



# Fenarimol solar degradation pathways and photoproducts in aqueous solution

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## Abstract

The degradation photoproducts of the fungicide fenarimol obtained from irradiation of aqueous solutions with sunlight were characterised. The photoproducts resulting from samples with different exposure times were extracted and separated using chromatographic techniques. Seven main photoproducts were detected using high performance liquid chromatography with a photodiode array detector, gas chromatography with mass spectrometry detector and Fourier transform infrared spectroscopy. Structures are suggested for possible photoproducts based on the characterisation results, minimum energy geometry of the parent compound, and the mass spectral behaviour of fenarimol. These correspond to the compounds with  $m/z$  328 (three structural isomers (a), (b) and (c)),  $m/z$  294 (two structural isomers (a) and (b)),  $m/z$  292, 278 and 190. Of the various major products detected, the isomer 328(a) is seen to be particularly unstable under the action of sunlight. The most stable photoproducts are found to be those with  $m/z$  294(a), 278 and 190. However, upon prolonged solar irradiation all of these break down to produce polar, low molecular weight compounds. Comparison with our own and other results on fenarimol photolysis indicate significant solvent effects on the process.

The combination of these structural characterisation results and previous data from spectroscopic and photodegradation kinetics studies allows us to suggest some possible mechanisms for the photodegradation of fenarimol under sunlight. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Fenarimol; Photodegradation; Photoproducts; Sunlight

## 1. Introduction

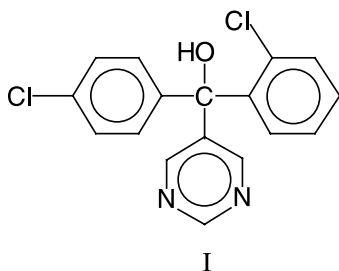
The direct photolysis of pesticides under sunlight is of considerable environmental importance, although they frequently only show UV/visible bands at relatively short wavelengths. However, although a number of possible pathways have been suggested for these pro-

cesses, there is still only a limited amount of data available on solar degradation of these compounds (Burrows et al., 2001), and there is a clear need for more studies both on aqueous solutions and model environmental systems. We report an extension of a study of the photodegradation of one such pesticide, fenarimol, following its behaviour under solar irradiation in water.

The fungicide fenarimol ( $\alpha$ -(2-chlorophenyl)  $\alpha$ -(4-chlorophenyl)-5-pyrimidine-methanol) (I) is commonly used in the form of a spray for treating mildew. However, it is known that it is photochemically unstable (Worthing, 1983).

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Previous spectroscopic and kinetic studies (Mateus et al., 1994, 1997, 2000) have shown that the photodegradation of this molecule occurs principally via its lowest excited singlet state. This has  $^1(n, \pi^*)$  character and corresponds to the excitation being located on the pyrimidine ring of fenarimol. Because of its low solubility in water, the initial approaches to identify photoproducts have used organic solvents irradiated either by sunlight (Mateus et al., 1994) or the UV output ( $>250$  nm) from high pressure mercury lamps (Sur et al., 2000). In the solar irradiation studies it is seen that the fenarimol photolysis rate constant decreases significantly in solvents containing hydroxyl groups, in agreement with the  $(n, \pi^*)$  character attributed to the first absorption band of fenarimol. In nonpolar solvents the formation of a precipitate is observed as the photodegradation proceeds, suggesting that the photodegradation products have a polar nature. This idea is supported by high performance liquid chromatography (HPLC) results, using a  $C_{18}$  column, which also indicates the formation of low molecular mass compounds.

Further valuable information comes from gas chromatography with mass spectrometry (GC–MS) analysis. Two compounds with  $m/z$  328 and 314 are formed in an initial phase of the photodegradation, and are most evident in hydroxylic solvents where the rate of photodegradation is slowest. In acetonitrile, where the rate of photodegradation of the pesticide is fastest, the most stable photoproduct is a compound with  $m/z$  190 (Mateus et al., 1994). Formation of a stable compound with  $m/z$  250 is favoured on photolysis in low polarity solvents, while a compound, or compounds, with  $m/z$  278 is an important photoproduct in alcohols (Sur et al., 2000) and water (this work) but is not a major photoproduct in nonpolar solvents.

For environmental considerations, the solar induced photodegradation of fenarimol in aqueous solutions is of particular interest. The marked solvent effects on the photoproducts show that caution must be exercised in extrapolation of data obtained with organic solvents to these conditions. In addition, the primary and secondary photoproducts from irradiation with light of wavelength less than 300 nm may be different from those observed on solar photolysis.

In this report, we extend our studies to obtain more information about the photoproducts produced on the

photodegradation of fenarimol in water by sunlight, with particular reference to the mechanisms, to whether excited states other than  $S_1$  may be involved, and what other photochemical transformations may be involved.

## 2. Materials and methods

### 2.1. Chemicals

**Solvents:** Solutions were prepared using water, which had been deionised and then distilled. Other solvents were of HPLC grade and were used without further treatment.

