Phototransformation of Propiconazole In Aqueous Media

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The photolysis of propiconazole in pure water, in water containing humic substances, and in natural water was investigated. The reaction rates were determined, and the main photoproducts were identified with the help of HPLC−mass spectrometry and by NMR. The quantum yield for direct photolysis was 0.11 ± 0.01 at the maximum of absorption (269 nm). Photocyclization after HCl elimination and photohydrolysis of the cyclized intermediate were the main reaction pathways at 254 nm. By contrast, oxidation prevailed over dechlorination in simulated or natural solar light. Humic substances (10 mg·L^{-1}) and naturally occurring chromophores contained in natural water enhanced the rate of propiconazole photodegradation in solar light. Half-life in June in Clermont-Ferrand (latitude 46°N) was found to be 85 ± 10 h in pure water and 60 ± 10 h in natural water; showing that photodegradation of propiconazole in natural waters involves both direct photolysis and photoinduced reactions.

Keywords: *Propiconazole; direct photolysis; photoinduced transformation; humic substances; natural water; solar light*

INTRODUCTION

The presence of pollutants in surface waters poses health and environmental risks. The European Union has listed the persistent and potentially toxic compounds for which more data are needed regarding their fate in the environment. Propiconazole (±)-1-[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-ylmethyl]-1H-1,2,4 triazole figures in this priority list (EEC/414/91). It is a systemic foliar fungicide with a broad range of activity. The toxicity is moderate: the acute oral LD_{50} is around 1500 mg/kg in rats. There is no report of long-term human exposure to propiconazole. This compound, however, has been classified as a possible human carcinogen (group C) by the U.S. Environmental Protection Agency (EPA, document no. 96-29020, 1996), on the basis of data from rodent studies.

Little is known on the fate of this compound in the environment. According to the literature (*1*), the compound's half-life in aerobic soils is 40−70 days, showing that intrinsic biodegradation processes are relatively slow. In surface waters, the half-life is shorter, suggesting that photochemical degradation might occur.

The phototransformation of a pollutant in surface water may result from light absorption by the pollutant itself (direct photolysis) or may be photoinduced by the dissolved natural organic matter (NOM) or nitrate ions present in water, as these chromophores are known to photoproduce reactive species (indirect photolysis) (*2*−*8*). Numerous studies have been reported in the literature (see for example refs *9*−*16*) showing that the relative importance of the two pathways depends on the pollutant structure. To get a better insight into the mechanism of propiconazole phototransformation, we tried to obtain relevant information on both photoproducts and photochemical kinetics under various experimental conditions. In a first step, we studied the direct photolysis of propiconazole using 254-nm radiation, artificial light simulating the solar light, and natural solar light. Identification of the main photodegradation products was based on ^{1}H NMR and HPLC−mass spectrometric (MS) analyses. Preliminary and detailed NMR studies (^{1}H and ^{13}C) on propiconazole itself were necessary. In a second step, we evaluated the ability of propiconazole to undergo humic-substances-mediated phototransformation when exposed to artificial or natural solar light. Finally, propiconazole was irradiated in natural water with solar light as close to natural conditions as possible.

MATERIALS AND METHODS

Chemicals and Water Samples. Propiconazole (98,4% purity) was purchased from Riedel de Haën−Fluka (Saint Quentin Fallavier, France) and used as received. It was a mixture of four stereoisomers because of the presence of two asymmetric carbons, i.e. two couples of enantiomers (RR+SS) and (RS+SR). Humic acids (technical grade) were supplied by Aldrich. Water was purified using a Milli-Q device (Millipore). Natural water was collected in June 1999 from Barrage de Villerest (Loire, France) using inactinic bottles. The pH was 8.5 and the dissolved organic carbon (DOC) concentration was 7.2 mg·L^{-1}. Samples were stored at 4 °C and filtered through 0.45-μm filters (cellulose acetate, Sartorius) before use. Solutions containing humic substances were adjusted to pH 7.0 by using phosphate buffers.

Photolyses. *Monochromatic Irradiations.* Aqueous solutions of propiconazole ($9.0 \times 10^{-5} - 3.0 \times 10^{-4}$ mol·L^{-1}) were irradiated at 254 nm using a device equipped with up to six germicidal tubes (Mazda TG 15W) and a quartz cylindrical

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reactor (14-mm i.d.). Quantum yield of photolysis was measured at 270 ± 3 nm using a 900-W xenon lamp equipped with a monochromator Spex 1681. Potassium ferrioxalate was used as a chemical actinometer.

