

## The Mass Spectra of Some Aliphatic Lactones

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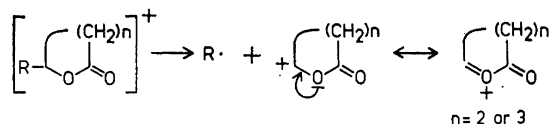
The mass spectra of eight  $\gamma$ -lactones and eight  $\delta$ -lactones have been determined. Both homologous series give rise to characteristic peaks at  $m/e = 85$  and  $99$  for  $\gamma$ - and  $\delta$ -lactones, respectively. The abundance of the molecular ion is in general very low and it is difficult to determine the molecular size of an unknown lactone on the basis of the mass spectra alone. The best criterion for this is the gas chromatographic retention time.

Gas chromatographic retention times in a poly(propylene glycol) column at  $175^\circ\text{C}$  for the  $\gamma$ - and  $\delta$ -lactones investigated are given.

In the course of studies on the flavour substances of milk we have found some lactone compounds. Since the mass spectrometric identification without any reference compounds, especially in the case of the higher lactones, is very difficult, we have determined the mass spectra of some saturated aliphatic  $\gamma$ - and  $\delta$ -lactones in the hope of obtaining more information about the fragmentation processes. At the time of writing only the spectra of  $\gamma$ -butyro- and  $\gamma$ -valerolactone appear in the literature.<sup>1</sup>

The mass spectra of the  $\gamma$ - and  $\delta$ -lactones are seen in Figs. 1-4. The peaks such as  $m/e = 28, 32,$  and  $40$ , originating partially from  $\text{N}_2, \text{O}_2,$  and  $\text{Ar}$ , respectively, have been removed from the spectra, since it is very difficult to estimate their true intensity by difference from the background.

As can be seen the most favoured cleavage is the rupture of the bond between the side chain and the ring. The cleavage of the carbon-carbon bond next to the hetero-atom is very common in this type of molecule. The free electron pair of the hetero-atom stabilizes the positive charge on the adjacent carbon atom.<sup>2</sup>



The intense peaks at  $m/e = 85$  and  $99$  are formed by this type of cleavage and are characteristic of  $\gamma$ - and  $\delta$ -lactones, respectively. The formation of the peak at  $m/e = 85$  in the spectra of  $\delta$ -lactones can arise from the easy rearrangement

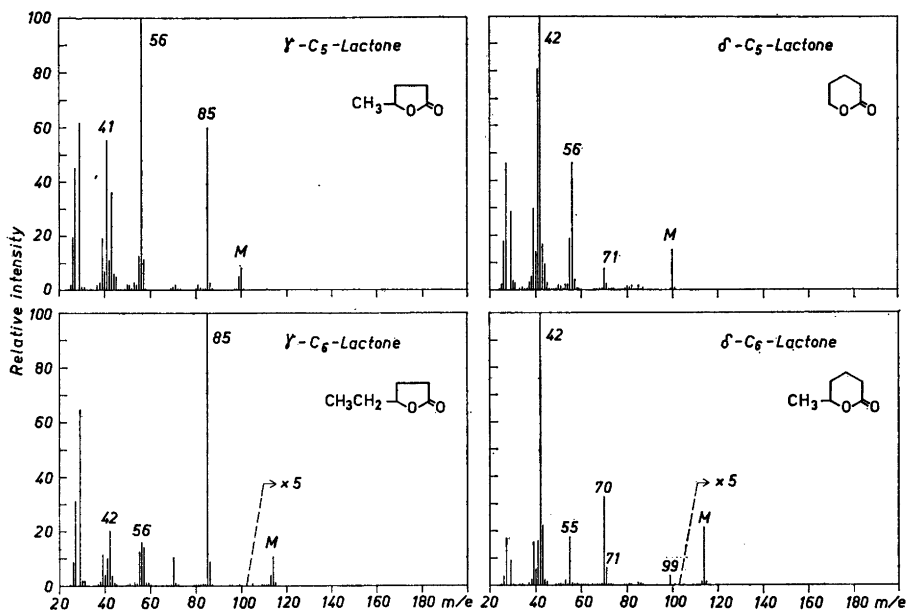


Fig. 1. Mass spectra of  $\gamma$ - and  $\delta$ -C<sub>5</sub>-C<sub>6</sub>-lactones.

