

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 publication¹⁰ 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 laboratory¹ 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

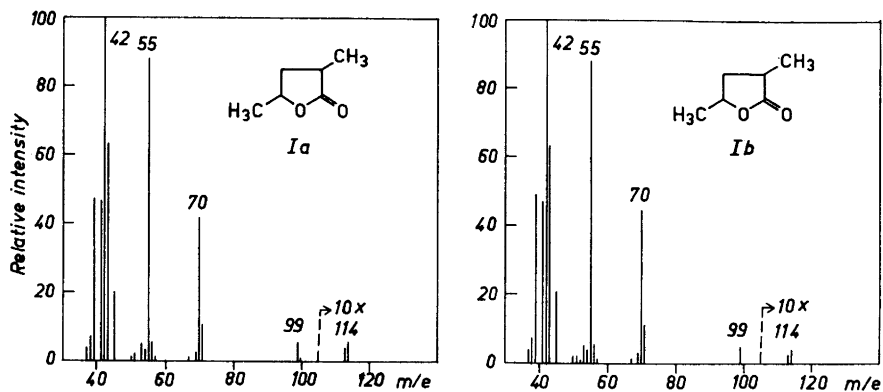


Fig. 1. Mass spectra of 2-methyl-4-hydroxypentanoic acid lactones; a. faster moving compound, b. slower moving compound.

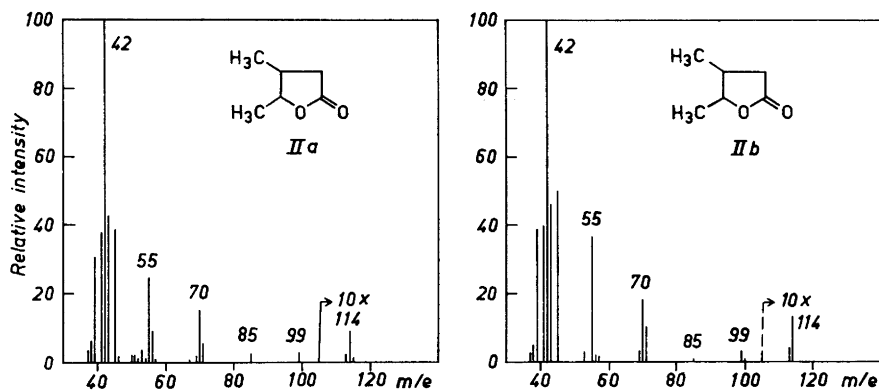


Fig. 2. Mass spectra of 3-methyl-4-hydroxypentanoic acid lactones; a. faster moving compound, b. slower moving compound.

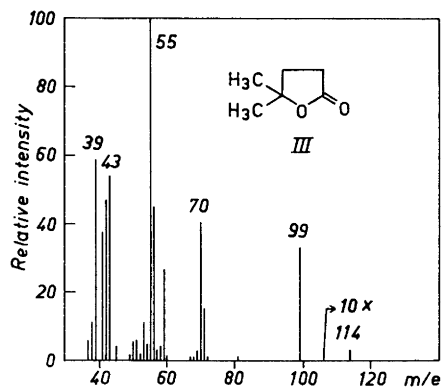


Fig. 3. Mass spectrum of 4-methyl-4-hydroxypentanoic acid lactone.

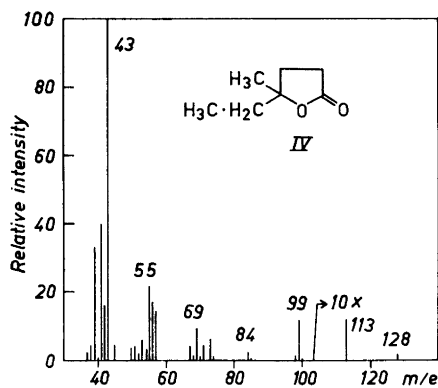


Fig. 4. Mass spectrum of 4-methyl-4-hydroxyhexanoic acid lactone.