Polychromatic Irradiations. Aqueous solutions of pure propiconazole (1.5×10^{-5} mol·L^{-1}) and mixtures of propiconazole (1.5×10^{-5} mol·L^{-1}) and humic substances (10 mg·L^{-1}) were irradiated using a "solarbox" (Cofranegra, Italy) equipped with a xenon lamp and a special glass filter restricting the transmission of wavelengths below 290 nm. The spectral distribution of this device was similar to that of solar light, and the average irradiation intensity was 750−800 W/m^2. The temperature was set at 25 °C. The solutions were irradiated for 60 h in a 130-mL Pyrex glass cylindrical reactor sealed with caps. Aliquots of 1 mL were removed at selected intervals and analyzed by HPLC−MS.

Solutions of propiconazole (1.5×10^{-5} mol·L^{-1}) in pure water, in neutral water containing humic substances added at a level of 10 mg·L^{-1}, and in natural water were filled into Pyrex glass reactors, attached on a rack inclined by about 15° from horizontal, and exposed to solar light between June 2nd and 8th, 1999 at Clermont-Ferrand (46° N, 3° E). At selected intervals, aliquots of 0.5 mL were removed from the three solutions and analyzed by HPLC−UV.

Analytical Procedures. Losses of propiconazole were monitored by HPLC−UV using a Waters apparatus equipped with two pumps (model 510), an autosampler, a photodiode array detector (model 996), and a C_{18} reversed-phase column (4.6 mm × 250 mm, Spherisorb S5 ODS2, Waters). The eluent was a mixture of water acidified with 0.1% of orthophosphoric acid (A) and acetonitrile (B) at a constant flow of 1 mL·min^{-1}. The following gradient was used: mixture of 50% A and 50% B kept constant for 5 min, linear increase of B content to 90% in 5 min, then decrease of B to 50% in 5 min, and mixture of 50% A and 50% B kept constant till the end of the analysis (20 min).

The mass spectrometric analyses of propiconazole and its photoproducts were performed by HPLC−MS using a Thermo Separation Products series gradient pump equipped with a 4.6 mm (i. d.) × 250 mm Alltech column packed with 5-μm Alltima C_{18} reversed-phase material, and thermostated at 20 °C. A mixture of water (C) and methanol (D) was used as mobile phase at a constant flow rate of 1 mL/min. The gradient program was the following: constant mixture of 50% C and 50% D for 5 min, then linear increase of D content to 90% in 10 min, and a mixture of 10% C and 90% D kept constant till the end of the analysis (25 min). The Finnigan MAT LCQ mass spectrometer was equipped with a standard atmospheric pressure chemical ionization (APCI) interface operating in positive ion mode. The parameter optimization was performed using the infusion technique at 25 μL/min with a solution of propiconazole in water (1.5×10^{-5} mol·L^{-1}). The mass selected in this operation was $m/z = 342$ corresponding to $[M+H]^+$. The following optimized conditions were obtained: APCI vaporizer temperature 450 °C; capillary temperature 150 °C; source voltage 6 kV; capillary voltage 25 V; source current 5 μA; sheath gas flow (N_2) 80 arbitrary units; auxiliary gas flow (He) 10 arbitrary units. The MS analyses were carried out in full scan mode, scanning the range from $m/z = 60$ to $m/z = 450$ in 1.1 s. Disappearance of propiconazole and formation of photoproducts were measured by HPLC−APCI−MS using integrated selected ion monitoring (SIM) signals corresponding to $[M+H]^+$ at the detected compounds.

