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Study of photodegradation of the pesticide ethiofencarb in aqueous and non-aqueous media, by gas chromatography–mass spectrometry

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Abstract

A comparative photodegradation kinetic study of ethiofencarb [2-ethylthiomethyl(phenyl)-*N*-methylcarbamate] in aqueous and non-aqueous media (hexane and methanol), is carried out. After irradiation, the aqueous samples are extracted with isobutyl methyl ketone. Ethiofencarb and its metabolites are analyzed by GC in combination with nitrogen–phosphorus detection and MS, respectively. The degradation kinetics depend on the solvent polarity; the quickest pesticide transformation is in the aqueous medium and the slowest in hexane. The photoproducts are also dependent on the solvents. In the case of the aqueous solution, photocleavage of the carbon–sulphur bond gives 2-(methyl)phenyl-*N*-methylcarbamate as the main product, while methanol and hexane solutions show different photoproducts.

Keywords: Photodegradation; Kinetic studies; Pesticides; Ethiofencarb; Carbamates

1. Introduction

The carbamates are a wide family of pesticides whose structures ($R_1OCONR_2R_3$) are derived from carbamic acid. Many of the insecticidal carbamates of commercial significance are phenyl carbamates: the R_1 group is an aromatic ring, although some enol and oxime carbamates are also used; R_2 is usually a methyl group and R_3 can be either hydrogen, methyl or a more complex group. Carbamate pesticides comprise an important group of pesticides noted for their relatively short persistence in the environment. The activity of carbamates is associated with inhibition of cholinesterase enzyme; they appear as an alternative to the highly persistent organochlorine and organophosphorus pesticides.

The principal degradation pathways for pesticides involve photolysis, hydrolysis, dehalogenation and oxidation. Photochemical degradation is one of the major transformation processes and one of the factors controlling the fate of pesticides and other chemicals in the environment.

It has been demonstrated that the use of different light sources (natural summer sunlight, the suntest apparatus and mercury lamps) under identical aqueous conditions, produces similar degradation products, the only difference being the kinetics of formation [1,2]. Natural sunlight photodegradation processes are usually compared with those obtained under controlled conditions, generally using a xenon arc lamp [3,4]. These studies allow the modelling of

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pesticide behaviour after its application, in order to obtain information about the degradation kinetic and half-life and to increase the information available about the degradation products that can be formed under natural conditions.

Since many chemicals do not exhibit good solubility in water, it is essential to use photochemically inert organic solvents, such as acetonitrile or methanol [5,6]. The irradiation time is also very variable, depending on the degradation kinetics of the compound under study, and may vary from 3 h to 72 h [7,8]. The irradiation energy is an important factor to be taken into account, because the photoproduct's final concentrations may change depending on it [9]. In aqueous solutions, the pH is another factor to take into account [10,11], in combination with the pesticide's characteristics [12].

Several solvents have been used in photodegradation studies of *N*-methyl carbamates. Climent et al. [13] studied photodegradation in aqueous media. Galadi et al. [14] studied the photodegradation of a mixture of pesticides in acetonitrile–water (3:1, v/v) including ethiofencarb. Raha et al. [15,16] carried out the photodegradation of carbofuran in solvents such as methanol, ethanol, acetonitrile chloroform and water, obtaining different photoproducts for the different solvents. Kopf and Schwack [9] studied the photoreactivity and possible photodegradation pathways of ethiofencarb on the plant surface, in the presence of cyclohexane, cyclohexene and isopropanol.

The main products reported for the aqueous photodegradation of *N*-methyl carbamate are the respective phenol and *N*-methylamine [17]. For *N*-methyl carbamate pesticides with C–S bonds, the photodegradation products depend on the energies of the C–O or C–S bonds [13]. The C–S bond is weaker (270 kJ mol^{-1}) than the C–O bond (360 kJ mol^{-1}) [18], and the thiyl and alkoxy radicals therefore display markedly different behaviors and the products of the reactions may differ appreciably.

The present work investigates the photodegradation of the carbamate pesticide ethiofencarb, in aqueous and non-aqueous media, using GC with nitrogen–phosphorus detection (NPD) to compare the photodegradation behavior and kinetic of ethiofencarb in terms of the polarity of the solvents used (water, methanol and hexane). Xenon arc lamp irradiation was used. The GC–MS system was used in order to determine and identify photoproducts in the resulting reaction mixtures. Determination of the photoproducts permitted the identification of the possible photolytic pathways of ethiofencarb.

Ethiofencarb [2-ethylthiomethyl(phenyl)-*N*-methylcarbamate] is a systemic insecticide widely used in agriculture due to its specific effect against aphids. A large number of papers have been published about the potential toxicity of ethiofencarb; the acceptable daily intake (ADI) for humans is 0.1 mg/kg body mass [19].

2. Experimental

2.1. Apparatus

A Hewlett-Packard HP 5890 gas chromatograph equipped with a nitrogen–phosphorus detector and an HP Ultra 2 fused-silica capillary column (cross-linked 5% phenylmethylsilicone gum phase of 0.33 μm film thickness, 25 m×0.2 mm I.D.) was used for determining the pesticide.

The operating conditions were as follows: injector temperature 250°C and detector temperature 275°C; the oven temperature programme had an initial temperature of 120°C for 3 min with the temperature programmed to rise at a rate of 60°C/min to a temperature of 225°C and be held for 7 min, followed by a second rise at the rate of 60°C/min to a temperature of 275°C and then held for 5 min. The nitrogen carrier gas flow-rate was 0.6 ml/min and the flow-rates for the nitrogen–phosphorus detector were 70 ml/min (air) and 4 ml/min (hydrogen); the auxiliary gas flow-rate (nitrogen) was 30 ml/min. Splitless injection was used and the sample volume injected was 1 μl.

