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Identification of 2-Chloroethyl Palmitate and 2-Chloroethyl Linoleate in French Dressing

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Utilizing gas liquid chromatography with microcoulometric detection, two unknown peaks were found in several composites of fats and oils from the Total Diet Program conducted by the Food and Drug Administration (MANSKE AND JOHNSON 1977). Upon analysis of individual commodities of these composites, the unknown peaks were found to occur only in French dressing. One sample of oleoresin from a manufacturer of French dressing was analyzed and found to contain two peaks with the same retention values as those in the French dressing. These unknowns were identified as 2-chloroethyl palmitate and 2-chloroethyl linoleate by gas chromatography-mass spectrometry (GC/MS). An acid catalyzed esterification reaction was utilized to synthesize 2-chloroethyl palmitate and 2-chloroethyl linoleate which were used as standards.

EXPERIMENTAL

The official methods currently used by the FOOD AND DRUG ADMINISTRATION (1975) for multiresidue analysis were applied to the analysis of the French dressing samples:

(a) The homogenized product was extracted with ethyl ether-petroleum ether and the solvent evaporated.

(b) The resulting fat residue was extracted with acetonitrile. An aliquot of the extract was diluted with water and, in turn, extracted with petroleum ether.

(c) Clean-up of the petroleum ether extract was accomplished with a Florisil column. The 2-chloroethyl palmitate and 2-chloroethyl linoleate eluted with 15% ethyl ether in petroleum ether. This eluate was analyzed by gas chromatography with microcoulometric detection (MC/GC).

Respective solutions of palmitic, linoleic, oleic and stearic acids in 2-chloroethanol were warmed on a steam bath after addition of a drop of concentrated hydrochloric acid. The reacted solutions were diluted with water and the esters extracted with methylene chloride. Following evaporation of the solvent, the residues were dissolved in petroleum ether and cleaned up with a Florisil column, as above. The resulting 2-chloroethyl esters used as standards were 99% free of their acid precursors.

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MC/GC: A Dohrmann 2400 gas chromatograph and a Barber Coleman gas chromatograph each equipped with a Coulson furnace and a microcoulometric detector were used for quantitative analysis. Column parameters were as follows:

(1) Pyrex, 1.8mx4mm (ID), packed with 3% OV-1 on Chromosorb WHP 80/100 mesh at 180°; with 80 ml/min N_2 flow,

(2) Pyrex, 1.8mx4mm (ID), packed with a mixture (1+1) of 10% DC-200 and 15% QF-1 on Chromosorb WHP 80/100 at 200°,with 120 ml/min N_2 flow.

GC/MS: A DuPont 491B mass spectrometer was interfaced through a glass jet separator to a Packard 838 gas chromatograph. Samples were injected on a 1.8mx2mm pyrex column packed with 3% OV-17 on Chromosorb WHP 80/100 mesh at 210° and 30 ml/min He flow. The injector temperature was 220°.

The data system was comprised of a Hewlett-Packard 2100A computer (16K), and 7900A disc drive, with Tektronix 4010 teletype port interface and 4610 hard copy unit.

Electron impact spectra (75 eV) were obtained at a scan rate of 2 sec/dec, scanning from 517 to 41 amu. The source was held at 240° with an accelerating voltage of 1.4 KV.

RESULTS AND DISCUSSION

The relative retentions (aldrin = 1.00) of these esters on columns used in the MC/GC systems are listed in Table 1.

TABLE 1
Relative Retention Times of Some 2-Chloroethyl Esters (Aldrin=1.00)

Ester	Relative Retention OV-1	Mixed
2-Chloroethyl Palmitate	2.75	2.02
2-Chloroethyl Linoleate	5.12	3.46
2-Chloroethyl Oleate	5.27	3.46
2-Chloroethyl Stearate	6.17	3.75

The compounds are much more responsive on the MC/GC system than on electron capture gas chromatography (EC/GC). With the MC sensitivity set to give 1/2 FSD for 5 ng of heptachlor epoxide and the EC sensitivity to give 1/2 FSD for 1 ng of heptachlor epoxide the following amounts of each ester are required for 1/2 FSD:

MC	100 ng
EC (^{63}Ni)	5 µg
EC (^{3}H)	75 µg

Quantitative analysis of three samples of French dressing plus one sample of oleoresin was accomplished using the MC/GC systems. The results of this study are listed in Table 2. Samples I, II, and the oleoresin are from the same manufacturer. Sample III is from another manufacturer.

TABLE 2

Results of analysis of three French dressing samples and one oleoresin sample using MC/GC. Values are expressed in ppm.