NMR Spectroscopy. Proton and carbon NMR spectra were collected on both 400 MHz AC 400 and 300 MHz DSX 300 Bruker spectrometers, depending on the program used. The NMR analysis of propiconazole was made difficult by the presence of the two couples of enantiomers (RR+SS) and the assignment of the resonances derived from the combination of several experiments. Concerning proton spectra, the main difficulty was to attribute the resonances of the 1,3-dioxolane group. Phase sensitive COSY-45 (correlation spectroscopy) sequence confirmed the multiple double irradiation experiments in the knowledge of connections in each stereoisomer. NOESY (nuclear Overhauser enhancement spectroscopy) spectrum was necessary to distinguish between the two couples of resonances of the triazole ring protons (the results are summarized in Figure 1). For ^{13}C peaks assignments, J-modulated, distortionless enhancement by polarization transfer (DEPT), heteronuclear correlation (HETCOR), and heteronuclear multiple bond correlation (HMBC) were used to attribute all the resonances (Table 1). To be noticed are the particular properties of the H−C bonds of the triazole ring: undecoupled ^{1}H/^{13}C correlation allowed measurement of the coupling constants. $^1J(CH)^3$ and $^1J(CH)^5$ are very high: 212 and 207 Hz, respectively. These unusual values (*17*) fit well with the fact that in the conventional J-modulated spectrum, C^3 and C^5 atoms resonances occur on the unexpected "wrong" side. Moreover, chemical shifts and coupling constants deduced from spectra were checked to fit well with those given in the literature (*18*).

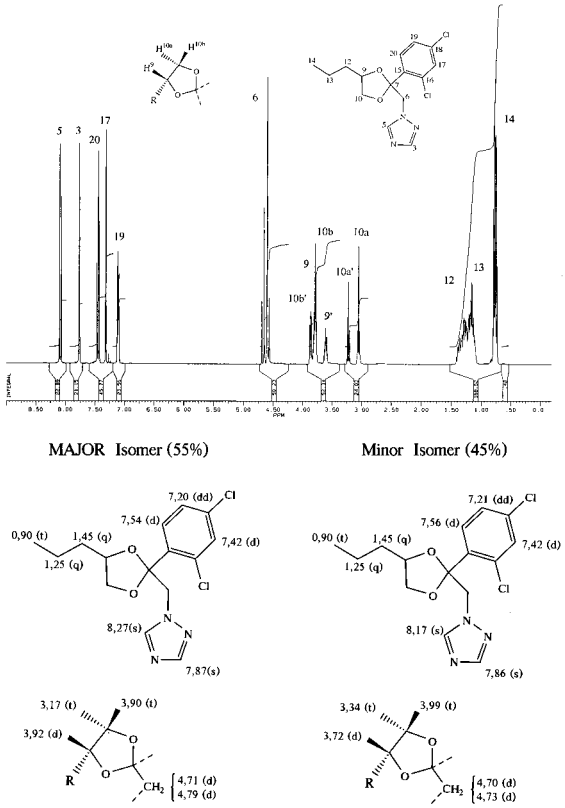


Figure 1. ^{1}H NMR data of propiconazole.

Other Analytical Methods. UV spectra were recorded on a Cary 3 Varian spectrophotometer. DOC measurements were performed by Institut Louise Blanquet (Clermont-Ferrand, France) using a standard titration method.

Analysis of Photoproducts. Irradiation of propiconazole in the different experimental conditions led to the formation of five detectable photoproducts. Products named **1** and **2** could be isolated and analyzed by ^{1}H NMR (Table 2) and HPLC−APCI−MS (Table 3). Products **3**, **4**, and **5**, produced in smaller amounts, were analyzed by HPLC−APCI−MS (Table 3) through injection of crude reactional mixtures. In addition, **5** could be produced independently by hydrolysis. The detailed procedures are described below.

Compound 1. A 100-mL solution of propiconazole (1.0×10^{-4} mol·L^{-1}) in acetonitrile was irradiated at 254 nm for 2 min in the device equipped with six tubes, yielding **1** as the single detectable photoproduct. Acetonitrile was evaporated until the sample volume was reduced to 1 mL. Compound **1** was separated from propiconazole by HPLC fractionation using a Beckmann HPLC equipped with a UV detector and a C_{18} reversed-phase column (4.6 mm × 250 mm, RP18 5-μm Lichrospher 100, Merck) by using isocratic conditions (35% water/65% acetonitrile) at a constant flow rate of 1.5 mL·min^{-1}. Retention time in condition of HPLC−APCI−MS analysis: 15 min; λ_{max} = 218 and 260 nm.

