Bull. Environ. Contam. Toxicol. 31, 116–119 (1983)

GC-MS Identification of Prothiophos in Imported Preserved Cabbage

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A residue of an insecticide subsequently identified by GC-MS as prothiophos [0-(2,4-dichlorophenyl) 0-ethyl S-propyl phosphorodithioate] was found at a level of 0.13 ppm in preserved cabbage imported from Thailand. Prothiophos (also known as tokuthion, NTN-8629, prothiofos, or dichlorpropaphos) is a broad spectrum contact-and stomach-poison insecticide. It is not registered for use in the United States, but it is recommended for use in other countries on apples, pears, grapes, citrus, vegetables, corn, potatoes, sugar cane, sugar beets, tea, tobacco, and hops to control numerous insects (THOMSON 1979). This paper reports the mass spectral identification, GLC characteristics, and recovery data for this compound.

MATERIALS AND METHODS

GC-MS-DS: Low resolution electron impact (EI), methane positive ion chemical ionization (PICI), and negative ion chemical ionization (NICI) mass spectra were determined using a Finnigan 9610 gas chromatograph interfaced to a Finnigan 4021 mass spectrometer as described previously (BARRY et al. 1982).

Accurate mass measurements were determined by GC-MS using the double beam technique employing 3,000 resolution for both the sample and reference beams on an AEI MS-30 double beam mass spectrometer as described previously (BARRY et al. 1982).

GC (Retention Time data): A Tracor Model 222 gas chromatograph equipped with a linearized Ni-63 electron-capture (EC) detector (in the constant current mode) and a Tracor Model 560 gas chromatograph equipped with a nitrogen/phosphorus (N/P) and a Hall Electrolytic Conductivity (HEC) detector were used for the analysis. Each gas chromatograph was fitted with 1.8 m x 4 mm i.d. glass column packed with (A) 5% OV-101 on 80-100 mesh Chromosorb WHP. The Tracor Model 222 was additionally equipped with (B) 4% SE-30/6% SP2401 on 100-120 mesh Supelcoport. Column temperatures (ca 200°C) were adjusted to permit elution of p,p'-DDT at 3.13 and 2.80 (retention time relative to chlorpyrifos) on Columns A and B, respecitvely, for EC detectors. For the N/P detector and Column (A), the column temperature (ca 200°C) was adjusted to permit elution of ethion at 2.56 relative to chlorpyrifos.

RESULTS AND DISCUSSION

An extract prepared for the analysis of preserved cabbage exhibited electron-capture as well as Hall electrolytic conductivity and nitrogen/phosphorous GLC responses; the peak of interest had relative retention times (chlorpyrifos=1) of 1.85 and 1.75 on 5% OV-101 and 4% SE-30/6% SP2401, respectively. The retention times did not correspond with those of any known domestic pesticides or industrial chemicals.

The mass spectral data (EI, PICI, and NICI) indicated that the compound had a molecular weight of 344 and contained 2 chlorine atoms. The "Mass Spectral Data Compliation of Pesticides and Industrial Chemicals" (CAIRNS et al. 1980) listed two compounds having these properties, prothiophos ($C_{11}H_{15}Cl_2O_2PS$) and oxadiazon ($C_{15}H_{18}Cl_2N_2O_3$). The fragmentation pattern of the unknown correlated better with the structural configuration of prothiophos rather than oxadiazon. A reference standard of prothiophos was subsequently obtained from the EPA, and both the mass spectral and retention time data agreed with the data for the sample component.

The EI spectrum (Fig. 1a) exhibits no molecular ion but does show prominent chlorine isotope clusters representative of one chlorine atom at m/z 309 $[M-Cl]^+$, and m/z 267 $[309-C_3H_6]^+$. The two chlorine atom isotope cluster at m/z 162 represents the dichlorophenol $[HO-C_6H_3Cl_2]^+$ fragment ion. Other prominent ions in the spectrum are m/z 183 $[C_2H_5O-P(S)-SC_3H_7]^+$, m/z 155 $[C_3H_7S-P(S)-OH]^+$, m/z 113 $[HS-P(S)-OH]^+$, m/z 63 $[PS]^+$, and m/z 43 $[C_3H_7]^+$. The elemental composition of the fragment ions were confirmed by accurate mass measurements.

The isotope cluster at m/z 239 seen in the low resolution EI spectrum has the appearance of a two chlorine atom isotope cluster; however, high resolution mass spectra recorded at 12,500 resolution (BRUMLEY et al. 1982) confirmed the suspicion that the cluster actually consisted of two overlapping chlorine isotope clusters. The ion at m/z 239 was confirmed as being $C_6H_5O_2ClS_2P$, while m/z 241 was composed of two ions, $C_6H_5O_2{}^{37}ClS_2P$ and $C_6H_4Cl_2S_2P$.

The methane PICI spectrum (Fig. 1b) exhibits the characteristic two chlorine isotope cluster for the protonated molecular ion at m/z 345 $[M+H]^+$, as well as the adduct ions at m/z 373 and 385, representative of $[M+C_2H_5]^+$ and $[M+C_3H_5]^+$, respectively. The prominent non-chlorinated peak at m/z 183 represents $[C_2H_5O-P(S)-SC_3H_7]^+$.

