Photochemistry of vinclozolin in water and methanol–water solution

Bernhard Schick, Pran N Moza,* Klaus Hustert and Antonius Kettrup

GSF - National Research Center for Environment and Health, Institute for Ecological Chemistry, Ingolstädter Landstraße 1, D-85758 Neuherberg, Germany

Abstract: The photolysis of the fungicide vinclozolin in aqueous and methanol–water (50+50 by volume) solution has been examined. Irradiation at λ=254 nm for 10 minutes resulted in <90% and ≤95% substrate transformation respectively. The dissipation of vinclozolin both in water and methanol+water was linear and the calculated half-lives were 1.01 and 2.0 min respectively. Irradiation (8 h) with UV light (λ≥290 nm) resulted in 10% degradation of the chemical, which is of the same magnitude as that of the control (not irradiated). Irradiation (8 h) under artificial sunlight (Suntest) in the presence of commercially available humic acid (K-salt) resulted in 55% degradation of the chemical. Photolysis leads to the opening of the 2,4-oxazolidine-dione ring, forming 3,5-dichlorophenyl isocyanate and 3,5-dichloroaniline. In addition, dechlorination and elimination of the —CH=CH_2 moiety takes place, and one or both the chlorine atoms are replaced by a methoxy group.

Keywords: vinclozolin; photochemistry

1 INTRODUCTION

Vinclozolin [3-(3,5-dichlorophenyl)-5-methyl-5-vinyl-1,3-oxazolidine-2,4-dione] (**I**, Fig 1) is a protectant fungicide. It is widely used for controlling fungal diseases caused by *Botrytis* spp, *Sclerotinia* spp, and *Monilinica* spp in grapes, fruits, vegetables, ornamentals, hops, rapeseed, and turfgrass.[1] The hydrolysis of vinclozolin has been well studied,[2–4] and two main degradation products, 2-[(3,5-chlorophenyl)carbamoyloxy]-2-methyl-3-butenoic acid and 3′,5′-dichloro-2-hydroxy-2-methylbut-3-enanilide have been reported. The decline of the residue of vinclozolin in different grape vines has been studied by Gennari *et al*[5] who reported that the minimum half-life was 1.2 days for the normal dose and 2.0 days for the double dose. An earlier study[6] of the long-time (14 days) photolysis of vinclozolin has described the formation of 3,5-dichlorophenyl isocyanate, 3,5-dichloroaniline, methyl 3,5-dichlorophenylcarbamate and 3-(3-chlorophenyl)-5-methyl-5-vinyl-oxazolidine-2,4-dione in methanol solution. Vinclozolin is a colourless crystalline solid and is only slightly soluble in water (1 mg litre^{-1} at 20 °C). In order to increase its solubility and to produce enough of the photoproducts for structural elucidation, irradiation experiments were carried out in methanol-water solution. To our knowledge very little is known on the influence of humic materials (present in soil and surface waters) on the photodegradation of vinclozolin. In the present work, a comparative study was made of the photodecomposition and chemical nature of the photoproducts of vinclozolin irradiated with UV light ($\lambda \geq 290$ and 254 nm) in water and methanol-water solution. In addition, the effect of commercially available humic acid (K-salt) on the rate of degradation of vinclozolin in artificial sunlight (suntest-apparatus, emitting light with a spectrum close to that of sunlight) was also examined.

2 EXPERIMENTAL

2.1 Materials

Vinclozolin, analytical standard grade (99%) was supplied by Dr Ehrenstorfer, Germany, and was purified further by recrystallization from hexane +ethyl acetate. Methyl chloroformate (99%), 3,5-dichloroaniline (98%), 3-chloroaniline (99%), 3-chlorophenyl isocyanate, *S*-(−)methyl lactate (98%) and triethylamine (99%) were obtained from Aldrich Chemical Co. 3-Methoxyphenyl isocyanate (98%) and humic acid (K-salt) were obtained from Fluka, Germany, and phenyl isocyanate (95%) was received from Merck, Germany. These chemicals were used to synthesize comparison products.

2.2 Apparatus

Concentrations of vinclozolin after various intervals of irradiation were measured by HPLC using a Gilson-Abimed Model 302 liquid chromatograph equipped with a Macherey–Nagel reversed-phase column

* Correspondence to: PN Moza, GSF - National Research Center for Environment and Health, Institute for Ecological Chemistry, Ingolstädter Landstrasse 1, D85758, Neuherberg, Germany

(*Received 5 November 1998; revised version received 24 May 1999; accepted 8 July 1999*)

