Methyl esters are by far the most widely used fatty acid derivatives for analysis in general, and a great deal of information is available on their chromatographic, physical and spectroscopic properties. However, as cautioned in the ‘Introduction’ to these documents, mass spectrometry with electron-impact ionization of methyl esters affords limited information only concerning the structures of fatty acids, especially double bond positions. For example, some limited information on double bond positions in polyenoic fatty acids may be ascertainable, but not for monoenes or dienes. No information can be obtained on the geometry of double bonds. However, the molecular weight is usually obtainable, and this is an important piece of information. If gas chromatographic retention data are added to this, it is often possible to be 90% certain of the identity of a fatty acid. In addition, the positions of structural features, such as branch points and oxygenated groups can usually be deduced. In this document, mass spectra of linear saturated fatty acids only are described.

The Spectra

Methyl esters of straight-chain fatty acids have characteristic spectra, and some representative examples are illustrated below with brief details of interpretation only. Those of the more common fatty acids were published in the early days of mass spectrometry (Ryhage, R. and Stenhagen, E. Mass spectrometric studies. I. Saturated normal long-chain methyl esters. Arkiv Kemi, 13, 523-542 (1959)).

The mass spectrum of methyl palmitate is shown below -
represents loss of a C₃ unit (carbons 2 to 4), via a complex rearrangement, while that at m/z = 74 is the McLafferty rearrangement ion. The latter has a special significance (see below), not least in that it gives further confirmation that the spectrum is that of a methyl ester. An ion at m/z = 241 ([M-29]+) is also diagnostic and worthy of note. The long homologous series of related ions (14 amu apart) at m/z = 87, 101, 115, 129, 143, 157, 199, etc. of general formula [CH₃-OCO(CH₂)n]+ is evidence that there are unlikely to be other functional groups in the chain. The origins of many of these ions are discussed below.

However, mass spectra of fatty acids with iso- and anteiso-methyl branches are easily confused with those of linear analogues (see the web page on methyl esters of branched-chain fatty acids). In the mass spectra of methyl esters of unsaturated fatty acids, hydrocarbon ions predominate, and the McLafferty ion becomes much less distinctive.

The mass spectrum of methyl docosanoate (22:0) is shown next –

In essence, it is shows all the same features as that of methyl palmitate except that the molecular ion and that for loss of the methyl group, etc. are shifted upwards by 84 amu. Other straight-chain saturated esters would be expected to be comparable in all essentials.

For example, the same features are seen in the mass spectra of methyl esters of fatty acids from methyl octanoate (8:0) –
- to methyl tricosanoate (30:0) -

However, the molecular ion can be very small and is often difficult to discern in the mass spectra of saturated short-chain methyl esters. The ion representing $[M-31]^+$ must then be used for identification purposes.

**Mechanistic Aspects**

Although these pages are not intended to be a treatise on mechanistic aspects of mass spectrometry, the McLafferty rearrangement ion is central to the identification of ester derivatives of most fatty acids, so some digression in this direction seems desirable here. In fact, the McLafferty rearrangement is one of the most widely occurring and thence most studied processes in mass spectrometry. The resulting ion is always important for identification purposes.

A site-specific rearrangement is involved in which a hydrogen atom from position 4 of the aliphatic chain migrates to the carbo-methoxy group as illustrated, presumably through a six-membered transition state, which is sterically favoured. If one of the hydrogen atoms on carbon 4 is substituted, then the McLafferty ion will be appreciably lower in intensity than expected. This may explain why it is less evident in the mass spectra of derivatives of unsaturated fatty acids with increasing numbers of double bonds, which can readily migrate to position 4 under electron bombardment. If both hydrogens on carbon 4 are substituted, the McLafferty ion cannot form (see for example the spectra of 4-thia fatty acids on the appropriate web pages as well as of the deuterated fatty acids below). If there is a substituent on position 2, the $m/z$ value of the McLafferty ion will be increased according to the size of the substituent. Of course, if the nature of the alcohol moiety varies, so will the size of the McLafferty ion, to $m/z = 88$ for ethyl esters, 151 for 3-pyrdycarbinol ('picolinyl') esters, and 113 for dimethyloxazoline and pyrrolidine derivatives, for example.
In addition to the McLafferty ion, there is a series of related ions, formed by losses of neutral aliphatic radicals, of general formula \([(\text{CH}_2)_n\text{COOCH}_3]^+\) of which that at \(m/z = 87\) is most abundant, followed by 101, 115, 129, 143 and so forth.

The ion at \([M-43]^+\) at \(m/z = 227\) is believed to be formed via a rearrangement of the chain and one hydrogen atom, followed by expulsion of a propyl radical (carbons 2 to 4), again via a six-membered transition state. Similarly, an ion at \([M-29]^+\) is presumed to arise in an analogous manner following an initial cleavage between carbons 3 and 4. These ions can be useful diagnostically when carbons 2 to 4 in a fatty acid chain are substituted.

Some of these features can be seen in the mass spectra of methyl palmitate deuterated in specific positions, which can be compared with that of the normal fatty acid above. In the first instance, the spectrum of methyl 2,2-dideutero-hexadecanoate is illustrated.

Both the molecular ion and the McLafferty rearrangement ion have increased by 2 units, the latter to \(m/z = 76\). As would be anticipated, the ion representing the loss of a methoxyl group is still at \([M-31]^+\) (\(m/z = 241\)). On the other hand, the ion representing loss of carbons 2 to 4 is now equivalent to the loss of 44 amu (at \(m/z = 228\)), as is explained by the accepted mechanism for the formation of this ion.

Next the spectrum of methyl 3,3-dideutero-hexadecanoate –
Now the McLafferty ion is at m/z = 74 again, but the ion for [CH$_3$OOC(CH$_2$)$_2$]$^+$, formerly at m/z = 87 has now increased to 89. The ion representing loss of carbons 2 to 4 is now at [M-45]$^+$ (m/z = 227). In this and the previous spectrum, the ions resulting from the loss of carbons 2 and 3 are now equivalent to [M-31]$^+$ and coincide with that for the loss of the methoxyl group (m/z = 241) in a low-resolution spectrum.

Finally, the spectrum of methyl 4,4-dideutero-hexadecanoate –

The McLafferty ion is now at m/z = 75 as one of the deuterium atoms from carbon 4 has been abstracted during the rearrangement. The ion representing loss of carbons 2 to 4 is again at [M-45]$^+$ (m/z = 227), while that for loss of carbons 2 and 3 has reappeared at [M-29]$^+$ (m/z = 243).

Spectra of many more methyl esters of saturated fatty acids (4:0 to 30:0), including some labelled with stable isotopes, can be accessed from our Archive pages (without interpretation).

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