Fungicides and Photochemistry: Photodegradation of the Dicarboximide Fungicide Vinclozolin

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To examine the potential of the fungicide vinclozolin to undergo photochemical reactions on plant surfaces, model experiments (λ > 280 nm) were performed in various organic solvents simulating the plant cuticle environment. On irradiation in 2-propanol and *n*-propanol vinclozolin was completely degraded within 1 h, but the degradation was substantially lower in benzene, cyclohexane, cyclohexene, ethanol, methanol, and *tert*-butyl methyl ether (TBME). In 2-propanol, *n*-propanol, and cyclohexane, the main reaction was photoaddition of the solvent molecules to the vinclozolin vinyl group; the photoproducts in further reactions were dechlorinated. In the presence of ethanol, photodehalogenation of the fungicide competed with photoaddition. On the other hand, in cyclohexene and benzene solutions, substitutions of the chlorines by solvent molecules were mainly observed. Photolysis in methanol or TBME yielded only dehalogenated photoproducts.

Keywords: *Dicarboximide fungicides; vinclozolin; photochemistry; photoproducts*

INTRODUCTION

Vinclozolin [3-(3,5-dichlorophenyl)-5-methyl-5-vinyl-1,3-oxazolidine-2,4-dione, Figure 1], like the other two dicarboximide fungicides iprodione and procymidone, has a wide range of applications in plant protection. In particular, it is applied to prevent gray mold in viniculture and on strawberries. According to data of the German Food Administration, vinclozolin belongs to the most detected pesticides in fruits and vegetables group (CLUA Freiburg, 1987–1991). Vinclozolin is formulated as an aqueous emulsion in Ronilan and is sprayed onto the plants. Being a contact poison (The Agrochemicals Handbook), it is essential that only minor parts of the fungicide penetrate into the inner layers of the plant cuticle. Hence, an important requirement for photodecomposition by sunlight is satisfied. Those UV components of the spectrum of sunlight that are not filtered by the atmosphere show a minimal wavelength of ~280 nm (Matsumura and Murti, 1982). Vinclozolin absorbs within a range of up to 300 nm (log ϵ 205 nm = 4.67, log ϵ 274 nm = 2.71; Figure 2), so photochemical reactions caused by sunlight irradiation can be presumed. Similar reactions concerning pesticides of various types have been reported (Schwack, 1990; Schwack, 1987; Schwack, 1988) and may lead to so-called *bound residues* that consist of addition products with components of the plant cuticle. Such degradation products cannot be identified with usual methods of residue analysis.

To date, there are only few papers on the photochemical reactivity of vinclozolin available in the literature (Clark and Watkins, 1984; Schwack and Bourgeois, 1989). Our aim was to establish a basis for possible reactions in the plant cuticle environment by irradiating vinclozolin in several organic solvents simulating this natural environment. Cyclohexane, cyclohexene, 2-propanol, *n*-propanol, ethanol, methanol, and TBME were selected to simulate saturated, unsaturated, alcoholic, and etheral functional groups of plant waxes, respectively (Walker, 1994).