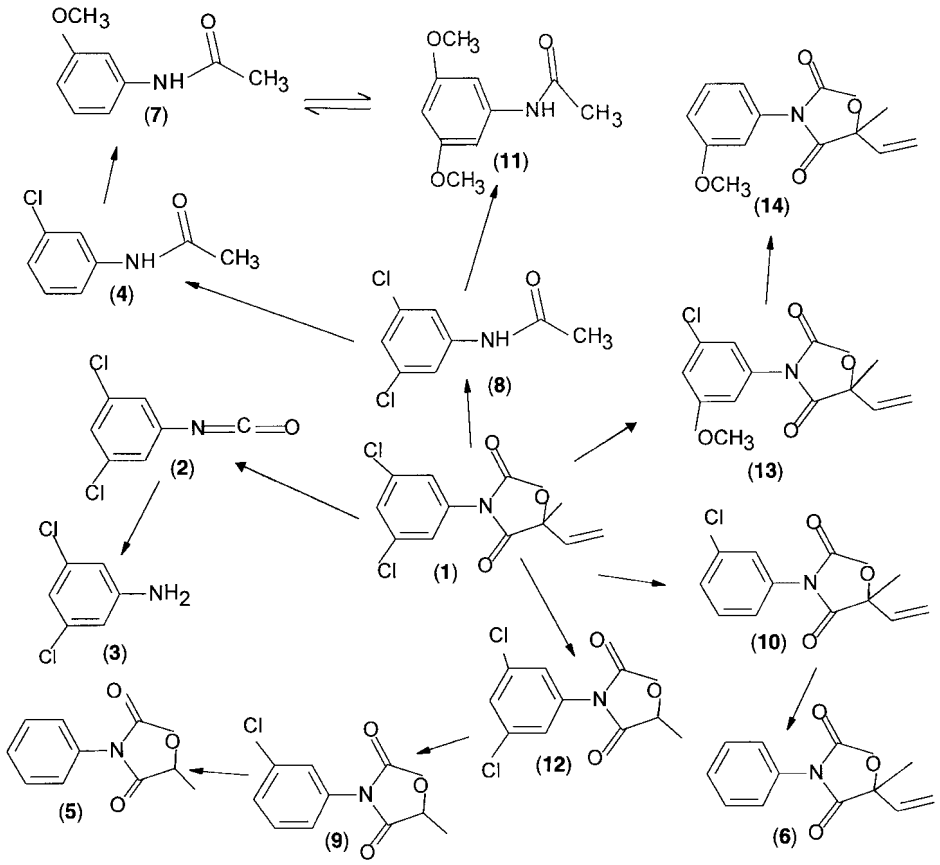

Figure 1. Photodegradation pathway of vinclozolin in methanol + water.

(Nucleosil C_{18}-CN; 5 μm, 20 × 0.4 cm ID) and a UV detector set at 210 nm. The solvent system used for monitoring the loss of the parent compound was acetonitrile + water (60 + 40 by volume) at a flow rate of 1 ml min^{-1}. For HPLC comparison (retention times) of the photoproducts with the standards, the instrument, the column and the detection wavelength were the same as for the quantitative analysis. The solvent system used was a gradient acetonitrile/water, flow chart given in Table 1.

Vinclozolin photoproducts were separated in various fractions by semi-preparative high performance liquid chromatography using a Microsorb C_{18} reversed-phase column (Rainin Instruments Co, USA, 5 μm, 25 cm × 1 cm ID). The pumps were Gilson Abimed Model 305 and 302 (in gradient mode of operation), with a UV detector Gilson Abimed Model 115 set at 210 nm. Optimal separation of the peaks was achieved with a 35 min gradient acetonitrile/water starting at 50 + 50 by volume and ending at 100% acetonitrile at a flow rate of 1 ml min^{-1}. The gradient flow chart is given in Table 1.

A Hewlett Packard Model 5995 GC-MS instrument at an ionization potential of 70 eV was used to obtain the MS spectra. The GC conditions were as follows: a Macherey–Nagel capillary column (Permabond; SE-52-DF-0.5, 25 m × 0.32 mm ID) coated with a 0.5 μm film of phenyl ethyl silicone; injector temperature 230 °C; carrier gas helium; temperature program 80–240 °C; 5 °C min^{-1}. Retention times of the photoproducts were compared with the standards on a Hewlett Packard model 5890 GC instrument. The GC conditions were the same as for GC-MS analysis except nitrogen (flow rate 1 ml min^{-1}) was used as carrier gas instead of helium.

[^{1}H] and [^{13}C]NMR spectra (400 and 100 MHz respectively) of deuterochloroform solutions were obtained on a Bruker AC-400 instrument with tetramethylsilane as an internal standard.