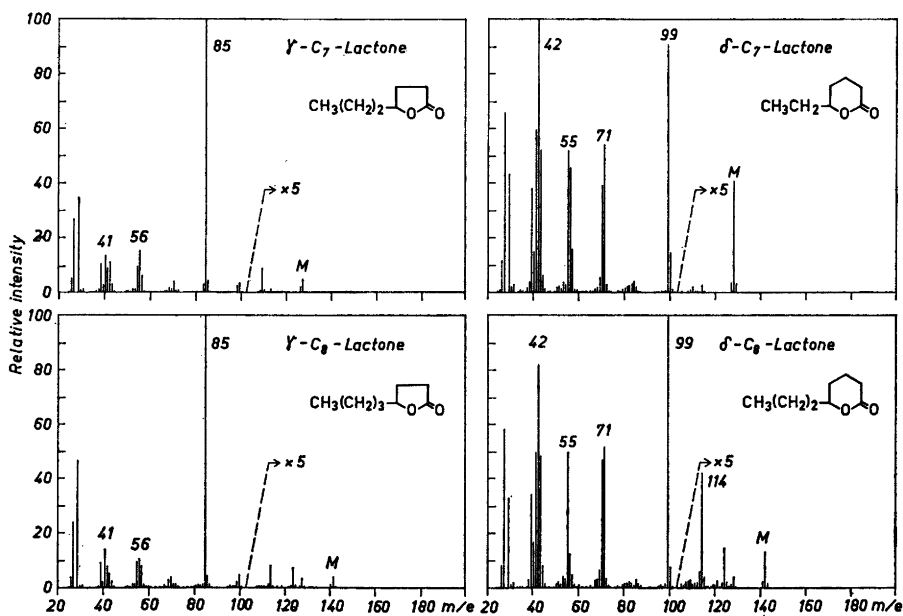
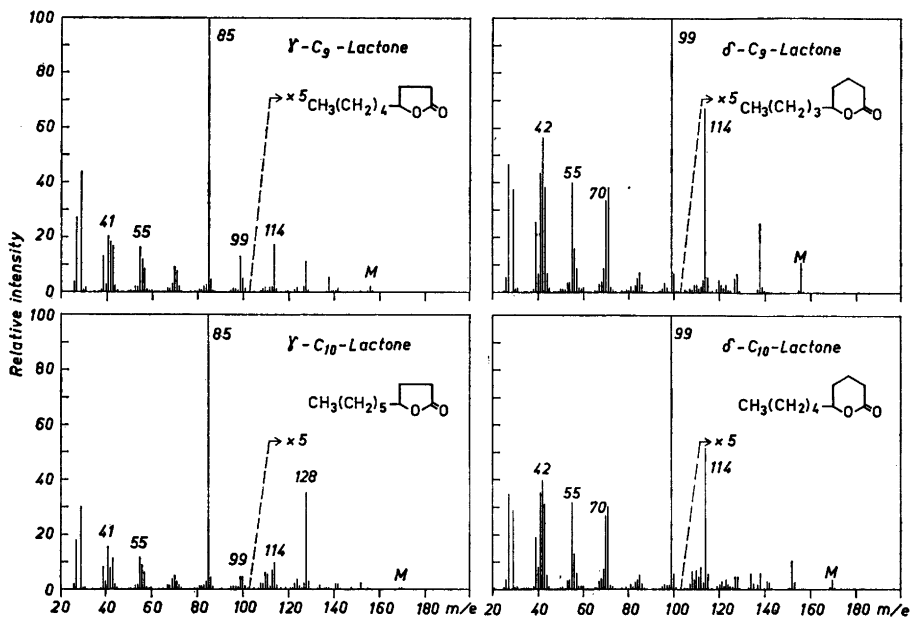
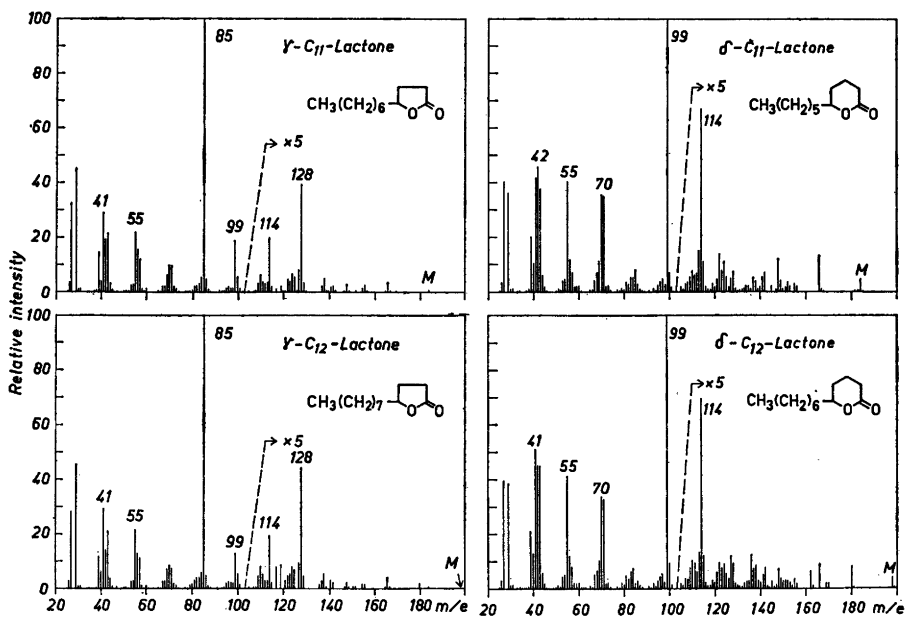


