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Degradation of chlorfenvinphos in carrots during storage

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In order to investigate the degradation products of chlorfenvinphos, organically grown carrots were treated with the pesticide. After storage at 5°C for 3 months, the following compounds were detected by gas chromatography–mass spectrometric (GC-MS) analysis: 1-(2′,4′-dichlorophenyl)ethan-1-ol, 2,4-dichlorobenzoic acid, and 2,2-dichloro-1-(2′,4′-dichlorophenyl) vinyl alcohol. The metabolic fate of the pesticide was also investigated by use of ^{14}C-ring-labelled chlorfenvinphos which was prepared using *o*-[^{14}C]dichlorobenzene as a starting material. After a month of storage at room temperature, the following compounds were determined in carrots and in sand in which the carrots were buried after treatment with [^{14}C]chlorfenvinphos: 2,2′,4′-trichloroacetophenone, 2,4-dichloroacetophenone and 2-chloro-1-(2′,4′-dichlorophenyl)vinyl alcohol. Separation of radioactive compounds was performed using high-performance liquid chromatography and a radioactivity flow detector. The identification of compounds was carried out by GC-MS. © 1997 Elsevier Science Ltd

INTRODUCTION

Chlorfenvinphos, 2-chloro-1-(2′,4′-dichlorophenyl)vinyl diethyl phosphate, is a widely used organophosphorus insecticide of low mammalian toxicity. It is used against soil-borne and foliage insects in both agricultural and horticultural crops and against ectoparasitic insects on livestock.

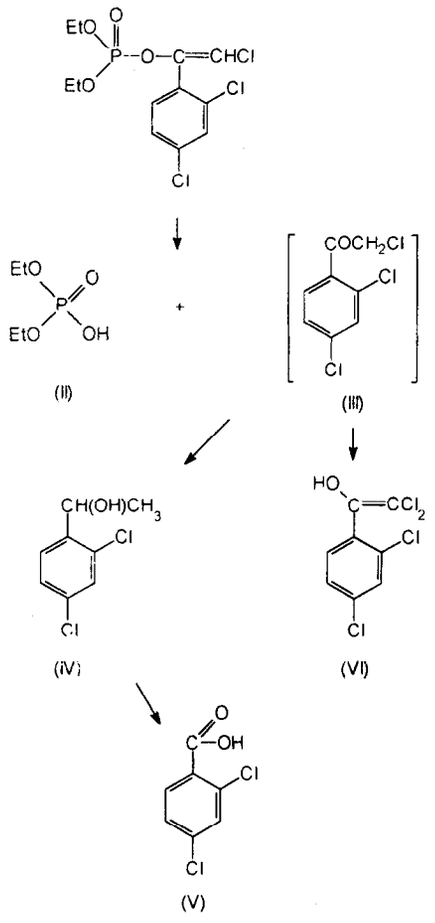
The metabolism of chlorfenvinphos in animals and in mammals has already been studied by Hutson (1980) and Hutson & Roberts (1985). Although a similar pathway was earlier demonstrated for plants and soil (Beynon *et al.*, 1973), the fate of chlorfenvinphos is not well-known in crops that are grown in soils treated with the pesticide.

It is important to distinguish between the primary metabolic process (triester to diester) and secondary process involving the further metabolism of the 'leaving group'. In plants, pesticides generally conjugate with sugars to form sugar conjugates as secondary metabolites. The alcohol groups of primary metabolites are usually readily conjugated (Edwards *et al.*, 1982). For instance, a small proportion of the sugar conjugate of 1-(2′,4′-dichlorophenyl)ethan-1-ol (IV, Scheme 1) derived from chlorfenvinphos has been found by Beynon *et al.* (1973) in soil.

The degradation products, which may be toxic, formed during storage of chlorfenvinphos-treated food products have not been reported and relevant mass spectral information has not been published. The information on the effect of storage on chlorfenvinphos in carrot is limited and further investigation is required into the relationship between the food components and the pesticide and its metabolites.

In this study, the decomposition of chlorfenvinphos in carrots during storage was investigated using organically grown carrots treated post harvest. The effect of storage on breakdown of the insecticide was examined in a variety of samples prepared after different periods of storage. Residues of chlorfenvinphos were determined using the technique of combined gas chromatography–mass spectrometry (GC-MS).

The investigation was also facilitated by use of a radioactively labelled chlorfenvinphos. The unique advantage of using a radiolabelled compound in a metabolism study is that it can be identified easily by its characteristic radiation. Beynon & Wright (1967) used [^{14}C]chlorfenvinphos labelled at each of the vinyl carbon atoms, and Burton & Sullivan (1972) synthesized [^{14}C]chlorfenvinphos specifically labelled in the alkoxy and vinyl groups. A label in the ethyl or vinyl carbon atoms gives no information on the eventual fate of the aryl group of chlorfenvinphos. Thus, the ring moiety was selected for labelling in this investigation. Ring-labelled chlorfenvinphos was synthesized from 1,3-[^{14}C]dichlorobenzene, obtained by isomerization of 1,2-[^{14}C]dichlorobenzene.



Scheme 1. The proposed breakdown route of chlorfenvinphos in carrot during cold storage.