**Organic compounds:** Fenarimol was obtained from Riedel (99.7%). This and all the other standards were used without further treatment: pyrimidine (Sigma, pure); chlorobenzene (Merck  $>99\%$ ); *o*-chlorotoluene (Merck p.a.); *p*-chlorotoluene (Merck p.a.); *o*-chlorobenzaldehyde (BDH p.a.); *p*-chlorobenzaldehyde (BDH p.a.).

### 2.2. Equipment and methods

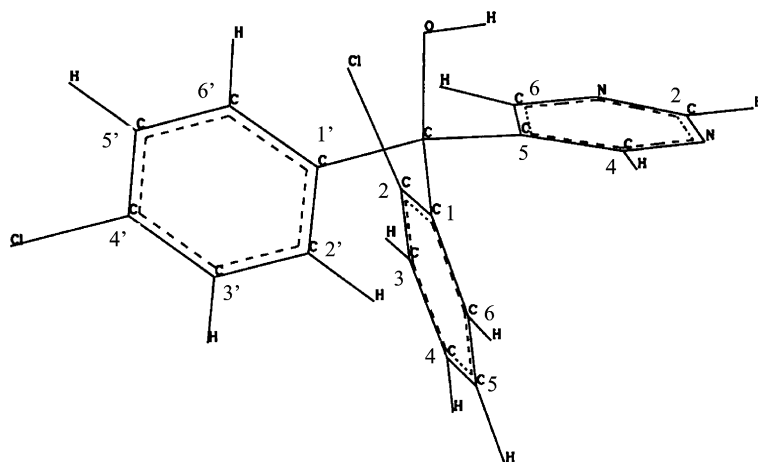
HPLC experiments were carried out using the Merck–Hitachi 655A-11 system with 655A-22 UV detector, or a Shimadzu UV–visible photodiode array (PDA, model SPD-M6A). Spectra were recorded of all the isolated fractions between 220 and 380 nm using the same conditions as used in isolation of the photoproducts.

All the GC–MS analyses were carried out by a Hewlett Packard “5890 series II” gas chromatograph with a 5971 series mass selective detector (MSD), and MS ChemStation. A Restex RTX-1701 column ( $20\text{ m} \times 0.2\text{ mm} \times 0.18\text{ }\mu\text{m}$ ) was employed to analyse all collected samples, and two different temperature programs used: (1) Marcexp.m: 1 min initial hold at  $140\text{ }^\circ\text{C}$ ,  $5\text{ }^\circ\text{C}/\text{min}$  at  $200\text{ }^\circ\text{C}$ ,  $10\text{ }^\circ\text{C}/\text{min}$  at  $250\text{ }^\circ\text{C}$ , 19 min final hold at  $250\text{ }^\circ\text{C}$ ; (2) Mateus02.m: 3 min initial hold at  $60\text{ }^\circ\text{C}$ ,  $6\text{ }^\circ\text{C}/\text{min}$  at  $250\text{ }^\circ\text{C}$ , 15 min final hold at  $280\text{ }^\circ\text{C}$ . The inlet temperature was  $280\text{ }^\circ\text{C}$ , the inlet pressure was 40 kPa, and the electron impact source temperature was  $280\text{ }^\circ\text{C}$ .

Infrared spectra were registered as KBr discs using Nicolet 740 Fourier transform infrared spectroscopy (FT-IR) (Coimbra) or Mattson 1000 FTIR (Faro) spectrophotometers.

#### 2.2.1. Characterisation of fenarimol

The UV/visible absorption and luminescence spectra of fenarimol have previously been discussed (Mateus et al., 1994, 1997).



	Angles between bonds attached to rings		Angles between the planes of the rings		Angles between the C-O bond and the rings	
	pyrimidine	<i>p</i> -CIBz	pyrimidine	<i>p</i> -CIBz	pyrimidine	<i>p</i> -CIBz
<i>o</i> -CIBz	114.05°		<i>o</i> -CIBz	64.1°	<i>o</i> -CIBz	97.77
<i>p</i> -CIBz	113.87°	103.4°	<i>p</i> -CIBz	69.1°	<i>p</i> -CIBz	111.98
						110.91

Fig. 1. Calculated minimum energy geometry of fenarimol.

A minimum energy geometry of fenarimol molecule was determined using the computer program INSIGHT/ DISCOVER: *Insight II Version 2.2, Discover Version 2.9 Biosym. Inc. San Diego CA, 1993*, and is shown in Fig. 1 with the appropriate geometrical parameters.

The mass spectrum of fenarimol has previously been presented (Mateus et al., 1994). A mechanism for the fragmentation in the spectrum on electron impact is given in Fig. 2.

