Bull. Environ. Contam. Toxicol. (1985) 35:285–290

Environmental Contamination and Toxicology

Identification of Fluchloralin in Imported Dried Fruit

Thomas L. Barry,[1] Glenn Petzinger,[1] and Mary Stenson[2]

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

A residue of an insecticide identified by GC/MS as fluchloralin [N-(2-chloroethyl)-2,6-dinitro-N-propyl-4-trifluoromethyl)benzenamine] was found at a level of 0.2 ppm in dried fruit imported from Asia. Fluchloralin (Basalin, BAS-392H) is a selective dinitroaniline compound used as a pre-plant herbicide. It is recommended for use for cotton, peanuts, and soybeans and is being tested for use with crops such as alfalfa, carrots, cucumbers, peas, beans, potatoes, and tomatoes (Thomson 1979). In July, 1982, the USEPA established tolerances for residues of fluchloralin of 0.05 ppm in or on seed and pod vegetables, and 0.1 ppm for forage and hay derived from these products (Cooper 1982).

MATERIALS AND METHODS

Electron impact (EI) mass spectra were obtained using a Finnigan 9610 gas chromatograph interfaced to a Finnigan 4021 mass spectrometer as described previously (Barry et al. 1982).

A Tracor model 222 gas chromatograph equipped with a linearized Ni-63 electron-capture detector (in the constant current mode) and 1.8 m 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 3.13 and 2.80 (relative to chlorpyrifos) on columns A and B, respectively.

RESULTS AND DISCUSSION

An analysis of an extract prepared from dried papaya produced electron-capture glc responses having relative retention times (chlorpyrifos=1) of 0.53 and 0.95 on 5% OV-101 and 4% SE-30/6% SP2401 columns, respectively. These retention times did not correlate with the data of any of the pesticides and industrial chemicals retained in the FDA databank.

The mass spectral data indicated that the unknown component had a molecular weight of 355, contained one chlorine atom, an odd number of nitrogen atoms (McLafferty 1973), and possible fluorine atoms. A computerized search of the NIH-EPA mass spectral library produced trifluralin [2,6-dinitro-N,N-dipropyl-4-(trifluoromethyl)benzenamine] as the best match. The fragmentation pattern and ion intensities suggested that the structure of the unknown component was very similar to that of trifluralin. The facts that the unknown component contained one chlorine atom and the molecular weight was 20 amu higher than trifluralin additionally suggested that the compound contained an N-propyl-N-chloromethyl group rather than an N,N-dipropyl group as in trifluralin. The unknown was tentatively identified as fluchloralin. A reference standard of fluchloralin was subsequently obtained from the USEPA, and both the mass spectral and retention time data agreed with the data for the sample component.

The EI spectrum of trifluralin (Fig. 1a) exhibits a molecular ion at m/z 335, a base peak m/z 306 $[M-C_2H_5]^+$, and an ion at m/z 264 representing $[M-(C_2H_5+C_3H_6)]^+$. Fragment ions representing loss of oxygen (16 amu) from both m/z 306 and 264 are observed at m/z 290 and 248, respectively. Other prominent ions appear at m/z 316 $[M-F]^+$, m/z 318 $[M-OH]^+$, and m/z 43 $[C_3H_7]^+$.

The EI spectrum of fluchloralin (Fig. 1b) exhibits a molecular ion having a characteristic one chlorine isotope cluster at m/z 355. The base peak, m/z 306 represents $[M-CH_2Cl]^+$, m/z 326 is $[M-C_2H_5]^+$, and