MATERIALS AND METHODS

Materials

Authentic chlorfenvinphos was obtained from Dr Ehrenstorfer, Augsburg (Germany). The 1,2-[^{14}C]dichlorobenzene (24.6 µl, initial activity 9.25 MBq) was purchased from Sigma (UK). Samples of the organically grown carrots were provided by a health food shop in the local market.

Synthesis of ^{14}C-ring-labelled chlorfenvinphos

The reactions used in the synthesis of the radiolabelled compound were:

1, 2–[^{14}C]Dichlorobenzene

1, 2 – [^{14}C]dichlorobenzene

→ 1, 3 – [^{14}C]dichlorobenzene

1, 4 – [^{14}C]dichlorobenzene

1, 3 – [^{14}C]Dichlorobenzene + dichloroacetylchloride

→ [^{14}C]tetrachloroacetophenone

[^{14}C]Tetrachloroacetophenone + triethylphosphate

→ [^{14}C]chlorfenvinphos

m-[^{14}C]Dichlorobenzene was obtained from the commercially available ^{14}C-labelled *o*-isomer (24.6 µl, initial activity 9.25 MBq). Before isomerization, the radiolabelled compound was diluted with unlabelled compound (approx. 600 mg) because the quantity of labelled dichlorobenzene was insufficient for the synthesis of the pesticide.

Isomerization was carried out according to Mattano (1955). *o*-[14C]Dichlorobenzene was isomerized, in the presence of aluminium chloride, to produce, principally, *m*-[^{14}C]dichlorobenzene, together with a small proportion of *p*-[^{14}C]dichlorobenzene. Gas-chromatographic analysis was then performed on the product. Separation of the fraction composed largely (approx. 60%) of *m*-[^{14}C]dichlorobenzene from the reaction mixture was achieved on a silica-gel column (50 cm×1 cm ID) using hexane as eluate. Liquid chromatography was performed by collecting 0.5 ml fractions from the column. Each fraction was then analysed by GC for determination of the 'dump volume' and range of fractions in which the *m*-isomer eluted from the column.

The intermediate [^{14}C]tetrachloacetophenone was prepared using the Friedel–Crafts ketone synthesis. This reaction was carried out using dichloroacetyl chloride and *m*-dichlorobenzene in the presence of aluminium chloride, and [^{14}C]chlorfenvinphos was synthesized by reacting the triethyl phosphite with [^{14}C]tetrachloroacetophenone according to Whetstone *et al.* (1966).

The activity of radioactive product was counted by a Packard Tricarb L600 TR liquid scintillation counter. Scintillation vials were prepared containing 10 ml of Emulsifier Scintillator 299 and 10 µl of radioactive sample. The total radioactivity was measured as counts per minute.

Fortification of carrots with chlorfenvinphos

Organically grown carrots (500 g) were fortified using a chlorfenvinphos solution (100 µg ml^{-1}) prepared in ethyl acetate (500 ml). The carrots were placed in the solution and the solvent was evaporated at room temperature in a fume cupboard. The samples were analysed after evaporation on the first day and then stored at 5°C for 3 months in a cold room. Samples were analysed for residues of chlorfenvinphos at approximately 15 day intervals.

Sample preparation

Extraction

Chopped carrots (50 g) were homogenized with ethyl acetate (50 ml) and anhydrous sodium sulphate (30 g) in a high-speed blender for 3 min. The homogenate was filtered and the residue twice extracted with ethyl

acetate (2×20 ml). The combined extracts were concentrated to approximately 20 ml using a rotary evaporator.

Clean-up by gel permeation chromatography (GPC)
An Anachem glass preparative chromatography column (45 cm×1 cm ID) fitted with a polytetrafluoroethylene (PTFE) bed support was packed with Bio-Beads SX-3 (mesh size 200–400) (Bio-Rad Labs). The prepared extract (1 ml) was injected onto the column via a Rheodyne PTFE rotary valve fitted with 1 ml sample loop. The eluent was ethyl acetate–cyclohexane (1:1) delivered at 1 ml min^{-1}. Eluent delivery was provided by a Kontron Model 420 high-performance liquid chromatography (HPLC) pump. The first 15 ml of the GPC eluate was dumped after injection; chlorfenvinphos and breakdown products were collected in the next 20 ml. The collected eluate was reduced to a small volume (100 µl) under nitrogen.

Chemical derivatization
Bis-(trimethylsilyl)trifluoroacetamide (BSTFA) (200 µl) as derivatizing agent was added to the cleaned extract (100 µl) and heated to 70°C for 1 h. The reaction mixture was kept for 20 min at this temperature after the addition of isopropanol (approx. 0.5 ml) to remove excess BSTFA.

Gas chromatography–mass spectrometry (GC-MS)

GC-MS was performed using a Kratos MS 80 RFA instrument directly coupled to a Carlo Erba 4200 gas chromatograph fitted with a BP-1 non-polar fused silica capillary column (25 m×0.32 mm ID, 0.5 µm film thickness) using helium carrier gas at a flow rate of 2 ml min^{-1}. The oven temperature programme was: initial temperature isothermal at 100°C for 5 min, then from 100°C to 260°C at 5°C min^{-1}, then 20 min at 260°C.

The operating parameters of the mass spectrometer were: ionization potential 70 eV, ion source temperature 150°C. The electron ionization (EI) and chemical ionization (CI) modes were used to obtain mass spectra of samples. Isobutane was chosen as a reagent gas for CI mode.

