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GC-MS Identification and Analytical Behavior of Procymidone in Imported Foods

Thomas L. Barry[1], Glenn Petzinger[1], and Jack Geltman[2]

[1] *U.S. Food and Drug Administration, New York Regional Laboratory, Chemistry Branch, New York, NY 11232, and* [2] *U.S. Food and Drug Administration, New York Import District, Laboratory Branch, New York, NY 11232*

Residues of a pesticide subsequently identified as procymidone [N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide] by gc-ms were found in fresh cucumbers and canned pimientos imported from Spain. Procymidone (also known as sumilex, sumisclex, dicyclidine, S-7131, or procymidox) has protective and eradicant properties and is used as a systemic foliar fungicide. It is recommended for application on most vegetables, fruit and field crops outside the United States to control Botrytis, Sclerotinia, Helminthosporium and Monilinia diseases (THOMSON 1979). Procymidone is not registered for use in the United States. This paper reports the mass spectral identification, glc characteristics, and recovery data for this compound.

MATERIALS AND METHODS

GC-MS-DS (Low Resolution Data): Analyses were performed on a Finnigan 9610 gas chromatograph interfaced to a Finnigan 4021 mass spectrometer by means of a glass jet separator. Data were acquired with an Incos data system. For electron impact (EI) analysis, the mass spectrometer was operated at 50 eV ionizing energy, 500 µA emission current, 250°C source temperature and was scanned over a mass range of 35-650 daltons in 3 sec. The separator and transfer lines were maintained at 205 and 210°C, respectively. For both positive ion (PICI) and negative ion chemical ionization (NICI), methane was used as a make-up gas with a forepump pressure guage reading of 0.2 torr and a source pressure of 5.7×10^{-5} torr. The mass spectrometer was operated at 50 eV ionizing energy, 100 µA emission current, 250°C source temperature, and was scanned over a mass range of 10-650 daltons (NICI) and 70-650 (PICI) in 3 sec. The gas chromatograph was equipped with a 6 ft x 2 mm i.d. glass column packed with 3% OV-101 on Chromosorb WHP 80/100 mesh and operated at column and injector temperatures of 200 and 220°C, respectively. The helium flow rate was 40 ml/min.

GC-MS-DS (Accurate Mass Measurements): Analyses were performed on a Pye 104 gas chromatograph interfaced to an AEI MS-30 Double Beam Mass Spectrometer by means of a silicone membrane separator. Data were acquired using an AEI DS50-DB data system. The mass spectrometer was operated at 70 eV ionizing energy, 4 kV accelerating voltage, 100 µA trap current, and 250°C source temperature. The separator and transfer lines were maintained at 220 and 210°C, respectively. Accurate mass measurements were obtained by gc-ms using the double beam technique employing 3,000 resolution for both the

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sample and reference beams and a scan rate of 3 sec/decade. The gas chromatograph was equipped with a 5 ft. x 4 mm i.d. glass column packed with 3% OV-101 on Chromosorb WHP 80/100 mesh and was operated at column and injector temperatures of 190 and 215°C, respectively. The helium flow rate was 40 ml/min.

GLC (Retention Time and Recovery Data): A Tracor model 222 gas chromatograph equipped with a linearized Ni-63 electron capture detector (in the constant current mode) and 6 ft. x 4 mm i.d. glass columns packed with (A) 5% OV-101 on Chromosorb WHP, 80/100 mesh and (B) 4% SE-30/6% SP2401 on Supelcoport 100/120 mesh. Column temperatures (ca 200°C) were adjusted to permit elution of p,p'-DDT at 3.03 and 3.28 (retention times relative to aldrin) on columns A and B, respectively.

RESULTS AND DISCUSSION

Extracts from the analyses of canned pimientos and fresh cucumbers both exhibited electron capture glc responses having relative retention times (aldrin = 1.0) of 1.34 and 2.32 on OV-101 and 4% SE-30/6% SP2401 columns, respectively. The retention times did not correlate 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 283, contained two chlorine atoms and an odd number of nitrogens atoms. The "Mass Spectral Data Compilation of Pesticides and Industrial Chemicals" (CAIRNS et al. 1980) listed two compounds which had these properties, nitrofen ($C_{12}H_7Cl_2NO_3$) and procymidone ($C_{13}H_{11}Cl_2NO_2$). Both the mass spectral and retention time data for nitrofen were known and did not agree with that of the sample component. Although there were no mass spectral or retention time data available for procymidone, accurate mass measurements indicated that the elemental composition of the sample component was $C_{13}H_{11}Cl_2NO_2$ (0.5 ppm).

A reference standard of procymidone was subsequently obtained by the EPA from Sumitomo Chemical Co. of Japan and both the mass spectral and retention time data agreed with the data for the sample component.

The EI spectrum of procymidone (Fig. 1a) exhibited a molecular ion representing two chlorine atoms at m/z 283. Other prominent two chlorine atom isotope clusters appeared at m/z 255, $[M-CO]^{+\cdot}$, m/z 240, $[M-(CO+CH_3)]^+$, m/z 212, $[M-(2CO+CH_3)]^+$ and m/z 145, $[C_6H_3Cl_2]^+$. The non-chlorinated base peak in the spectrum m/z 96, $[C_6H_8O]^{+\cdot}$, resulted from loss of dichloroisocynate from the molecular ion. The elemental composition of the fragment ions were confirmed by accurate mass measurement data (0.5 ppm).

