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Persistence and Metabolism of Aldicarb in Fresh Potatoes

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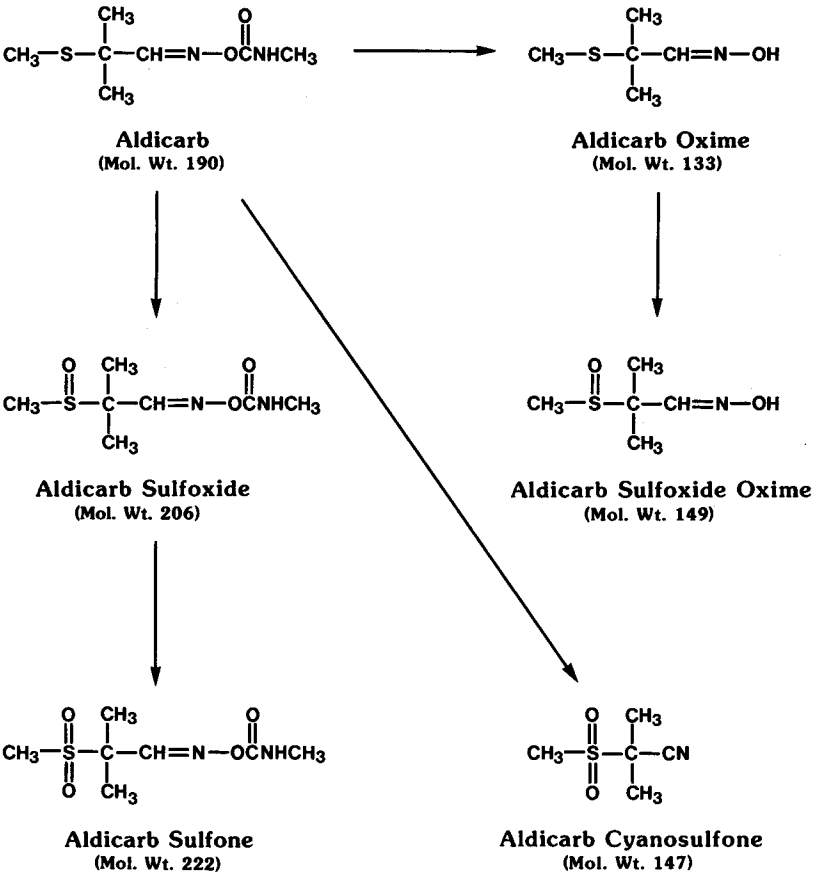
Before the U.S. federal registration of aldicarb [(2-methyl-2-methylthio)propionaldehyde O-(methylcarbamoyl)oxime] in 1970 for use on the cotton plant as broad spectrum soil-applied systemic pesticide for the control of insects, mites and nematodes, a detailed metabolic study on the cotton plant (Gossypium hirusutum) revealed an interesting insight into its mode of action (Metcalf et al. 1966). Initial metabolic attack was a rapid and complete oxidative conversion to aldicarb sulfoxide followed by a much slower oxidation to the sulfone (Scheme 1). Degradation of aldicarb to its corresponding oxime or nitrile was also indicated. Two important facts were established which have relevance to pesticide residue chemistry. The complete conversion of aldicarb to its sulfoxide and sulfone resulted in an increase in the cholinesterase inhibition. The persistence of aldicarb sulfoxide in the plant, combined with slow oxidation to the corresponding sulfone, accounted for the observed prolonged systemic activity. A reinvestigation of aldicarb metabolism in the cotton plant confirmed these findings and concentrated on the nature and toxicity of the highly polar conjugated residues (Bartley et al. 1970) which accounted for the major residue at final harvest. In a translocation study (Iwata et al. 1977) in oranges, the total carbamate residue remaining (sulfoxide and sulfone combined) in the soil after about 80 days was less than 1 ppm.

This paper describes a recent incidence involving fresh potatoes where the major carbamate residue detected and confirmed by methane and ammonia chemical ionization (CI) gas chromatography mass spectrometry (GCMS) was aldicarb sulfone at about 1 ppm with a minor contribution from aldicarb sulfoxide.

MATERIALS AND METHODS

All spectra were obtained on a Finnigan Model 3300 quadrupole mass spectrometer equipped with a CI source and INCOS Data System; operating conditions: 45 cm x 2 mm i.d. glass column packed with



Scheme 1. Metabolic pathway of aldicarb.