Application of the labelled pesticide on carrots

Sliced organically grown carrots (300 g), shown not to contain residues of pesticides, were painted with radioactive pesticide solution prepared in ethyl acetate (10 ml, total activity 0.143 mCi). Carrots treated with [^{14}C]chlorfenvinphos were buried in sand and stored in a desiccator at room temperature for a month.

Preparation of the radioactive samples for HPLC

After storage, degradation products of the radioactive pesticide were extracted from the carrots using excess amount of ethyl acetate (250 ml ×3) to ensure the complete extraction of the residues. The solvent was then removed by evaporation and the reduced volume of crude extract (approx. 1 ml) was subjected to radio-HPLC analysis without further clean-up.

The sand was washed three times with 250 ml of ethyl acetate, and excess solvent was then removed by rotary evaporation. The concentrated sample (1 ml) was analysed by HPLC.

The radioactive products of [^{14}C]chlorfenvinphos were determined in each sample by GC-MS analysis. The total amount of radioactivity introduced into the GC-MS system was very small (< 8000 Bq). Consequently, the laboratory air was unlikely to become contaminated because any lost products would be trapped by pump oil.

Radio-HPLC

Reversed-phase HPLC was performed under isocratic conditions using a Bio-Rad dual solvent pump equipped with an Apple microcomputer. A 10 µl loop was connected to the injector and a 10 µm C_{18} Spherisorb 10ODS2 (25 cm×4.6 mm ID) column. Methanol–water (9:1) was the mobile phase at a flow rate 1 ml min^{-1}.

A Ramona-D radioactivity flow detector was used for continuous measurement of beta-activity in the HPLC column effluent. The detector provided homogeneous counting in which the eluate from the HPLC column was mixed with Monoflow 3 liquid scintillation fluid (1:1) and the resulting solution was continuously passed through the counting cell set between a pair of photoelectron multiplier tubes. The monitor used coincidence counting. The radioactivity flow detector was interfaced to an IBM PC with printer attached and provided a real-time on-line graphics presentation. The radioactive signal was plotted against elution time as counts per second (CPS) and chromatographic peaks were detected with a minimum of about 30 CPS.

RESULTS AND DISCUSSION

Degradation of unlabelled chlorfenvinphos in carrots

The effect of storage on breakdown of chlorfenvinphos in carrot was examined at intervals of about 15 days during 3 months of storage at 5°C in a cold room. The compounds were identified from their mass spectra and, where possible, assignments were confirmed by comparison with available standards. In other cases, the structures of unknowns were postulated using molecular weight information from CI spectra and fragment ions from EI spectra.

The proposed breakdown route of chlorfenvinphos in carrot is given in Scheme 1. The stored carrot samples did not exhibit any residue other than unchanged

chlorfenvinphos on the first day of analysis of the treated carrots, as was expected. At the 15th day of storage, the GC-MS results (Fig. 1(a)) of fortified carrot with chlorfenvinphos (I) showed the presence of diethyl phosphate (II), which is one of the primary metabolites of the pesticide. It has been found as a major metabolite of the pesticide in liver slices from various animals (Hutson, 1980), but it has not been reported in soils or plants.

Diethyl phosphate was formed by hydrolysis of the ester bond of chlorfenvinphos (P–O–C) and was identified as diethyltrimethylsilyl phosphate (RT = 21.09) (Fig. 1(b)). Under EI conditions, the molecular ion for this derivative of diethyl phosphate appeared at *m/z* 226 and then the loss of a methyl group gave a peak at *m/z* 211. The base peak at *m/z* 155 was formed by cleavage of the ester bond between the trimethylsilyl (TMS) group and the diethyl phosphate oxygen. Chromatograms of blank carrot samples, which contained no pesticide, did not show a diethyltrimethylsilyl phosphate peak before or after storage.

2,4-Dichlorobenzoic acid (V), 1-(2′,4′-dichlorophenyl)-ethan-1-ol (IV) and 2,2-dichloro-1-(2′,4′-dichlorophenyl)-vinyl alcohol (VI) (Scheme 1) were found as secondary metabolites in carrots at the 40th day of storage. 2,4-Dichlorobenzoic acid, derived from chlorfenvinphos, was excreted by some animals as its glycine conjugate, but it was not detected in plant. Although 1-(2′,4′-dichlorophenyl)ethan-1-ol has been suggested as a major breakdown product of the pesticide, it was not found in plant or soil (Beynon *et al.*, 1973). 2,2-Dichloro-1-(2′,4′-dichlorophenyl)vinyl alcohol has not previously been reported.

The total ion chromatogram of derivatized carrot samples is given in Fig. 2(a). No molecular ion was observed for the TMS ester of dichlorobenzoic acid (RT = 15.08 min) in the chromatogram. It was detected by tracing the ions of *m/z* 173 and 145 (dichlorobenzoyl ion $[C_6H_3Cl_2CO]^+$ and dichlorobenzyl ion $[C_6H_3Cl_2]^+$, respectively) which are important fragmentation ions of the compound (Fig. 2(b)). The base peak at *m/z* 247