2.3 Irradiation

Vinclozolin (**1;** 0.2 mg) in 200 ml deionized water was irradiated for 10 min with a high-pressure mercury lamp (HPK 125 W, Philips) jacketed with a water-cooled quartz filter to get maximum intensity of UV light down to $\lambda = 254$ nm. Similar experiments with **1** were performed in methanol + water (50 + 50 by volume) ($\lambda = 254$ nm). Samples of the solution of **1** were held in the dark as controls. To investigate the effect of humic acid on the photodecomposition of

Table 1. Gradient flow chart for the separation of peaks by HPLC

Time (min)	*0*	*5*	*10*	*15*	*20*	*25*	*30*	*35*
Solvent acetonitrile/water (by volume)	50/50	50/50	60/40	70/30	80/20	90/10	100/0	100/0

vinclozolin, 5 mg of humic acid (potassium salt) was added to an aqueous solution (1 mg litre^{-1}) of the pesticide, and the solution was irradiated in a Suntest apparatus (Heraeus, Hanau, Germany). According to the manufacturer's specifications, the lamp emits light with a spectrum close to that of sunlight (300–800 nm). Similar experiments were carried out with a high-pressure mercury lamp jacketed with a water-cooled pyrex filter ($\lambda \geq 290$ nm). Samples of **1** in aqueous solutions with and without humic acid were held in the dark as controls.

2.4 Preparation of comparison compounds

*2.4.1 Methyl 3-methoxyphenylcarbamate (***7***, Fig 1)*

Methyl chloroformate (0.747 g, 5 mmol) in dry toluene (10 ml) was added slowly to a solution of 3-methoxyaniline (1.23 g, 10 mmol) in dry toluene (20 ml), and the mixture was heated at reflux for 3 h, cooled to room temperature, poured into ice-water and acidified with hydrochloric acid (1 M). The organic phase was washed with water and dried over anhydrous sodium sulfalt. After removal of the solvent at reduced pressure, the resulting brown product was purified by column chromatography on silica gel 60 with chloroform+hexane (50+50 by volume), yielding colourless crystals (0.24 g, 27%), mp 126–128 °C. [^{1}H]NMR δ 3.79 (s, 3 H), 3.76 (s, 3 H), 6.92 (s, 1 H), 6.6 (ddd, J=8.28 Hz, J=2.48 Hz, J=0.86 Hz, 1 H), 6.87 (dd, J=8.03 Hz, J=0.91 Hz, 1 H), 7.11 (s, 1 H), 7.18 (t, J=8.15 Hz, 1 H). [^{13}C]NMR δ 52.2 (OCH_3), 55.1 (CH_3), 104.5 (CH), 109.1 (CH), 110.9 (CH), 129.6 (CH), 139.1, 154.0 (C=O).

*2.4.2 Methyl 3,5-dimethoxyphenylcarbamate (***11***, Fig 1)*

To a stirred mixture of 3,5-dimethoxyaniline (0.766 g; 5 mmol) in dry toluene (20 ml) was added methyl chloroformate (0.237 g; 2.5 mmol) dissolved in toluene (10 ml). The reaction mixture was heated at reflux for 2 h. The usual work-up followed by recrystallization (hexane+ethyl acetate, 10+1 by volumn) afforded **11** as a colourless crystalline substance, 0.43 g (81%), mp 31–34 °C, bp 245–247 °C.

*2.4.3 Methyl 3-chlorophenylcarbamate (***4***, Fig 1)*

To a stirred mixture of 3-chloroaniline (0.64 g, 5 mmol) in dry toluene (20 ml) was slowly added methyl chloroformate (0.237 g; 2.5 mmol) in toluene (10 ml) and the mixture was refluxed for 2 h. Work-up of the reaction mixture as in the case of compound **11** yielded yellowish plates (0.44 g, 95%), mp 136–138 °C. [^{1}H]NMR δ 3.77 (s, 3 H), 6.69 (s, 1 H), 7.01 (m, 1 H), 7.20 (m, 2 H), 7.48 (s, 1 H). [^{13}C]NMR δ 52,5 (OCH_3), 116.6, 118.8, 123.5, 130.0 (aromatic carbons), 153.8 (C=O).

*2.4.4 Methyl 3,5-dichlorophenylcarbamate (***8***, Fig 1)*

Methyl chloroformate (0.74 g, 5 mmol) in dry toluene (10 ml) was added to a solution of 3,5-dichloroaniline in dry toluene (20 ml), and the mixture was heated at reflux for 2 h and cooled to ambient temperature. The usual work-up followed by recrystallization (hexane +ethyl acetate, 1+1 by volume) afforded a crystalline substance (0.46 g, 83%), mp 173–174 °C. [^{1}H]NMR δ 3.77 (s, 3 H), 6.91 (s, 1 H), 7.02 (t, J=1.82 Hz, 1 H), 7.32 (d, J=1.74 Hz). [^{13}C]NMR δ 52.7 (OCH_3), 116.9, 123.4, 135.4, 139.8 (aromatic carbons), 153.6 (C=O).