#### 2.2.2. Irradiation of fenarimol in aqueous solution under sunlight

Because the low solubility of fenarimol in water implies the dissolution of the pesticide during several hours under a heating source, aqueous solutions (5 mg/l– $1.5 \times 10^{-5}$  M) were prepared using about 1% of acetonitrile as co-solvent. At low concentrations acetonitrile is generally accepted to be photochemically inert related to pesticide photodegradation (Lemaire et al., 1982; Mill et al., 1982; Leifer, 1988), which agrees with our previous results using fenarimol in water without co-solvent (Mateus, 1997). At this percentage we believe that there is no significant effect on the photodegradation pathways. Samples were photolysed in 1 l crystallisation dishes, covered with a thin transparent plastic film (transmittance at 290 nm  $\approx$  80%). For solar irradiation studies samples were maintained in a water bath located on a terrace free of shadows. Samples were analysed after 4.5, 7, 21 and 50 days irradiation with sunlight to follow the evolution of photoproducts with exposure

time, until almost total degradation of the fungicide had occurred.

#### 2.2.3. Photoproduct extraction

Two different methods were used to separate the photoproducts from water:

(a) Individual irradiated samples were extracted with 10 ml of dichloromethane followed by 10 ml of hexane. The organic phase was evaporated and the residue redissolved in 2 ml of acetonitrile.

(b) To get a more efficient recovery of the low molecular weight photoproducts, a different extraction process was developed, using a Merck RP-18 cartridge solid-phase extraction system. The cartridge was washed twice with methanol and once with water adjusted to pH 2. The aqueous fenarimol solutions were filtered and the adsorbed compounds were eluted with 2 ml of methanol. This method proved more direct and did not involve any significant reduction in the relative amounts of photoproducts recovered.

#### 2.2.4. Photoproduct isolation

In initial studies, the fenarimol photoproducts were separated by HPLC/UV with a 125-4-Lichrospher 100 RP-18 (5  $\mu$ m) analytical column, using the following conditions: mobile phase: CH<sub>3</sub>CN/H<sub>2</sub>O, 40/60 (v/v); flow rate: 1.5 ml/min; volume of sample injected: 25  $\mu$ l; detection wavelength: 220 nm. To obtain a better separation of the compounds with shorter retention times, the conditions were modified by using the following

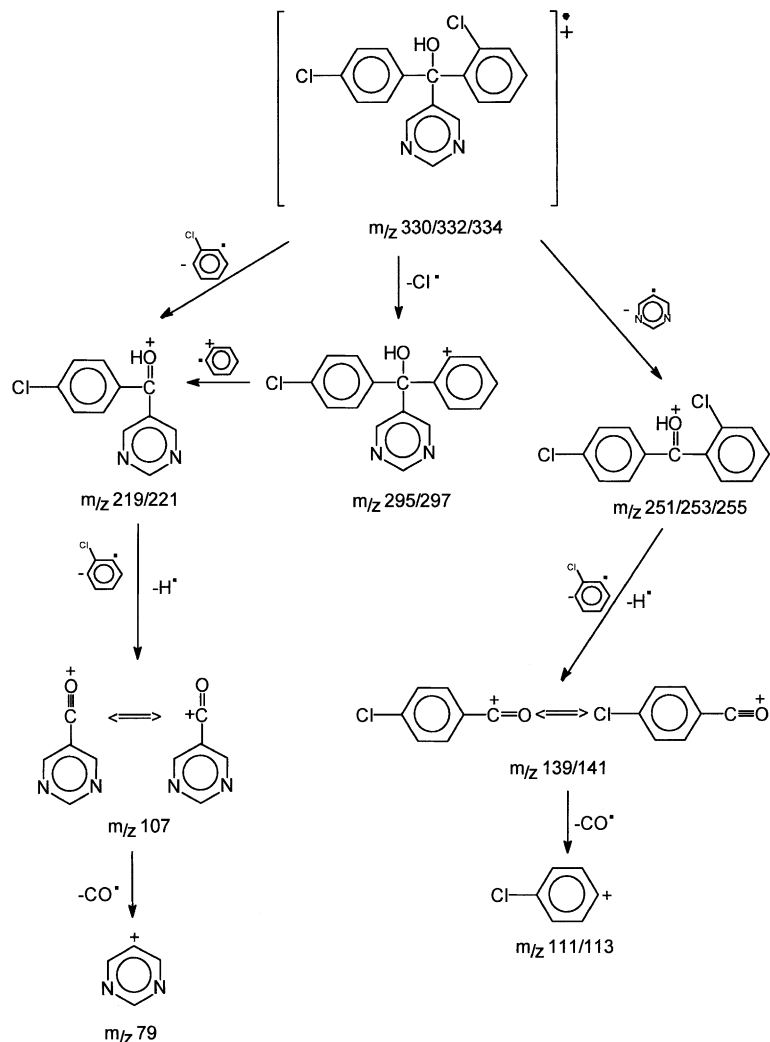


Fig. 2. Suggested fragmentation pattern for fenarimol in mass spectrum on electron impact.

elution gradient program for the mobile phase: 0.5 min with  $CH_3CN/H_2O$  25/75, 12.5 min with  $CH_3CN/H_2O$  40/60, and final 4 min again with  $CH_3CN/H_2O$  25/75.

Samples corresponding to well defined chromatographic peaks were collected and extracted with 20% dichloromethane. After centrifugation (5000 rpm for 10 min), the organic phase (dichloromethane and acetonitrile) was separated and concentrated to a volume of 1 ml (mainly acetonitrile solution).