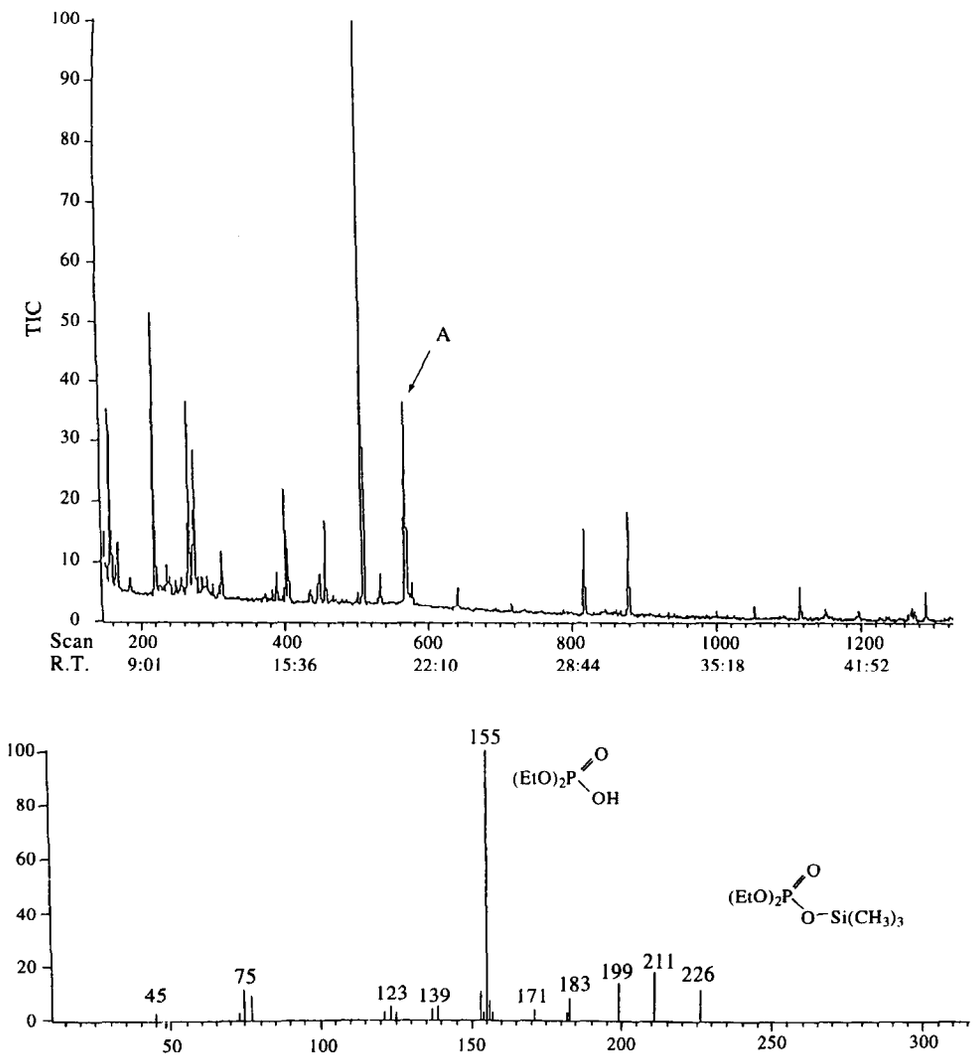


Fig. 1. (a) Total ion chromatogram of GC-MS analysis of carrot fortified with chlorfenvinphos at 15th day of storage; extract treated with BSTFA. Temperature programme: 50°C for 5 min, 15°C min^{-1} to 230°C. Peak A: diethyl phosphate. (b) Corrected mass spectrum of diethyl trimethylsilyl phosphate, RT = 21.09 min in (a).