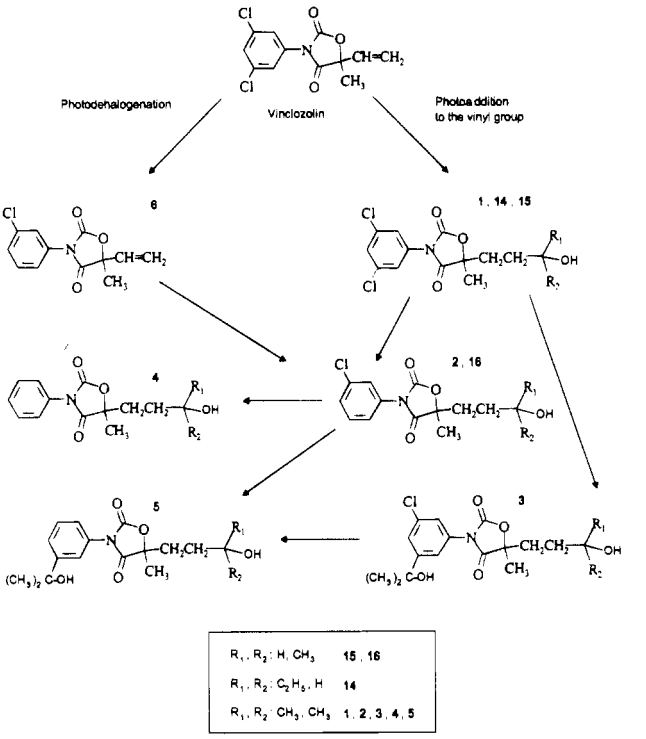

Figure 1. Photodegradation pathway of vinclozolin in the presence of ethanol, 2-propanol, or *n*-propanol.

EXPERIMENTAL PROCEDURES

Chemicals. Vinclozolin was isolated by extraction of Ronilan (BASF AG, Ludwigshafen, Germany) with CH_2Cl_2 and was further purified by repeated crystallization from *n*-hexane. The solvents used for photolyses were of analytical grade (Merck, Darmstadt, Germany); cyclohexane and cyclohexene were rectified over P_2O_5.

Apparatus and Chromatography. Vinclozolin degradation rates were determined on a Knauer (Bad Homburg, Germany) HPLC system equipped with a Knauer variable wavelength detector and a GAT autosampler (Bremerhaven,

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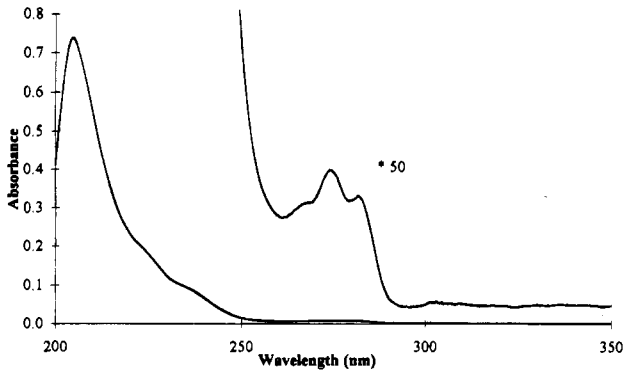

Figure 2. UV absorption spectrum of vinclozolin in 2-propanol.

Germany). For purity checkings and spectrum information, a Shimadzu (Kyoto, Japan) photo diode array detector (SPD M6a) was adapted to the HPLC system. A Nucleosil (Knauer) R 100, 5-μm, C18 reversed-phase column (4.6 i.d. × 250 mm) was used and eluted with methanol:water (70:30) at a flow rate of 1 mL/min. Quantification was performed by external standard mode, and 10 μL of the reaction mixtures were injected.

Proton (250 MHz) NMR spectroscopy was carried out with a Bruker Cryospec WM 250 (Karlsruhe, Germany), ^{1}H (400 MHz) NMR spectroscopy and ^{13}C (100 MHz) NMR spectroscopy with a Bruker WM 400 in $CDCl_3$ or CD_3CN solution. Spectra are reported in ppm downfield from TMS as internal standard.

The IR spectroscopy was performed on a IR spectrometer model PE 882 (Perkin Elmer, Überlingen, Germany) using KBr pellets. High-resolution mass spectrometry (HRMS) was carried out on a Finnigan MAT 90 (Breman, Germany).

Gas chromatography/mass spectrometry (GC/MS) was carried out on a GC 6000 Vega Series (Carlo Erba, Mainz, Germany), equipped with a fused silica quartz capillary column (10 m, stat. phase: OV1), coupled to a Finnigan MAT, model ITD 800 (Bremen, Germany). The temperature program was as follows: 150 °C for 2 min followed by increases of 10 °C/min, and then 280 °C for 5 min. The elemental analysis was performed with an Carlo Erba EA model 1106 (Milano, Italy).