The methane PICI spectra (Fig. 1b) produced the characteristic two chlorine isotope cluster for the protonated molecular ion at m/z 284, $[M+H]^+$, as well as the adduct ions at m/z 312 and 324 representing $[M+C_2H_5]^+$ and $[M+C_3H_5]^+$, respectively. The one chlorine atom isotope cluster at m/z 248 represents loss of HCl from the protonated molecular ion. The one chlorine isotope cluster at m/z 264 was unexpected. It is presently thought to arise from loss of HCl from the adduct ion $[M+CH_5]^+$. Studies with CD_4 are being undertaken to further investigate this possibility.

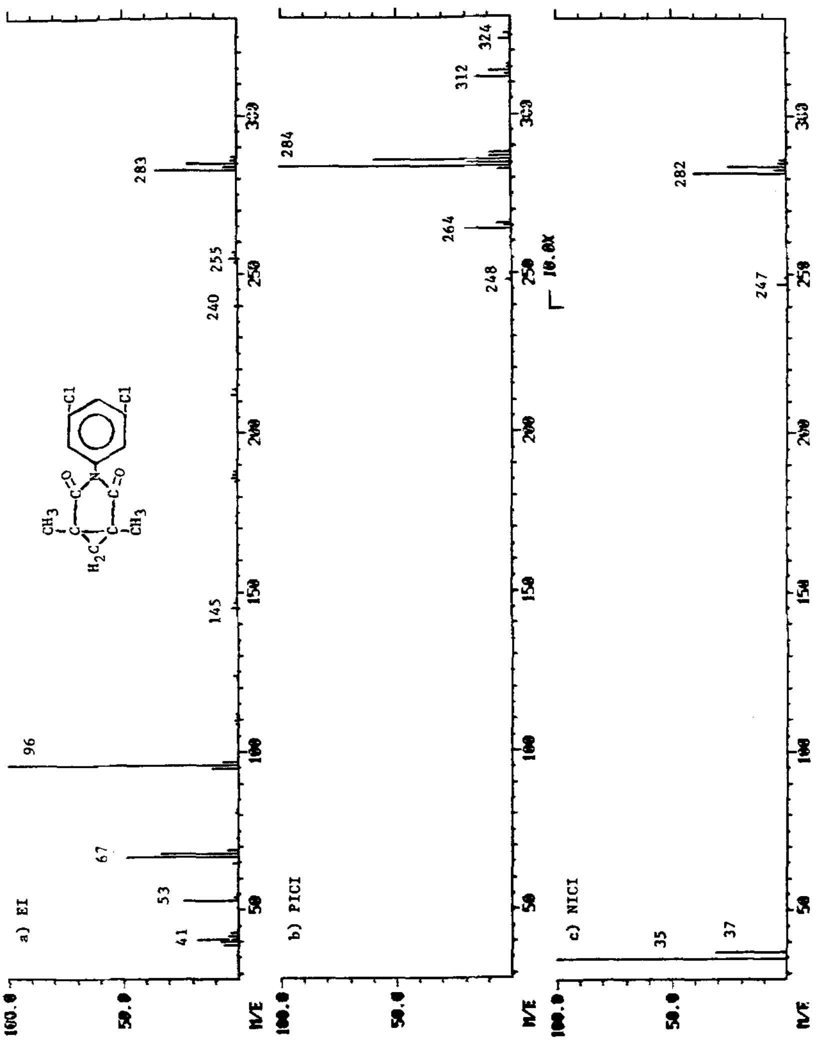

Fig. 1. Mass spectra of procymidone a) EI, b) PICI, c) NICI.

The methane NICI spectra (Fig. 1c) produced a prominent $[M-1]^-$ ion representative of two chlorine atoms at m/z 282. The $[M-1]^-$ is formed by dissociative resonance capture and is common for compounds with moderate electronegativity. Generally only compounds with strong electronegative functional groups produce $[M]^-$ ions.

The retention times of procymidone on 5% OV-101 were 1.34 and 1.37 relative to aldrin and chlorpyrifos, respectively. The corresponding relative retention times on 4% SE-30/6% SP2401 were 2.32 and 1.98. Procymidone exhibited a sensitivity of 11.5 nanograms for half-scale deflection (heptachlor epoxide = 1 ng).

Procymidone was recovered (74.8 and 77.5%) from cheese fat spiked at 0.85 ppm by the official pesticide multiresidue procedure for fatty foods (AOAC, Chap. 29, 1980). Recoveries by the non-fatty food procedure (AOAC, Chap. 29, 1980) were 81.1 and 86.5% for tomatoes spiked at 0.29 ppm. Procymidone eluted from the Florisil column in the 15% ethyl ether/petroleum ether fraction. Recoveries by the Luke procedure (LUKE et al. 1975) at 0.29 ppm in tomatoes were 92.0 and 96.7%.

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