Fig. 2. Mass spectra of  $\gamma$ - and  $\delta$ -C<sub>7</sub>-C<sub>8</sub>-lactones.

Fig. 3. Mass spectra of  $\gamma$ - and  $\delta$ -C<sub>9</sub>-C<sub>10</sub>-lactones.Fig. 4. Mass spectra of  $\gamma$ - and  $\delta$ -C<sub>11</sub>-C<sub>12</sub>-lactones.

of the molecular ion to the corresponding  $\gamma$ -lactone ion and similarly the peak at  $m/e = 99$  in the spectra of  $\gamma$ -lactones from the rearrangement of the  $\gamma$ -lactone molecular ion to the  $\delta$ -lactone ion. The peak at  $m/e = 99$  of  $\gamma$ -lactones is very weak up to the  $C_8$ -lactone, but intensifies then somewhat.

The intensity of the molecular ion is in general very low, but even so it is, with the  $\delta$ -lactones about 2–3 times greater than with the corresponding  $\gamma$ -lactones. The determination of the size of the side chain by difference is not easy, especially if some higher molecular weight impurities are present. For example, an alkyl substituent does not lead to a significant fragment. This being the case, the best criterion for the molecular size of an unknown lactone is the gas chromatographic retention time.

For distinguishing the  $\gamma$ - and  $\delta$ -lactones some other characteristic peaks besides  $m/e = 85$  and  $99$  are also seen in the spectra. The moderately intense peak pair at  $m/e = 70$  and  $71$  together with the strong peak at  $m/e = 42$  are typical of  $\delta$ -lactones. The fragment at  $m/e = 42$  occurs in very low intensity in the spectra of  $\gamma$ - $C_5$ - $C_{12}$ -lactones, but is, however, for  $\gamma$ -butyrolactone the second strongest peak in the spectrum.<sup>1</sup> This fragment ( $C_2H_2O^+$ ), which is formed by the rupture of two bonds of the ring, contains the carbonyl oxygen.<sup>1</sup> The peaks at  $m/e = 70$  and  $71$  are formed possibly from the fragment at  $m/e = 99$  by the expulsion of CO (or HCO) yielding perhaps a tetrahydrofuryl ion.

