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GC-MS Identification and Analytical Behavior of Pirimiphos-Methyl in Imported Foods

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Residues of an organophosphorus pesticide subsequently identified as pirimiphos-methyl by gc-ms were found in several samples of imported foods. This compound is a broad spectrum contact insecticide used to control stored grain pests, cockroaches, mosquitoes, lice, fleas, bedbugs, houseflies, ants and many fruit and vegetable pests (THOMSON 1979). It is not registered for use in the United States. This paper reports the mass spectral identification, GLC characteristics, and recovery data for this compound along with residue findings in various imported foods.

MATERIALS AND METHODS

GC-MS-DS: Analyses were performed on a Finnigan 9610 gas chromatograph interfaced to a Finnigan 4021 mass spectrometer by means of a jet separator. Data was acquired with an Incos data system. The mass spectrometer was operated at 70eV ionizing energy, 500 uA emission current, 250°C source temperature and was scanned over a mass range of 35-650 daltons in 3 sec. The gas chromatograph was equipped with a 6 ft x 2 mm i.d. glass column packed with 4% SE-30/6% OV-210 on Chromosorb WHP 80/100 mesh and operated at column and injector temperatures of 200 and 220°C, respectively. The helium flow rate was 30 ml/min. The separator and transfer lines were heated at 205 and 210°C, respectively.

GLC (for retention time and recovery data): A Tracor Model 222 gas chromatograph equipped with a flame photometric detector and a Tracor Model 560 gas chromatograph equipped with a nitrogen/phosphorus detector were used for the analyses. Each gas chromatograph was fitted with 6 ft x 4 mm i.d. glass columns packed with (A) 10% OV-101 on Chromosorb WHP, 80/100 mesh, and (B) 1:1 mixture of 10% OV-101 and 15% OV-210 on the same support. Column temperatures (ca. 200°C) were adjusted to permit elution of carbophenothion at 2.83 and 3.33 (retention times relative to parathion) on columns A and B, respectively. The detector responses were adjusted to provide one-half full scale deflection for two ng of parathion.

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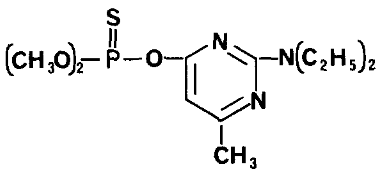
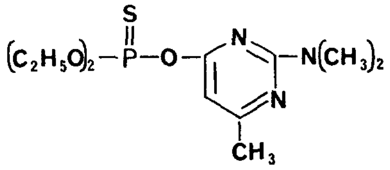
RESULTS AND DISCUSSION

An extract from the analysis of dried legumes exhibited a glc response having relative retention times (parathion = 1.0) of 0.85 and 0.55 on columns A and B respectively. These retention times did not correlate with those of any known domestic pesticide or industrial chemical. Responses obtained with flame photometric and nitrogen/phosphorus detectors indicated that the compound contained phosphorus. GC-MS analyses indicated the molecular weight of the compound was 305 and it contained an odd number of nitrogen atoms. The isotope abundance ratio of the $(M+2)^{+\cdot}$ ion also suggested the presence of sulfur and oxygen. A search of the literature for possible pesticide or industrial chemicals fitting the above criteria indicated that the identity of the unknown could be pirimiphos-methyl [0,0-dimethyl 0-(2-diethylamino-6-methyl-4-pyrimidinyl) phosphorothionate] or pyrimithate [0,0-diethyl 0-(2-dimethylamino-6-methyl-4-pyrimidinyl) phosphorothionate].



