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The Mass Spectra of Methyl Oleate, Methyl Linoleate, and Methyl Linolenate

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In connexion with studies on the mass spectra of esters of long-chain fatty acids we have examined a number of unsaturated esters. In general, unsaturated esters give more complex spectra than esters of saturated, normal-chain acids [1,2]. In order to interpret the spectrum of methyl oleate we have examined the isomeric 2-, 6-, 8-, 10-, 13- and 17-octadecenoates, but it has proved desirable to study also the ester of an acid with the double bond at position 4:5 or 5:6. None of these acids has been described in the literature. Synthetic work will therefore have to be undertaken and may also be required for the interpretation of the spectra of the di- and triethenoid esters. In view of the common occurrence of oleic, linoleic, and linolenic acids, however, and the analytical possibilities afforded by the mass spectrometer [3], a brief description of the mass spectra of their esters will be made.

The mass spectrum of methyl oleate (Fig. 1a) shows that the introduction of a double bond in the hydrocarbon chain leads to a fragmentation pattern considerably different from that of saturated methyl esters. Compared with methyl stearate [2], the peaks in the low-mass range due to fragments containing an intact methoxycarbonyl group are much less prominent than those due to hydrocarbon fragments. The peak at $m/e = 55$ ($C_4H_7^+$) is of the same order of magnitude as the rearrangement peak at $m/e = 74$. In the sequence of the higher-methoxycarbonyl-type fragments, the peak at $m/e = 87$ is the most prominent one (45 % of the base peak). The higher members of this series of peaks do not show the marked rhythmic variation in height which is characteristic of methyl esters of normal-chain saturated acids. In the high-mass range, marked peaks are found at $m/e = 296$, 264, 222, and 180. The peak due to the molecule-ion at $m/e = 296$ is relatively small, and the base peak at $m/e = 264$ corresponds to a fragment formed with the loss of 32 mass units. A comparison with the ethyl ester shows that the molecule-ion loses a methoxyl group and one hydrogen atom (formally, this corresponds to the loss of one molecule of methanol). The peak at $m/e = 265$ is higher than expected for the isotope peak corresponding to the peak at $m/e = 264$, which shows that ions are also formed with the loss of the methoxyl group only. The peak at $m/e = 222$ ($= M-74$) is due to a fragment formed by the loss of methylene-methoxycarbonyl, $-CH_2COOCH_3$, of mass 73, together with one hydrogen atom. The appearance of fairly marked peaks at $m/e = 180$, 222, 264, and 265 in both the methyl and the ethyl esters shows that the corresponding ions do not contain the ester alkoxy group.

The mass spectrum of methyl elaidate is practically indistinguishable from that of methyl oleate. Methyl esters of *cis-* and *trans-*petroselinic acids were both found to be indistinguishable from that of methyl oleate. Even a shift of the double bond to the 17:18

position has little effect upon the mass spectrum. On the other hand, the mass spectra of the *cis-* and *trans-* $\Delta^{2:3}$ isomers differ considerably from each other and from those of esters in which the double bond is at position 6:7 or beyond.

The results just described show that it is in general not possible to determine the position of the double bond in a monoethenoid acid by direct mass spectrometric analysis. The position of the double bond may be determined, however, after deuteration by means of hydrazine-d_4 [4] or after hydroxylation [5].

The spectrum of methyl linoleate (Fig. 1b) shows prominent peaks due to hydrocarbon fragments at $m/e = 67$ (base peak), 81, and 95. In general, the 'hydrocarbon' peaks are much stronger than those due to oxygen-containing fragments. The peak at $m/e = 294$ due to the molecule-ion is very prominent; the

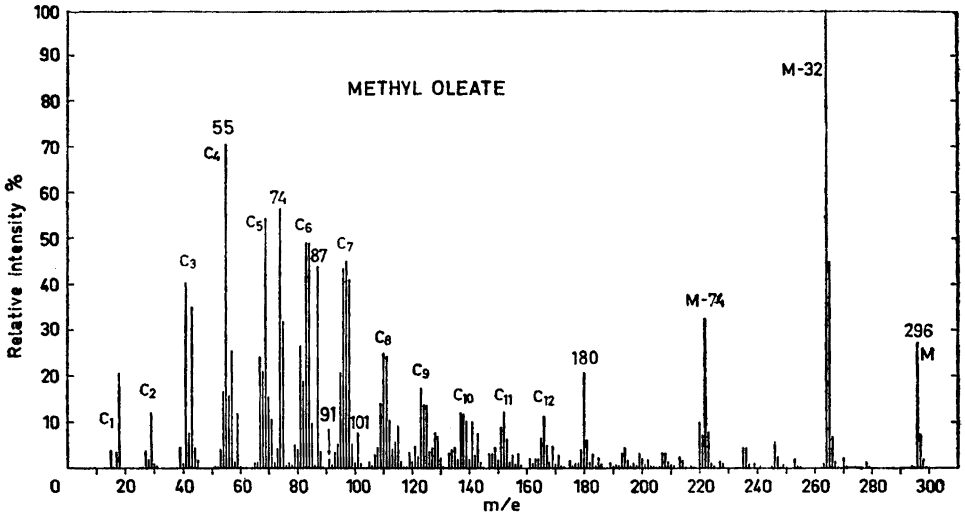

Fig. 1 a.