2% DEGS on 80/100 mesh Chromosorb W; carrier gas and reagent gas for chemical ionization, 30 mL methane/min; column inlet, 180°C; column temperature, 120°C, isothermal.

Sample (58 g) was extracted by the Luke procedure (Luke et al. 1981). For identification by GCMS, the sample extract was further cleaned up by elution through carbon (Luke & Doose 1983) and concentrated to 0.1 mL using a stream of dry nitrogen. 3 uL of this extract representing 0.3 g of sample was then used for analysis.

RESULTS AND DISCUSSION

The sample extract was first examined by gas chromatography using a flame photometric detector in the sulfur mode (FPD-S) and was suspected of containing aldicarb sulfoxide [RR_t = 0.2 relative to phorate]. For confirmatory purposes, the extract was then reduced in volume (to 0.1 mL) in preparation for examination by GCMS. Before such an examination, however, the mass spectral characteristics of aldicarb sulfoxide and aldicarb sulfone were obtained at the expected concentration level (about 1 ppm) to be encountered in the sample (Figure 1). Previous studies (Muszkat & Aharonson 1982) had indicated that isobutane CI may provide abundant protonated molecular ions [MH^+] as well as several diagnostic ions for residue confirmation. As can be observed from the GCMS data illustrated in Figure 1, no ions coresponding to MH^+ were observed under methane or ammonia CI conditions. This absence of MH^+ ions was not altogether unexpected since the previous workers had introduced their standards at much higher concentration levels via an unheated direct inlet probe. The present studies involved injections of less than 100 ng on column for GCMS, i.e. according to the sample protocol to be used for residue confirmation. While the former probe analyses can give strong indications as to the behavior of some compounds on GCMS-CI, the extrapolation of such results to actual residue work can be disappointing, particularly when dealing with molecules known to suffer from potential thermal lability. In the present study, the possibility of thermal degradation did exist and was explored via sample introduction by spotting on the liquid chromatographic (LC) moving belt interface (Cairns et al. 1983) at various flash evaporization temperatures (100°C to 200°C) with an ambient mass spectrometer source temperature of 180°C. The conclusions derived from that preliminary study indicated that the molecules under study survived a flash evaporization temperature of 140°C, 20°C above the GC temperature selected for the analyses. This data confirmed that aldicarb sulfoxide and aldicarb sulfone would be chromatographed intact at least as far as the source of the mass spectrometer set at 180°C where the potential for thermal degradation could occur. A previous study of these compounds via LCMS (Wright et al. 1982) also concluded that these carbamates were not thermally degraded at 120°C.

In the case of aldicarb sulfoxide (Figure 1A), the base peak is m/z 143, corresponding to the loss of CH_3SO from the protonated molecular ion (Scheme 2). The appearance of ions at m/z 171 and m/z 183 (in the methane spectrum) corresponded to adduct species derived from the reagent ions present in the source. However, the presence of an ion at m/z 148 can only be explained as belonging to be protonated aldicarb cyanosulfone. Since the retention times for the sulfoxide and sulfone were very close together, the probability that the reference standard contained a small amount of sulfone was a feasible explanation. In the ammonia CI spectrum of aldicarb sulfoxide (Figure 1A), the evidence for the

