Bull. Environm. Contam. Toxicol. 30, 117–121 (1983)

Incidence of *cis*-4-Cyclohexene-1,2-dicarboximide in Fruit Crops Treated with Captan

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The multiresidue procedure (LUKE et al. 1975, 1981) adopted for use in our pesticide monitoring program for fruits and vegetables uses a Hall electrolytic conductivity detector (HECD) for organohalogen, organonitrogen, and organosulfur pesticides and a flame photometric detector (FPD-P) for organophosphorus pesticides. The sensitivity of these detectors is now in the sub-nanogram range. During such routine regulatory analyses, it is often necessary to employ gas chromatography-mass spectrometry (GCMS) to gain structural information which is not available from gas chromatography alone. In many cases, the concentration level of the unknown analytical response (UAR) is extremely low (below 1 ppm), and multiple ion detection (MID) must be used to achieve the necessary and parallel level of sensitivity of element-selective GC detectors originally used to detect the UAR. The analytical approach adopted to structurally elucidate such UARs via chemical ionization GCMS has been described in detail elsewhere (CAIRNS et al. 1983).

This paper describes a recent and interesting case history involving the identification of a UAR in peaches as a breakdown product of the fungicide, captan, cis-N-[(trichloromethyl)thio]-4-cyclohexene-1,2-dicarboimide. Identification was unambiguously confirmed as cis-4-cyclohexene-1,2-dicarboximide.

MATERIALS AND METHODS

Mass Spectral Data. All spectra were obtained on a Finnigan Model 3300 quadrupole mass spectrometer equipped with a CI source and INCOS Data System; operating conditions: 30 cm x 2 mm i.d. glass column packed with 2% DEGS on 80/100 mesh Chromosorb W; carrier gas and reagent gas, 30 mL methane/min; column inlet, 250°C; column temperature, 180°C, isothermal.

0007-4861/83/0030-0117 $01.00

Sample Preparation. Sample was extracted by the Luke procedure (LUKE et al. 1975, 1981), eluted through charcoal, concentrated to dryness using a stream of dry nitrogen, and then diluted to 100 uL with acetone; 3 uL of this extract representing 1.7 g of sample was then used for analysis.

RESULTS AND DISCUSSION

The sample extract was examined using methane chemical ionization GCMS (Figure 1). Of major concern was the compound eluting at 0.8 min (peak B) corresponding to the retention time of the UAR on HECD. Perhaps the most notable problem encountered in GCMS work is the impaired ability to sometimes detect the compound of interest among so many other endogenous sample peaks. While the high sensitivity and selectivity of the HECD can be a distinct advantage to the pesticide chemist in residue work, the concentration level of the suspected organonitrogen UAR in this particular case was low enough that initial investigation of the extract was unproductive. Sample clean-up through charcoal was undertaken and permitted the GCMS analysis to be performed successfully (Figure 1).

The compound under investigation (Figure 1, peak **B**, spectrum **B**) was clearly dominant above other sample compounds. With the base peak at *m/z* 152 and the appearance of ions at *m/z* 180 and 192 (corresponding to +28 and +40 daltons relative to *m/z* 152), the initial conclusion was to assign the compound a molecular weight of 151. Lack of fragmentation precluded any further deductive reasoning as to its structure. However, also present in the sample extract was a compound eluting at 2.5 mins (Figure 1, peak **A**, spectrum **A**) which was easily identified from retention time and mass spectral characteristics as captan (molecular weight 299). Admittedly, the protonated molecular ion at *m/z* 300 is of extremely low relative abundance, but the ion at *m/z* 264 respresenting the loss of HCl from MH^+ is clearly visible as a two chlorine containing entity. This loss of HCl after protonation has been observed to be prevalent when dealing with chlorine-containing pesticides (CAIRNS et al. 1981). However, of much greater significance was the appearance of the base peak at *m/z* 152 and the two ions at *m/z* 180 and 192 (corresponding once again to +28 and +40 daltons relative to *m/z* 152). It was this obvious similarity with the UAR mass spectrum (spectrum **B**) that provided the first clue as to its identity, i.e. a possible