A Hewlett-Packard HP 5890 Serie II gas chromatograph, equipped with an electron impact ionization (EI) and positive chemical ionization (PCI) mass spectrometer 5989 B, was used for GC–MS. The chromatographic conditions were the same as described above. Helium was the carrier gas at a flow-rate of 0.1 ml/min. Splitless injection was used and the sample volume injected was 1 μl.

A rotary vacuum evaporator a Heidolph VV 2000 (Kelheim, Germany), was used to evaporate the solvent.

An Oriel solar simulation unit was used (Oriel, Stratford, USA, ref. 66001/68805), with a 150 W Xe arc lamp (Oriel, ref. 6253), and a quartz sample cell of 25 ml capacity.

2.2. Reagents

All pesticide standards, certified and 99.9% pure, were obtained from Riedel-de Häen (Seelze, Germany). All the solvents used were HPLC or PRS grade quality; isobutyl methyl ketone (IBMK) from Fluka (Baker, Deventer, The Netherlands), methanol and hexane from Carlo Erba (Milan, Italy). The anhydrous calcium chloride was obtained from Carlo Erba.

2.3. Solutions

Pesticide solutions: Stock solutions of 1.00 mg/ml of diazinon; 10.2 mg/ml of ethiofencarb and 20.7 mg/ml of malathion were prepared in water, methanol and hexane. The more dilute solutions were prepared by dilution with the solvent required.

The aqueous and non-aqueous solutions were prepared by dissolving 2.50 ml of a 10.2 mg/ml solution of ethiofencarb in 50 ml of the selected solvent; the ethiofencarb concentration was 510 μg/ml in every case. This concentration was chosen because it is recommended for the application of the commercial formulation of ethiofencarb.

2.4. Quantification and extraction procedure

For the aqueous media, a liquid–liquid extraction method was chosen [20], as it is a simple and reliable method for quantification of pesticides in water. For extracting the ethiofencarb from the aqueous phase, the extraction solvent chosen was IBMK, with a stirring time of 15 min. Malathion was used as the internal standard for the extraction procedure. Quantitative determinations of ethiofencarb and malathion solutions in IBMK were carried out by the internal standard method (diazinon 2.00 μg/ml). Peak areas were used for the quantification.

In the non-aqueous media, the samples were directly analysed and quantified, using a previous internal standard addition (diazinon).

2.5. Photochemical procedure in the laboratory

In the photolytic degradation study, an Oriel solar simulation unit was used; this system has been previously reported for pesticide photodegradation studies, under controlled conditions, with similar results to solar photodegradation [21].

The sample was placed in a quartz cell of 25 ml capacity, at 5 cm from the source and the radiation was directed to the centre of the cell. A possible rise in the solution temperature was measured, but no significant effects were observed.

2.6. Photolysis experiments

Aqueous and non-aqueous ethiofencarb solutions of 510 μg/ml prepared as described above, were kept in the total absence of light except for the source. Samples were taken at different times (h). The sample treatment procedure was the following:

2.6.1. Aqueous medium

The internal standard (malathion) was added to an aliquot of one ml of the reactive solution, at a final concentration ranging from 10.0 μg/ml to 305 μg/ml, depending on the posterior dilution required for the sample. The extraction procedure was then applied. The organic phase was dried with anhydrous calcium chloride. An aliquot of between 25 μl and 100 μl (increased volume with degraded pesticide) was taken and diazinon was added to obtain a final concentration of 2.00 μg/ml in all cases. This final volume was adjusted to obtain a dilution ranging from 1/40 (highest concentrations of ethiofencarb) to 1/1.25 (lowest concentrations of ethiofencarb). The solutions obtained were injected into the chromatograph.

2.6.2. Non-aqueous media: methanol and hexane

An aliquot of between 25 and 100 μl (increased volume with degraded pesticide) was taken and

diazinon was added to obtain a final concentration of 2.00 μg/ml in all cases. This final volume was adjusted to obtain a dilution ranging from 1/40 (highest concentrations of ethiofencarb) to 1/1.25 (lowest concentrations of ethiofencarb). The solutions obtained were injected into the chromatograph.

2.7. Determination of kinetics parameters.

In order to determine the degradation kinetics, plots of concentration against time were made. An exponential regression analysis was then performed on each data set. The rate constant, *K*, was calculated from the first-order rate equation:

$$(\%\, C_{\text{ethiofencarb}})_t = (\%\, C_{\text{ethiofencarb}})_0\, e^{-kt} \quad (1)$$

where $(\%\, C_{\text{ethiofencarb}})_t$ represents the percentage of pesticide at time *t*, $(\%\, C_{\text{ethiofencarb}})_0$ represents the initial concentration percentage and *k* is the degradation rate constant. When the concentration falls to 50% of its initial amount, the half-life ($t_{1/2}$) can be determined by $t_{1/2} = 0.693/k$. The confirmation of the first-order rate kinetics was derived from the linearity of the plots of ln $(\%C_{\text{ethiofencarb}})_t$ against time.

2.8. Degradation products obtained

The treatment of the sample for product identification differed depending on the media used in the degradation.