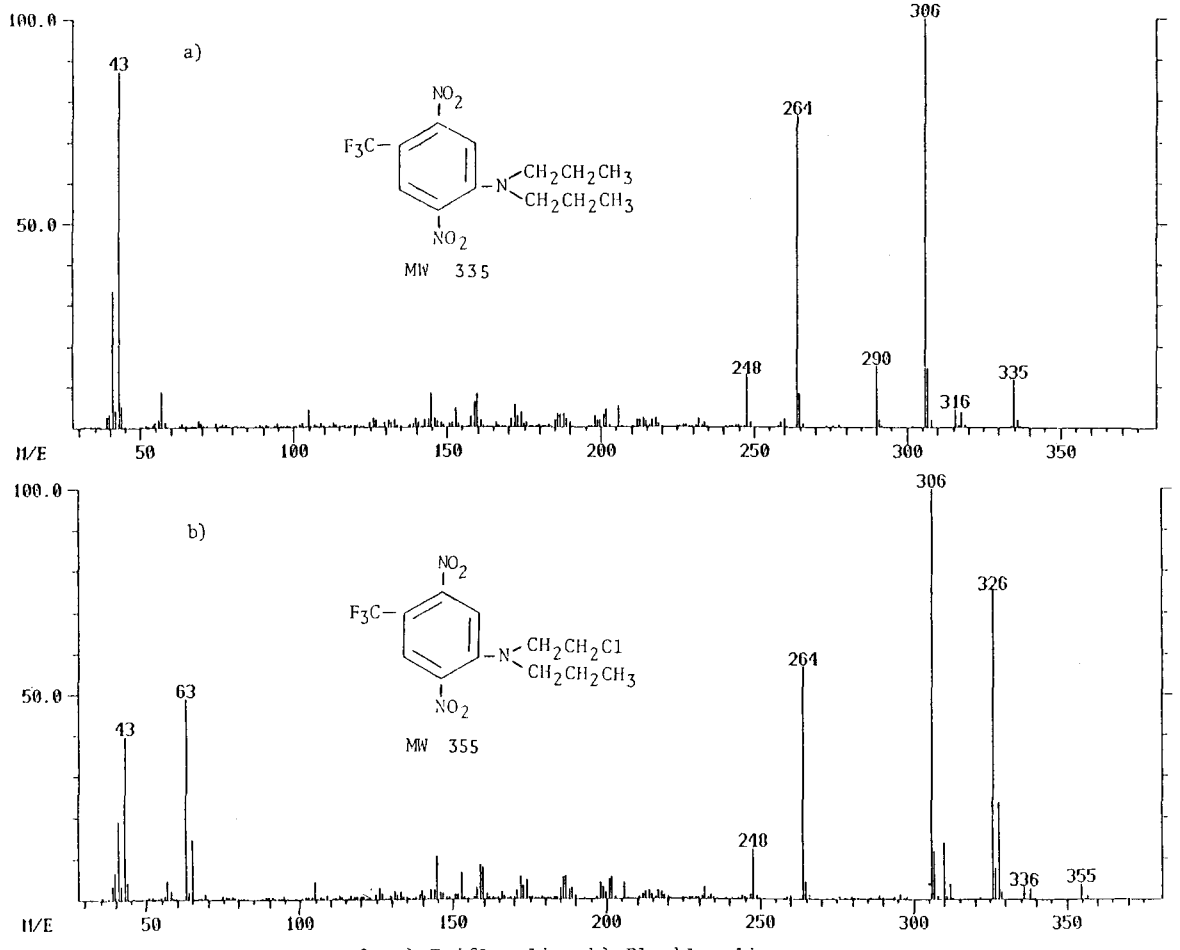

Fig. 1. Mass Spectra of a) Trifluralin, b) Fluchloralin

m/z 264 represents both $[M-(C_2H_5+C_2H_3Cl)]^+$ and $[M-(CH_2Cl+C_3H_6)]^+$. Fragment ions representing the loss of oxygen (16 amu) from both m/z 326 and 264 are observed at m/z 310 and 248, respectively. Other prominent ions appear at m/z 336 $[M-F]^+$, m/z 338 $[M-OH]^+$, m/z 43 $[C_3H_7]^+$, and m/z 63 $[CH_2CH_2Cl]^+$.

In the fragmentation mechanism proposed for trifluralin, the base peak, m/z 306, is formed by loss of an ethyl radical from the molecular ion as a result of α-cleavage of the alkyl carbon-carbon bond attached to the nitrogen atom as shown in figure 2a (Plummer & Klingbiel 1974). The base peak fragments further by cleavage of the carbon-nitrogen bond resulting in loss of propylene to form the ion at m/z 264.

Fluchloralin follows a fragmentation pathway similar to trifluralin. However, since there are two different alkyl groups on the nitrogen atom in fluchloralin, two different α-cleavage pathways are observed (Fig. 2b). Loss of an ethyl radical from the molecular ion results in formation of the ion at m/z 326. This ion then loses vinyl chloride as a result of carbon-nitrogen bond cleavage to form m/z 264. Alternatively, loss of a chloromethyl radical from the molecular ion results in formation of the base peak, m/z 306, which then loses propylene as a result of carbon-nitrogen bond cleavage forming m/z 264. Thus both α-cleavage pathways lead to formation of the same m/z 264 ion.

The relative retention times of fluchloralin (chlorpyrifos=1.0) on 5% OV-101 and 4% SE-30/6% SP2401 are 0.53 and 0.95, respectively. Fluchloralin exhibits a sensitivity of 1.7 ng for a half-scale deflection (heptachlor epoxide= 1 ng) for the electron-capture detector.

Fluchloralin is recovered from raisins fortified at 0.35 ppm by the official pesticide multiresidue procedure for non-fatty foods (Horwitz 1980). Recovery by the fatty food procedure (Horwitz 1980) is essentially zero for cheese fortified at 0.4 ppm. Fluchloralin elutes from Florisil columns in the 6% diethyl ether/petroleum ether fraction.