Photolyses Equipment and Photolysis Procedure. For kinetic experiments, vinclozolin solutions (50 mg/50 mL) were irradiated in a quartz tube (120 × 28 mm) with a 150 W high-pressure mercury lamp (TQ 150, Hanau Quarzlampen GmbH, Germany) equipped with a quartz glass water-cooling jacket. The UV light was filtered by glass filters WG 295 (λ > 280 nm), WG 305 (λ > 295 nm), and WG 320 (λ > 300 nm) (Schott Glaswerke, Mainz, Germany). For preparative product isolation, vinclozolin was irradiated at concentrations of 150 mg/50 mL.

Isolation of Photoproducts. The reaction mixtures were evaporated to dryness under reduced pressure. The residue was redissolved in 2 mL of CH_2Cl_2 and chromatographed on silica gel (LOBAR B column filled with LiChroprep Si 60; Merck) with petroleum ether:diethyl ether (70:30) (flow rate 8 mL/min) as eluent. For purity checkings, 20 μL of these fractions were diluted with 200 μL of methanol and subjected to analytical HPLC.

Identification of Photoproducts. *3-(3,5-Dichlorophenyl)-5-(3-hydroxy-3-methylbutyl)-5-methyl-1,3-oxazolidine-2,4-dione (1)*; colorless crystals. IR (KBr) 3610, 3080, 2980, 2940, 2880, 1820, 1760, 1590, 1580, 1390, 1370, 1230, 1180, 1145, 1090, 1070, 1030, 920, 840, and 780 cm^{-1}; MS (70 eV) *m/z* 345 (2%, M^+, Cl_2), 330 (3%, Cl_2), 287 (4%, Cl_2), 259 (15%, Cl_2), 187 (8%, Cl_2), 59 (100%), and 43 (64%); ^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 7.45 (2H, d, phenyl-H, J_{meta} = 1.8 Hz); 7.41 (1H, t, phenyl-H, J_{meta} = 1.8 Hz); 2.09 (2H, m, $-CH_2CH_2C(CH_3)_2OH$); 1.69 (3H, s, $-CH_3$); 1.67 and 1.47 (je 1H, m, $-CH_2-CH_2C(CH_3)_2OH$); 1.50–1.60 (1H, −OH, exchangeable with D_2O); 1.25 (6H, s, $-(CH_3)_2OH$); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 173.8 (C=O); 152.4 (C=O); 135.6 (aromatic C); 132.8 (aromatic C); 128.9 (aromatic C); 123.7 (aromatic CH); 86.0 (quart. C); 69.9 (quart. C); 36.3 (CH_2); 31.8 (CH_2); 29.4 (CH_3); 29.3 (CH_3); 22.6 (CH_3).

3-(-3-Chlorophenyl)-5-(3-hydroxy-3-methylbutyl)-5-methyl-1,3-oxazolidine-2,4-dione (2). IR (KBr) 3575, 3080, 2980, 2940, 2870, 1805, 1740, 1590, 1570, 1480, 1450, 1430, 1405, 1380, 1360, 1350, 1320, 1280, 1170, 1130, 1070, and 1030 cm^{-1}; MS (70 eV) *m/z* 311 (7%, M^+, Cl_1), 296 (5%, Cl_1), 253 (10%, Cl_1), 225 (36%, Cl_1), 153 (20%, Cl_1), 125 (20%, Cl_1), 59 (100%), 43 (70%); ^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 7.45–7.52 (1H, m, phenyl-H); 7.33–7.44 (3H, m, phenyl-H); for the remaining proton signals, see product **1**.