In the aqueous medium, and after 28 h of irradiation, the ethiofencarb solution was extracted with 25 ml of ethyl acetate. The aqueous solution that remained after extraction was evaporated to dryness and the residue was dissolved in 2 ml of ethyl acetate. The solution was then concentrated under vacuum.

The different fractions obtained were analysed by GC–MS using the experimental conditions described for ethiofencarb determination in previous studies. The chromatogram for the aqueous solution showed one trace peak, identified as the remaining ethiofencarb.

For the non-aqueous media, the pesticide solution was directly concentrated under vacuum after the decay study. This solution was injected into the GC–MS system, obtaining a mixture of several

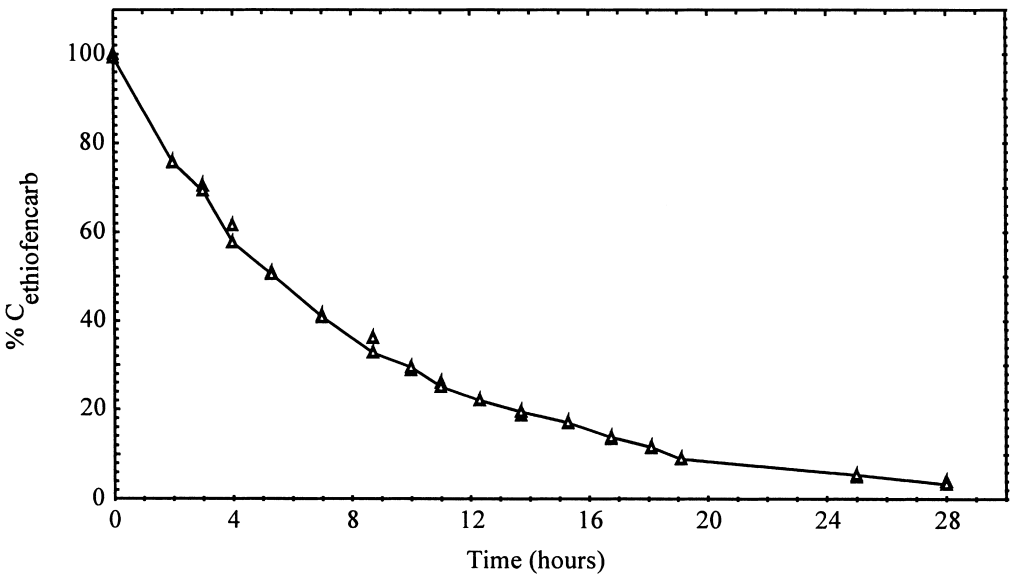

Fig. 1. Decay of ethiofencarb in aqueous medium.

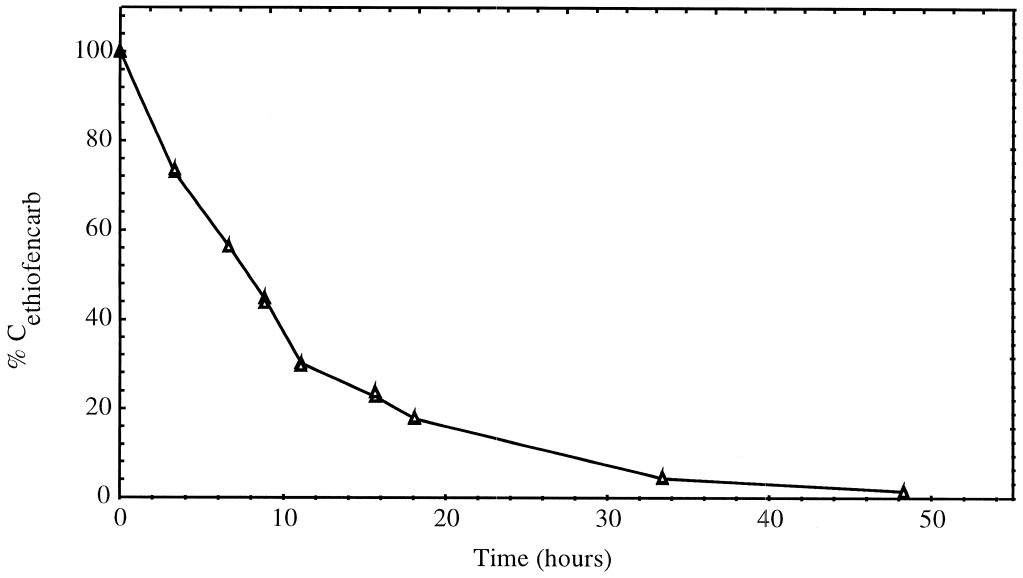

Fig. 2. Decay of ethiofencarb in methanol.