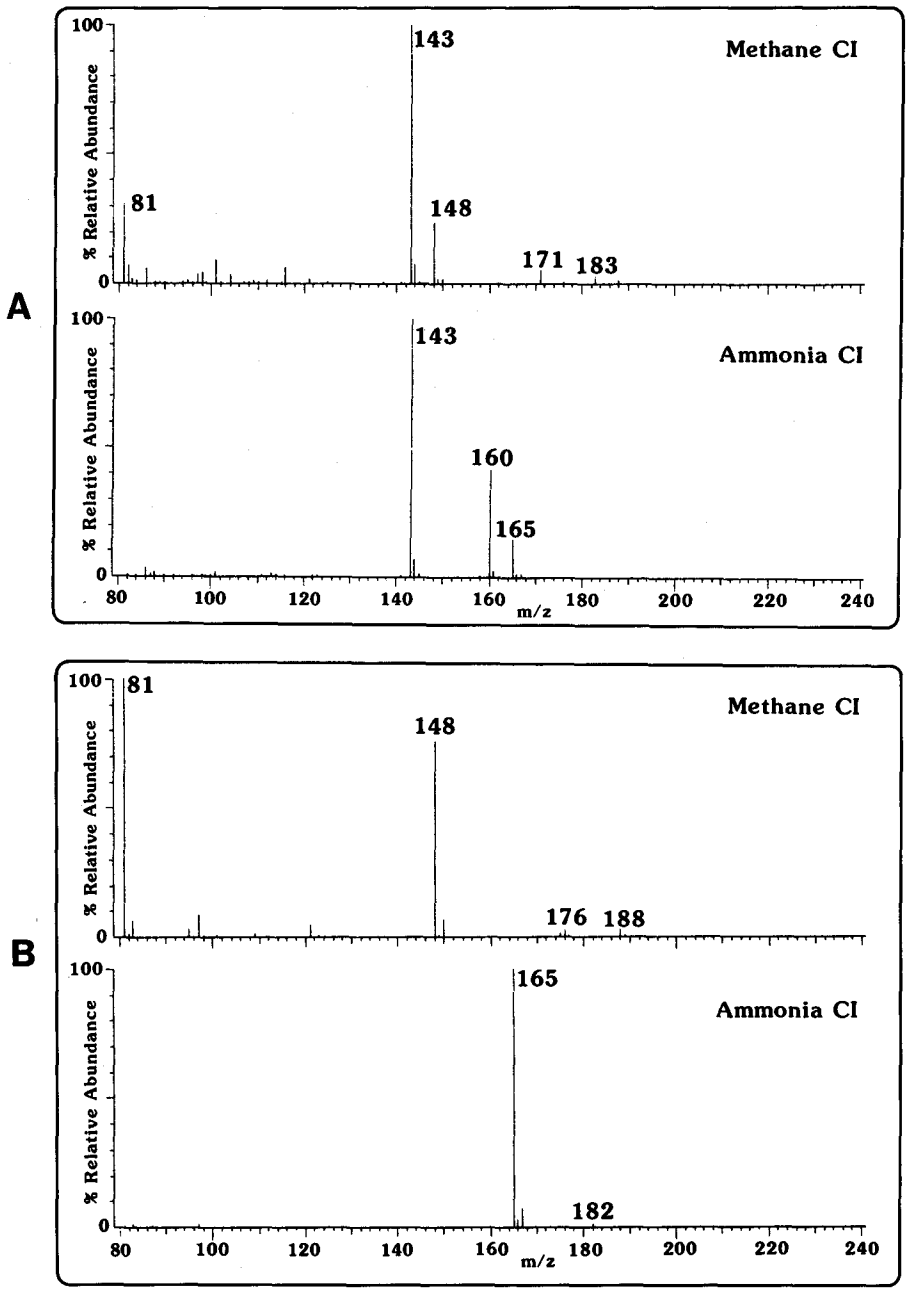
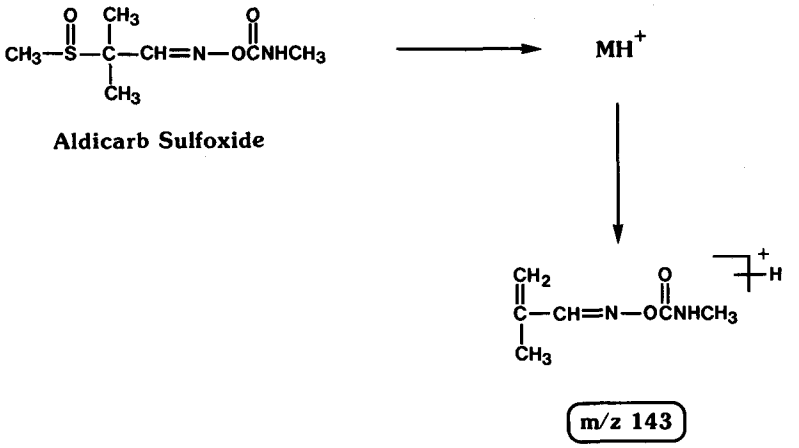
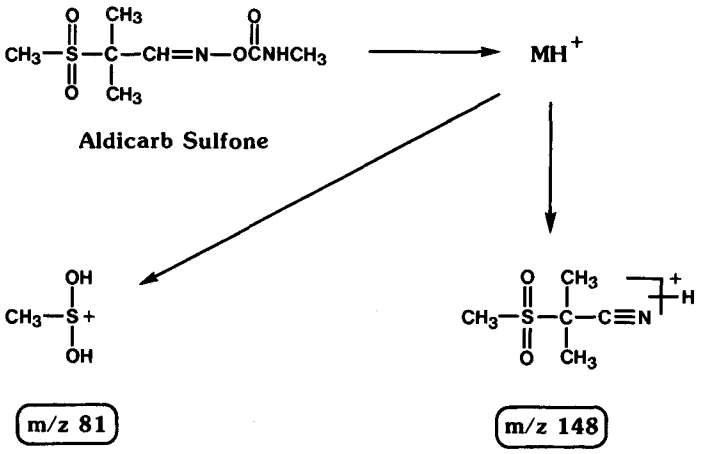