#### 2.2.5. Photoproduct characterisation

General details of the HPLC/PDA and GC-MS analysis of collected samples are given in Section 2.2.

To help identify possible photoproducts, standard solutions of chlorobenzene, pyrimidine, *ortho* and *para*-chlorobenzaldehyde were prepared. In addition, 2,2'-

dichlorobenzil and 4,4'-dichlorobenzil were synthesised, from *ortho* and *para*-chlorobenzaldehyde, using literature procedures (Vogel, 1956). The photoproducts were compared with these standards using GC-MS, HPLC/PDA and FTIR. In spite of the low concentrations of photoproducts, the high sensitivity of these analytical methods allowed good reproducibility between experiments.

### 3. Results and discussion

#### 3.1. Photoproducts of fenarimol in aqueous solutions

Chromatographic results of the products of photolysis of aqueous solutions of fenarimol with sunlight for 7

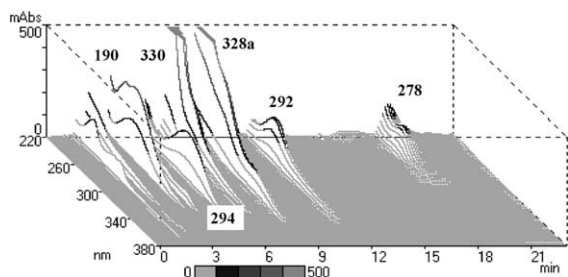


Fig. 3. Chromatogram of photolysis products of an aqueous fenarimol solution (5 mg/l) obtained by HPLC with a multi-channel detector (PDA). The solution was irradiated with sunlight for 7 days.

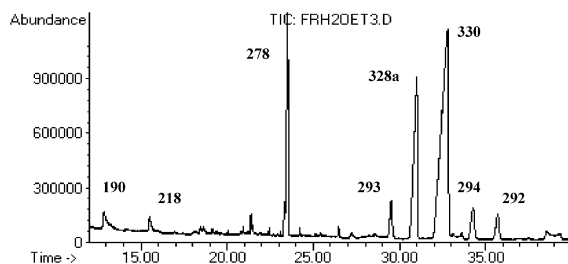


Fig. 4. Chromatogram of photolysis products of an aqueous fenarimol solution (5 mg/l) obtained by GC–MS. The solution was irradiated with sunlight for 7 days.

days, followed by extraction using  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$  are shown in Fig. 3 (HPLC/PDA) and Fig. 4 (GC/MS). Previous studies (Mateus et al., 1994) had shown that there is no degradation in the absence of light. In Table 1, data are given for the characterisation of the five major isolated photoproducts ( $m/z$  190, 278, 292, 294(a) and 328(a)), together with suggested structures, based on the HPLC/PDA data, IR spectra and MS fragmentation patterns.

Using two different gas chromatographic temperature programs, three more photoproducts could be ob-

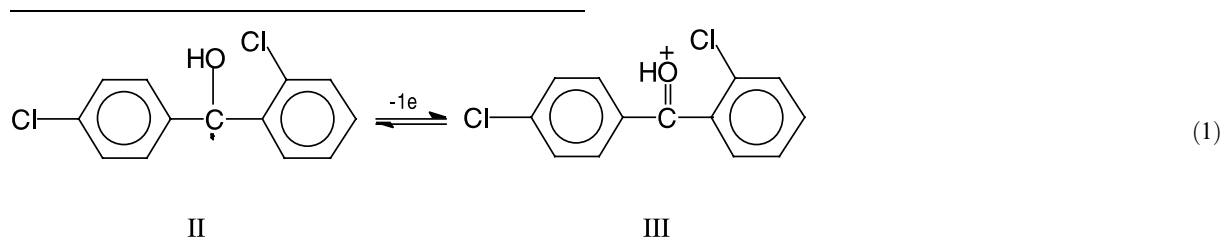
Traces of three more compounds were also detected in single experiments, but subsequent attempts to repeat their detection were not successful. These are a compound with  $m/z$  250, which could be dichlorobenzophenone, as suggested by Sur et al. (2000), a compound with  $m/z$  314 with unknown molecular structure and a compound with  $m/z$  218. This latter compound possibly results from cleavage of a chlorobenzene ring of fenarimol and formation of a pyrimidine-chlorobenzophenone pyrimidine-chlorophenone photoproduct. Further photodegradation experiments, using exclusively water as solvent, showed two GC–MS peaks with  $m/z$  218, in a very initial step of the photodegradation process, which may correspond to structural isomers with different chlorobenzene rings.

### 3.2. Time-evolution of photodegradation products

The time evolution of photoproducts generation as observed by the two extraction methods is presented in Table 2. The MS results show that all the isolated compounds have lower molecular masses than fenarimol, showing the importance of cleavage processes on the fenarimol photolysis.