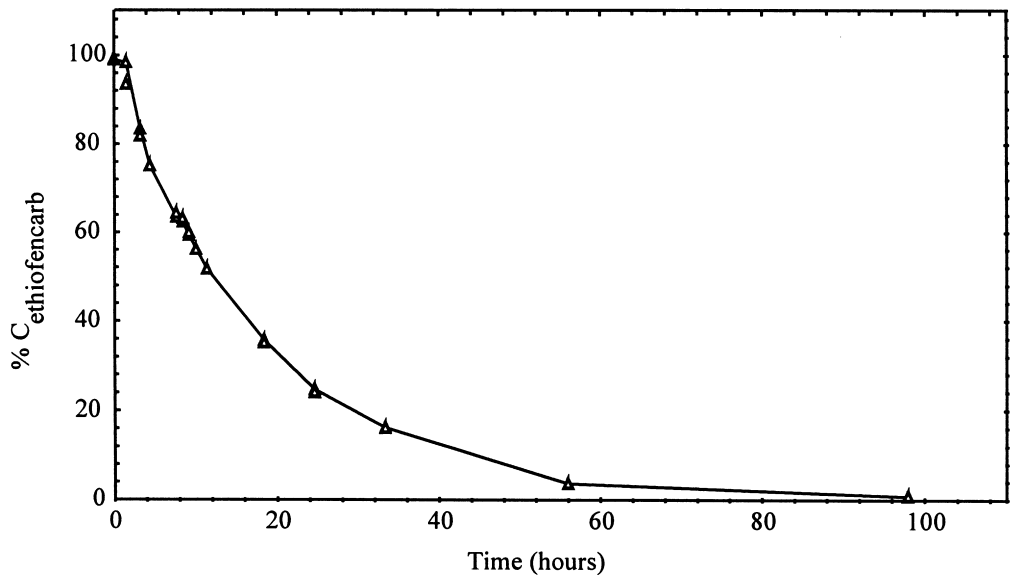

Fig. 3. Decay of ethiofencarb in hexane.

compounds. The solution was also investigated by GC–PCI–MS in order to determine the molecular masses of the photoproducts.

3. Results and discussion

3.1. Decay study and kinetics

The results obtained for the different samples permitted the determination of the pesticide behaviour over time. The irradiation time for each medium depended on the ethiofencarb degradation rate and continued until total pesticide loss.

Figs. 1–3 show the degradation of ethiofencarb for the different solvents; the data is expressed as the percentage of ethiofencarb remaining in the solution. The decay was rapid for the aqueous media (Fig. 1), the most polar solvent studied; total loss of the pesticide signal was obtained at a time below 30 h of continuous irradiation. The lowest reactivity was shown for the least polar solvent, hexane (Fig. 3); in this medium, the pesticide was totally degraded in more than 98 h. An intermediate behaviour was observed for the methanolic solution (Fig. 2), in which ethiofencarb was not detected after 50 h of irradiation.

Results were obtained for $ln\ (\%C_{\text{ethiofencarb}})$ versus irradiation time, giving a first order kinetic for the pesticide photolysis. From the first order Eq. (1) calculated for the degradation of the ethiofencarb, values were obtained for the constants and the half-lives. These were: $k = 3.32 \cdot 10^{-5}\ s^{-1}$ (water), $k = 2.53 \cdot 10^{-5}\ s^{-1}$ (methanol) and $k = 1.56 \cdot 10^{-5}\ s^{-1}$ (hexane), and $t_{1/2}$ (h) 5.57, 7.17 and 12.41, respectively.

3.2. Identification of ethiofencarb photoproducts

The structures of the photoproducts were established, in some cases, by comparison of their spectral properties with those of authentic samples. Table 1 shows their GC retention times and MS fragmentation patterns.

3.2.1. Photodegradation in water

The ethyl acetate extracted solution also showed the presence of a main compound (II) and the remaining pesticide. The GC–PCI–MS determination of the extract gave a molecular mass for this compound of 165. Its structure and mass spectra are shown in Fig. 4. It was identified as 2-methylphenyl-N-methylcarbamate.

3.2.2. Photodegradation in methanol

Table 1 shows retention times, molecular masses and characteristic ions with their relative abundance. The mass spectra and structures proposed for these compounds are shown in Fig. 4.

Table 1
Mass fragmentation pattern and retention time of ethiofencarb (I) and its photoproducts

Structure no.	Compound	Solvent system	t_R (min)	M_r	Characteristic peaks in mass spectrum[a]
I	Ethiofencarb		8.17	225	168(14), 107(100), 77 (24), 58(20)
II	2-Methylphenyl-N-methylcarbamate	Water Methanol	6.14	165	108(100), 107(36), 77(30)
III	3-Methylbenzo[*e*][1,3]oxazine-2,4-dione	Methanol Hexane	6.76	177	177(52), 120(100), 92(47)
IV	3-Methyl-benzo[*e*][1,3]oxazine-2-one	Methanol Hexane	6.91	163	163(98), 106(100), 78(94)
V	Unidentified compound	Methanol	7.55	152	152(57), 120(100), 92(51)
VI	Unnamed compound	Methanol	8.53	219	162(53), 120(21), 107(100), 91(22), 77(40)
VII	Sulphone of ethiofencarb phenol	Methanol	11.35	200	107(100), 77(27)
VIII	2-Methylbenzo[*e*](1,3)oxathio?	Hexane	5.99	166	166(28), 107(67), 78(100), 59(43)
IX	Ethiofencarb phenol	Hexane	6.14	168	168(20), 108(24),107(100),77(51)
X	2-*n*-butylphenol?	Hexane	6.21	150	106(42), 78(100), 51(22)

[a] Relative abundance in parenthesis.