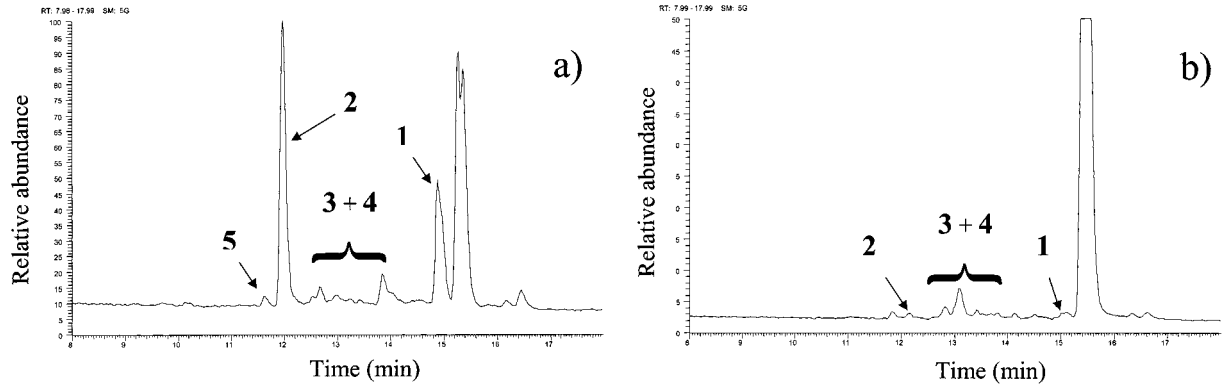
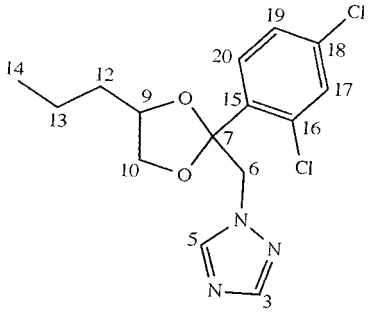


Figure 2. HPLC−APCI−MS chromatograms of aqueous propiconazole (1.5×10^{-5} mol·L^{-1}) irradiated (a) at 254 nm, and (b) in simulated solar light.

Table 1. ^{13}C Chemical Shifts of Propiconazole ($CDCl_3$ as Internal Reference: $\delta = 77$ ppm, downfield from TMS; Calculated Resonances Were Obtained from ChemWindow Software)



	Measured Major isomer	Measured Minor isomer	Calculated
3	151,2	151,3	147,4
5	144,6	144,5	147,4
6	54	54,4	62,1
7	107	107	108,2
9	76,6	78,2	80,2
10	70,1	70,1	74,9
12	34,4	34,8	34,2
13	18,8	18,9	17,2
14	13,8	13,8	14,3
15	134,8	134,8	135,7
16	135,6	135,5	134,3
17	129,5	129,3	129,2
18	133,1	133	134,3
19	127	127	126,9
20	131,2	131	130,4

Table 2. Differences in ^{1}H NMR Signals between Propiconazole and Compounds 1 and 2

	δ ppm (multiplicity)		
	propiconazole	**1**	**2**
H^{8a}; H^{8b}	3.17 (t); 3.90 (t)	3.75 (t); 4.30 (t)	between 1 and 1.5
H^9	3.92 (t)	4.25 (t)	between 1 and 1.5
H^{6a}; H^{6b}	4.71 (d); 4.79 (d)	4.40 (d); 4.50 (d)	-
H^{20}	7.54 (d)	8.10 (d)	8.10 (d)
H^5	8.27 (s)	none	none
H^3	7.87 (s)	7.95 (s)	8.00 (s)
CH_3	-	-	3.70 (s)[a]
CH_n-OH	-	-	5.10 (m)[a]

[a] New resonances.

Compound 2. A 200-mL solution of propiconazole (4.5×10^{-5} mol·L^{-1}) in pure water was irradiated at 254 nm for 2 min in the device equipped with six tubes. Photoproducts were extracted with three 5-mL portions of dichloromethane. Then, the solvent was removed by evaporation to dryness. The resulting mixture was dissolved in 1 mL of a water−acetonitrile (50/50, v/v) mixture. Compound **2** was isolated by HPLC fractionation in the same conditions as **1**. Retention time in condition of HPLC−APCI−MS analysis: 12 min; $\lambda_{max} = 240$ nm.

