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Note

Gas chromatography–mass spectrometry of the flophemesyl derivatives of a series of fatty acid methyl ester chlorohydrins

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The formation and assessment of pentafluorophenyldimethylsilyl ether (shortened to flophemesyl) derivatives for the gas chromatographic (GC) analysis of steroids was first reported by Morgan and Poole[1,2], who subsequently extended their work and showed the sensitivity obtainable for analysis by electron-capture detection of flophemesyl derivatives of alcohols, phenols, amines and carboxylic acids[3,4]. They also demonstrated that flophemesyl ethers have good mass spectral (MS) properties showing some marked differences to the trimethylsilyl (TMS) ethers of steroids[5]. Our own investigations of methyl ester chlorohydrins have previously led us to report the GC–MS analysis of the TMS derivatives[6], but in practice we have subsequently found that for trace analysis of chlorohydrins in polymer systems[7] the flophemesyl derivatives are a better alternative, enabling sensitive electron-capture detection and producing simple but very characteristic MS fragmentation patterns. In this note we report the ease of formation, and stability of the flophemesyl derivatives of a series of chlorohydrin fatty acid methyl esters, their electron-capture limits of detection and MS fragmentation patterns.

EXPERIMENTAL

The preparation of the fatty acid ester chlorohydrins was previously described[6], and the flophemesyl derivatives were formed quantitatively by addition of equal volumes of pyridine and flophemesylamine (Lancaster Synthesis, St. Leonard Gate, Lancaster, Great Britain) allowing to stand at room temperature for a few minutes, for complete reaction.

GC was performed on a Pye Series 104 equipped with flame ionisation and ^{63}Ni electron-capture detectors. The glass column (1.5 m × 0.6 cm O.D.) packed with 3% OV-1 on Diatomite CLQ (100–120 mesh) was operated at 260° with a nitrogen carrier gas flow-rate of 60 ml/min. The electron-capture detector was operated at 300° in a pulsed mode with a spacing of 150 μsec.

Combined GC–MS was carried out on a DuPont Model 21-490B mass spectrometer interfaced with an all glass jet separator to a Varian 2700 gas chromatograph. The separator and connecting lines were held at 270°, the ion source at 230° and mass spectra were obtained at 70 eV scanning over the mass range from *m/e* 20 — 800 at 4 sec per decade.

RESULTS AND DISCUSSION

Flophemesyl derivatives of fatty acid ester chlorohydrins exhibited good GC properties with sharp peaks, an absence of tailing and no evidence of decomposition. Solutions of the derivatised chlorohydrins were stable at room temperature in diethyl ether solvent for up to 72 h without evidence of any hydrolysis to the parent compound. The electron-capture detector was approximately 10^3 times more sensitive than the flame ionisation detector to equal amounts of flophemesyl chlorohydrins with a practical working limit of detection by electron capture of the order of 5 pg.

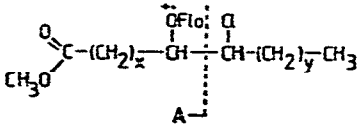
TABLE I

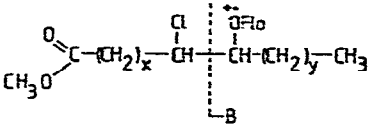
CHARACTERISTIC IONS FROM FLOPHEMESYL CHLOROHYDRINS

Spectra were obtained by combined GC–MS.

Starting material	*Fragmentation ions*			
	A		*B*	
	m/e	*Relative intensity (%)*	*m/e*	*Relative intensity (%)*
Methyl 9,10-epoxyoctadecanoate	411	100	367	71
Methyl 9,10-epoxyhexadecanoate	411	100	339	84
Methyl 6,7-epoxyoctadecanoate	369	100	409	82
Methyl 11,12-epoxyoctadecanoate	439	100	339	36
Methyl 11,12-epoxyeicosanoate	439	100	367	77
Ethyl 9,10-epoxyoctadecanoate	425	100	367	50

The mass spectra of the flophemesyl chlorohydrins showed few small fragment ions but in each case produced two intense characteristic ions the (two major ions in each spectra). These ions A and B (shown in Table I) were due to cleavage between the adjacent carbons bearing the chlorine and O-flophemesyl groups.





Analogously to the TMS chlorohydrins[6] the formation of positional chlorohydrin isomers by reaction of hydrogen chloride with epoxides is again illustrated by this fragmentation pattern. The spectra are characterised by (i) an absence of other ions of major intensity, (ii) the absence of molecular ions —in contrast to the MS behaviour of simple flophemesyl alcohols[3], (iii) the M — 15 ion being absent— or occasionally present at very low intensity, (iv) the M — 31 ion commonly being the highest ion present (intensity commonly between 3 and 8%). A typical mass spectrum of the flophemesyl derivative of the reaction product of HCl with methyl 9,10-epoxyoctadecanoate is illustrated in Fig. 1.

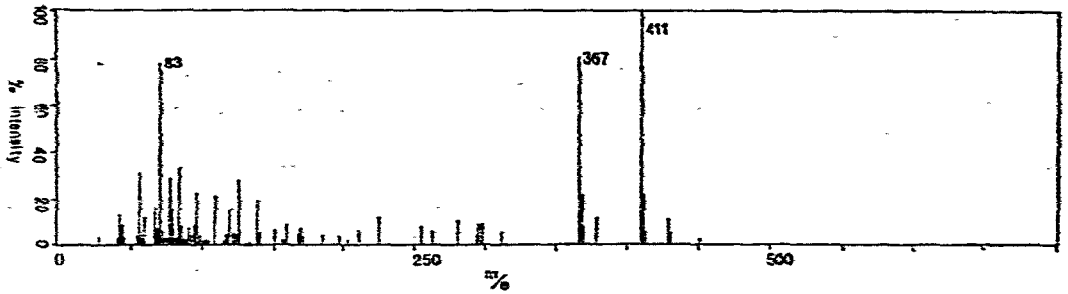


Fig. 1. Mass spectrum of the flophemesyl derivative of the reaction product of methyl 9,10-epoxyoctadecanoate with HCl.

In these laboratories flophemesyl derivatives have been routinely employed for the electron-capture capillary GC analysis of chlorohydrins isolated from polymer systems[7] and have proved well suited for quantitation at high sensitivity.

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