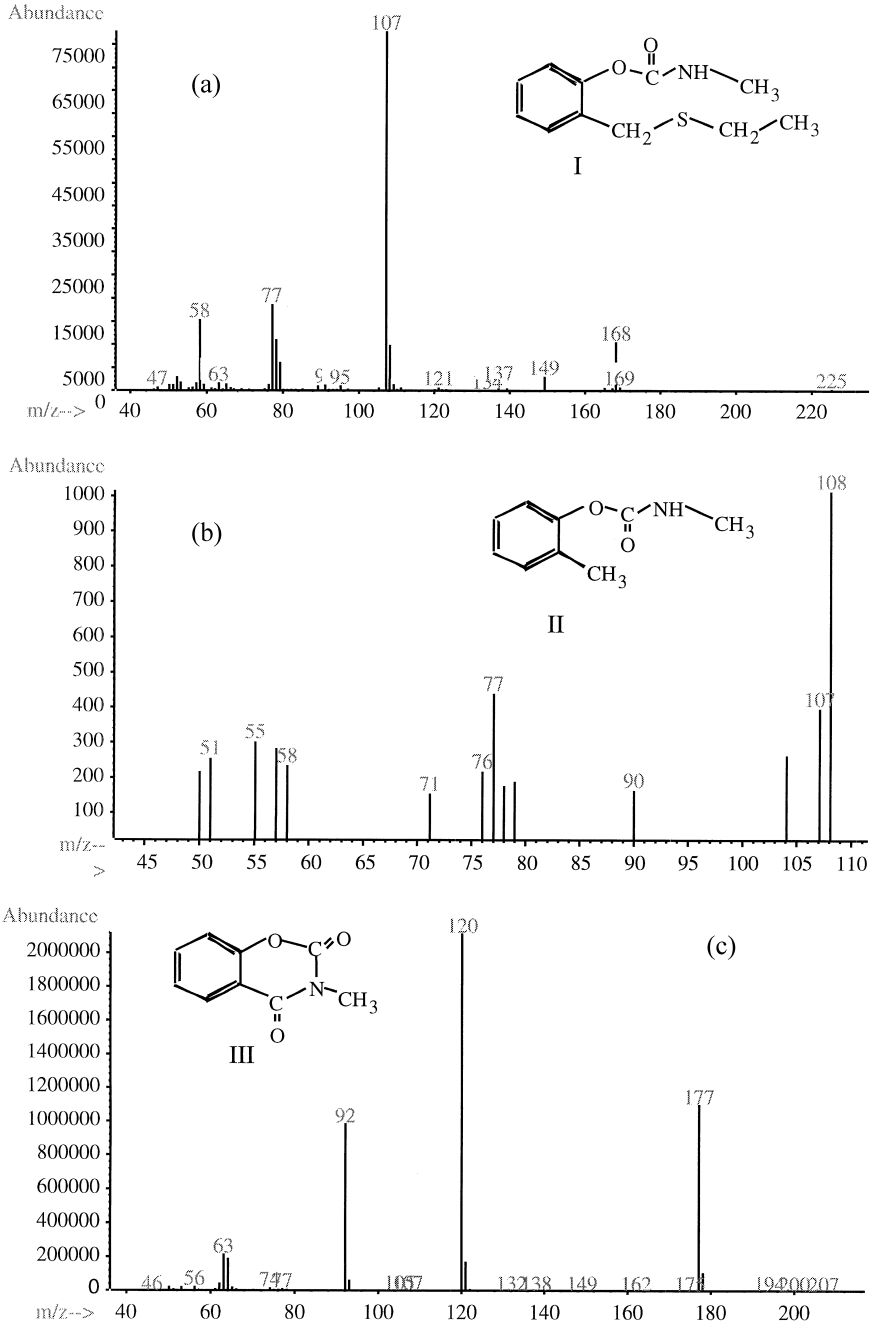

Fig. 4. Mass spectra and proposed structures: I = Ethiofencarb; II = 2-methylphenyl-*N*-methylcarbamate; III = 3-methylbenzo[*e*][1,3]oxazine-2,4-dione; IV = 3-methylbenzo[*e*][1,3]oxazine-2-one; V = unidentified compound; VI = un-named compound; VII = sulphone of ethiofencarb phenol; VIII = 2-methylbenzo[*e*][1,3]oxathio?; IX = ethiofencarb phenol; X = 2-*n*-butylphenol?.