The methane NICI spectrum (Fig. 1c) does not exhibit any $[M]^-$ or $[M-1]^-$ ions. The ion at m/z 308 represents $[M-HCl]^-$. Other prominent one chlorine fragment ions are the m/z 280 $[M-(HCl+C_2H_4)]^-$ and the base peak m/z 237 $[M-(HCl+C_5H_{11})]^-$. Characteristic two chlorine isotope clusters are observed at m/z 301 $(M-C_3H_7)^-$, m/z 269 $[301-S]^-$, m/z 177 $[S-\emptyset-Cl_2]^-$, and m/z 161 $[O-\emptyset Cl_2]^-$. Other

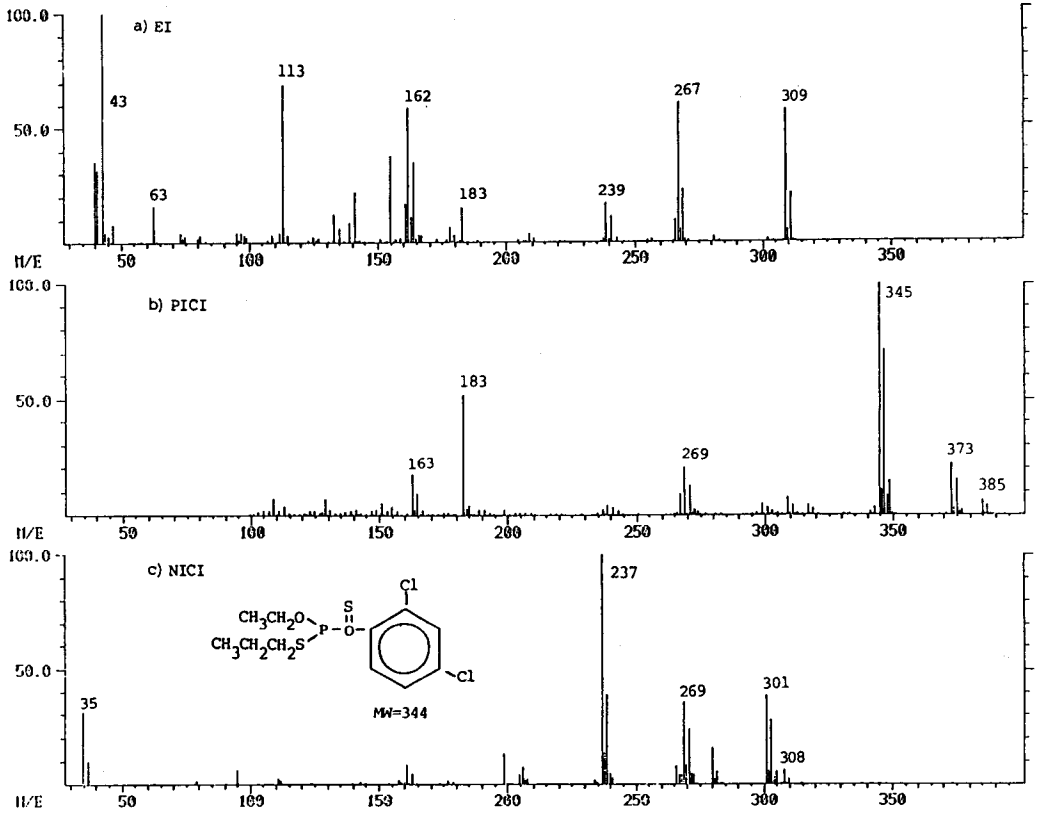

Fig. 1 Mass Spectra of Prothiophos a) EI, b) PICI, c) NICI

prominent ions occur at m/z 199 $[C_2H_5O\text{-}P(S)(O)\text{-}SC_3H_7]^-$, m/z 111 $[PS_2O]^-$, m/z 95 $[PSO_2]^-$ and m/z 35 $[Cl]^-$.

The retention times of prothiophos reference standard were 1.85 and 1.75 relative to chlorpyrifos on 5% OV-101 and 4% SE-30/6% SP2401, respectively, as had been determined for the sample component. Prothiophos exhibited a sensitivity on the EC detector of 2.5 nanograms for half-scale deflection (heptachlor epoxide = 1 ng).

Prothiophos was recovered (94%) from cheese fortified at 1.0 ppm by the official pesticide multiresidue procedure for fatty foods (AOAC, Chap. 29, 1980). Recovery by the non-fatty food procedure was 92% for endive fortified at 0.04 ppm. Prothiophos eluted from Florisil columns in the 6% diethyl ether/petroleum ether fraction.

Subsequent to this initial finding of prothiophos, we have confirmed by GC-MS the presence of 0.25 ppm prothiophos in red barlinka grapes imported from South Africa (YOUNG 1982).

ACKNOWLEDGMENT

We wish to thank J.D. Rosen, Science Advisor, FDA, New York and Research Professor of Food Science, Cook College, Rutgers University, New Jersey, for his help in the preparation of this paper, and W. Brumley and J. Sphon for obtaining the high resolution data on the chlorine isotope cluster at m/z 239 and 241.

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Accepted December 27, 1982