A comparative analysis of data presented in Table 2, and consideration of the mass spectrum of fenarimol itself, suggests that two distinct routes may be involved in the photodegradation:

- Homolytic cleavage of the bond from the carbinol carbon to the pyrimidine group of fenarimol, resulting in formation of a pyrimidyl radical and a dichloroketyl radical (II).
- Homolytic cleavage of the carbon–chlorine bond in the *ortho* position relative to the central carbon in fenarimol, followed by cyclisation and loss of a chlorine atom.
- The first pathway seems to be particularly important for the photodegradation process from the lowest excited singlet state  $^1(n, \pi^*)$ . The dichloroketyl radical may participate in the redox equilibrium (Eq. (1)):



served ( $m/z$  = 293, 294(b), 328(b)), although, because of their low yields, they could not be isolated (see Table 1).

which may either, involve electron transfer to fenarimol ( $E_{1/2} = -0.86$  V (Mateus et al., 2000)) or

Table 1  
Analytical data and suggested structures of photoproducts of fenarimol in water

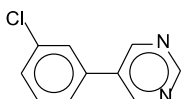
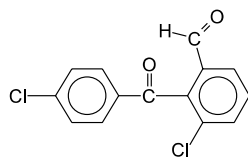
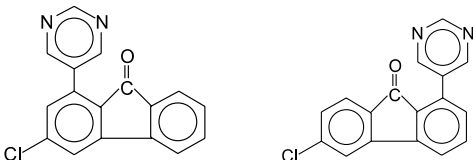
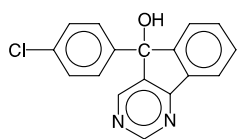
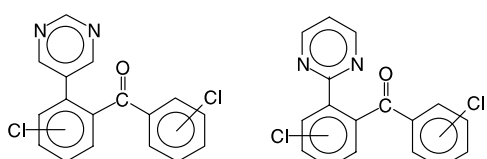
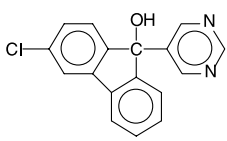
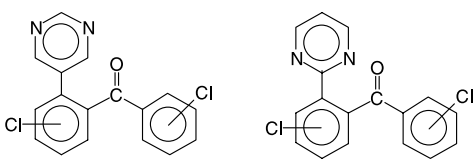
Suggested structure	Analytical characterisation
 m/z 190	HPLC/PDA: retention time—3.8 min; $\lambda_{\max}$ —255 nm GC: retention time—12.8 min MS spectrum: 190/192 ( $M^+$ , 100%); 155 (6.3); 136/138 (59.6); 101 (12.8)
 m/z 278	HPLC/PDA: retention time—19.65 min; $\lambda_{\max}$ —242 nm IR: strong peak at $1766\text{ cm}^{-1}$ GC: retention time—23.5 min MS spectrum: 278/280/282 ( $M^+$ , 24%); 249/251/253 (3.6); 243/245 (17); 215/217 (2.4); 199/201 (33); 139/141 (100); 111/113 (24.4)
 m/z 292	HPLC/PDA: retention time—12.09 min; $\lambda_{\max}$ —250 nm IR: peak at $1661\text{ cm}^{-1}$ GC: retention time—35.4 min MS spectrum: 292/294 ( $M^+$ , 100%); 264/266 (97); 229 (8.2)
 m/z 294(a)	HPLC/PDA: retention time—5.81 min; $\lambda_{\max}$ —280 nm GC: retention time—34.0 min MS spectrum: 294/296 ( $M^+$ , 52%); 259 (2); 183 (100); 155 (6.2); 139/141 (43.8); 128 (20.8); 111/113 (16.7)
 m/z 328(a)	HPLC/PDA: retention time—8.63 min; $\lambda_{\max}$ shoulder—300 nm IR: strong peak at $1666\text{ cm}^{-1}$ GC: retention time—30.7 min MS spectrum: 328/330/332 ( $M^+$ , 26.5%); 299/301/303 (26); 293/295 (100); 217/219 (24); 190/192 (6); 139/141 (62); 111/113 (40)
 m/z 294(b)	GC: retention time—34.0 min MS spectrum: 294/296 ( $M^+$ , 93%); 277/279 (22.7); 259 (47.7); 215/217 (100), 152 (54.5)
 m/z 328(b)	GC: retention time (GC programme MATEUS02)—43.8 min MS spectrum: 328/330/332 ( $M^+$ , 41.8%); 293/295 (3); 117/119 (51); 139/141 (100); 111/113 (27.6)

Table 1 (continued)

Suggested structure	Analytical characterisation
<p style="text-align: center;">m/z 328(c)</p>	HPLC/PDA: retention time (programme with elution gradient)—4.22 min; $\lambda_{\text{shoulder}}$ —280 nm GC: retention time (GC programme MATEUS02)—44.4 min MS spectrum: 328/330/332 ( $M^+$ , 50%); 293/295 (14.8); 217/219 (100)

Table 2

Evolution of products of solar irradiation of aqueous solutions of fenarimol with irradiation time using different extraction procedures