Figure 1. Chemical ionization mass spectra obtained under GCMS conditions for A, aldicarb sulfoxide; and B, aldicarb sulfone.



Scheme 2. Fragmentation pathway for aldicarb sulfoxide.



Scheme 3. Fragmentation pathway for aldicarb sulfone.

sulfone impurity was clearly illustrated by the appearance of an ion at m/z 165 corresponding to the adduct species formed with the ammonium ion by the aldicarb cyanosulfone moiety. The ion at m/z 160 can be attributed to the ammonium adduct ion formed with the structure represented by the m/z 143 ion in the methane spectrum. Finally, the mass spectral data for aldicarb sulfone (Figure 1B) indicated that the major fragmentation pathway was to the protonated aldicarb cyanosulfone (Scheme 3) at m/z 148 in the

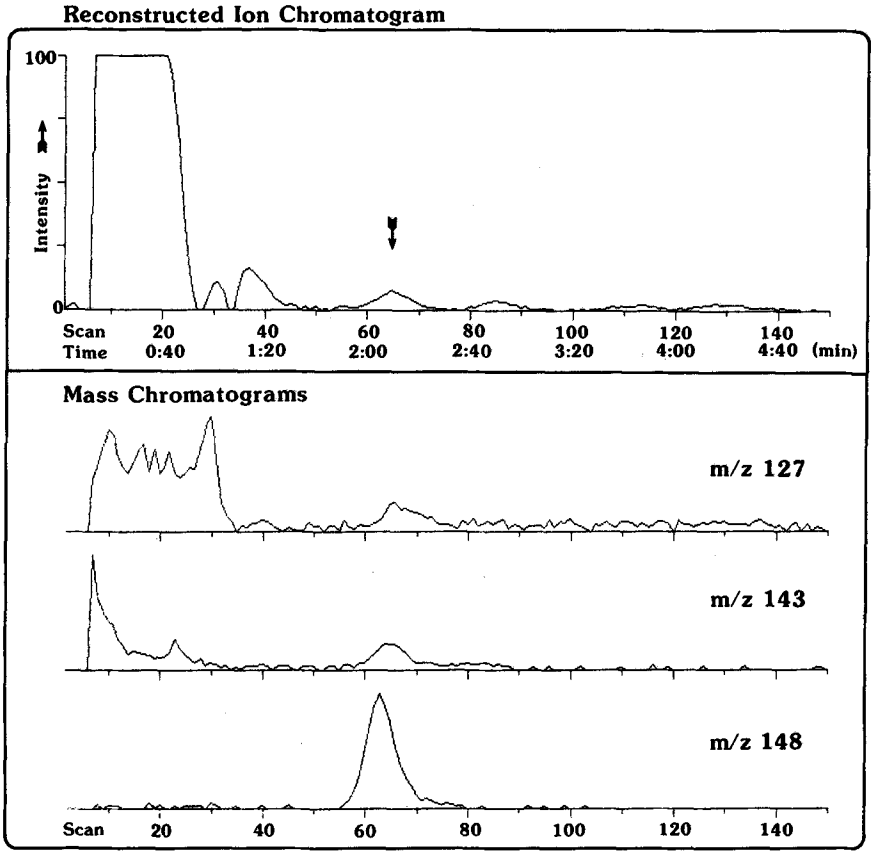


Figure 2. Total ion chromatogram for potato extract under chemical ionization conditions with mass chromatograms to indicate the peak of interest.