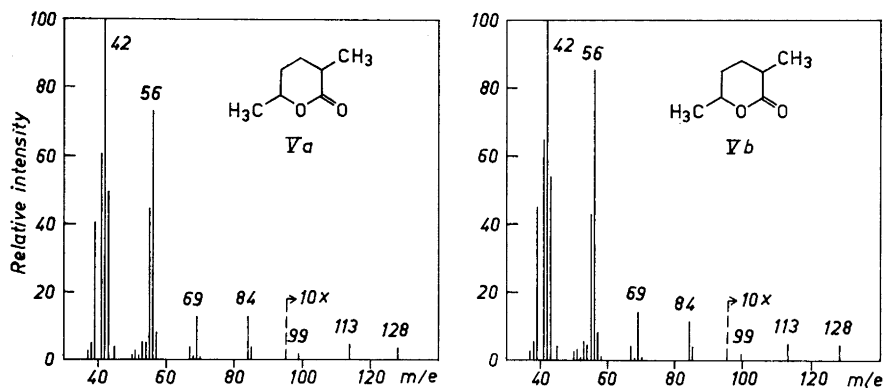


Fig. 5. Mass spectra of 2-methyl-5-hydroxy hexanoic acid lactones; a. faster moving compound, b. slower moving compound.

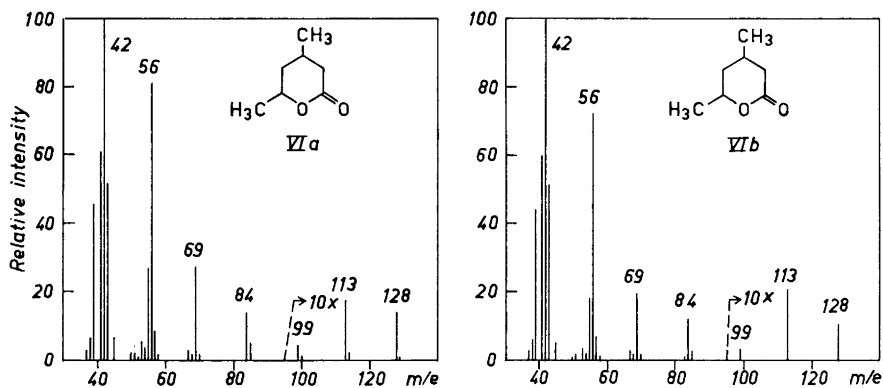


Fig. 6. Mass spectra of 3-methyl-5-hydroxy hexanoic acid lactones; a. faster moving compound, b. slower moving compound.

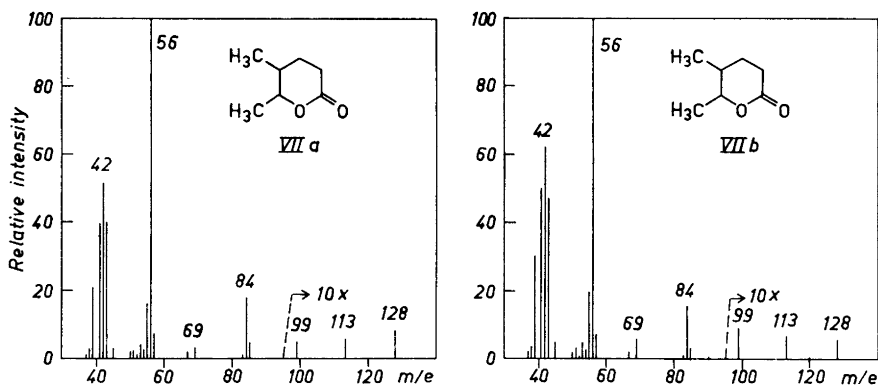


Fig. 7. Mass spectra of 4-methyl-5-hydroxyhexanoic acid lactones; a. faster moving (*trans*) compound, b. slower moving (*cis*) compound.

acid lactone (VIII), which has a tertiary carbon atom at the position 5, is the peak at $m/e=84$ negligible. Of the normal γ - and δ -lactones^{2,3} only the γ -C₄, γ -C₅, and δ -C₅ lactones show loss of carbon dioxide. The mass spectra of the lactones with a tertiary carbon atom (III, IV, and VIII) differ from the other

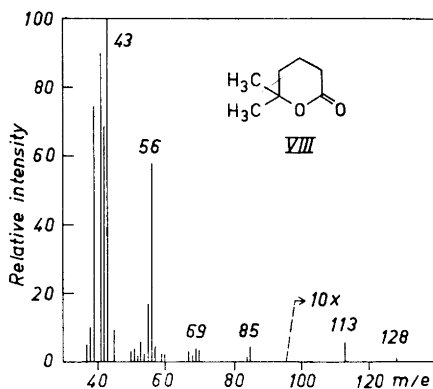


Fig. 8. Mass spectrum of 5-methyl-5-hydroxyhexanoic acid lactone.

compounds to a certain extent. The peak at $m/e=M-29$ ($m/e=85$ or 99) is completely absent in the spectra of compounds III and VIII and in addition the peak at $m/e=99$ ($M-15$) compound III has a considerably higher intensity than other γ -lactones. The intense peak at $m/e=43$ of VIII also is typical of this compound only.