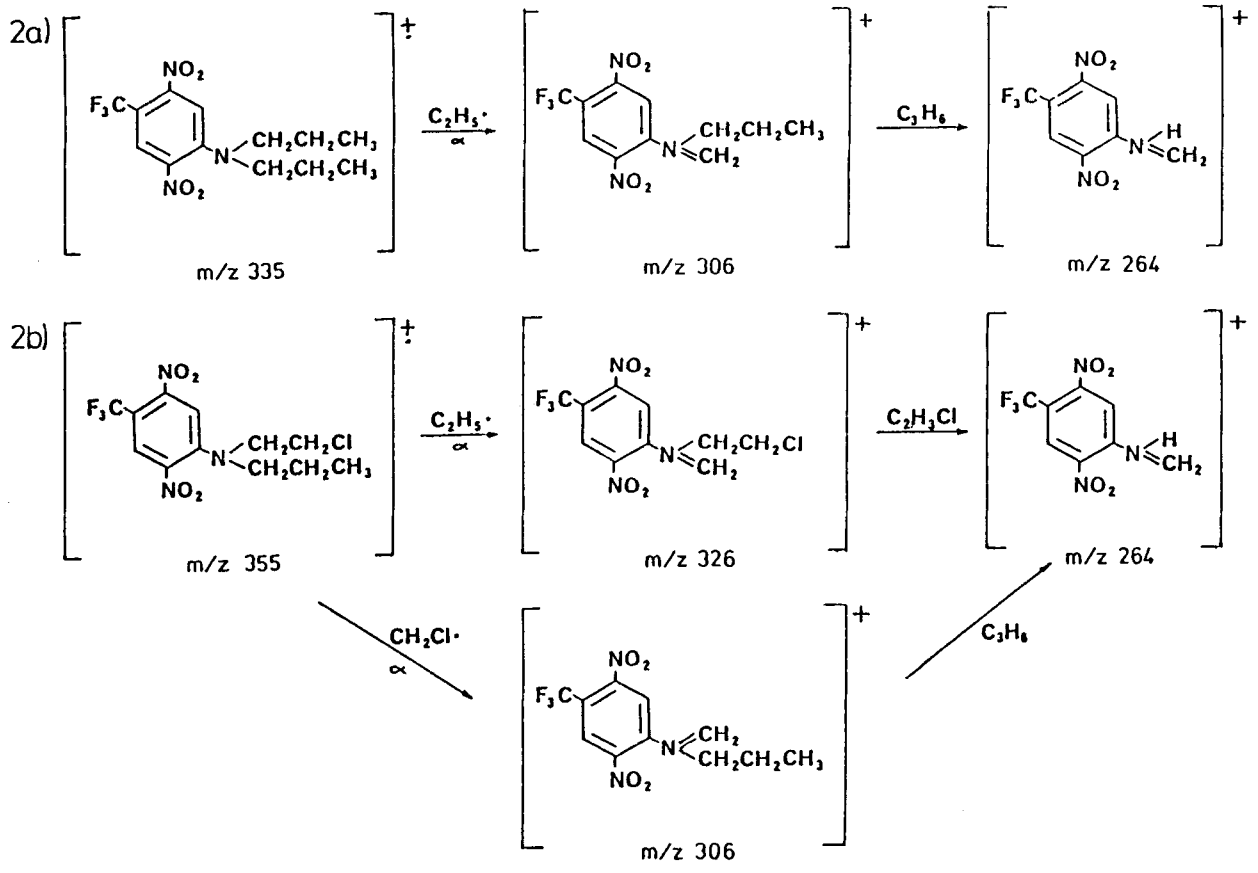

Fig. 2. EI Mass Fragmentation Pathways of a) Trifluralin, b) Fluchloralin

Acknowledgements. We 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.

REFERENCES

Barry TL, Petzinger G, Geltman J (1982) GC-MS identification and analytical behavior of procymidone in imported foods. Bull Environm Contam Toxicol 29: 611-614

Cooper C (ed) (1982) Pesticide and Toxic Chemical News. Food Chemical News Inc, Washington D.C., 10(36): 5-6

Horwitz W (ed) (1980) Official methods of analysis of the association of official analytical chemists, 13th edn. Association of Official Analytical Chemists, Washington D.C., pp 466-496

McLafferty FW (1973) Interpretation of mass spectra, 2nd edn. WA Benjamin, Reading, Massachusetts, pp 31-39

Plimmer JR, Klingbiel UI (1974) The application of mass spectrometry to the study of nitroaniline derived herbicides. In: Hague R, Biros, FJ (eds), Mass spectrometry and nmr spectroscopy in pesticide chemistry. Plenum Press, New York, pp 99-112

Thomson WT(1979) Agricultural chemicals, book II - herbicides. Thomson Publications, Fresno, California, pp 44-45

Received May 8, 1984; accepted August 1, 1984