Irradiation time	Photoproduct ( <i>m/z</i> )											
	190	218	250	278	292	293	294(a)	294(b)	314	328(a)	328(b)	328(c)
<i>Extraction with dichloromethane and hexane</i>												
7 days	4.7	22	vest.	24	5.5	5.9	(a + b) = 7.7	vest.	41.7	0.51	n.d.	
21 days	182	n.d.	n.d.	118	10	10	133	n.d.	n.d.	10	42	54
<i>Extraction with C18 cartridges</i>												
4.5 days	1.6	n.d.	vest.	0.92	n.d.	vest.	(a + b) = 1.1	2.3	7.9	vest.	vest.	
21 days	371	n.d.	n.d.	326	vest.	12	177	n.d.	n.d.	n.d.	41	87
50 days	118	n.d.	n.d.	164	n.d.	n.d.	26	n.d.	n.d.	n.d.	vest.	n.d.

n.d.—not detected; vest.—traces.

The values given correspond to the % area of photoproduct relative to the area of the fraction of fenarimol in each chromatogram obtained by GC–MS using the method MATEUS02.

disproportionation by deprotonation of the cation (III) producing 2,4'-chlorobenzophenone (*m/z* 250). This has been shown to be a major product on photolysis in alcohol–water mixtures (Sur et al., 2000). However, only traces of this compound are observed with some of the samples on solar photolysis of aqueous solutions, suggesting other pathways for these radicals. The major reaction in this case appears to be recombination of the pyrimidyl and dichloroketyl radicals by ring addition to form the structural isomers designated 328(a) and (b). Although the two compounds have similar HPLC retention times, they show different GC–MS behaviour. In addition, although compound 328(a) is fully degraded within 21 days, compound 328(b) persists.

Although GC–MS results of fenarimol photoproduct evolution shows that compound 328(a) is the main initial photoproduct produced and is unstable to photolysis, the experimental data obtained do not allow us to distinguish unequivocally between the two isomers (a) and (b). To attempt to clarify the assignment, we have carried out a minimum energy geometry analysis (Fig. 1) which suggests that the most favourable positions for forming new C–C bonds with free pyrimidyl radical are position 6 of the *o*-chlorobenzene and positions 2' and 6' of the *p*-chlorobenzene ring, with formation of the correspondent isomers. The alternative structures for these

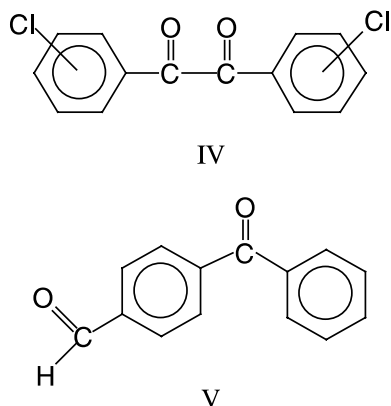
compounds are represented in Table 1 and are just given as guides.

Other experimental studies on the effect of acidity on the formation of the isomers of compound *m/z* 328 in the presence of oxygen show a decrease in the yield of compound 328(a) with a decrease in the solution pH (Mateus et al., 1994). This may be due to the protonation equilibrium (Eq. (1)) with consequent inhibition of radical recombination.

It is well known that in the absence of low lying  $^1(\pi, \pi^*)$  or charge transfer states, benzophenones show a high  $S_1(n, \pi^*) \xrightarrow{\text{ISC}} T_1(n, \pi^*)$  intersystem crossing efficiency (Turro, 1978). Considering the structures of compounds 328(a) and (b), the presence of the carbonyl group is likely to make these sensitive to photodegradation through their lowest triplet states. Support for this comes from increased photochemical stability of these compounds in presence the triplet state quencher sorbic acid (Mateus et al., 1994, 2000). There are no indications of formation of substituted benzopinacol derivatives, which would be expected for hydrogen atom abstraction by excited carbonyl compounds (Scaiano, 1973; Turro, 1978; Gilbert and Baggott, 1991; Formosinho and Arnaut, 1991; Wagner and Park, 1991; March, 1992). However, it is known that hydrogen atom abstraction from water is difficult, due to the high O–H bond energy

(Ledger and Porter, 1972) and it is likely that other photochemical pathways for excited carbonyl compounds are important.