*2.4.5 5-methyl-3-phenyloxazolidine-2,4-dione (***5***, Fig 1)*

To a mixture of phenylisocyanate (1.14 g, 10 mmol) and methyl lactate (0.884 g; 10 mmol) in dry toluene (30 ml) was added triethylamine (1.01 g; 10 mmol) in toluene (10 ml). The reaction mixture was heated at reflux for 12 h and cooled to room temperature. The mixture was filtered and the crystals of $(C_2H_5)_3N$ OCH_3 were washed with toluene. The filtrate and the washings were combined and washed with water (3 × 20 ml). The organic phase was dried over sodium sulfate, and the solvent was removed at reduced pressure. The residue, a transparent liquid, was triturated with methanol and a white solid separated out. Crystallization from hexane+ethyl acetate (1+1 by volume) yielded 0.81 g (42%), mp 113–116 °C, of a white powder. [^{1}H]NMR δ 1.71 (d, J=7 Hz, 3 H), 5.01 (q, J=7 Hz, 1 H), 7.45 (m, 5 H). [^{13}C]NMR δ 16.7 (CH_3), 75.9 (CH), 129.3, 128.9 (aromatic carbons), 153.9 (N-COO), 172.4 (N-CO-R).

*2.4.6 3-(3-chlorophenyl)-5-methyloxazolidine-2,4-dione (***9***, Fig 1)*

Triethylamine (2.02 g; 20 mmol) in toluene (10 ml) was added to a mixture of 3-chlorophenylisocyanate (3.07 g, 20 mmol) and methyl lactate (1.79 g, 20 mmol) in toluene (20 ml). The reaction mixture was heated at reflux for 12 h. Work-up of the reaction mixture as in the case of compound **8** yielded an oil, which upon cooling gave a solid, recrystallized from hexane+ethylacetate (1+1 by volume) yielded a white powder (0.81 g; 36%), mp 166–169 °C. [^{1}H]NMR δ 1.69 (d, J=7.01 Hz, 3 H), 5.01 (q, J=7.02 Hz, 1 H), 7.39 (m, 3 H), 7,5 (dt, J=1.84 Hz, J=0.76 Hz, 1 H), [^{13}C]NMR δ 16.7 (CH_3), 75,9 (CH), 123.5, 125.6, 129.1, 130.2, 131.9 (aromatic carbons), 134.9 (CN), 153.3 (N-COO), 171.9 (N-CO-R).

2.5 Isolation and identification of photoproducts

To produce enough of the photoproducts for structural elucidation, **1** (10 mg) in methanol+water (50+50 by volume; 1 litre) was irradiated in five batches (2 mg in 200 ml for 10 min through a quartz filter. The irradiated solutions were combined and the solvent removed at reduced pressure and finally freeze-dried. The residue, dissolved in methanol (2 ml) showed upon GC analysis a number of substances in addition to a very small amount of vinclozolin. Separation of the unchanged vinclozolin and its photoproducts was attempted by semipreparative HPLC (100 µl per injection). Gradient elution (Table 1) was performed with water (eluant A) and methanol (eluant B). Nine

main fractions (1–9 in order of increasing retention times) were collected. Corresponding eluates from several injections were combined, and the solvent was removed on a rotary evaporator.

2.5.1 Identification of fractions

2.5.1.1 Fraction 1. (Colourless liquid, R_t 13.49 min) upon GC and GC-MS analysis was found to be a mixture of two compounds. One (GC R_t 19.24 min), molecular ion *m/z* 191 and fragment ions at *m/z* 119 (M^+-CO_2-C_2H_4), 91 (M^+-CO_2-C_2H_4-CO_2), and 64 (M^+-CO_2-C_2H_4-CO_2-HNC) was identified as 5-methyl-3-phenyl-1,3-oxazolidine-2,4-dione (**5**, Fig 1) by chromatography (GC and HPLC) and MS comparison with an authentic sample of this compound synthesized as described above. The other compound (GC R_t 29.24 min), molecular ion *m/z* 247 and fragments at *m/z* 160 (M^+-CO_2-CO-CH_3) and 149 (M^+-CO_2-C(CH_3)-CH=CH_2) has been assigned the tentative structure 3-(3-methoxyphenyl)-5-methyl-5-vinyl-1,3-oxazolidine-2,4-dione (**14**, Fig 1).

2.5.1.2 Fraction 2. (liquid, R_t 14.55 min) was also a mixture of two compounds (GC R_t 20.08 and 25.58 min). The compound GC R_t 20.08, molecular ion *m/z* 181, fragment ions at *m/z* 149 (M^+-COCH3), 122 (M^+-$HOCH_3$-CO+1) and 93 (M^+-$HOCH_3$-HNC-1) was identified as methyl 3-methoxyphenyl-carbamate (**7**, Fig 1) by GC and MS comparison with an authentic sample of this compound. GC retention time (25.58 min) molecular ion *m/z* 211 and fragment ions at *m/z* 179 (M^+-$HOCH_3$), 150 (M^+-$HOCH_3$-CO-1) and 136 (M^+-$HOCH_3$-CO-CH_3) of the second component were in good agreement with those of methyl 3,5-dimethoxyphenylcarbamate (**11**, Fig 1).