methane CI spectrum and at m/z 165 in the ammonia CI spectrum corresponding to the adduct with the ammonium ion. Whether or not the aldicarb cyanosulfone moiety is produced thermally from the aldicarb sulfone on entry to the mass spectrometer source at 180°C cannot be addressed. Since the methane CI spectrum provided diagnostic ions to detect the presence of sulfoxide (m/z 143) versus sulfone (m/z 148) the potato extract was then examined under similar conditions as the standards discussed above (Figure 2). The eluting peak of interest was determined by retention time and mass chromatograms for m/z 143 and m/z 148 (in methane CI) respectively. Once properly located, full spectral scans were obtained (Figure 3). In the case of methane CI, the predominant ions were m/z 148 and m/z 81 indicating the presence of aldicarb sulfone. However, an ion at m/z 143 (about 10% relative abundance) would seem to indicate the presence of aldicarb sulfoxide. Admittedly the two compounds have similar

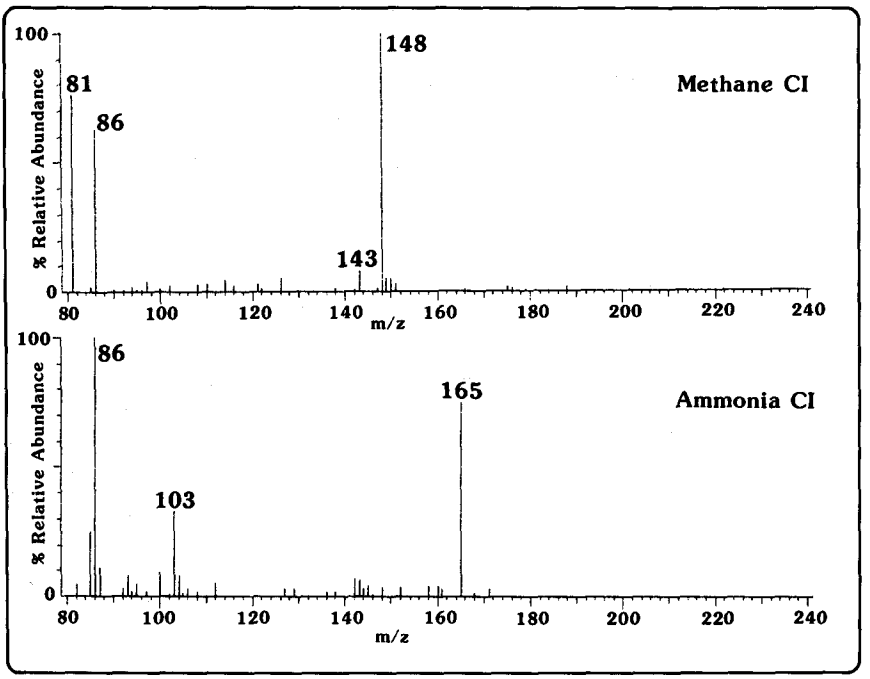


Figure 3. Total mass spectral scans obtained from potato extract at scan numer 65.

retention times, but the ion profile for m/z 143 is shifted about 5 scans higher than the peak apex for m/z 148, adding confirmation to the presence of a smaller amount of the sulfoxide.

While the detection of aldicarb and its metabolites has been previously established (Wright et al. 1983) by LCMS in water samples, the complexity in dealing with a potato extract is somewhat more difficult experimentally. Indeed the ion monitored by LCMS for quantitation of sulfone was also m/z 148 (methane CI). However, the biological matrix of the potato would not permit the use of this ion for low residue level work because of endogenous background interferences. In the present study, the confirmation obtained by two different ionization modes (methane and ammonia) has provided the needed reinforcement to guarantee the relability of the findings reported.

The presence of aldicarb sulfone in fresh potatoes is interesting for two reasons. First, the increased level of sulfone relative to sulfoxide would seem to indicate that sufficient time had lapsed to permit the slow oxidation of sulfoxide to sulfone to occur. Second, the demonstrated translocation to the upper

leaf sets (Iwata et al. 1977) should have greatly diluted the sulfone concentration. The detected residue level of about 1 ppm would suggest that such a translocation is by no means a complete process and that root crops such as potatoes are susceptible to residue levels of aldicarb metabolites. There was no evidence to support the presence of any other metabolites such as the oximes and nitriles (Scheme 1).

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