It can be seen from Table 2 that the decay of compound 328(a) is accompanied by formation of compounds with  $m/z$  278 and 190. This behaviour can be explained assuming a Norrish type I reaction (Gilbert et al., 1991; March, 1992), with the consequent formation of the respective chlorobenzoyl ion and the compound  $m/z$  190. The chlorobenzoyl radicals would be expected to recombine to form dichlorobenzil ( $m/z$  278). 2,4'-dichlorobenzil has been shown to be one of the products of photolysis of fenarimol in alcohol–water mixtures (Sur et al., 2000). The other isomers 2,2'-chlorobenzil and 4,4'-chlorobenzil were synthesised and compared with the photoproduct  $m/z$  278. However, analytical data from HPLC/PDA, GC–MS and IR spectroscopy show that these are three distinct compounds, with different retention times and spectra. In particular, the MS spectrum for photoproduct  $m/z$  278 is much more complex than those obtained from the dichlorobenzil isomers (IV), although the compounds have the same mass. In addition, the IR spectra for these dichlorobenzils and for other benzil derivatives (Sadler book, 1978) show carbonyl C=O stretching peaks typically in the region 1650–1680  $\text{cm}^{-1}$ , while the compound with  $m/z$  278 shows a band at 1766  $\text{cm}^{-1}$ , more typical for a compound with an aldehyde functional group. Further, the UV absorption spectra of benzil shows absorptions up to 450 nm (Murov et al., 1993), whilst the compound 278 only absorbs significantly below 300 nm. We, therefore, assign the structure given in Table 1. Previous studies by Rao and Turro (1989), using 313 nm photolysis of a benzaldehyde- $\beta$ -cyclodextrin complex as a solid, shown that compound (V) could be generated with a 24% yield if  $\text{O}_2$  was present.



We believe that the dominant photoproduct with  $m/z$  278 in aqueous solutions has a similar chemical structure (Table 1). As with the system discussed by Rao and Turro, the fact that the molecule  $m/z$  328(a) is three

times less stable in the presence of  $\text{O}_2$  may be significant in the formation of the aldehyde functional group.

In additional experiments irradiating solutions of 4-chlorobenzaldehyde, 2-chlorobenzaldehyde, or equimolar mixtures of 4-chlorobenzaldehyde and 2-chlorobenzaldehyde in methanol/water (50/50 v/v), we found the products were the corresponding dichlorodiphenyl-ethane-1,2 diols rather than compound V, in agreement with previous studies referred to by Turro and Rao in ethanol solution. These results strongly suggest another mechanism is involved in the photochemical generation of compound  $m/z$  278. One possibility involves photooxidation by fragmentation of the pyrimidine ring in compounds 328(a) and/or (b). Some support for this comes from the mass spectra of compounds  $m/z$  190, 292, 294(a), 328(a) and 328(b), where it can be seen that fragmentation involves cleavage within the pyrimidine ring. The C–C bond from the pyrimidine to the chlorobenzene ring remains intact, possibly because of a very high bond energy.

Table 2 shows that the compound  $m/z$  278 is one of the most stable fenarimol photoproducts. As suggested in related systems (Wagner, 1967, Lewis et al., 1975), this may be due to some particularly effective vibronic coupling between the aldehyde and the excited ketone carbonyl groups, giving efficient radiationless deactivation to the ground state in competition with chemical reaction(s) to yield products. This idea provides further support to the recombination of the photocleaved pyrimidine radical with one the carbon atoms in *ortho* position, leading preferentially to one of the isomers of 328, as suggested from the higher statistical probability. However, it is not enough to distinguish between isomers (a) and (b).

Starting from Eq. (1), another possible pathway involves recombination of the pyrimidine radical, initially formed, with the quaternary carbon and one of the chlorobenzene rings to generate photoproduct  $m/z$  328(c). This compound is more stable under solar irradiation than the photoproduct 328(a), as we can see in Table 2, and its higher polarity (confirmed by chromatographic data) is in agreement with it maintaining the hydroxyl group. Furthermore, an increase in the structure of the UV spectrum of the isomer 328(c), relative to isomer 328(a), is consistent with the loss of planarity resulting from a more conjugated system formation that might involve fusion between the pyrimidine and chlorobenzene rings (Catalan et al., 1992).

In addition to homolytic cleavage of the bond between the carbinol group and pyrimidine, a second, less important, route involves the homolytic cleavage of the carbon–chlorine bond in the *ortho* position relative to the central carbon of fenarimol molecule, followed by cyclisation and loss of  $\text{Cl}^-$ . This process leads directly to two isomers (a) and (b) with  $m/z$  294, and indirectly to the compound 292, after loss of one chlorine atom from



compound 328(a) or (b) followed by condensation of the two benzene rings.

Photochemical chlorine loss, during fenarimol photodegradation process, was confirmed analysing an irradiated solution of fenarimol. By addition of a  $\text{AgNO}_3$  solution a white precipitate of  $\text{AgCl}$  was observed and by using a chloride selective electrode an increase in chloride concentration in solution was detected.

This mechanism may be associated with a higher dissociative excited state associated with the chlorobenzene ring (absorption band 230–280 nm). This lies above the  $^1(\pi, \pi^*)$  pyrimidine transition, and is probably only significant for irradiation with short wavelength light. Because the photoproduct yield was very low, it was very difficult to follow the respective photodegradation kinetics, and it was not possible to reach any conclusion about the nature of the excited state responsible.