2.5.1.3 Fraction 3. (R_t 16.92 min). The amount of this fraction was so small that, except for mass analysis, no spectral data could be obtained. The mass spectrum, molecular ion *m/z* 217, fragments at *m/z* 173 (M^+-CO_2), 144 (M^+-CO_2-CH_3-CH_2), 119 (M^+-CO_2-C(CH_3)-CH=CH_2) and 91 (M^+-CO_2-C(CH_3)-CH=CH_2-CO) showed absence of chlorine atoms in the molecule. The fragments suggest the compound is 5-methyl-5-vinyl-3-phenyl-1,3-oxazolidine-2,4-dione (**6**, Fig 1). Furthermore, the fragmentation pattern of this compound was similar to vinclozolin except for that the main fragments were without chlorine atoms.

2.5.1.4 Fraction 4. (yellowish solid, R_t 19,5 min); molecular ion *m/z* 185, fragment ions at *m/z* 153 (M^+-$HOCH_3$), 125 (M^+-$HOCH_3$-CO) and 98 (M^+-$HOCH_3$-CO-HNC). The mass spectra, NMR and GC (R_t 19.24 min) data were in good agreement with those of the standard methyl 3-chlorophenylcarbamate (**4**, Fig 1).

2.5.1.5 Fraction 5. (R_t 21.36 min); the molecular ion *m/z* 251 had an isotope ratio indicative of one chlorine atom. On the basis of fragments *m/z* 207 (M^+-CO_2), and 153 (M^+-CO_2-C(CH_3)-CH=CH_2), which is similar to that of vinclozolin except that the major ions contained one chlorine atom, the structure 3-(3-chlorophenyl)-5-methyl-5-vinyl-1,3-oxazolidine-2,4-dione (**10**, Fig 1) was assigned to this molecule.

2.5.1.6 Fraction 6. (R_t 23.39 min); molecular ion 281, fragments at *m/z* 237 (M^+-CO_2), 208 (M^+-CO_2-CH_3-CH=CH_2) and 174 (M^+-CO_2-Cl-C_2H_3+1). The mass spectrum was similar to that of vinclozolin except that the major ions contained one chlorine atom. The structure of this compound was assigned as 3-(3-chloro-5-methoxyphenyl)-5-methyl-5-vinyl-1,3-oxazolidine-2,4-dione (**13**, Fig 1).

2.5.1.7 Fraction 7. (R_t 24.04 min); molecular ion *m/z* 225, fragments at *m/z* 153 (M^+-CO_2-$CHCH_3$) and 125 (M^+-CO_2-$CHCH_3$-CO). This was identified as 3-(3-chlorophenyl)-5-methyl-1,3-oxazolidine-2,4-dione (**9**, Fig 1) by direct chromatographic (GC and HPLC) and mass spectrum comparison with an authentic sample of this compound synthesized as described above.

2.5.1.8 Fraction 8. (R_t 25.46 min); molecular ion *m/z* 161, fragments at *m/z* 126 (M^+-Cl), 99 (M^+-Cl-CNH) and 63 (M^+-Cl-HNC-1). This compound was identified as 3,5-dichloroaniline (**3**, Fig 1) by direct chromatographic (GC R_t 15.4 min) and MS comparison with the authentic standard.

2.5.1.9 Fraction 9. (R_t 26.36 min). This fraction upon GC and GC-MS analysis was found to be a mixture of three components.

The first component (GC R_t 11.8 min), showed a molecular ion *m/z* 187 and the presence of two chlorine atoms. On the basis of the fragments *m/z* 159 (M^+-CO), 124 (M^+-CO-Cl), 97 (M^+-CO-Cl-CNH) and 61 (M^+-CO-Cl-CNH-Cl) the compound was identified as 3,5-dichlorophenyl isocyanate (**2**, Fig 1).

The second GC component (R_t 23.58 min); molecular ion *m/z* 219, fragments at *m/z* 187 (M^+-$HOCH_3$), 159 (M^+-$HOCH_3$-CO), 124 (M^+-$HOCH_3$-CO-Cl) and 97 (M^+-$HOCH_3$-CO-Cl-HNC) was identified as methyl 3,5-dichlorophenyl-carbamate by direct chromatographic GC and MS comparison with the synthesized compound (**8**, Fig 1).

The third GC component (R_t 28.7 min); molecular ion *m/z* 259, fragments at *m/z* 187 (M^+-CO_2-CH-CH_3), and 159 (M^+-CO_2-CH-CH_3-CO), was assigned the tentative structure 3-(3,5-dichlorophenyl)-5-methyl-1,3-oxazolidine-2,4-dione (**12**, Fig 1).

