

Mass Spectrometry of Aldehyde Esters

Eight aldehyde esters were investigated in a combined gas chromatograph-mass spectrometer. All compounds gave rise to characteristic ions at $M - 18$, $M - 28$, $M - 31$, $M - 32$, $M - 44$,

$M - 50$, $M - 59$, $M - 60$ and at m/e 59 and m/e 74. Several metastable peaks were observed, allowing the confirmation of certain fragmentation patterns.

In our work on the autoxidation of polyunsaturated fatty acids we identified a series of saturated and unsaturated aldehyde esters. The formation of the C9:0 semialdehyde in the autoxidation of lipids has been previously reported (Frankel *et al.*, 1961; Horvat *et al.*, 1966; Yassuda *et al.*, 1968). Semialdehydes are also major products in reductive ozonolysis of unsaturated fatty acids, a convenient method frequently used in determining the location of double bonds. Mass spectrometry provides a reliable means for the identification of aldehyde esters. However, the spectrum of only methyl azelaaldehyde has been published (Horvat *et al.*, 1966; Yassuda *et al.*, 1968). In this report the mass spectra of some aldehyde esters varying in chain length and degree of unsaturation are presented.

EXPERIMENTAL

The C4:0, C9:0, C7:1, C12:1, C10:2, C15:2, C13:3, and C16:4 aldehyde esters were synthesized by ozonization of the appropriate methyl esters, followed by fission of the ozonides as described by Pryde *et al.* (1960). For this purpose methyl 4-pentenoate, methyl linolenate, and methyl 4,7,10,13,16,19-docosahexaenoate were used as substrates. The aldehyde esters were separated by gas chromatography and their identity verified by infrared spectrophotometry. Using a 6-ft \times $\frac{1}{8}$ -in. o.d. 10% silicone rubber SE-30 and a 10-ft \times $\frac{1}{8}$ -in. 10% methyl silicone OV-1 column, the compounds were analyzed in a Hitachi Perkin-Elmer combined gas chromatograph-mass spectrometer, Model RMU-6A. The operative conditions of mass spectral analyses were the same as described previously (LeTellier and Nawar, 1971).

RESULTS AND DISCUSSION

The mass spectra of the eight synthesized compounds are presented in Figure 1. Spectral patterns of aldehyde esters show fragmentation characteristics of both functional groups. The aldehydic fragments, $M - 18$ (loss of H_2O), $M - 28$ (expulsion of ethylene), $M - 44$ (β -cleavage with hydrogen rearrangement), and the methyl ester ions at $M - 31$ (loss of $-OCH_3$), $M - 32$ ($M-CH_3OH$); and at m/e 74 (McLafferty rearrangement) and m/e 59 ($-COOCH_3$)⁺ are observed in the mass spectra of all eight compounds. Also typical are ions resulting from the combined losses of two fragments

from the molecular ion, giving rise to peaks at $M - 50$ (loss of $CH_3OH + H_2O$), $M - 59$ (loss of ethylene + a methoxy radical) and $M - 60$ (loss of ethylene + CH_3OH). Several metastable peaks which confirm the above fragmentation pathways are frequently seen in the spectra of aldehyde esters.

As the chain length increases, fragments characteristic of the two functional groups become smaller and ions arising from the hydrocarbon chain predominate. A stronger molecular ion is observed in case of the unsaturated compounds and the ion pattern of the series (C_nH_{2n-5}) and (C_nH_{2n-7}) is observed for the highly unsaturated aldehyde esters. Small peaks at $M - 2$ are also observed for most of the compounds studied.

The spectrum of the C4:0 aldehyde ester is unique because of its short carbon chain. The two most intense peaks appear at m/e 85 ($M - 31$) and m/e 88 ($M - 28$). The molecular ion is absent. The peak at m/e 74 is extremely small due to lack of hydrogen available for rearrangement on the fourth carbon. Three metastable peaks were observed in this spectrum, one at m/e 38.2 and two at approximately 36.9. According to the calculated values tabulated by Beynon *et al.* (1965) a metastable peak at m/e 38.22 corresponds to the transition $85^+ \rightarrow 57^+ + 28$, while peaks at m/e 36.92 and at m/e 36.89 indicate the transitions $88^+ \rightarrow 57^+ + 31$ and $85^+ \rightarrow 56^+ + 29$, respectively.

The spectrum of the C9:0 compound is different, due to the longer alkyl chain separating the aldehyde and the methyl ester groups. Fragments at m/e 59, 74, 87, 101, 115, 129, and 143 are clearly seen, with those at m/e 87 and 143 strongly favored as typical of the longer chain fatty acid methyl esters (Budzikiewicz *et al.*, 1967). A metastable peak at m/e 86.16 corresponds to the loss of methanol from the fragment at m/e 143 ($143^+ \rightarrow 111^+ + 32$) and a subsequent loss of 28 mass units from the ion at m/e 111 is indicated by a metastable peak at m/e 62.06 ($111^+ \rightarrow 83^+ + 28$).