Compounds 3 and 4. A 100-mL aliquot of an aqueous solution containing propiconazole (8.0×10^{-5} mol·L^{-1}) and $K_2S_2O_8$ (1.0×10^{-3} mol·L^{-1}) was irradiated at 254 nm in the device equipped with one tube. HPLC−APCI−MS analysis indicated that **3** and **4** each have several isomers and show isotopic clusters at $m/z = 356$, 358, and 360 for the former, and $m/z = 358$, 360, and 362 for the latter. In both cases, isomers were eluted within the range 12.4−14.2 min.

Compound 5. HPLC−APCI−MS analysis of a solution of propiconazole (4.5×10^{-5} mol·L^{-1}) irradiated at 254 nm for 2 min in the device equipped with six tubes gave $m/z = 256$, 258, and 260. The same product was obtained on acidic hydrolysis of propiconazole using $HClO_4$ at a level of 0.5 mL in 5 mL of acetonitrile. Retention time in condition of HPLC−APCI−MS analysis: 11.7 min; $\lambda_{max} = 252$ nm with shoulder at 290 nm.

RESULTS

Direct Photolysis at Short Wavelength. Propiconazole shows a maximum of absorption at 269 nm ($\epsilon = 200$ mol^{-1}·L·cm^{-1}). The quantum yield of photolysis at this wavelength was found to be 0.11 ± 0.01 in aerated medium.

Figure 2 shows the typical HPLC−APCI−MS chromatogram of a solution of propiconazole irradiated at 254 nm for 2 min. The two main photoproducts, compounds **1** and **2**, could be identified on the basis of ^{1}H NMR (Table 2) and HPLC−APCI−MS (Table 3) data. Proposed structures are given in Figure 3. Mass spectrometric analyses proved that these compounds are monochlorinated through the presence of M and M+2 in the ratio 1:3. The molecular ions obtained correspond to the loss of HCl in the former case and to the loss of HCl plus addition of H_2O in the latter. Unlike propiconazole that loses triazole by MS^n collision-induced dissociation (CID), compound **1** loses the aliphatic chain and part of dioxolane, and compound **2** loses first H_2O and then the dehydrated alkyl chain R. These results indicate a higher degree of bonding of the triazole-ring in the photoproduct than in propiconazole. The ^{1}H NMR spectrum of compound **1** indicates that the missing

Table 3. HPLC−APCI−MS Data of Propiconazole and Photoproducts in Positive Mode Ion (MS−MS Fragments Obtained on the Italicized Molecular Ion)

	molecular ions *m/z*	major fragments (relative abundance)
propiconazole	*342* $[M+H]^+$−344−346	273 (24); 237 (48); 205 (54); 159 (100)
1	*306* $[M+H]^+$−308	220 (100)
2	*324* $[M+H]^+$−326	306 (100); 238 (84)
3	*356* $[M+H]^+$−358−360	256 (80); 159 (4)
4	358 $[M+H]^+$−360−362	
5	*256* $[M+H]^+$−258−260	187 (100); 159 (22)

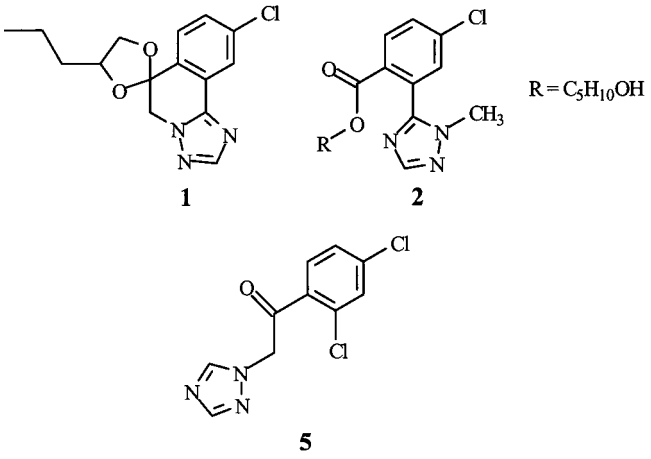


Figure 3. Structure of identified photoproducts.