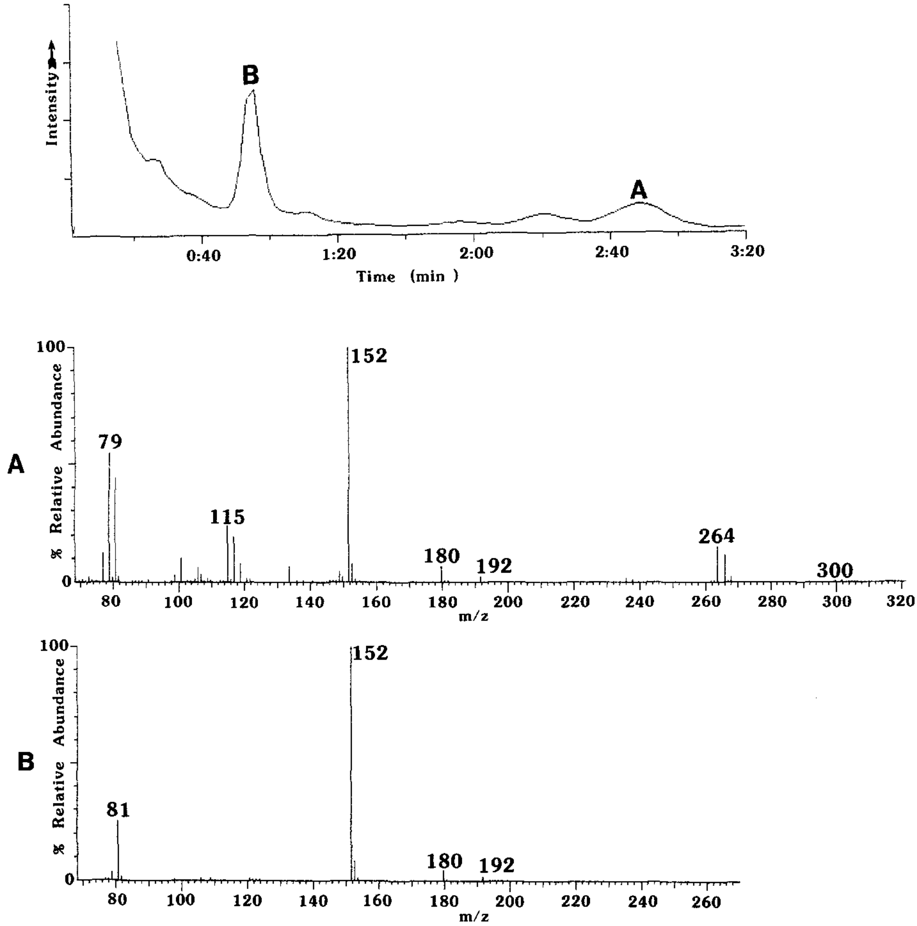
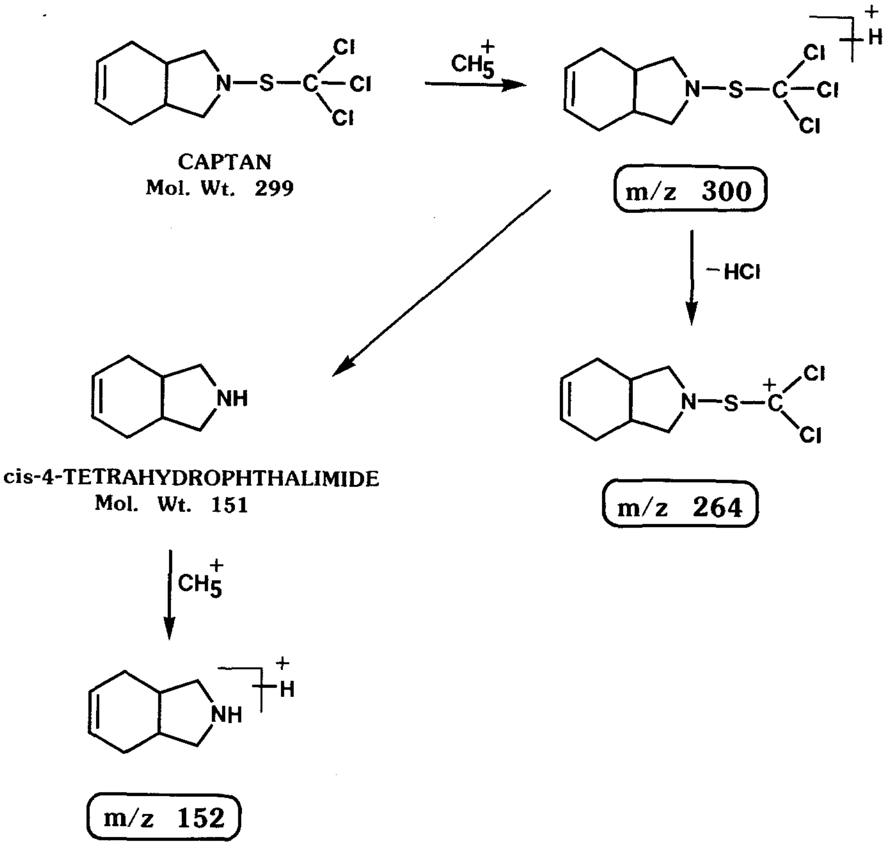


Figure 1. Total ion chromatogram (*m/z* 80-350) obtained using methane CI conditions of sample extract with representative mass spectra of the two components of interest, labeled A and B.

breakdown product of captan. For the UAR to have a molecular weight of 151, then the side chain of the captan molecule would have to be lost via breakdown or weathering, i.e. loss of $-SCCl_3$. A reference material of this proposed structure was available and the identification confirmed as *cis*-4-cyclohexene-1,2-dicarboximide.

The only unanswered question left was why the methane CI mass spectrum of captan should exhibit a protonated species of this breakdown product as well as adduct ions at *m/z* 180 and 192. It is now proposed that a neutral molecule of this breakdown product is formed in the ion source of the mass spectrometer from ionization by CH_5^+, etc. (Scheme 1). The prevalence of such reactions is slowly being recognized (CAIRNS et al. 1982) and their importance in structural analysis has increased the potential of methane CI as a method of choice to obtain molecular weight information as well as structural diagnosis.



Scheme 1. Proposed fragmentation pathway for captan.

The incidence of this breakdown product in the sample extract was then the subject of discussion as regards to origin and causes. Using a captan reference standard no such breakdown was observed on column or injection port of the GCMS system. Therefore, the issue of thermal degradation was ruled out completely. The fact that the sample extract contained a relatively small amount of captan relative to breakdown product was a clear indication that the weathering of the pesticide in situ was probably the most logical explanation. Results from this study have now provided an analytical protocol to ascertain the presence of both captan and its breakdown products in future samples to obtain a knowledgeable profile of their persistence in fruits and vegetables treated with this fungicide.

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Accepted November 23, 1982