The fragmentation of the C7:1 aldehyde ester gives rise to a number of metastable peaks. The loss of water from the molecular ion is represented by a metastable peak at m/e 122.08 corresponding to the transition $156^+ \rightarrow 138^+ + 18$. The fragment at m/e 124 results from the loss of methanol from M^+ as indicated by the metastable peak at m/e 98.56. This fragment further undergoes loss of 28 mass units to produce a peak at m/e 96, as shown by the metastable peak at m/e 74.32 ($124^+ \rightarrow 96^+ + 28$). A metastable peak at

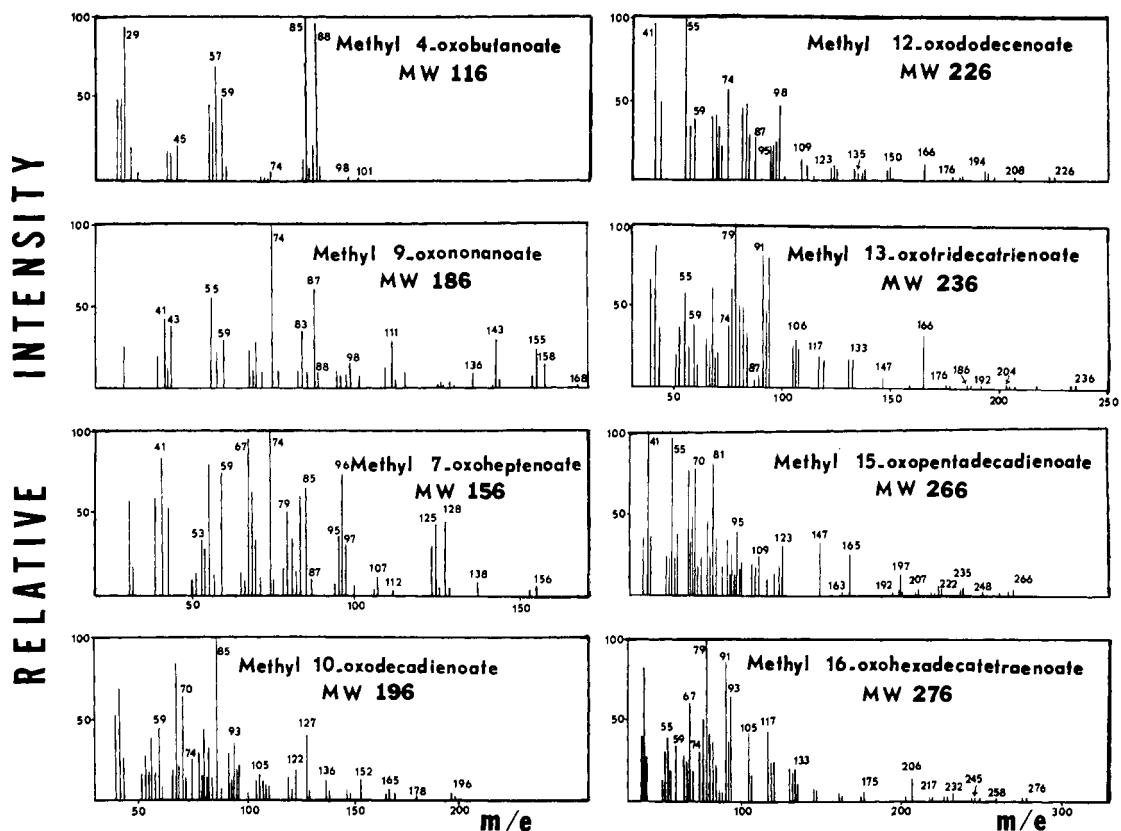


Figure 1. Mass spectra of aldehyde esters

m/e 91.58 corresponds to the loss of water from the peak at m/e 125 ($125^+ \rightarrow 107^+ + 18$). Similarly a metastable peak at m/e 73.73 represents the loss of 29 mass units from the peak at m/e 125 ($125^+ \rightarrow 96^+ + 29$). In addition, metastable peaks at m/e 73.5 and 72.0 correspond to the losses of 31 and 32 mass units, respectively, from the ion at m/e 128 ($128^+ \rightarrow 97^+ + 31$ and $128^+ \rightarrow 96^+ + 32$).

The general features of the remaining unsaturated compounds are similar to those discussed above. In addition, the ion at m/e 122 ($M - 74$) in case of the C10:2 aldehyde ester may result from the loss of the ester rearrangement group as observed in unsaturated methyl esters (Creveling and Jennings, 1970). The intense peak at m/e 127 may be formed by a 6-7 bond cleavage with the charge remaining on the ester fragment. Cleavage of the same bond with hydrogen rearrangement may account for the intense ion at m/e 70. In case of the C13:3 aldehyde ester, the base peak at m/e 79 is probably due to the unsaturated hydrocarbon chain fragment as in ethyl trienoates (Creveling and Jennings, 1970).

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