3 RESULTS AND DISCUSSION

UV irradiation at λ=254 nm of a 1.0 mg litre^{-1} methanol-water (50+50 by volume) solution of vinclozolin (**1**, Fig 2) resulted in rapid decomposition

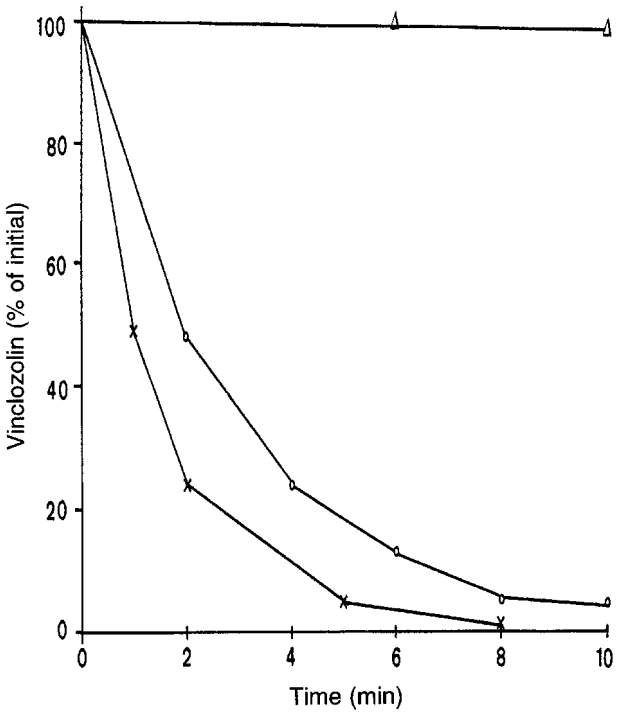

Figure 2. Photodegration of vinclozolin in (○) methanol+water (1+1 by volume) and (×) water at 254nm. (△) Control.

(90 (±3)%, average of three runs) in 10min. Similar experiments in deionized water also resulted in more than 90% substrate decomposition, whereas the compound degraded slowly (10% in 8h) when irradiated at $\lambda \geq 290$nm as shown in Fig 3. The high decomposition rate at $\lambda = 254$nm is due to direct photolysis near the absorption maximum (240nm). In control experiments there was no degradation in 10min, whereas the compound under similar conditions decomposed approximately 10% in 8h. The results of the irradiated ($\lambda \geq 290$nm) and non-irradiated aqueous solutions of **1** being of the same magnitude (*c* 10%), it is presumed that the compound is more susceptible to hydrolysis than to irradiation with light close to the solar spectrum. The photolysis rates in water and methanol+water (50+50 by volume) when **1** is irradiated with UV light $\lambda = 254$nm fit a first-order reaction model

$$\ln(c_t/c_o) = -kt$$
$$\text{with a half-life } t_{1/2} = \ln(2)/k$$

where c_o and c_t are the concentrations of **1** at times 0 and t respectively, and k is the photolysis rate constant. The slope of a linear plot ln c_t/c_o versus time gives the photolysis rate constant of **1** in water ($k = 1.14 \times 10^{-3}\,s^{-1}$) which is greater than in methanol-water ($k = 5.77 \times 10^{-3}\,s^{-1}$) and the calculated half-lifes were 1.01 and 2.0min respectively. Irradiation of **1** ($\lambda = 290$nm) in the presence of humic acid (K-salt) led to faster degradation (50%, observed-control, 8h, Fig 3) than in its absence (10%, Fig 3). A similar experiment in the Suntest equipment showed sub-

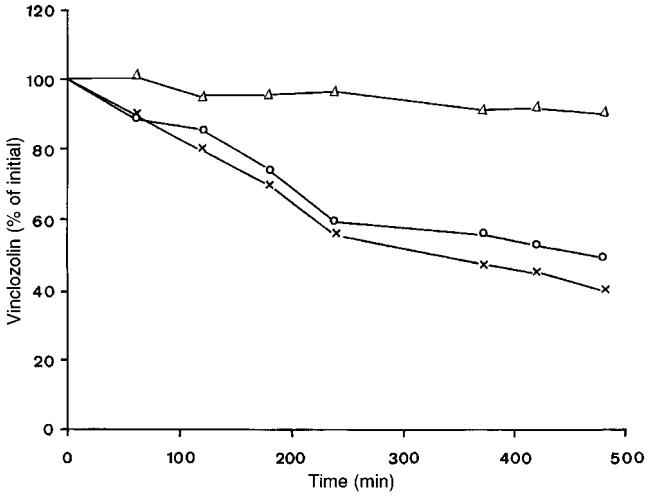

Figure 3. Photodegradation of vinclozolin (○) in the presence of humic acid ($\lambda = 290$nm) and (×) in Suntest equipment. (△) Control.

strate transformation of 60% in 8h (Fig 3). In control experiments (not irradiated) with and without humic acid, it was of the same magnitude (10%) as was observed in methanol-water solution.

