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# UTILITY OF DICYANOMETHYLENE DERIVATIVES IN STRUCTURAL STUDIES OF LONG-CHAIN ALIPHATIC ACIDS BY MASS SPECTROMETRY

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Comparison of the mass spectrum* of a methyl ester of a long-chain aliphatic acid with that of the corresponding methyl ether of its dicyanomethylene (DCM) derivative ($-(OCH_3)C{=}C(CN)_2$) reveals a striking contrast between their patterns of fragmentation. In this communication it is suggested that, the mass spectra of these DCM derivatives can be used to advantage in the identification and structural elaboration of such molecules.

The reaction of $n\text{-}CH_3(CH_2)_{16}COCl$ with $CH_2(CH)_2$, using pyridine as catalyst, yielded a product, which on treatment with $CH_2N_2$ gave the compound $n\text{-}CH_3(CH_2)_{16}(OCH_3)C{=}C(CN)_2$, whose mass spectrum is characterized by an abundant series of fragment ions extending uniformly to the molecular ion (Fig. 1). High resolution data show that these ions have an elemental composition corresponding to $(CH_2)_n\text{-}(OCH_3)C{=}C(CN)_2$, and could be derived from the molecular ion by loss of alkyl groups from the chain. The M-15 fragment, however, is apparently formed almost exclusively by loss of $CH_3$ from $OCH_3$, since, in the spectrum of the corresponding ethyl ether, formation of the M-29 fragment is the predominant process. The periodicity (1,2) found in the fragmentation of long-chain esters (cf. Fig. 2) is absent in the spectrum of the DCM derivatives.

The abundant series of peaks resulting from loss of progressively larger alkyl units from the molecular ion of a DCM derivative would appear to provide information relevant to the location of secondary or (potentially) tertiary carbon atoms in the chains of unknown

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* Determined on LKB 9000 gas chromatograph-mass spectrometer with ion source temp. 250° C, 70 eV; and chromatographic column of 6 ft of 1% OV-1 on Gas Chrom Q at 210° C.

branched-chain compounds. By analogy with the spectra of branched-chain methyl esters (3,4), one might expect a decided preference for formation of the ion resulting from cleavage of a main-chain C-C bond on the "hydrocarbon" side of the branch point of a DCM derivative. In addition, one might also expect the virtual absence of an ion having a mass of 14 a.m.u. less. As shown in the mass spectrum (Fig. 3) of the methyl ether of the DCM derivative of 4,8,12-trimethyloctadecanoic acid, formation of the ions arising by fragmentation at the branch points is indeed preferred, although ions having masses of 14 a.m.u. less do not completely disappear. The recognition of the branch at C-4 (numbering as in parent acid), is not as evident as those at C-8 and C-12, although some diminution of the peak at m/e 149 is observed. While branch-points in methyl 4,8,12-trimethyloctadecanoate are suggested in its mass spectrum by slightly enhanced fragmentation, the secondary carbonium ions (deriving from fragmentation at the branch-point) lead to peaks of comparable intensity originating through the elimination of $CH_3OH$ (4). By contrast, the branch-points in the DCM derivative are characterized in its mass spectrum by peaks which are 10 times more intense (compare $\%\Sigma$ in Figs. 3 and 4) than the corresponding peaks in the spectrum of the methyl ester.

The features shown in these spectra are typical of those of other similar DCM derivatives observed in our laboratories. Deuterium labelling of C-2, C-3, C-4 indicates that the ions producing the groups of peaks near m/e 135 and 149 may be derived by several mechanisms. The primary mechanism producing the major series of ions from long-chain DCM derivatives is still under investigation. Preliminary studies indicate that DCM derivatives may find valuable applications in structural studies relating to various other long-chain or alicyclic molecules.