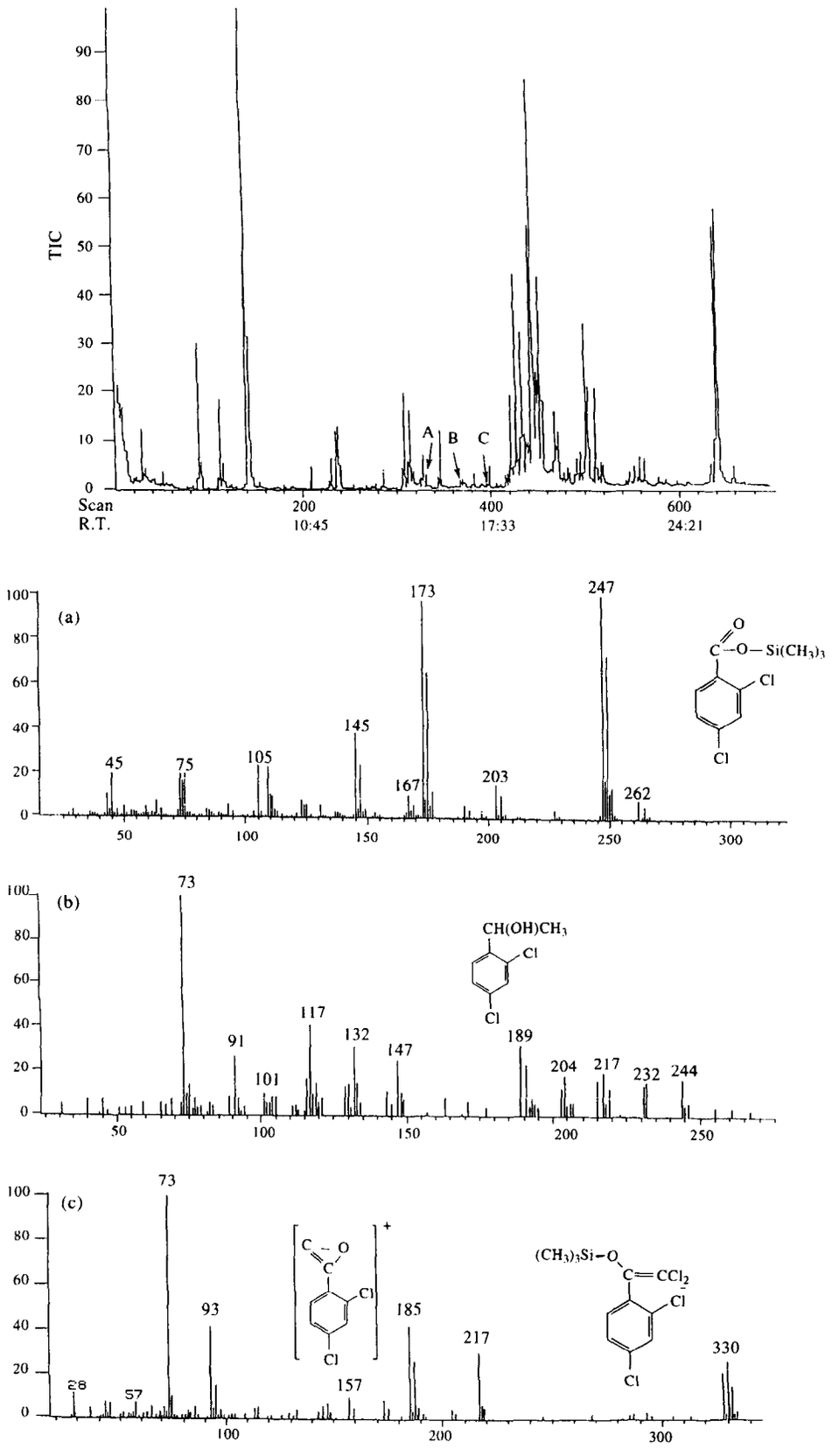


Fig. 2. (a) Total ion chromatogram of GC-MS analysis of the fortified carrot with chlorfenvinphos at 40th day of storage; extract treated with BSTFA. Temperature programme: 2 min at 50°C, 10°C min^{-1} to 250°C. Peak A, trimethylsilyl (TMS) derivative of dichlorobenzoic acid; peak B, TMS derivative of 1-(2′,4′-dichlorophenyl)ethan-1-ol; peak C, TMS derivative of 2,2-dichloro-1-(2′,4′-dichlorophenyl)vinyl alcohol. (b) Corrected mass spectrum of TMS derivative of dichlorobenzoic acid, RT = 15.08 min in (a). (c) Corrected mass spectrum of TMS derivative of 1-(2′,4′-dichlorophenyl)ethan-1-ol, RT = 16.44 min in (a). (d) Corrected mass spectrum of TMS derivative of 2,2-dichloro-1-(2′,4′-dichlorophenyl)vinyl alcohol, RT = 17.17 min in (a).

represents the ion corresponding to $[M-15]^+$, which arises from the molecular ion (*m/z* 262) by loss of a methyl group.

In this study, the breakdown route of chlorfenvinphos in carrot can be postulated as 2,2′,4′-trichloroacetophenone (III) hydrolysed to 1-(2′,4′-dichlorophenyl)ethan-1-ol (IV), which could be conjugated, although no identification was achieved. Then the free alcohol derivative could be oxidized to the corresponding dichlorobenzoic acid derivative. This postulate is based on the compound that was observed at a retention time of 16.44 min in the GC-MS chromatogram of the carrot extract at the 40th day of storage (Fig. 2(a)).

The ion *m/z* 189 appears (Fig. 2(c)) to be an $[M-1]^+$ ion which would show a typical ion cluster for two chlorine atoms. The intense ion at *m/z* 73 is the characteristic TMS ion $[Si(CH_3)_3]^+$ of the TMS derivative of the ethan-1-ol.

In the carrot extract at the 40th day of storage, another metabolite of the insecticide was detected which has not previously been reported. In the EI spectrum (Fig. 2(d)) of the peak at retention time 17.17 min, the ion at *m/z* 328 could originate from the TMS derivative of 2,2-dichloro-1-(2′,4′-dichlorophenyl)vinyl alcohol (VI) (Scheme 1) whose molecular weight is 256. The isotope ratio of the ions of *m/z* 328, 330, 332, 334 indicated that the peak contained four chlorine atoms. The small peak at *m/z* 293 could be formed by loss of a chlorine atom from the ion at *m/z* 328.

The chlorine isotope ratio of the ion cluster *m/z* 185, 187, 189 showed two chlorine atoms. A possible structure of the ion cluster *m/z* 185 could be the species $[O(C???C)\text{-}C_6H_3Cl_2]^+$. The ions at *m/z* 93 and 95 appear to represent the species $[Cl\text{–}Si(CH_3)_2]^+$.

Unfortunately, molecular weight verification of (IV) and (VI) could not be obtained from the CI spectra. Because of the very small quantity of the compound present, CI spectra could not be obtained and EI spectra showed many interferences and low intensity of the ions.