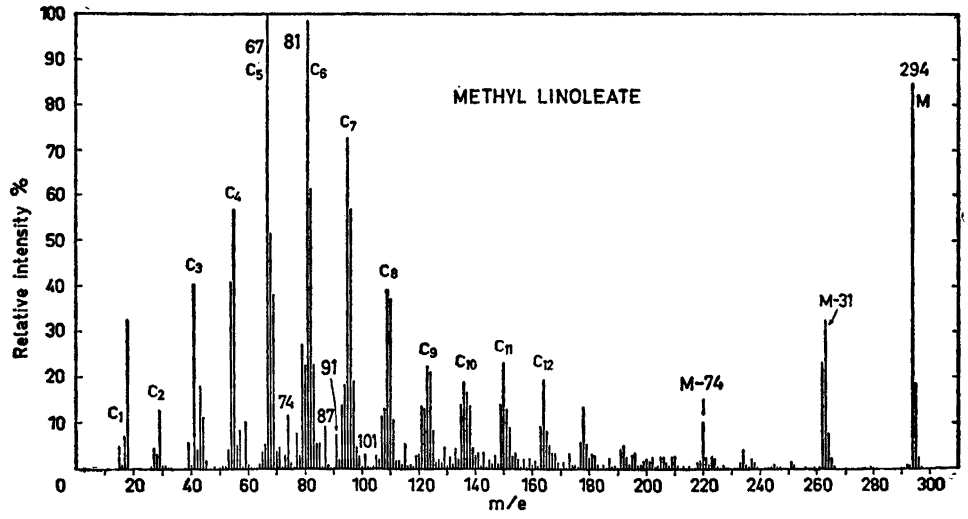

Fig. 1 b.

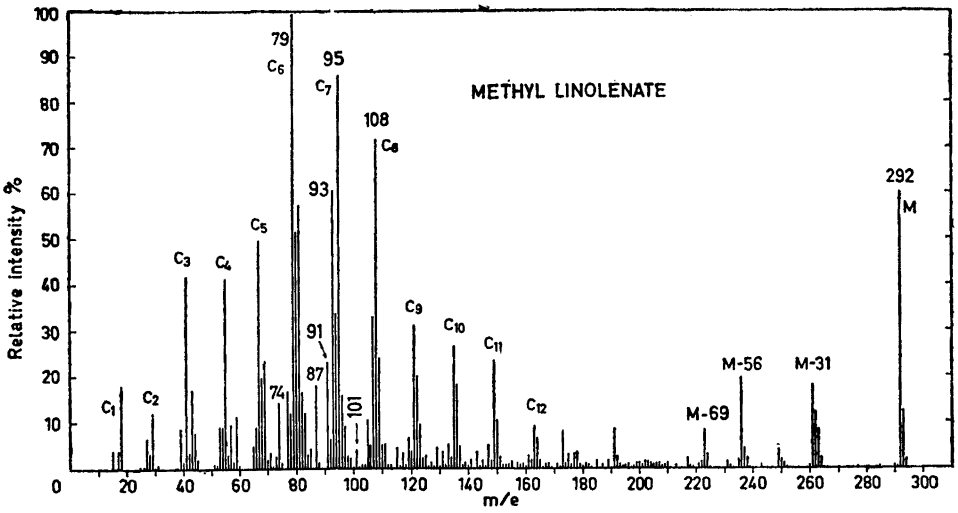

Fig. 1 c.

peak at $m/e = M-31$ is higher than that at $m/e = M-32$; and the peak at $m/e = 220$ (M−74) is obviously analogous to that at $m/e = 222$ in the spectrum of methyl oleate.

In the spectrum of methyl linolenate (Fig. 1c), the base peak is at $m/e = 79$ ($C_6H_7^+$). The 'methoxycarbonyl' peaks are relatively small. In the high-mass range, the molecule ion at $m/e = 292$ gives the most prominent peak, followed by the peaks at $m/e = M-56$ and $m/e = M-31$. The peak at $m/e = M-56$ is probably formed by cleavage between carbon atoms 14 and 15, with rearrangement of one hydrogen atom, leading to the formation of a neutral molecule of 1-butene and an ionized fragment of $m/e = 236$. In the spectrum of methyl linolenate there is a peak at $m/e = 91$ the height of which is about 20 % of that of the base peak. This peak, which may be due to tropylium ions [6] formed by cyclization and rearrangement, is very high in the spectra of methyl esters of unsaturated acids with many double bonds. It is the base peak in the case of a methyl docosahexaenoate which we have examined.

Experimental. The mass spectrometer and the general procedure have been described previously [7]. The intake system was kept at 200°, and the energy of the electrons was 70 eV.

The esters used in order to obtain the spectra shown in Fig. 1 were purchased from Mann Research Laboratories, New York. Their purity was checked by gas chromatography on a Reoplex 400 column with an efficiency approaching 5 000 plates. The oleate contained 1 % of palmitate, and the linoleate about 1 % of oleate. No significant amount of impurity was found in the linolenate. We are indebted to Dr. W. L. Courchene, The Procter & Gamble Company, Cincinnati, for samples of octadecenoic acids synthesized by Huber [8], to Dr. L. Crombie, University of London King's College, for the 2-octadecenoic acids, to Dr. R. T. Holman of the Hormel Institute of the University of Minnesota for the methyl docosahexaenoate, and to Mr. Ng. Dinh-Nguyen for the preparation of several esters. Grants from *Gustaf och Tyra Svenssons Stiftelse* and the *Swedish Medical, Natural Science,* and *Technical Research Councils* are gratefully acknowledged.

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