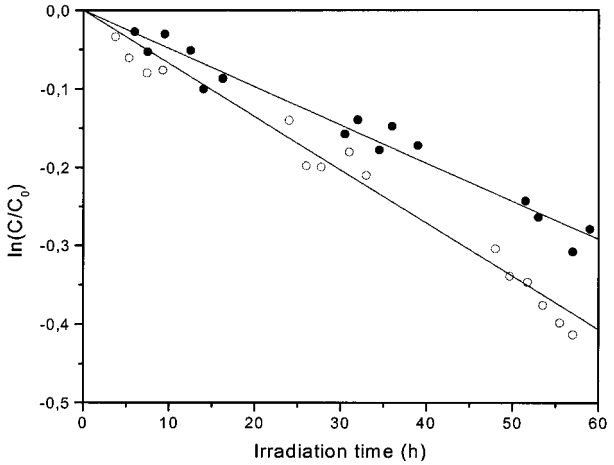


Figure 4. Phototransformation of propiconazole (1.5×10^{-5} mol·l^{-1}) in simulated solar light. Plot of $\ln(c/c_0)$ vs the irradiation time: ●, pure water; ○, water containing humic acids (10 mg/L).

Table 4. Kinetic Parameters Measured in Simulated and Natural Solar Light

conditions	first-order rate constant measured in simulated solar light (h^{-1})	half-life measured in solar light (h)
pure water	5×10^{-3}	85 ± 10
humic substances (10 mg·L^{-1})	7×10^{-3}	73 ± 10
natural water		60 ± 10

proton is the homologous of H^5 of triazole, as a consequence of a six-membered new ring formation. All other signals fit well with the proposed cyclic structure. The ^{1}H NMR spectrum of compound **2** is greatly simplified compared to that of propiconazole: signals from dioxolane ring are not observed, and the typical double AB spectrum from the (CH_2—N) groups (one for each isomer) is also missing. On the other hand, new signals appear: a singlet at 3.70 ppm corresponding to three equivalent protons and a multiplet at 5.10 ppm. The singlet is attributed to the methyl group linked to triazole, and the multiplet is attributed to a proton geminated with a hydroxyl group in the alkyl chain R.

Product **5** was identified to the ketone (Figure 3) on the basis of several results. By MS^n CID fragmentation, this compound loses first the triazole ring, just as propiconazole, and then CO. Moreover, its UV spectrum is very similar to that of 2,4-dichloroacetophenone (λ_{max} = 252 nm with shoulder at 290 nm). This assignment was confirmed by a complementary experiment: the acidic hydrolysis of propiconazole, that is known to remove 1,3-dioxolane used as a carbonyl protecting group producing therefore the ketone, also yielded **5**.

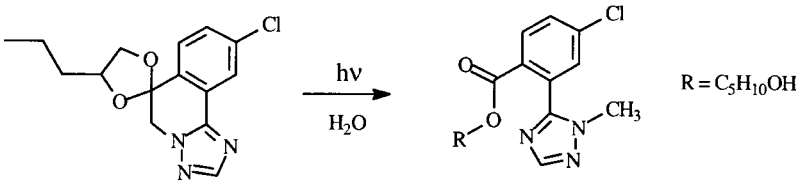
The two other photoproducts named **3** and **4** have the particularity to show several isomers by HPLC−APCI−MS eluted at retention times lying between 12.4 and 14.2 min (Figure 2). They have isotopic clusters at *m/z* = 356, 358, and 360 for the former and *m/z* = 358, 360, and 362 for the latter and are therefore dichlorinated photoproducts. The molecular mass of **3** $[M+14+H]^+$ may correspond to the addition of an oxygen atom with loss of two protons, whereas that of **4** $[M+16+H]^+$ corresponds to the addition of an oxygen atom only. It can be proposed that **3** and **4** are oxidation photoproducts: **3** might be a ketone and **4** might be an alcohol.

Phototransformation in Simulated or Natural Solar Light. Results are shown in Table 4.

In Pure Water. The absorption of propiconazole at wavelengths longer than 290 nm is very weak. Phototransformation, however, occurred. The irradiation of propiconazole (1.5×10^{-5} mol·L^{-1}) in simulated solar light led to a decrease in concentration equal to 30% after 60 h. The plot of $\ln(c/c_0)$, where c represents the concentration of propiconazole at time t and c_0 represents the initial concentration, against the irradiation time was linear in accordance with a first-order kinetics (Figure 4). The apparent first-order rate constant was equal to 5.0×10^{-3} h^{-1}.