Degradation of [^{14}C]chlorfenvinphos in carrot and sand

The investigation of chlorfenvinphos metabolism in carrot was conducted with radiolabelled pesticide as well as with the unlabelled compound. After storage, the carrots and sand were analysed for the breakdown products of the radioactive pesticide. Measurement of the radioactivity was performed using radio-HPLC (i.e. the HPLC system included a radioactivity flow detector which was connected to a data system).

[^{14}C]Chlorfenvinphos (A) and two other radioactive compounds (B and C) appeared as peaks on chromatograms of the carrot and sand extracts (Fig. 3). The separation between the pesticide and unknown compounds was incomplete. Although the radioactive degradation products of chlorfenvinphos were not well separated on radio-HPLC, they were resolved and identified by GC-MS in both carrot and sand extracts. The total ion chromatograms of derivatized carrot and sand extracts are given in Figs 4(a) and 5(a), respectively.

After a month's storage of the carrots in sand, the following compounds were detected in trimethylsilylated carrot and sand extracts: 2,2′,4′-trichloroacetophenone (III), 2,4-dichloroacetophenone (VII), and the TMS derivative of 2-chloro-1-(2′,4′-dichlorophenyl)vinyl alcohol (VIII) (Scheme 2).

The major degradation product was the trichloroacetophenone detected in both carrot and sand extracts. It was confirmed by comparison of the EI spectrum (Fig. 4(b)) of the compound at retention times of 17.38 and 17.36 min with the mass spectrum of the standard. Reductive dehalogenation of trichloroacetophenone to give dichloroacetophenone (Fig. 4(c)) occurred in carrots, and traces of (VII) were also determined in sand extract.

In sand, a breakdown product of chlorfenvinphos was detected which has not previously been reported. It was suggested to be 2-chloro-(2′,4′-dichlorophenyl)vinyl alcohol (VIII). This assignment is based on the molecular weight information of the compound ($[M+H]^+$, *m/z* 295) obtained from the CI spectrum (Fig. 5(b)), and the measured accurate masses of some fragment ions (*m/z*: 93, 95; 294 and 296) in the EI spectrum (Fig. 5(c));

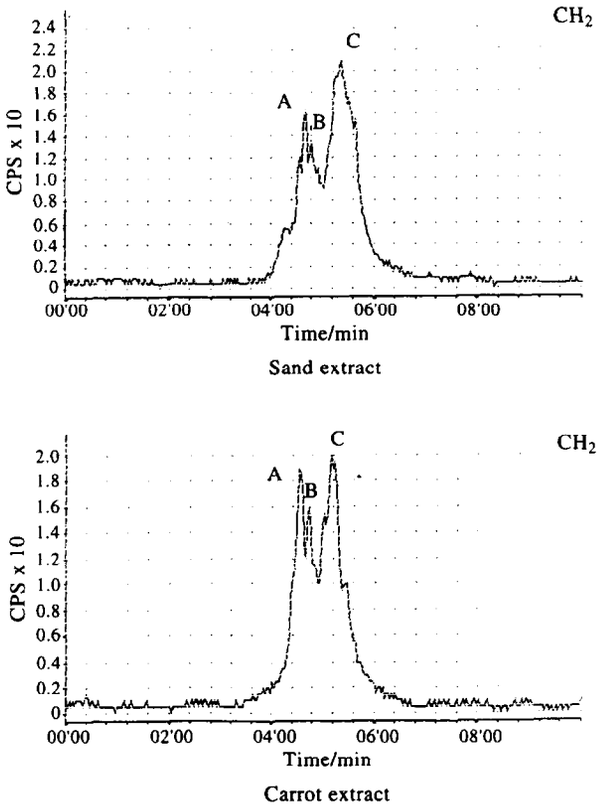


Fig. 3. Separation of ^{14}C-labelled products formed from [^{14}C]chlorfenvinphos. Column, Spherisorb 10ODS2; flow rate, 1 ml min^{-1}; mobile phase, methanol–water (9:1, v/v). Peak A, chlorfenvinphos; peaks B and C, unknown compounds.

accurate mass measurement enabled the molecular formula [$C_{11}H_{13}Cl_3OSi$] to be calculated and aided interpretation of the mass spectrum.

The molecular ion contained the TMS group, as shown by the ion at *m/z* 294, and the isotope peak ratios *m/z* 294:296:298 indicated three chlorine atoms in the molecule. The small peak at *m/z* 223 could have been formed by cleavage of the ester bond between the TMS group and oxygen.

An alternative mode of fragmentation for the m/z 294 ion gives the m/z 259 ion by loss of a chlorine. The isotope abundance of the ions m/z 259:261:263 indicated that two chlorine atoms are present in the molecule.