Humic acid is an important ingredient of soil and many surface waters contain organic matter, such as humic materials. These materials may sensitize the photodegradation of pesticides by several indirect processes[7] and soil has been reported to produce active oxygen species.[8–10] Compounds **2** and **12** (Fig 1) were the main photoproducts identified after **1** was irradiated ($\lambda = 290$nm and in Suntest) in the presence of humic acid.

The oxazolidine ring of vinclozolin opens in ethanol, methanol and water suspension and leads to the formation of *N*-(2-hydroxy-2-methyl-1-oxo-buten-3-yl)-3,5-dichlorophenylcarbamic acid and its decarboxylation product.[2] In our experiments in the presence of humic acid none of the above-mentioned products was identified, instead **2** and **3** (Fig 1) were isolated and characterized. This study demonstrates the photosensitized formation of **2, 3** and **12** from vinclozolin in aqueous solution of humic acid.

A photolysed ($\lambda = 254$nm) methanol-water solution of **1** revealed on HPLC analysis a number of products and, upon semi-preparative HPLC separation on a RP-18 reversed-phase column, nine main fractions were collected. Fraction 1 upon GC-MS analysis was found to be a mixture of **4** and **13** (Fig 1), fraction 2 was a mixture of **6** and **10** and fraction 9 was found to contain compounds **2, 7** and **11** (Fig 1). It is observed that the clean separation of these compounds on semi-preparative RP-18 column was not achieved. Probably the compounds have very close polarities. Compounds **4** and **10** are the major photoproducts, followed by **2, 7, 8, 11** and **12**.

Vinclozolin contains a 3,5-dichlorophenyl and a 2,4-oxazolidine-dione moiety. It was expected that the oxazolidine-dione ring would open and produce 3,5-dichloroaniline (**3**) and 3,5-dichlorophenyl isocyanate

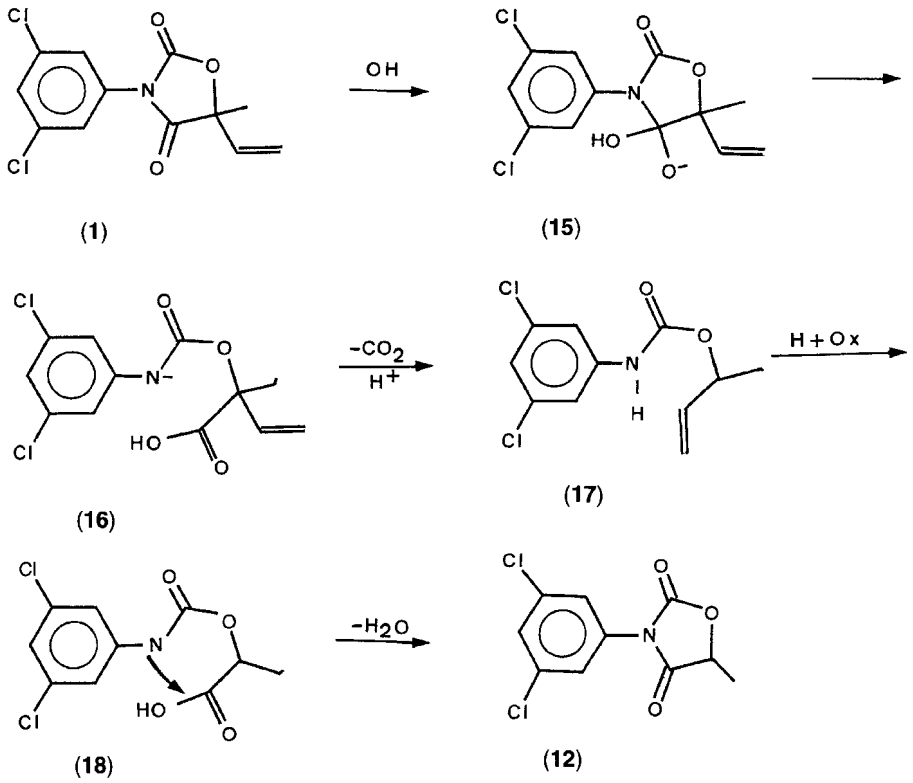

Figure 4. Proposed reaction mechanism for the formation of **12**.

(**2**). In fact, both **2** and **3** were identified and confirmed on photolysis ($\lambda = 254$ nm) of **1**. Long-time (14 days) photolysis of **1** by previous workers[6] also showed the formation of these two compounds.

