MASS SPECTRA OF DERIVATIVES OF CYCLOPROPYL AND CYCLOPROPENYL FATTY ACIDS

The document does not aim to be a complete account of mass spectrometry of cyclopropyl and cyclopropenyl fatty acids, but rather is a personal account of our experience of those encountered during our research activities and for which we have spectra available for illustration purposes. Spectra of methyl esters, 3-pyridylcarbinol (‘picolinyl’) esters, DMOX derivatives and pyrrolidides are described in the same document. Where we are aware of prior illustrations of mass spectra in the literature, the appropriate papers are cited. These notes are a practical guide rather than a mechanistic account. The occurrence and biological properties of cyclic fatty acids were reviewed by Sébédio and Grandgirard (1989).

Cyclopropyl Fatty Acids

Cyclopropyl fatty acids are common constituents of bacterial lipids and may accompany cyclopropene fatty acids as minor components of certain seed oils. Mass spectra of methyl esters of cyclopropyl fatty acids are not very informative as the ring appears to rearrange under electron bombardment in the mass spectrometer to give a double bond. Spectra are thus indistinguishable from those of monoenic fatty acids with an alkyl chain one carbon longer (Christie and Holman, 1966). The mass spectrum of methyl 9,10-methylene-hexadecanoate is illustrated as an example –

The spectrum is in essence identical to that of methyl 9-heptadecenoate. Although there have been suggestions in the literature that subtle differences exist between the mass spectra of cyclopropanes and monoenes that might serve for diagnosis, these are not very convincing to this author. They may work with a limited range of pure model compounds, but are less likely to be of practical value in the analysis of complex mixtures, especially when instrumental variations are taken into account. The GC retention times of methyl esters of monoenioic and cyclopropanoic fatty acids are very different, and this can be useful information in deciding between possible structures.
3-Pyridylcarbinol esters are by far the most useful derivatives for characterization of cyclopropane fatty acids, as they give distinctive cleavages that permit facile location of the cyclopropane ring. As an example, the mass spectrum of 3-pyridylcarbinyl 9,10-methylene-octadecanoate is illustrated next.

There are the usual ions in the lower molecular weight region at m/z = 92, 108, 151 and 164, typical of a 3-pyridylcarbinol ester, but the [M-1]^+ ion is more abundant than the molecular ion (m/z = 387) itself. The distinctive ion that permits location of the ring is odd-numbered (uncommon) at m/z = 247, representing cleavage at the ring as shown (Harvey, 1984).

In the spectrum of 3-pyridylcarbinyl 11,12-methylene-octadecanoate (lactobacillic acid), illustrated next, the distinctive ion has shifted 28 amu as expected to m/z = 275.

DMOX derivatives are of much less value for the structural analysis of cyclopropyl fatty acids since they appear to undergo a rearrangement to form monoenes in a similar manner as occurs with methyl esters (Zhang et al., 1987). This view of the mechanism is too simplistic but is serviceable. This is one of only a few examples where DMOX derivatives fail.
As an example, the mass spectrum of the DMOX derivative of 9,10-methylene-octadecanoate is illustrated -

Although the structure can in theory be deduced from the fact the rearranged double bond in position 9 gives a characteristic gap of 12 amu between $m/z = 196$ and 208, this presupposes that the analyst is already aware that the fatty acid contains the ring structure - not a double bond (see the webpage dealing with DMOX derivatives of monoenes). On the other hand, gas chromatographic (GC) retention times may indicate that an unusual fatty acid is present.

The DMOX derivative of 11,12-methylene-octadecanoate (or lactobacillate) has the mass spectrum –

Again the position of the ring can be deduced from the gap of 12 amu (between $m/z = 224$ and 236), assuming we recognize that it is a cyclopropyl acid not a monoene.

The mass spectra of pyrrolide derivatives of cyclopropane fatty acids closely resemble those of the DMOX derivatives, and like them give ambiguous spectra that are almost indistinguishable from those of monoenes one carbon longer in chain-length. The same caveats apply in interpreting the spectra. I am not aware of publication elsewhere.
For example, the mass spectrum of the pyrrolidide of 9,10-methylene-octadecanoate is almost identical to that of 9-nonadecenoate, and the gap of 12 amu between \( m/z = 196 \) and 208 is that expected for a double bond in position 9 of the chain.

The mass spectrum of the pyrrolide of 11,12-methylene-octadecanoate (or lactobacillate) is –

Although the position of the ring can in theory be deduced from this from first principles (from the gap of 12 amu between \( m/z = 224 \) and 236), in practice it may be better to regard it simply as a fingerprint. Again, GC retention times of DMOX or pyrrolide derivatives of monoenoic and cyclopropanoic fatty acids are very different, and this can be useful information in deciding between possible structures.

Alternative mass spectrometric methods for locating cyclopropane rings in fatty acids involve ring opening by vigorous hydrogenation or by reaction with boron trifluoride-methanol (see the online ‘Gas Chromatography and Lipids’).

**Cyclopropenyl Fatty Acids**

It was long thought that GC and thus GC-MS of derivatives of cyclopropenyl fatty acid was impossible because of thermal degradation on the GC column. However, modern capillary columns
are relatively inert, and analysis by GC is straightforward, provided that appropriate derivatization methods are employed, i.e. that acidic conditions are avoided.

The mass spectra of methyl ester derivatives of cyclopropenoid fatty acids tend to resemble those of dienoic fatty acids, so methyl sterculate (9,10-methylene-octadec-9-en oate) has a spectrum (see below) that differs in minor ways only from that of methyl nonadecadienoate, and there are no obvious ions that serve to locate the ring (Pawlowski et al., 1974).

The mass spectrum of 3-pyridylcarbinyl sterculate is distinctive, however, and it is illustrated next (see also Spitzer et al., 1994).

In this instance, the diagnostic cleavages occur on either side of the ring and beta to it, giving distinctive ions at \( m/z = 220 \) and 286. There is also an ion that appears to be characteristic at \( m/z = 293 \) (though not found apparently by Spitzer et al., 1994). This has now been identified as containing the fatty acyl chain without the 3-pyridylcarbinyl moiety, i.e. it represents a distinctive type of fragmentation that appears to be unique to and diagnostic for cyclopropene rings (Knothe et al., 2011). As might be expected, the analogous diagnostic ions in the mass spectrum of 3-pyridylcarbinyl malvalate (8,9-methylene-heptadec-8-en oate) are all 14 amu lower.
The mass spectrum of DMOX derivatives are less helpful, and resemble those of an acetylenic fatty acid with the triple bond in position 9 and one carbon longer, presumably because rearrangement occurs in the mass spectrometer (Spitzer, 1991). For example, the mass spectrum of the DMOX derivative of sterulic acid is illustrated next. The key diagnostic ions are for a gap of 10 amu between m/z = 196 and 206.

The spectrum of the pyrrolidide of sterulate is very similar to this (unpublished), although the ions in the high mass range are less abundant, and it is illustrated below.

The key diagnostic ions are again for a gap of 10 amu between m/z = 196 and 206. The corresponding ions in the mass spectrum of the malvalate derivative are all 14 amu lower.

The simplest alternative mass spectrometric method for locating cyclopropene rings in fatty acids involves addition of methane thiol across the double bond (see the online 'Gas Chromatography and Lipids').

Mass spectra of more derivatives of cyclopropyl and cyclopropenyl fatty acids are available in our Archive pages.
References


**William W. Christie**

James Hutton Institute (and Mylnefield Lipid Analysis), Invergowrie, Dundee (DD2 5DA), Scotland

Last updated: March 6th, 2014