Sample No.	2-Chloroethyl Palmitate	2-Chloroethyl Linoleate
I	1.3	14.0
II	0.74	6.1
III	0.0	0.0
IV	trace	5.0

The mass spectra of 2-chloroethyl palmitate and 2-chloroethyl linoleate are shown in Figure 1 and Figure 2, respectively. These spectra are essentially identical to the mass spectra recorded from the analysis of French dressing.

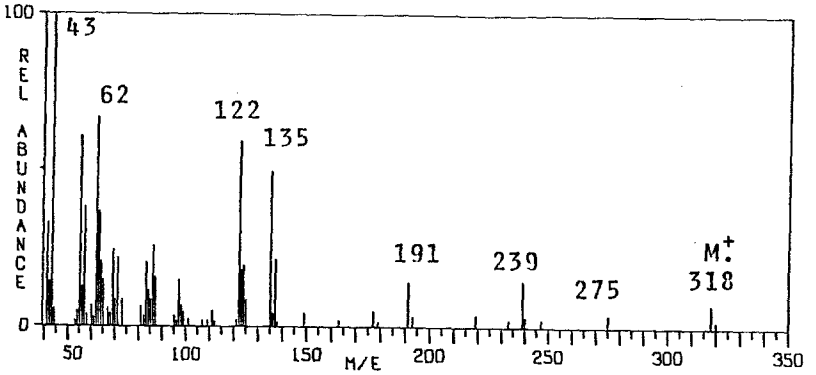

Figure 1-Electron impact mass spectrum of 2-Chloroethyl Palmitate

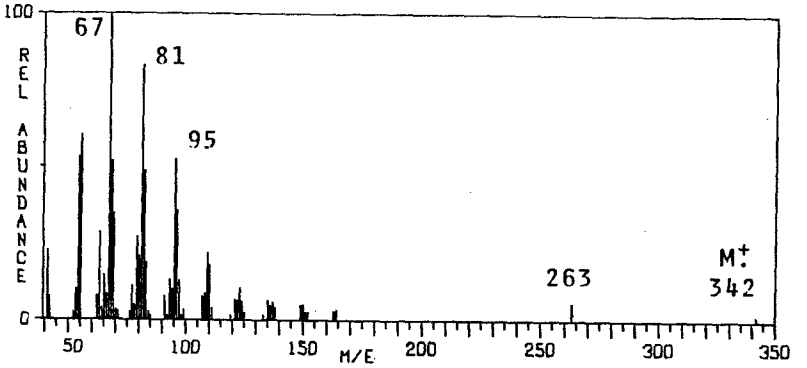

Figure 2-Electron impact mass spectrum of 2-Chloroethyl Linoleate

The fragmentation of 2-chloroethyl palmitate produces many chlorine containing ions. A suggested fragmentation scheme is shown in Figure 3. By contrast, the spectrum of 2-chloroethyl linoleate shows little chlorination aside from the molecular ion and the chloroethyl ion. Indeed, the fragmentation pattern resembles that of the unchlorinated ester.

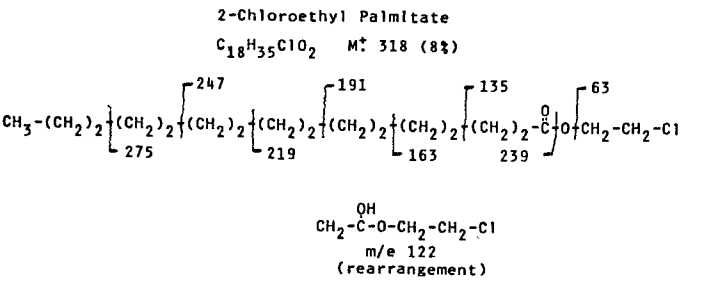

Figure 3-Suggested fragmentation scheme for 2-Chloroethyl Palmitate

French dressing samples fortified with the 2-chloroethyl esters of palmitic and linoleic acids and taken through the procedure described under "Experimental", showed recoveries of 50% and 73%, respectively.

None of the samples analyzed showed evidence of 2-chloroethyl oleate or 2-chloroethyl stearate.

2-Chloroethanol (ethylene chlorohydrin) has been formed in whole and ground spices after fumigation with ethylene oxide. The fumigant combines with moisture and natural inorganic chloride to form the corresponding chlorohydrin (WESLEY et.al 1965).

It is suggested that the 2-chloroethyl palmitate and 2-chloroethyl linoleate detected are the reaction products of 2-chloroethanol and natural fatty acids of oleoresins used in the manufacture of French dressing.

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