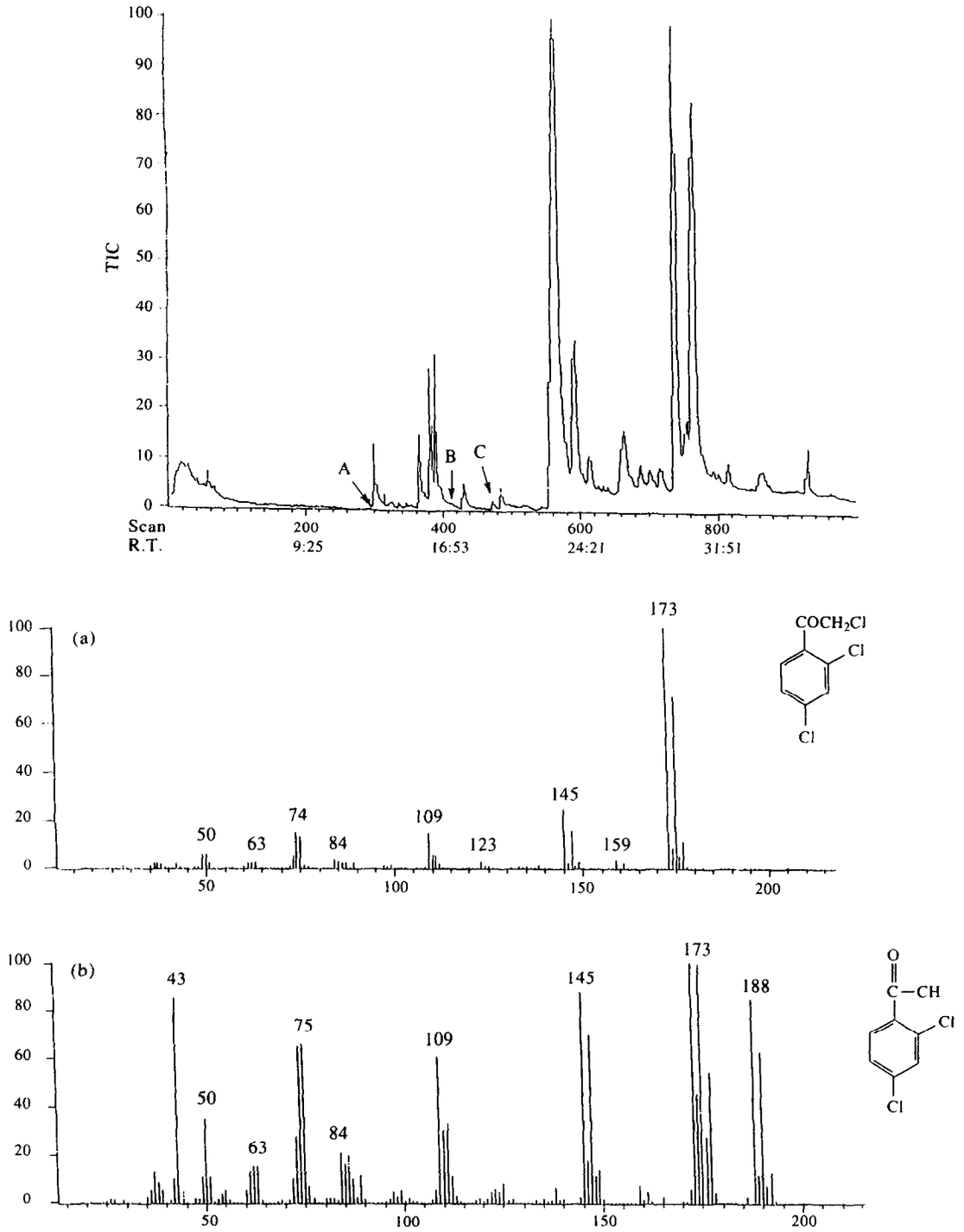


Fig. 4. (a) Total ion chromatogram of GC-MS analysis of the carrot extract containing [^{14}C]chlorfenvinphos. Temperature programme: 100°C for 5 min, 5°C min^{-1} to 260°C. Peak A, 2,4-dichloroacetophenone; peak B, 2,2′,4′-trichloroacetophenone. (b) Corrected mass spectrum of 2,2′,4′-trichloroacetophenone, RT = 17.38 min in (a) and RT = 17.36 min in Fig. 5(a). (c) Corrected mass spectrum of 2,4-dichloroacetophenone, RT = 12.08 min in (a) and RT = 11.59 min in Fig. 5(a).