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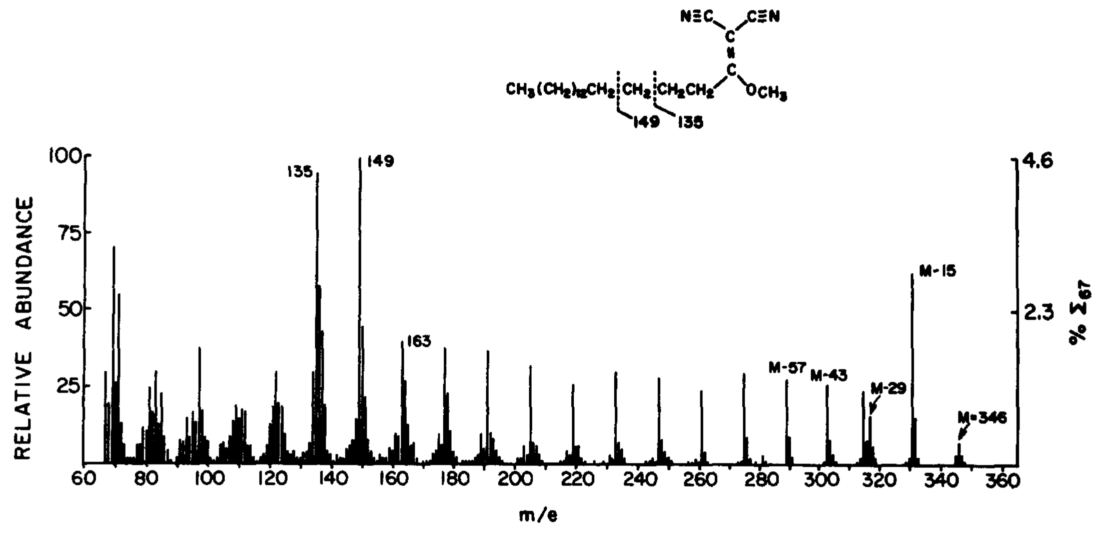
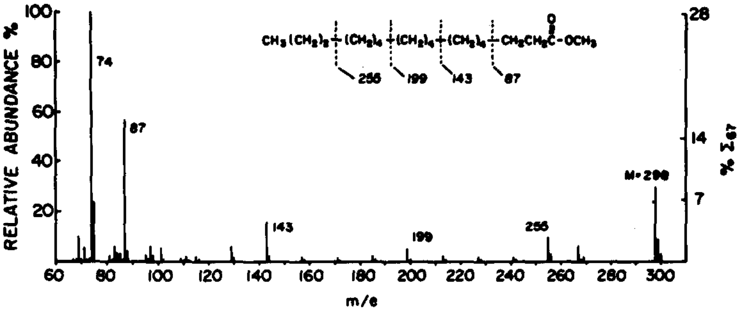
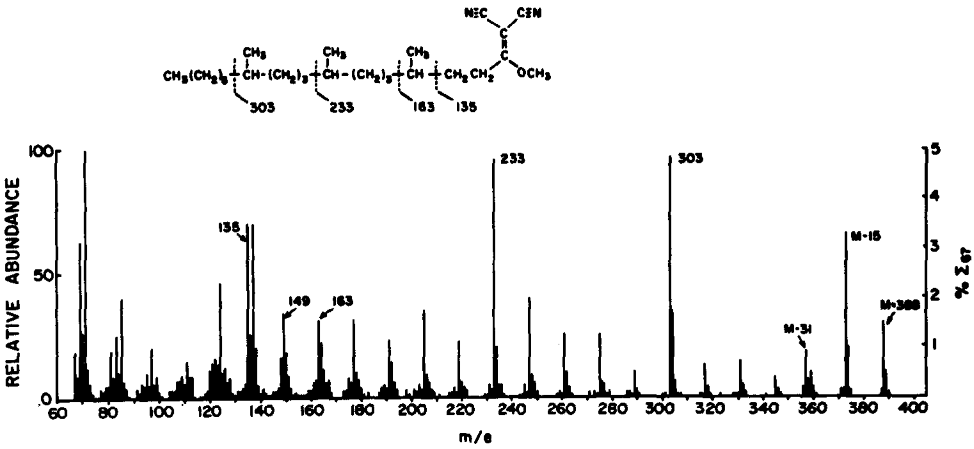


Figure 1. Mass spectrum of the methyl ether of the dicyanomethylene derivative of octadecanoic acid. This spectrum and those in the other figures were obtained under the conditions listed at the bottom of the title page.





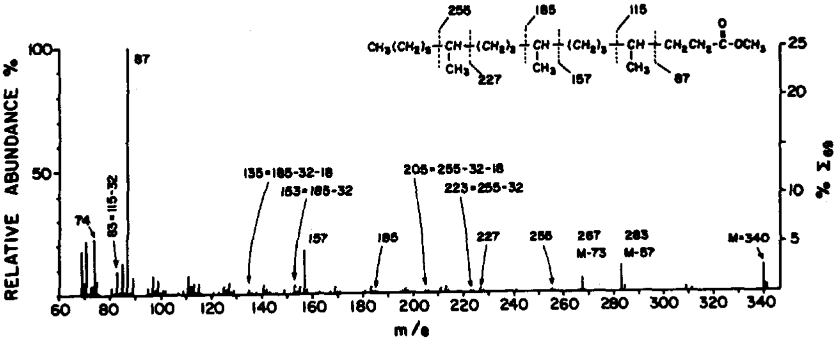


Figure 2 (Top) mass spectrum of methyl stearate

Figure 3 (Middle) mass spectrum of methyl ether of dicyanoethylene derivative of 4,8,12 trimethyloctadecanoic acid

Figure 4 (Bottom) mass spectrum of methyl ester of 4,8,12 trimethyloctadecanoic acid