Tetrahedron Letters No.18, pp. 1063–1067, 1964. Pergamon Press Ltd.
Printed in Great Britain.

THE MASS SPECTROMETRY OF LARGE MOLECULES I.
THE TRIGLYCERIDES OF STRAIGHT CHAIN FATTY ACIDS.

M. Barber and T. O. Merren.

A.E.I. Ltd. Scientific Apparatus Department, Manchester

W. Kelly

Unilever Research Laboratory, Colworth House, Sharnbrook, Bedford

(Received 18 March 1964)

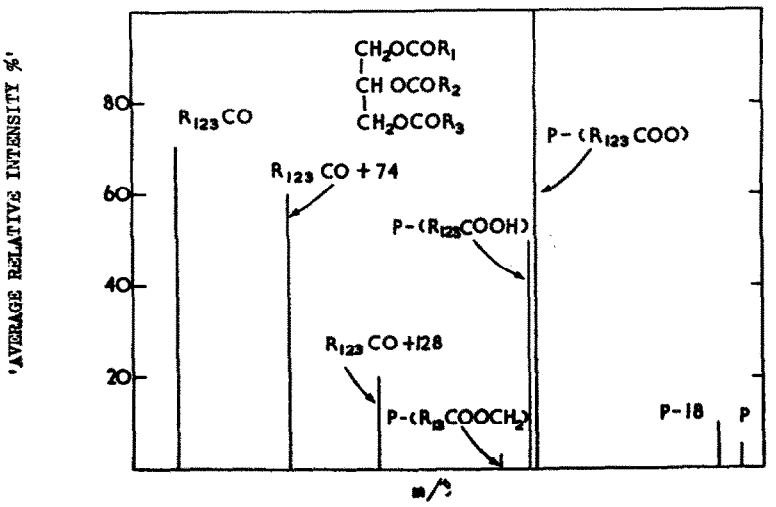
Ryhage and Stenhagen have published the spectrum of one mixed triglyceride (1). They commented on the difficulty which they experienced in 'pump out' and 'memory' effects caused by such compounds, and no other work has been published on them, presumably for this reason.

We wish to give here a preliminary account of work which is being done by us on the correlation of mass spectra with structure of some known, pure triglycerides. No difficulty has been encountered with 'memory' or 'pump out', and, with the direct inlet system used, introduction of the compounds without thermal cracking has been easily achieved. In each case a parent peak has been observed, of sufficient intensity for accurate mass measurement at high resolving power, even for triglycerides of molecular weight as high as 1058 (glycerol tribehenate).

The spectra which have been obtained are very characteristic, and all the major peaks are readily interpreted in terms of triglyceride structure. The major features are outlined briefly below, and the main cleavages in the molecule shown schematically in Fig. 1.

1. The base peak is in most cases due to the loss of an acyloxy group from the complete molecule (see Figs. 1 & 2). This is also perhaps the most important peak from the point of view of structure determination. In the case of mixed triglycerides a peak is obtained from the loss of each acyloxy group present in the molecule (see Fig.3).

FIG 1



Cracking pattern of a triglyceride

2. The second most intense peak is usually that of the positively charged acyl ion (Fig. 1 & 2). Once again there is an ion corresponding to each fatty acid present in the molecule.

3. Associated with the $P-R_{123}COO$ peak are peaks of smaller intensity 14 mass units lower. One of these peaks, the $P-(R_2COO + 14)$ is significantly smaller than the $P-R_1COOCH_2$ and the $P-R_3COOCH_2$ peaks. This characteristic fragmentation, first noted by Ryhage (1), is clearly illustrated in Fig. 3. The peaks at m/e 565 and 537, due to