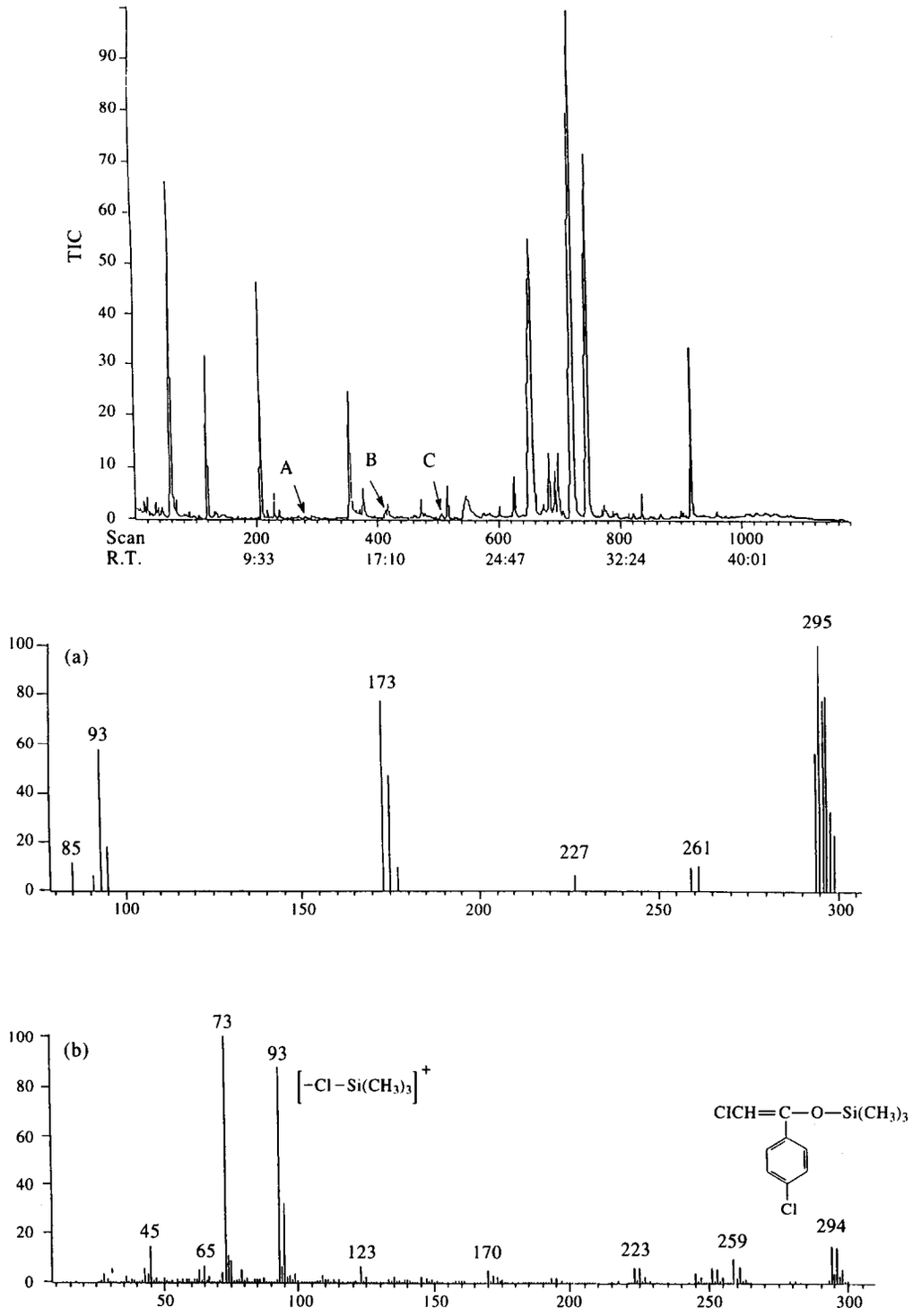
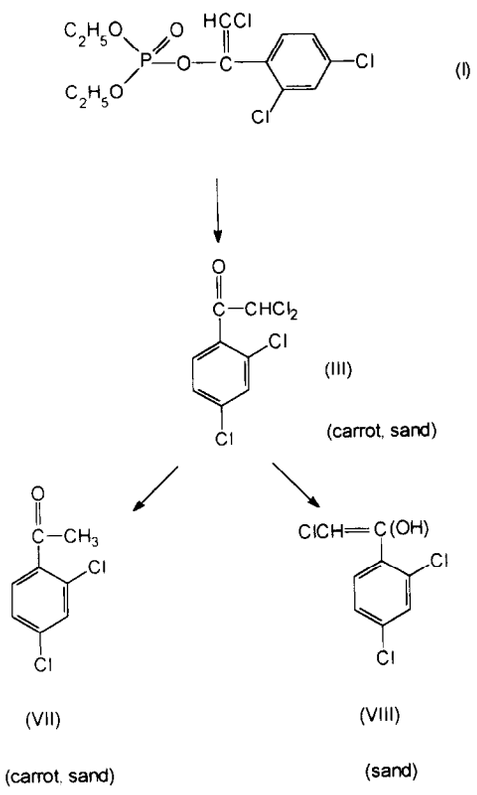


Fig. 5. (a) Total ion chromatogram of GC-MS analysis of the sand extract containing [^{14}C]chlorfenvinphos. Temperature programme: 100°C for 5 min, 5°C min^{-1} to 260°C. Peak A, 2,4-dichloroacetophenone; peak B, 2,2′,4′-trichloroacetophenone; peak C, 2-chloro-1-(2′,4′-dichlorophenyl)vinyl alcohol. (b) Corrected CI spectrum of 2-chloro-1-(2′,4′-dichlorophenyl)vinyl alcohol. (c) Corrected mass spectrum of 2-chloro-1-(2′,4′-dichlorophenyl)vinyl alcohol, RT = 21.35 min in (a).

CONCLUSION

The breakdown products of chlorfenvinphos were investigated using organically grown carrots treated post harvest. The effect of storage on breakdown of the insecticide was examined in a variety of carrot samples, fortified with unlabelled chlorfenvinphos and [^{14}C]chlorfenvinphos.

The use of radiolabelled compound in this investigation was based on the assumption that the radiolabelled molecule would be metabolized in the same manner as the unlabelled molecule. However, the different break-



Scheme 2. The proposed breakdown route of [^{14}C]chlorfenvinphos in carrot and sand.

down products that were determined in carrots fortified with unlabelled and labelled pesticide could be explained by the storage conditions—i.e. in air as compared to sand.

The breakdown of chlorfenvinphos on carrot was found to take place mainly by hydrolysis of the P–O–C linkage to form diethyl phosphate, which was detected in carrot during cold storage, and trichloroacetophenone, which was determined in carrot and sand extracts after a month of storage at room temperature. The present study indicates that metabolism of chlorfenvinphos is significantly affected by different storage conditions.

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