3-[3-Chloro-5-(1-hydroxy-1-methylethyl)phenyl]-5-(3-hydroxy-3-methylbutyl)-5-methyl-1,3-oxazolidine-2,4-dione (3). IR (KBr) 3650, 3560, 3080, 2980, 2940, 2870, 1805, 1740, 1620, 1580, 1450, 1380, 1370, 1280, 1220, 1190, 1170, 1140, 1120, and 1050 cm^{-1}; MS (70 eV) *m/z* 369 (12%, M^+, Cl_1), 336 (100%, Cl_1), 265 (45%, Cl_1), 196 (25%, Cl_1), 123 (41%), 113 (83%), 69 (31%), 59 (86%), 55 (18%); ^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 7.49 (1H, t, phenyl-H, J_{meta} = 1.8 Hz); 7.47 (1H, t, phenyl-H, J_{meta} = 1.8 Hz); 7.32 (1H, t, phenyl-H, J_{meta} = 1.8 Hz); 2.09 (2H, m, $-CH_2CH_2C(CH_3)_2OH$); 2.00 (1H, s, −OH, exchangeable with D_2O); 1.69 (3H, s, $-CH_3$); 1.67 and 1.47 (1H each, m, $-CH_2-CH_2C(CH_3)_2OH$); 1.59 (6H, s, isopropyl-CH_3 at the aromatic ring); 1.50–1.60 (1H, −OH, exchangeable with D_2O); 1.25 (6H, s, $-C(CH_3)_2OH$).

3-Phenyl-5-(3-hydroxy-3-methylbutyl)-5-methyl-1,3-oxazolidine-2,4-dione (4). IR (KBr) 3560, 3080, 2980, 2940, 2870, 1805, 1740, 1590, 1570, 1480, 1450, 1430, 1405, 1380, 1360, 1350, 1320, 1280, 1170, 1130, 1070, and 1030 cm^{-1}; MS (70 eV) *m/z* 277 (33%, M^+), 262 (18%), 225 (13%), 219 (13%), 191 (100%), 125 (21%), 119 (50%), 113 (31%), 59 (100%); ^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 7.39–7.55 (5H, m, phenyl-H); for the remaining proton signals, see product 1.

3-[3-(1-Hydroxy-1-methylethyl)phenyl]-5-(3-hydroxy-3-methylbutyl)-5-methyl-1,3-oxazolidine-2,4-dione (5). MS (GC/MS) *m/z* 335 (52%, M^+), 302 (10%), 258 (10%), 231 (12%), 188 (3%), 162 (7%), 123 (11%), 113 (41%), 95 (11%), 59 (28%), 43 (100%).

3-(3-Chlorophenyl)-5-ethenyl-5-methyl-1,3-oxazolidine-2,4-dione (6). MS (70 eV) *m/e* 251 (100%, M^+, Cl_1), 207 (8.1%, Cl_1), 178 (69.7%, Cl_1), 164 (70.4% Cl_1), 153 (77.7%, Cl_1), 144 (52.4%, Cl_1), 125 (21.9%, Cl_1), 111 (18%, Cl_1), 90 (23.8%), 53 (26.4%); ^{1}H NMR (250 MHz; $CDCl_3$, ppm) δ 7.46–7.52 (1H, m, phenyl-H); 7.33–7.44 (3H, m, phenyl-H); 6.05 (1H, dd, $-CH=CH_2$); 5.62 (1H, d, $-CH=CH_2$); 5.43 (1H, d, $-CH=CH_2$); 1.76 (3H, s, $-CH_3$). Elemental analysis ($C_{12}H_{10}NO_3Cl$): C, found 57.2% (calculated 57.3%); H, found 4.02% (calculated 3.98); N, found 5.61% (calculated 5.57%); Cl, found 14.1% (calculated 14.0%).

3-Phenyl-5-ethenyl-5-methyl-1,3-oxazolidine-2,4-dione (7). MS (70 eV) *m/z* 217 (100%, M^+), 173 (6%), 145 (40.5%), 144 (49.3%), 130 (45.1%), 119 (52.2%), 104 (6.5%), 91 (17.4%), 77 (13.8%); ^{1}H NMR (250 MHz; $CDCl_3$, ppm) δ 7.39–7.55 (5H, m, phenyl-H); for the remaining proton signals, see product **6**. Elemental analysis ($C_{12}H_{11}O_3N$): C, found 66.25% (calculated 66.36%); H, found 5.12% (calculated 5.07%); N, found 6.47% (calculated 6.45%).