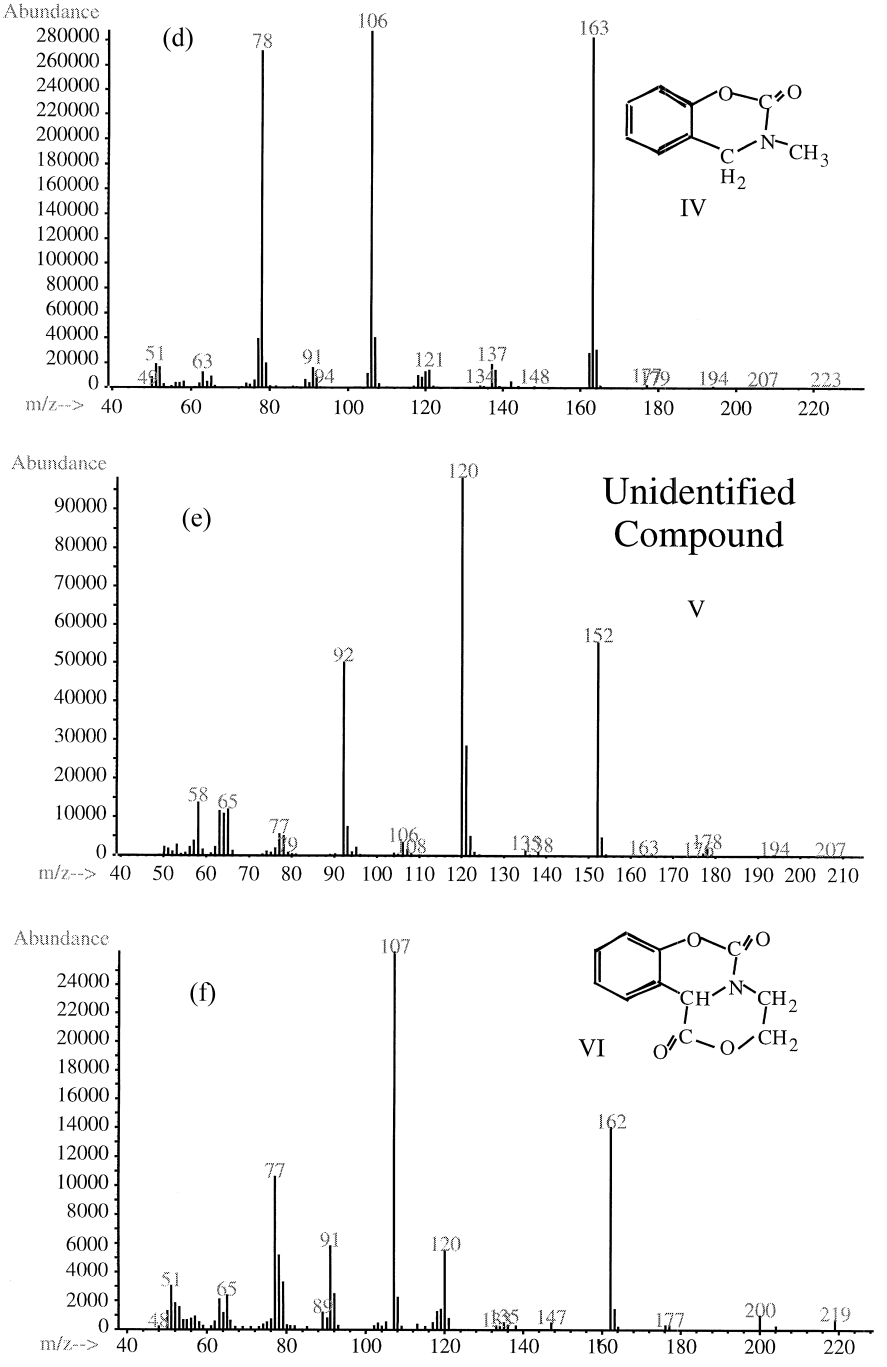

Fig. 4. (*continued*)

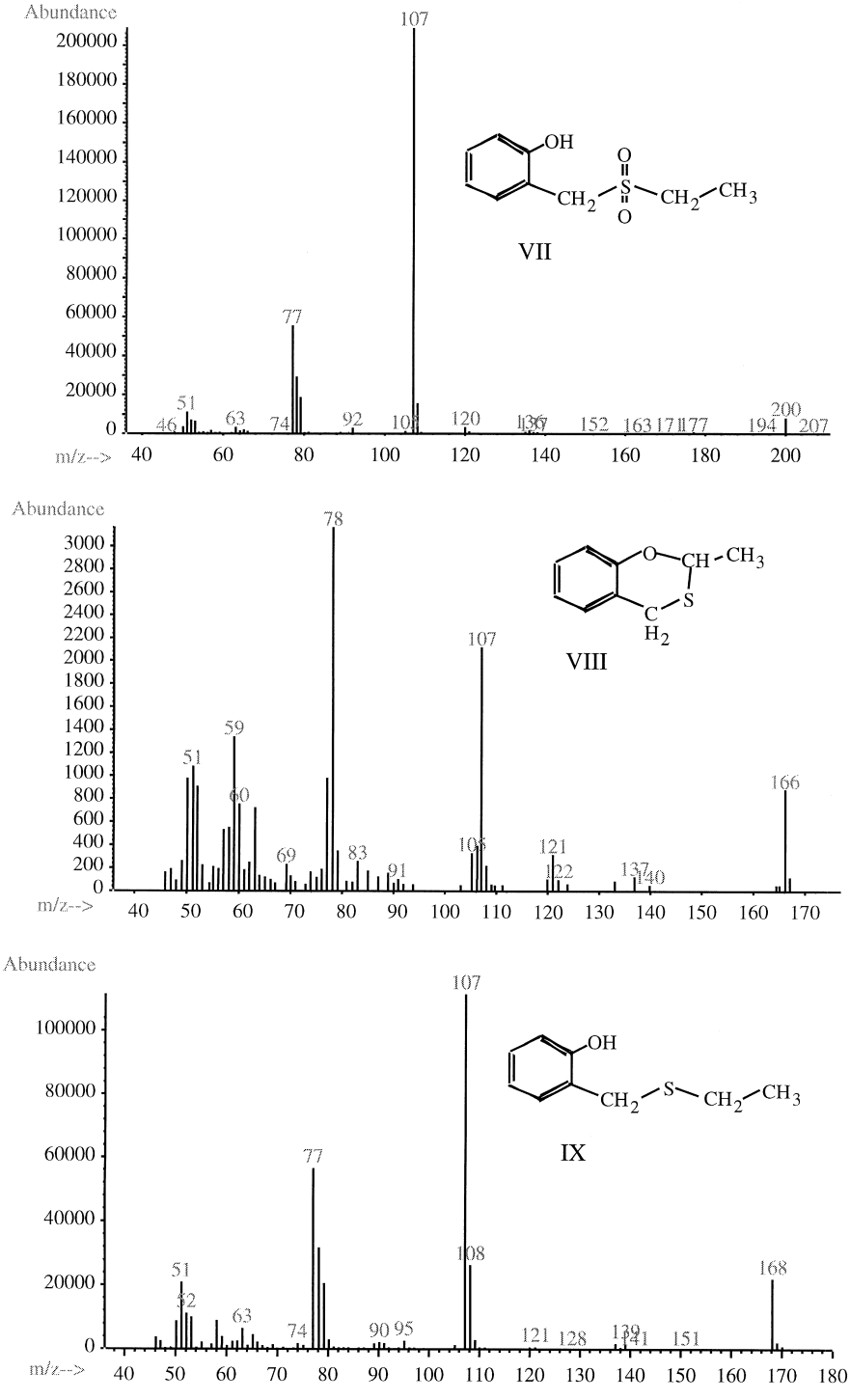

Fig. 4. (*continued*)