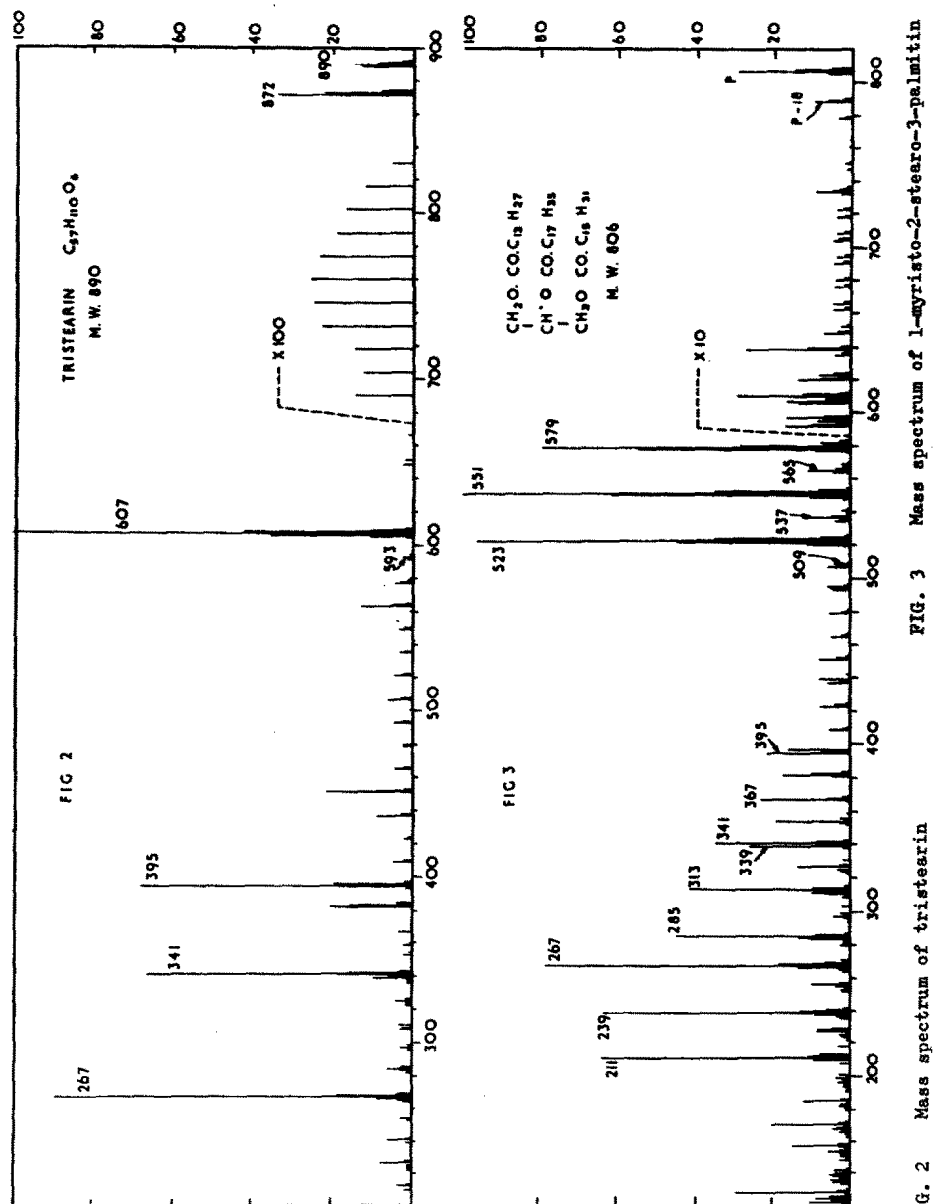


FIG. 2 Mass spectrum of tristearin

FIG. 3 Mass spectrum of 1-myristo-2-stearo-3-palmitin

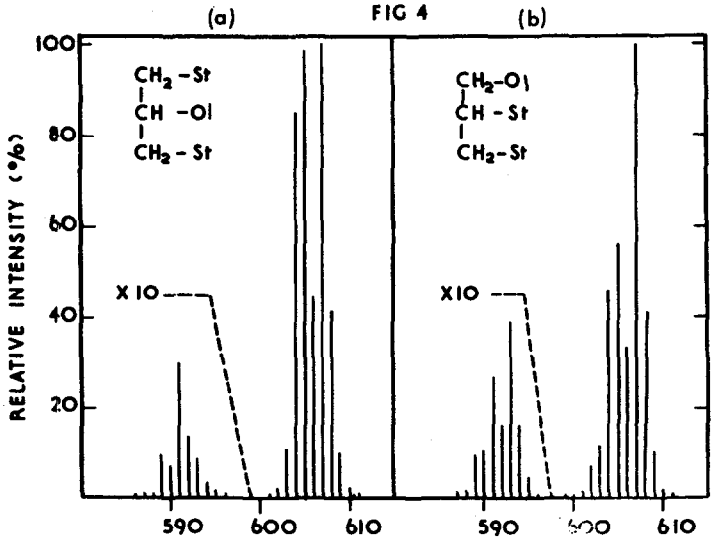
the loss of the myristic and palmitic fragments are three times the intensity of the peak at m/e 509 due to the loss of the stearic fragment.

4. Corresponding to each P-$R_{123}COO$ peak is a peak of slightly lower intensity one mass number lower. Mechanistically this P-$R_{123}COOH$ ion is particularly interesting since it is the precursor of many of the fragment peaks of lower mass.

5. A set of peaks are also formed in these compounds 74 and 128 mass numbers higher than each acyl ion peak. These peaks are quite characteristic of an acid being attached directly to the glycerol skeleton and are therefore useful for establishing this fact.

6. A peak is always observed at P-18. However it should be noted that a prominent metastable is also observed corresponding to the transition P ⟶ P-18, indicating that this peak is due largely to ionic fragmentation and not to thermal cracking.

FIG 4



Portion of mass spectrum of (a) 2-oleo distearin (b) 1-oleo distearin

From the above observations it would appear that it is possible to carry out a complete structural analysis of triglycerides containing straight chain fatty acids. The sensitivity of the method is well illustrated by the ability to distinguish between the isomeric 1- & 2- oleo distearins. This is shown in Fig. 4(a) and 4(b). The present method has considerable advantages in economy of time and material over the normal methods of glyceride analysis, such as chemical or enzymatic hydrolysis, followed by methylation of the fatty acids obtained and gas chromatography. Glycerides containing branched chain and oxygenated fatty acids are at present being studied. The results of this work together with further details of the mechanisms of fragmentation will be published shortly.

All these spectra were run on an A.E.I. MS9, double focussing mass spectrometer (2). The samples were introduced by direct evaporation into the ionization chamber from the end of a ceramic rod. The rod fitted flush with the walls of the ion chamber and the temperature was controlled by means of heaters fitted into the ion chamber itself. For the majority of compounds studied, a satisfactory rate of evaporation was obtained at temperatures between 170°C and 200°C.

REFERENCES

(1) R. Ryhage & E. Stenhagen, J. Lipid Res., 1, 382 (1960)

(2) R. D. Craig, B. N. Green & J. D. Waldron, Chimia, 17, 33 (1963)