3-(3,5-Dichlorophenyl)-5-(2-cyclohexylethyl)-5-methyl-1,3-oxazolidine-2,4-dione (8). IR (KBr) 3090, 3080, 2930, 2850, 1820, 1760, 1590, 1580, 1460, 1430, 1400, 1240, 1180, 1160, 1145, 1090, 1070, 1030, 920, 840, and 780 cm^{-1}; MS (70 eV) *m/z* 369 (36%, M^+, Cl_2), 259 (100%, Cl_2), 187 (20%, Cl_2), 165 (20%), 94 (21%), 83 (16%), 67 (8%), 55 (20%); ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.45 (2H, d, phenyl-H, J_{meta} = 1.8 Hz); 7.41 (1H, t, phenyl-H, J_{meta} = 1.8 Hz); 1.97 (2H, m, $-CH_2CH_2C_6H_{11}$); 1.60–1.80 (6H, m, cyclohexyl-H); 1.67 (3H, s, $-CH_3$); 1.35 and 1.13 (1H each, m, $-CH_2CH_2C_6H_{11}$); 1.10–1.30 (3H, m, cyclohexyl-H); 0.84–0.97 (2H, m, cyclohexyl-H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 173.9 (C=O); 152.5 (C=O); 135.5 (2 aromatic C); 132.8 (aromatic C); 128.9 (aromatic C); 123.7 (2 aromatic C); 86.4 (quart. C); 37.4 (CH-cyclohexyl); 34.6 (CH_2); 33.1 (CH_2); 33.0 (CH_2); 30.2 (CH_2); 26.4 (CH_2); 26.2 (2 × CH_2); 22.6 (CH_3).

3-(3-Chlorophenyl)-5-(2-cyclohexylethyl)-5-methyl-1,3-oxazolidine-2,4-dione (9). MS (GC/MS): *m/z* 335 (9%, M^+, Cl_1), 225 (59%, Cl_1), 153 (35%, Cl_1), 83 (19%), 81 (22%), 55 (100%).

3-(3-Chloro-5-cyclohexylphenyl)-5-ethenyl-5-methyl-1,3-oxazolidine-2,4-dione (10). MS (70 eV) *m/z* 333 (100%, M^+, Cl_1),

285 (17%, Cl_2), 178 (26%, Cl_1), 83 (10%), 81 (10%), 55 (17%), 53 (14%); ^1H NMR (250 MHz, $CDCl_3$, ppm) δ 7.25–7.32 (2 × (1H, t, phenyl-H); 7.18 (1H, t, phenyl-H, J_{meta} = 1.8 Hz); 1.05–2.60 (11H, cyclohexyl-H); for the remaining proton signals, see product **6**.

3-(3-Chloro-5-cyclohexenylphenyl)-5-ethenyl-5-methyl-1,3-oxazolidine-2,4-dione (11/12). MS (70 eV) *m/z* (331 (100%, M^+, Cl_1), 281 (6%), 81 (19%), 72 (42%), 67 (18%), 59 (64%), 55 (29%); ^1H NMR (250 MHz, $CDCl_3$, ppm) δ 7.29 (1H, t, phenyl-H, J_{meta} = 1.8 Hz); 7.20 (1H, t, phenyl-H, J_{meta} = 1.8 Hz); 7.15 (1H, t, phenyl-H); for the remaining proton signals, see product **6**.