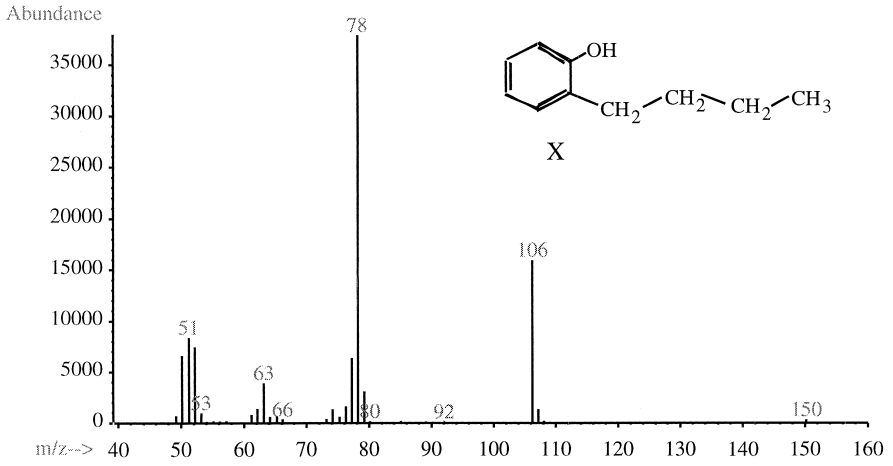

Fig. 4. (*continued*)

Compound II was identified as the same compound obtained in the aqueous medium, as it had the same retention time and the same EI and PCI spectra.

Compound III showed characteristic peaks at m/z 120 and m/z 92, indicating the presence of $[C_6H_4OCO]^+$ and $[C_6H_4O]^+$; its molecular mass was 177. It was identified as 3-methylbenzo[*e*][1,3]oxazine-2,4-dione. The proposed structure has been reported previously for the photodegradation of ethiofencarb in other solvents [9,14].

Compound IV was identified as 3-methylbenzo[*e*][1,3]oxazine-2-one. The compound showed major peaks at m/z 106 and 163, corresponding to the ion $[C_6H_4CH_2O]^+$ and the molecular ion, respectively.

The structure for compound V was not determined.

The mass fragments obtained for compound VI were determined, and a proposed structure is given in Fig. 4. Given its complexity, we have not indicated a name for this compound.

Finally, the structure proposed for VII was the sulphone of ethiofencarb phenol.

3.2.3. Photodegradation in hexane

The data obtained for the photodegradation compounds is shown in Table 1. The mass spectra and proposed structures are shown in Fig. 4. Compounds III and IV are also shown.

Compound I was identified as the remaining ethifencarb.

Compounds III and IV were identified as the same compound obtained in methanolic solution.

Compound IX was identified as ethiofencarb phenol (by comparison with a pure standard).

For compounds VIII (2-methylbenzo[*e*][1,3]oxathio?) and X (2-*n*-butylphenol?), the proposed structures are shown in Fig. 4; the spectral information obtained from the mass spectra of these compounds was not sufficient to confirm these structures. A further isolation of these compounds, as well as V, will be necessary in order to confirm their structures from NMR and their IR spectra.

3.2.4. Photodegradation scheme

The tentative photodegradation schemes for ethiofencarb in water, methanol and hexane solutions are shown in Fig. 5.

4. Conclusions

The photolytic degradation in aqueous and non aqueous (methanol and hexane) of samples of ethiofencarb pesticide, using a solar simulation unit, allows different residues of the pesticide to be studied. It seems that the degradation pathways depend to a large extent on the media used; the main

