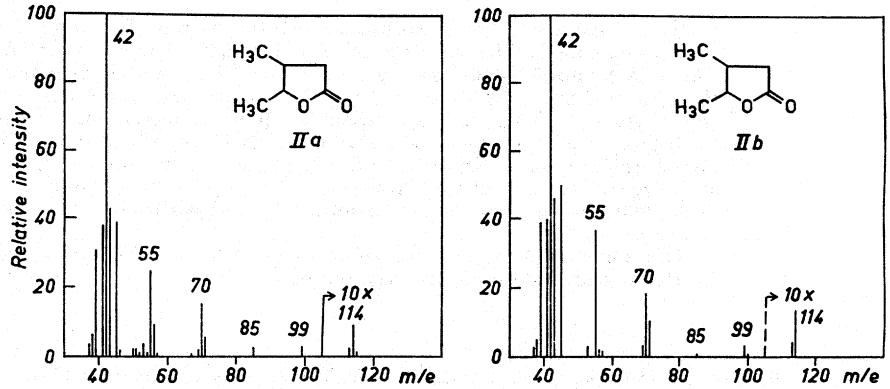

Fig. 2. Mass spectra of 3-methyl-4-hydroxypentanoic acid lactones; a. faster moving compound, b. slower moving compound.

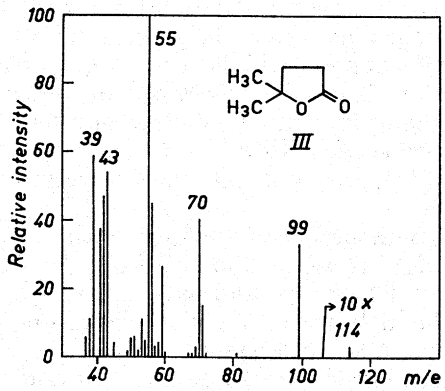

Fig. 3. Mass spectrum of 4-methyl-4-hydroxypentanoic acid lactone.

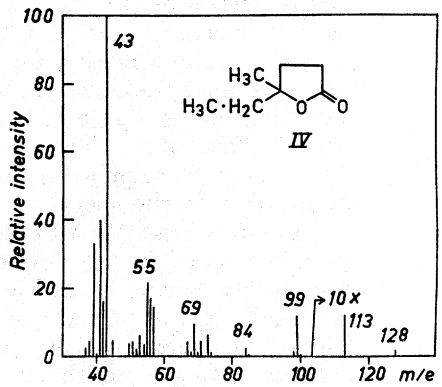

Fig. 4. Mass spectrum of 4-methyl-4-hydroxyhexanoic acid lactone.

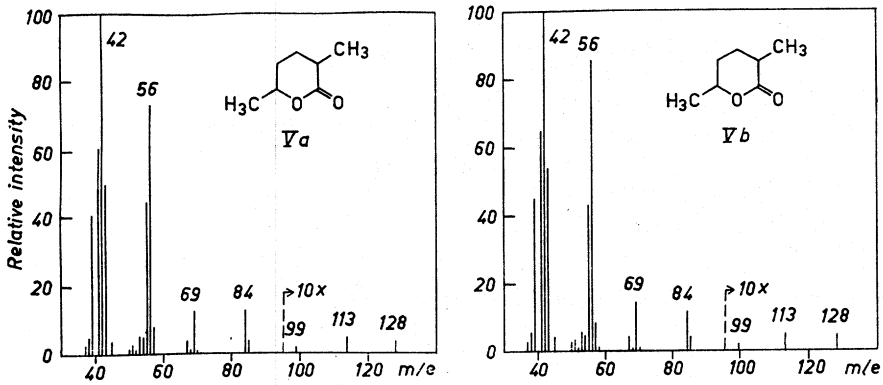

Fig. 5. Mass spectra of 2-methyl-5-hydroxy hexanoic acid lactones; a. faster moving compound, b. slower moving compound.

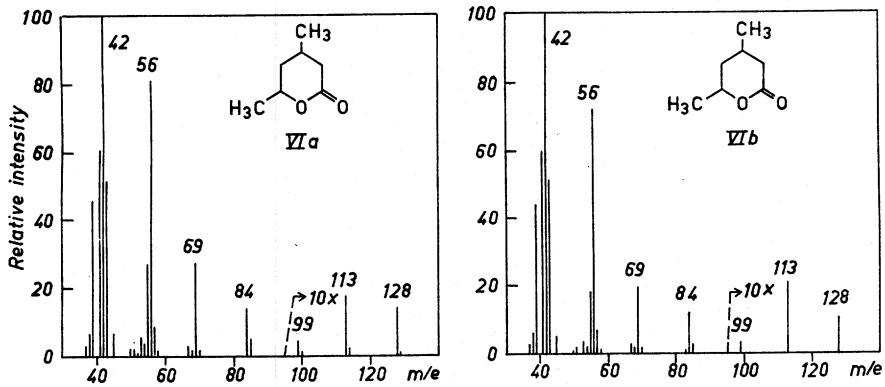

Fig. 6. Mass spectra of 3-methyl-5-hydroxy hexanoic acid lactones; a. faster moving compound, b. slower moving compound.

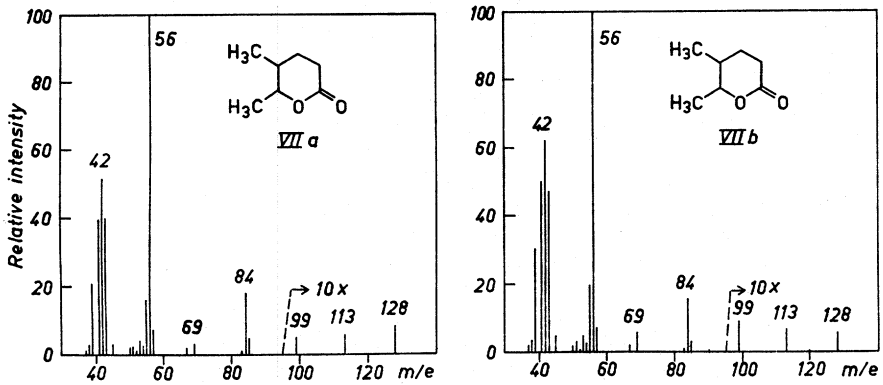

Fig. 7. Mass spectra of 4-methyl-5-hydroxyhexanoic acid lactones; a. faster moving (*trans*) compound, b. slower moving (*cis*) compound.

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