The photodecomposition of vinclozolin involves opening of the oxazolidine-dione ring, dechlorination and the elimination of —CH=CH_2 moieties. The formation of compound **13** is probably the result of C-Cl bond cleavage and abstraction of a hydrogen radical from the medium. The replacement of chlorine by a methoxy group in a number of photoproducts (Fig 1) could be explained either by a radical process or by photonucleophilic displacement, analogous to the displacement of an NO_2 group by OH.[11] Furthermore, analysis of methanol-water solution of **1** after irradiation ($\lambda = 254$ nm) yielded **4, 5, 6, 7, 9, 11, 12** and **14**. Urethane (**8**) could be formed from isocyanate (**2**) and methanol present in the medium. We are of the opinion that this compound is derived from the intermediate **12** by decarboxylation and elimination of the hydrogen radical from the medium and not from the intermediate **2**. Urethane synthesis[12] involves reagents free of water and reaction temperature over 80 °C. The other carbamates (**4, 7**) are probably derived from **8** by a free radical mechanism[13] and **11** by nucleophilic substitution.

A plausible pathway for the formation of compound **12** is drawn in Fig 4. Szeto *et al*[4] have identified intermediate **16** as one of the hydrolysis products of vinclozolin. Decarboxylation of **16** leading to **17** can be explained by the free radical and intermolecular processes that occur in organic acids upon photolysis.[14,15] The photolysis of simple alkenes, upon direct excitation or by sensitized processes, is quite complex.[16] The participation of the (π, π^*) state results in *cis-trans* isomerization, [1,3] hydrogen shift or hydration. It is presumed that —CH=CH_2 is hydrated and subsequently photo-oxidized to **18** before intramolecular cyclization to **12** takes place. Photoproducts **9** and **5** are derivatives of **12**. Previous investigation[6] has shown formation of only one compound (**10**, Fig 1) when a methanolic solution of **1** was photolysed with UV light ($\lambda = 254$ nm). Furthermore, analysis of an aqueous solution of **1** after irradiation at 254 nm revealed the formation of **2, 5, 7** and **9; 2** was identified as one of the products by previous workers.[6]

Considering the photodecomposition of vinclozolin in artificial sunlight and in the presence of humic acid when irradiated with UV light ($\lambda \geq 290$ nm) to yield polar compounds in the presence of dissolved humic material, it appears reasonable to expect these compounds to be found in soil, plants or water exposed to the fungicide.

ACKNOWLEDGEMENTS

Our thanks are due to Mrs Eva Schindlbeck for recording [^{1}H] and [^{13}C]NMR and mass spectra.

REFERENCES

1 Spencer EY, *Guide to the Chemicals used in Crop Protection*, 7th

edn, Publication 1043, Agricultural Canada Research Branch, Ottawa, Canada. p 585 (1982).
2 Clark T, The stability of vinclozolin in the presence of ethanol, methanol and water. *Chemosphere* **12**:1363–1369 (1983).
3 Melkebeke G, De Spiegeleer F, Strubant W and Dejonckheere W, A kinetic study of the chemical hydrolysis of the fungicides iprodione, vinclozolin and metalaxyl. *Med Fac Landbouww Rijksuniv Gent* **1**:319–329 (1986).
4 Szeto SY, Burlinson NE, Rettig SJ and Trotter J, *J Agric Food Chem* **37**:1103–1108 (1989).
5 Gennari M, Zanini E, Cignetti A, Bicci D, D'Amato A, Taccheo MB, Spessoto C, De Paoli M, Flori P, Imbroglini G, Leandri A and Conte E, Vinclozoline decay on different grapevines in four different Italian areas. *J Agric Food Chem* **33**:1232–1237 (1985).
6 Clark T and Watkins AMD, Photolysis of vinclozolin. *Chemosphere* **13**:1391–1396 (1984).
7 Crosby DG, *Proc Internat Symp Pestic Soil Ecol Degradation Movement*, Michigan State University (1971).
8 Gohre K and Miller GC, Singlet oxygen generation on soil surfaces. *J Agric. Food Chem* **31**:1104–1108 (1983).
9 Smith CA, Iwata Y and Gunther FA, Conversion and disappearance of methidathion on thin layers of dry soil. *J Agric Food Chem* **26**:959–962 (1978).
10 Slawinski J, Puzyna W and Slawinska D, Chemiluminescence during photooxidation of melanins and soil humic acids arising from a singlet oxygen mechanism. *Photochem Photobio.* **28**:459–463 (1978).
11 Havinga E and Kronenberg ME, Some problems in aromatic photosubstitution. *Pure Appl Chem* **16**:137–152 (1968).
12 Culvert JG and Pitts JN Jr, Photochemistry of polyatomic molecules, in *Photochemistry*, Wiley, New York. p 477 (1967).
13 McMurry S, Polyurethanes, in *Organic Chemistry*, 2nd edn, Books/Cole Publishing Company, California. p 1129 (1988).
14 Kopecky J, Photochemistry of alkenes, in *Organic Photochemistry*, VCH, Weinheim, Germany. p 60 (1992).
15 Ausloos P and Steacie ENR, *Can J Chem* **33**:1530–1535 (1955).
16 Clusius K and Schanzer W, *Chem. Ber* **75**:1795–1799 (1942).