PIRIMIPHOS-METHYL



PYRIMITHATE

The mass spectral data supported the structure representing pirimiphos-methyl based on the following observations. The fragment ions at m/z 79 $(CH_3O\text{-}P\text{-}OH)^+$, 93 $((CH_3O)_2P)^+$, 109 $((CH_3O)_2P(O))^+$, and 125 $((CH_3O)_2P(S))^+$ are characteristic of methyl ester phosphorothionates (SAFE 1973). The extremely large relative abundance of m/z 290 $(M\text{-}CH_3)^+$ results from beta cleavage of the aliphatic nitrogen (BUDZIKIEWICZ 1967) indicating a N-diethyl rather than a N-dimethyl group. The ion at m/z 233 suggested $[M\text{-}N(C_2H_5)_2]^+$. Final confirmation of the identity of the unknown as pirimiphos-methyl was subsequently made by gc-ms comparison to an authentic reference material (Fig. 1a). A mass spectrum of pyrimithate reference material was also recorded (Fig 1b) for comparison purposes.

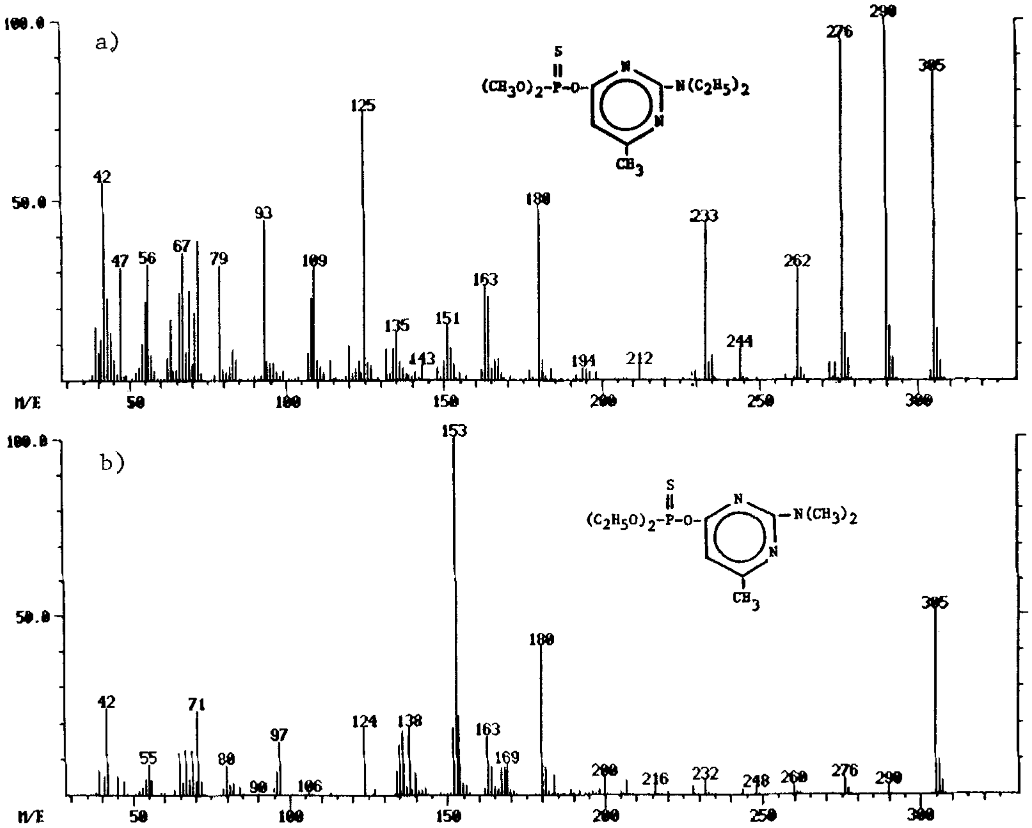
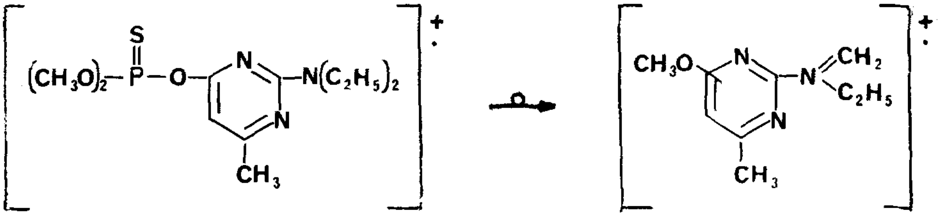