The weak peak at  $m/e = M-18$  by the higher lactones indicates the loss of water from the molecular ion. This elimination must be a very complicated process, involving several bond ruptures and rearrangements, for example with cyclohexanone.<sup>3</sup>

After the sending in of this report, another study of the mass spectra of  $\gamma$ -,  $\delta$ - and  $\epsilon$ -lactones has been published.<sup>6</sup> The mass spectra in both investigations are in general very similar. In our spectra the intensity of the peaks at  $m/e = 85$  by  $\delta$ -lactones and at  $m/e = 99$  by  $\gamma$ -lactones are considerably greater. Since the  $\gamma$ - and  $\delta$ -lactones are separated very well in the gas chromatographic column used, it is not possible that the sample contains the corresponding  $\gamma$ - or  $\delta$ -lactone as impurity. It is most likely that the isomerisation has taken place, after the collection of the sample, under the influence of water,

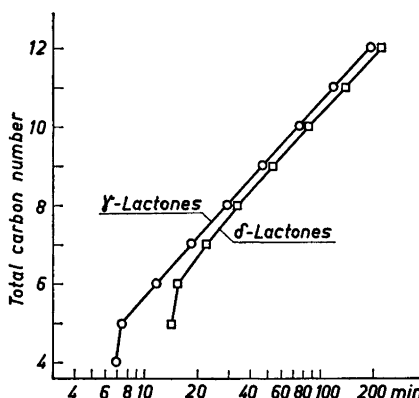


Fig. 5. Gas chromatographic retention times of the  $\gamma$ - and  $\delta$ -lactones investigated in a poly(propyleneglycol) (LB-550-X, 20%) column ( $\phi$  4.5 mm, 120 cm) at  $175^\circ\text{C}$  with a  $N_2$  flow of 45 ml/min. Air = 0.

which is always present in the effluent gas emerging from a polypropylene glycol column. Later it was observed that, if the sample was collected from an apiezon grease column having much less resolving power than the polypropylene glycol column, the intensity of the peak at  $m/e = 85$  by  $\delta$ -lactones and at  $m/e = 99$  by  $\gamma$ -lactones decreased considerably.

### EXPERIMENTAL

The mass spectra were determined with a mass spectrometer, modified CEC Model 21-401, under following conditions: 70 V electrons, ionizing current of 100  $\mu$ A and ion source temperature of 150°C, exponential voltage scan. A condenser (400  $\mu$ F) was first charged to 1500 V and discharged then through the voltage divider network of the Isatron control ( $R = 50$  k $\Omega$ ). The spectra were recorded in 20-40 sec with an oscillograph "Visicorder 1706" using an "Atlas DC 60" direct current amplifier.

The substances were first subjected to gas chromatography. Both homologous series were separated very well at 175°C in a relatively short (120 cm) poly(propylene glycol) column as can be seen in Fig. 5. The pure samples were collected in a small glass trap in liquid nitrogen and then connected with a Teflon tube to the sample inlet valve of the mass spectrometer.

The  $\gamma$ -lactones were synthesized from the corresponding 2-alkenoic acids, obtained by the Knoevenagel reaction from aldehydes and malonic acid, by the action of 85 % sulphuric acid at 85°C according to Ota *et al.*<sup>4</sup> The purity of the  $\gamma$ -lactones formed, containing less than 1 % of the corresponding  $\delta$ -isomer, was in general over 99 %.

The  $\delta$ -valerolactone was prepared from glutaric acid ethyl ester chloride by sodium borohydride reduction in diglyme followed by hydrolysis and acidification. The other  $\delta$ -lactones were obtained from the corresponding 5-oxoalkanoic acids<sup>6</sup> by sodium borohydride reduction in water. The products contained only the  $\delta$ -isomer desired.

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