Shimoda et al. studies, in gas phase (Shimoda et al., 1979a,b), shown that the fluorescence quantum yield of *p*-chlorotoluene is superior to that of *o*-chlorotoluene, while Ichimura et al. (Ichimura et al., 1984, 1985a,b, 1994) have shown that the photodecomposition of *p*-chlorotoluene is more sensitive to collisional quenching than that of the *ortho* isomer. These results suggest a greater photochemical reactivity for the *ortho* isomer, in agreement with our structural data, which suggest that photoproducts predominantly arise in fenarimol from homolytic cleavage at the *ortho*-position. This will also be favoured by the strong steric repulsion between the chlorine atom in the *ortho* position and the central oxy-

gen. Although some studies with chloroaromatics suggest that photonucleophilic substitution is the main reaction in hydroxylic solvents such as water (Tissot et al., 1983; Dulin et al., 1986; Boule et al., 1987), our results suggest that with fenarimol intramolecular photocyclisation is energetically the most favourable route after homolytic cleavage of the carbon–halogen bond (Choudhry and Webster, 1986; Davidson et al., 1984). This is possibly because of the proximity of the aromatic rings, as seen from the minimum energy geometry. This route ends mainly with production of compounds *m/z* 294(a) and (b). The lower photostability of isomer (b) (Table 2) is probably associated with the greater reactivity of the free pyrimidine ring compared to that fused to the aromatic ring in isomer (a).

Chromatographic and spectroscopic results were compared with standard solutions of pyrimidine, *ortho*- and *para*-chlorobenzaldehyde, chlorobenzene. None of these substances were detected in the extracts of irradiated fenarimol solutions, suggesting that upon prolonged solar irradiation, all the photoproducts break down to produce polar, low molecular weight compounds, which are eluted with the solvent front.

#### 4. Conclusions

From the above discussion on the products of photodegradation of fenarimol in water by sunlight, we suggest the mechanism in Fig. 5, which we believe gives both the primary and subsequent breakdown pathways

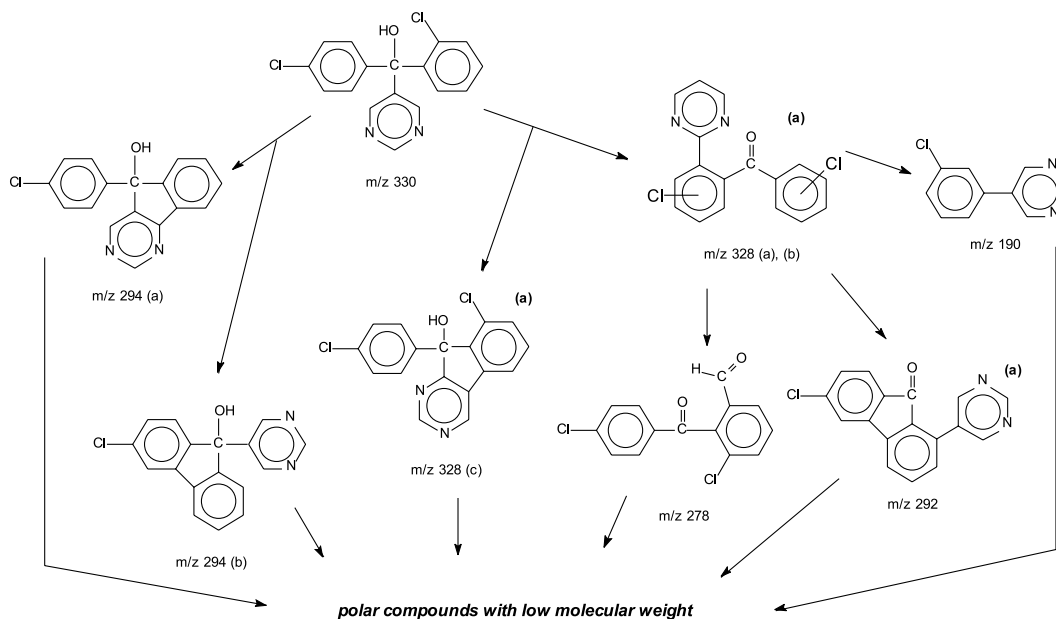


Fig. 5. Photodegradation process of fenarimol by sunlight in aqueous solution. (a) We are only presenting one of the possible isomers.

for the fungicide. Although the results we have previously reported for the photodegradation of this compound in organic solvents (Mateus et al., 1994) provide indications of the basic photodegradation pathways, the results shown in Table 2 for the time evolution of the products of solar photodegradation in water indicate preferential formation of the compound  $m/z$  328(a) in the initial step in water, while the compound  $m/z$  250, attributed to 2,4'-dichlorobenzophenone (Sur et al., 2000), is not formed significantly in water, but appears to be a major product of photolysis in organic solvents. The products with  $m/z$  278 and 190 are common to photolysis in both water and in most organic solvents. In water, the products  $m/z$  294(a) and (b) are observed, and result from homolytic cleavage of the carbon–chlorine bond and subsequent cyclisation. These products are not important in organic solvents, although in hexane and acetonitrile, there is formation of a product with  $m/z$  293 resulting from C–Cl cleavage. In this case the compound  $m/z$  278 is not formed. The differences in behaviour between photodegradation of fenarimol in aqueous solutions using sunlight and in organic solvents using ultraviolet light in the UV-C region emphasize the importance of using conditions as close as possible to environmental ones when trying to understand the natural photodegradation of pesticides.

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