The distribution of photoproducts was different from that obtained at a shorter wavelength. In particular, the formation of photoproducts **1** and **2** was found to be drastically reduced, while that of products **3** and **4** was favored. Comparing the peak area obtained by integrating HPLC−APCI−MS signals in the SIM mode enabled us to get ratios between the area measured after irradiation in simulated solar light and the area measured after irradiation at 254 nm. We found 0.07 for compound **1**, 0.02 for compound **2**, and 2.19 for compounds **3** and **4**. As seen on the chromatogram b of Figure 2, the major photoproducts in solar light are compounds **3** and **4**, whereas compounds **1** and **2** prevail at 254 nm (chromatogram a of Figure 2). The kinetics of photoproducts formation was monitored by HPLC−APCI−MS. From the shape of the formation curves (Figure 5), it can be deduced that compounds **1**, **3**, and **4** are primary photoproducts, whereas compound **2** is a secondary photoproduct.

Scheme 1



1 **2**

When exposed to solar light, propiconazole underwent a slow photodegradation (Figure 6). The half-life in June was estimated at 85 ± 10 h.

In the Presence of Humic Substances. The presence of humic substances (10 mg·L^{-1}) increased the rate of propiconazole disappearance when irradiated both in simulated (Figure 4) and natural solar light (Figure 6). In the former case, the apparent first-order rate constant deduced from the plot $\ln(c/c_0)$ vs t was found to be equal to 7×10^{-3} h^{-1}, i.e., 40% higher than that in pure water. In the latter, the half-life was estimated as 73 ± 10 h, compared to 85 ± 10 h in pure water.

Photoproducts were similar to those observed in pure water, but the distribution pattern was different. The presence of humic substances reduced the formation rate of compounds **1** and **2** (Figure 5a) but enhanced that of **3** and **4** (Figure 5b). These quantitative data confirm that humic acids are able to photoinduce the degradation of propiconazole.

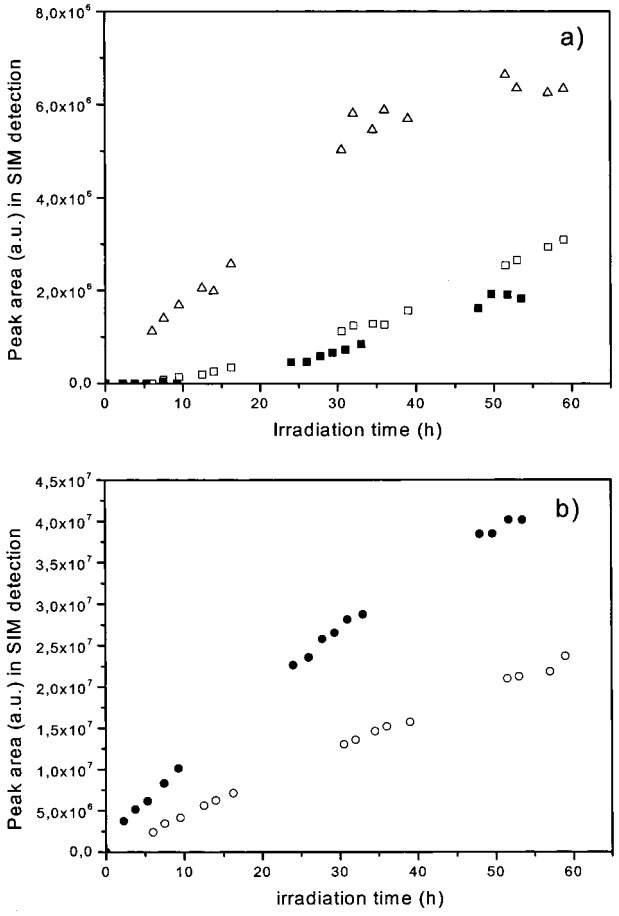


Figure 5. Formation of **1**, **2** (a) and **3** + **4** (b) over time upon irradiation of propiconazole (1.5×10^{-5} mol·L^{-1}) in simulated solar light. (△): **1** in pure water; (□): **2** in pure water; (■): **2** in water containing humic substances (10 mg/L); (○): **3** + **4** in pure water; (●) **3** + **4** in water containing humic substances (10 mg/L).