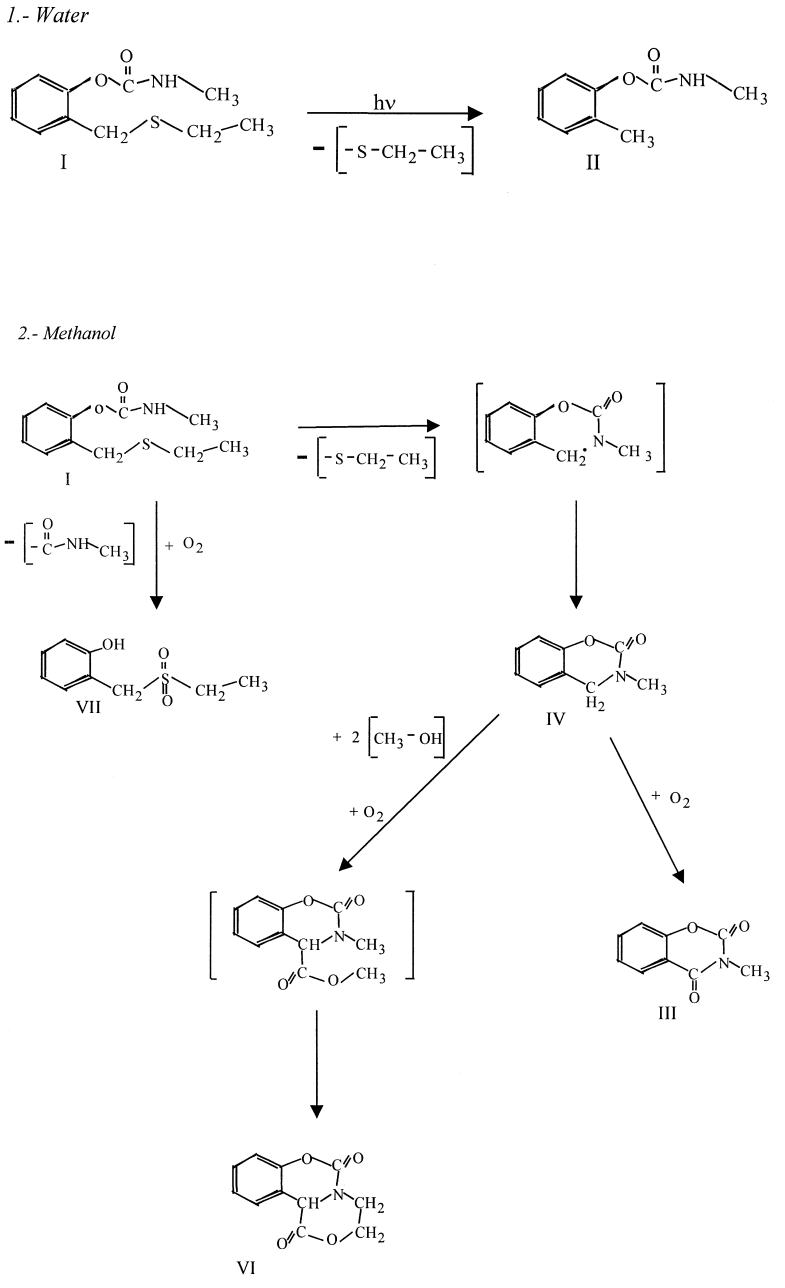

Fig. 5. Photodegradation schemes for ethiofencarb in water, methanol and hexane solutions.

compounds obtained are different, as is the process complexity. The results obtained clearly indicate that ethiofencarb degradation occurs in an exponential way over time.

Kinetic photodegradation of the pesticide depends on the solvent media; the kinetics can be fitted to a first-order rate equation independently of the medium. The greatest velocity is seen with solvents of highest polarity.

Total degradation of the pesticide, in irradiation

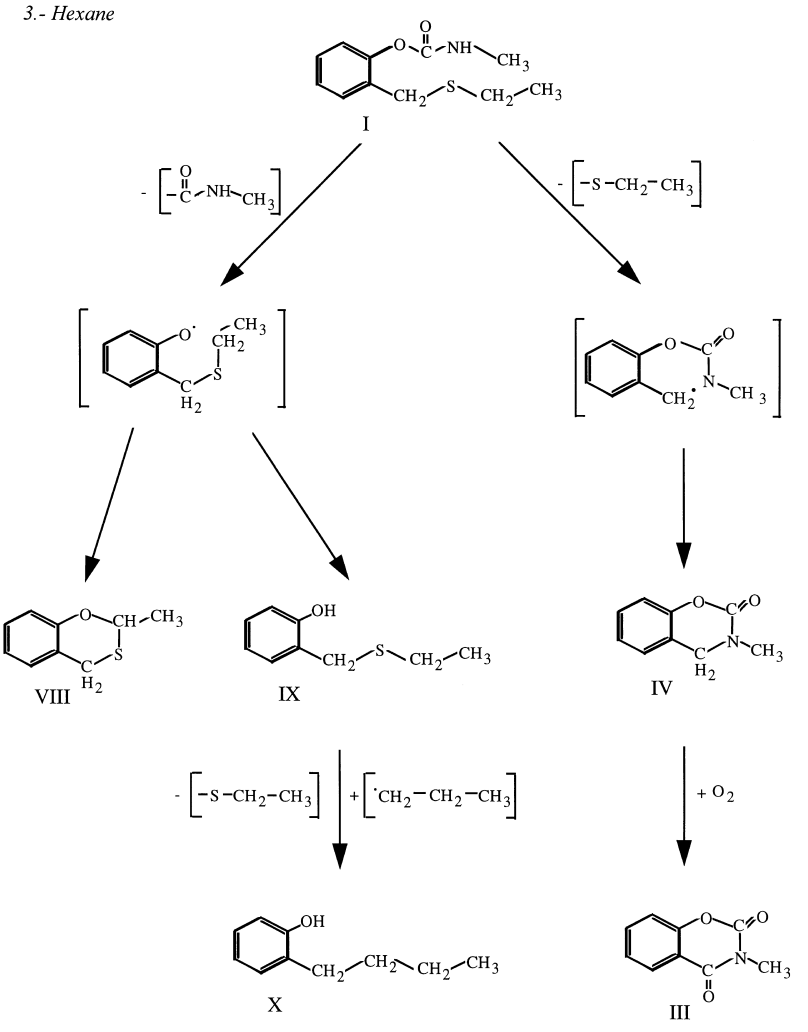

Fig. 5. (*continued*)

time, depends on the solvent media: $t_{water} < 30$ h, $t_{methanol} < 50$ h and $t_{hexane} < 98$ h.

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