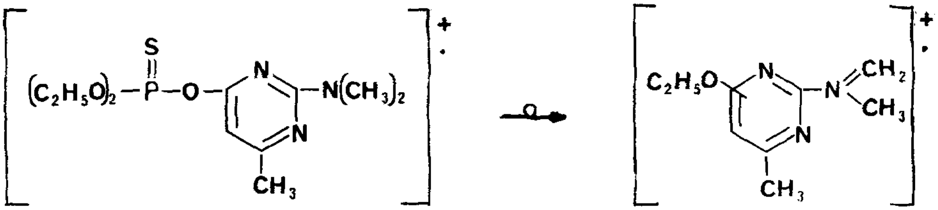
Fig. 1. Mass Spectrum of a) Pirimiphos-Methyl, b) Pyrimithate

It is interesting to note that both compounds exhibit ions at m/z 180. These ions are probably formed by the same type of mechanism proposed by DAMICO (1966) for the formation of m/z 179 in the mass spectrum of diazinon [O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothionate]. For both pirimiphos-methyl and pyrimithate, the formation of m/z 180 involves migration of an alkyl (or alkoxy) group, followed (or preceeded) by loss of a methyl radical from the N-diethyl group, or a hydrogen atom from the N-dimethyl group, respectively.



PIRIMIPHOS-METHYL

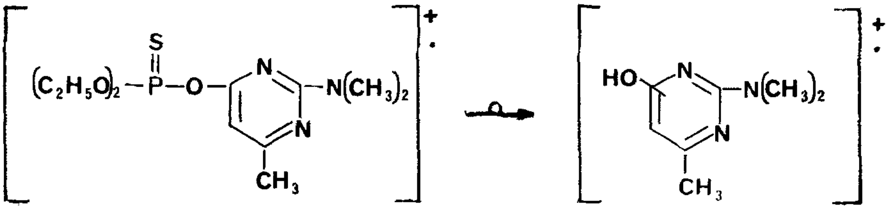
m/z 180



PYRIMITHATE

m/z 180

The most intense ion in the mass spectrum of pyrimithate, m/z 153, was initially thought to be $[(C_2H_5O)_2\text{-}P(S)]^+$ which would have corresponded to the m/z 125 ion, $[(CH_3O)_2\text{-}P(S)]^+$, in pirimiphos-methyl. However, accurate mass measurements indicated that m/z 153 had an elemental composition of $C_7H_{11}N_3O$. The formation of this ion probably involves a hydrogen rearrangement from the ethyl group to the pyrimidinyl oxygen atom.



PYRIMITHATE

m/z 153

Such a mechanism was proposed by DAMICO (1966) for the formation of the analogous ion, m/z 152, in diazinon. The corresponding rearrangement for the methyl ester, pirimiphos-methyl, was not observed.

To date, this laboratory has found pirimiphos-methyl in imported foods at the levels indicated in Table 1.

Table 1. Pirimiphos-Methyl Residues in Imported Foods

Food	Country of Origin	Concentration (ppm)
Chick Peas	Australia	0.02
Pigeon Peas	Kenya	0.19
Moong Dall	Tanzania	0.03
Peanut Butter	South Africa	0.23
Split Peas	Kenya	0.10-0.17[a]
Sardo Cheese	Argentina	0.21-1.4[a,b]

[a] Determined on a fat basis

[b] Represents range found in multiple samples of the same commodity

Another FDA district laboratory has reported finding a 3 ppm. residue of pirimiphos-methyl in dried green peas from Australia (LASKI 1981).

Recovery studies indicate that pirimiphos-methyl can be quantitatively recovered (97 and 101%) from dried legumes at the 0.1 ppm level by the official pesticide multi-residue procedure for non-fatty foods (AOAC 1980). The pesticide elutes from a Florisil column in the 15% ethyl ether/petroleum ether fraction.

ACKNOWLEDGMENT

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