In Natural Water. In a last step, propiconazole was dissolved in natural water and exposed to solar light. As illustrated by Figure 6, the disappearance was faster in natural water than in pure water, showing that propiconazole was subject to enhanced photodegradation due to indirect processes in natural water. The half-life was estimated as 60 ± 10 h in natural water compared to 85 h in pure water.

DISCUSSION AND CONCLUSION

We show that propiconazole photodegrades in solar light. The phototransformation is faster by about 30% in natural water than in pure water. It proves that both direct photolysis and photoinduced processes contribute to the degradation reaction under environmentally relevant conditions. Humic matter contained in natural waters is likely to be involved in the photoinduced reactions as the phototransformation of propiconazole was shown to be enhanced by humic acids.

An important part of the work was devoted to product studies using APCI mass spectrometry and high-field NMR ^{1}H and ^{13}C. The analytical aspects of this work reaction are interesting in several ways.

The full attribution of NMR signals needed preliminary and detailed studies on propiconazole itself. The two isomers of propiconazole both could be well characterized (Figure 1).

Propiconazole undergoes several ways of phototransformation on excitation in pure water. We prove that photo-cyclization accompanied by elimination of HCl occurs, especially upon irradiation at short wavelength. Such a reaction was quite unexpected even though other examples of photo-cyclization accompanied by elimination of HCl or HBr already have been reported in the literature (*19*−*22*). The mechanism of cyclization is not yet clear. The concerted removal of H and Cl atoms is

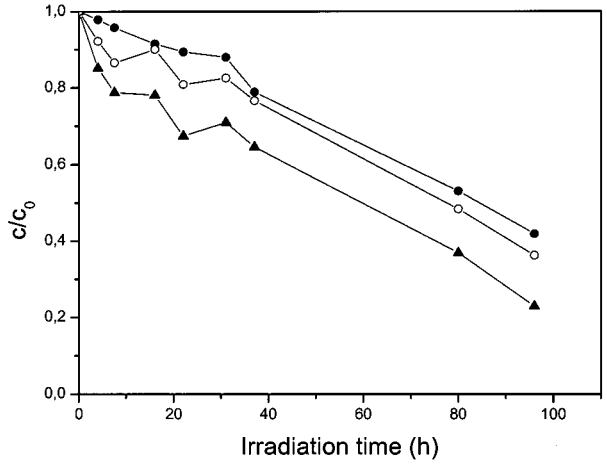


Figure 6. Phototransformation of propiconazole (1.5×10^{-5} M) in solar light. ● pure water; ○ water containing humic acids (10 mg/L); ▲ natural water.

conceivable, because molecular models show that the chlorine atom attached to C^{16} is very close to the hydrogen atom H^5. The compound **2** that has the mass of **1**+18 and shows a secondary formation kinetic is likely to result from a multistep and uncomplete hydrolysis of the dioxolane group of product **1** (Scheme 1). This reaction, which is not observed in the dark, is most probably light-induced. The formation of ketone **5** is less surprising because this compound corresponds to the hydrolysis of the 1,3-dioxolane protecting group. The analysis of irradiated mixtures by HPLC−APCI−MS allowed the detection of photoproducts **3** and **4** that have the particularity to each have several isomers. They are likely to be oxidation photoproducts; however, full assignment could not be achieved. The mechanism of direct photolysis is clearly wavelength dependent: photocyclization is the major pathway at short wavelength, whereas oxidation mainly occurs in solar light.

The photoinduced transformation by humic substances yields mainly compounds **3** and **4**. Oxidant species photogenerated by humic material seem able to abstract electrons or hydrogen atoms from propiconazole with subsequent formation of oxidation products. The oxidation is more difficult to explain in the case where propiconazole is irradiated in pure water. Oxidation of triplet excited states of propiconazole might take place. As an alternative, photoinduction involving primary photoproducts might occur. For example, compound **5** might photoinduce the oxidation of propiconazole as it is known that excited triplet states of aromatic ketones have oxidant properties (*23*−*25*).

Supporting Information Available: Carbon spectra, J-modulated, COSY, NOESY, (in order to distinguish between H^3 and H^5, through their different interactions with (CH2)6, depending on their relative space proximity), traditional and undecoupled HETCOR (over one bond), and heteronuclear multiple bond correlation (HMBC, set to long-range correlation) were acquired with gradient selection, if necessary. This material is available free of charge via the Internet at http://pubs.acs.org.

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