Although the mass spectra of the positional isomers in γ - and δ -lactone series are so similar, it is possible to distinguish all the isomers on the basis of the different peak intensity ratios. Distinguishing between the geometrical isomers is in contrast very difficult. Only in the spectra of the isomers of 4-methyl-5-hydroxyhexanoic acid lactones can small differences be detected with certainty. In the *trans*-isomer¹ (VIIa) the peak intensities increase in the order $m/e=99$, 113, and 128, while these intensities of the *cis*-isomer (VIIb) decrease in the same order.

The intensities of the molecular ions of branched-chain lactones are, as is to be expected, lower than those of the corresponding straight-chain lactones, and those of the compounds with tertiary carbon atoms (III, IV, and VIII) are lower still.

The geometrical isomers of these lactones with the exception of the isomers of 2-methyl-4-hydroxypentanoic acid lactone (Ia and Ib), are in general separated very well by gas chromatography on an FFAP-column ($1/8'' \times 4$ m). The retention times of these lactone compounds on Carbowax 20M and FFAP columns are presented in Table 1.

Table 1. Gas chromatographic retention times (in min) of the synthesized branched-chain γ - and δ -lactones on Carbowax 20M and FFAP columns.

Compound	20 % Carbowax 20 M (1/8" \times 2 m) at 150°C		20 % FFAP (1/8" \times 4 m) at 190°C	
	a	b	a	b
I	4.6	4.7	17.5	17.8
II	5.3	6.9	19.9	25.7
III	4.9	—	18.7	—
IV	7.1	—	26.6	—
V	7.9	9.0	30.3	33.7
VI	10.0	10.7	35.7	37.7
VII	12.1	14.2	41.8	48.3
VIII	10.1	—	36.2	—

EXPERIMENTAL

The mass spectra were determined with a gas chromatograph-mass spectrometer (modified CEC Model 21-401) unit operated under the following conditions: 70 V electrons, ionizing current 100 μ A and ion source temperature 150°C, exponential voltage scan. A 1/8" \times 4 m 5 % FFAP column and temperature programming 2°C/min from 60°C to 230°C were used in the gas chromatography apparatus. The gas chromatograph was connected to the mass spectrometer *via* a molecular separator made from Teflon tubing⁴ (ID 0.3 mm, OD 0.6 mm, 10 m long) placed in a heated (280–290°C) vacuum chamber. About 90 % of the effluent gas (He, 10 ml/min) was pumped out in the molecular separator. The spectra were recorded in 20 sec with a Visicorder 1706 oscillograph using an Atlas DC 60 direct current amplifier.

4-Methyl-4-hydroxypentanoic (III), 4-methyl-4-hydroxyhexanoic (IV), and 5-methyl-5-hydroxyhexanoic (VIII) acid lactones were synthesized by the reaction of two moles of methyl- or ethylmagnesium iodides with the corresponding 4- or 5-ketoacids, according to Porter.⁵

2-Methyl-4-hydroxypentanoic acid lactone (I) was obtained by the condensation of ethyl 2-bromopropionate with ethyl 3-ketobutanoate followed by acid hydrolysis, reduction with sodium borohydride and acidification. This compound has been previously prepared by Trave and Garanti⁶ by another route. The following lactones were synthesized by an analogous procedure: 3-Methyl-4-hydroxypentanoic acid lactone (II) from ethyl bromoacetate and ethyl 2-methyl-3-ketobutanoate.

2-Methyl-5-hydroxyhexanoic acid lactone (V), from methyl 2-methyl-3-bromopropionate and ethyl 3-ketobutanoate. Mohr⁷ obtained this lactone by the reaction of potassium cyanide with 2,5-dibromohexane followed by hydrolysis.

3-Methyl-5-hydroxyhexanoic acid lactone (VI) from ethyl 3-bromobutyrate and ethyl 3-ketobutanoate. Longley *et al.*⁸ have prepared this compound by catalytic hydrogenation of 2-methoxy-4-methyl-3,4-dihydropyrene.

4-Methyl-5-hydroxyhexanoic acid lactone (VII) from ethyl 3-bromopropionate and ethyl 2-methyl-3-ketobutanoate.⁹

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