3-(3-Chlorobiphenyl-5-yl)-5-ethenyl-5-methyl-1,3-oxazolidine-2,4-dione (13). IR (KBr) 3085, 2990, 2940, 1820, 1740, 1640, 1600, 1585, 1570, 1500, 1465, 1435, 1395, 1290, 1240, 1220, 1180, 1160, 1075, 1045, 1017, 980, 940, 865, 820, 765, 745, 725, 700, 680, 650, and 625 cm^{-1}; MS (70 eV) *m/z* 327 (100%, M^+, Cl_1), 254 (26%, Cl_1), 240 (36%, Cl_1), 229 (40%, Cl_1), 220 (39%), 166 (23%), 152 (37%), 84 (16%), 81 (14%), 57 (16%), 55 (18%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, t, phenyl-H, J_{meta} = 1.8 Hz); 7.54–7.58 (3H, m, phenyl-H); 7.38–7.49 (4H, m, phenyl-H); for the remaining proton signals, see product **6**.

3-(3,5-Dichlorophenyl)-5-(3-hydroxypentyl)-5-methyl-1,3-oxazolidine-2,4-dione (14). MS (70 eV) *m/z* 345 (31.7%, M^+, Cl_2), 316 (51.5%, Cl_2), 259 (100%, Cl_2), 230 (17.5%, Cl_2), 187 (36.8%, Cl_2), 112 (49%), 101 (65.9%), 59 (61%); ^1H NMR (250 MHz, $CDCl_3$, ppm) δ 7.45 (2 H, d, phenyl-H); 7.41 (1H, t, phenyl-H); 3.49–3.61 (1H, m [broad], $-CH_2CH_2CH(OH)CH_2CH_3$); 2.18 and 2.01 (2H, m, $-CH_2CH_2CH(OH)CH_2CH_3$); 1.69 (3H, s, $-CH_3$); 1.67 and 1.47 (2H, m, $-CH_2CH_2CH(OH)CH_2CH_3$); 1.50 (2H, m, $-CH(OH)CH_CH3$); 1.27 (1H, −OH, exchangeable with D_2O); 0.95 (3H, t, $-CH(OH)CH_2CH_3$).

3-(3,5-Dichlorophenyl)-5-(3-hydroxybutyl)-5-methyl-1,3-oxazolidine-2,4-dione (15). MS (70 eV) *m/z* 331 (30.7%, M^+, Cl_2), 259 (100%, Cl_2), 230 (18.4%, Cl_2), 187 (50.4%, Cl_2), 98 (54.1%); HRMS: $C_{14}H_{15}NO_4{}^{37}Cl_2$ calculated, 333.0348; found, 333.0331; ^1H NMR (250 MHz, $CDCl_3$, ppm) δ 7.45 (2H, d, phenyl-H); 7.41 (1H, t, phenyl-H); 3.78–3.91 (1H, m [broad], $-CH_2CH_2CH(OH)CH_3$); 2.18 and 2.01 (each 1*H*, m, $-CH_2CH_2-R$); 1.69 (3 H, s, $-CH_3$); 1.67 and 1.47 (each 1H, m, $-CH_2CH_2CH(OH)CH_3$); 1.30–1.36 (1H, −OH, exchangeable with D_2O); 1.25 (3H, d, $-CH_2CH_2CH(OH)CH_3$).

3-(3-Chlorophenyl)-5-(3-hydroxybutyl)-5-methyl-1,3-oxazolidine-2,4-dione (16). MS (70 eV) *m/z* 297 (43.2%, M^+, Cl_1), 225 (100%, Cl_1), 153 (72.6%), 109 (36%, Cl_1), 99 (70.2%), 81 (21.5%), 43 (80%); HRMS $C_{14}H_{16}NO_4Cl$ calculated; 297.0767; found, 297.0754; ^1H NMR (250 MHz, CD_3CN, ppm) δ 7.49–7.54 (3H, m, phenyl-H); 7.42 (1H, m, phenyl-H); for the remaining proton signals, see product **15**.

Biphenyl (17). MS (GC/MS) *m/z* 154 (100%, M^+), 63 (15%), 51 (34%), 50 (29%), 39 (23%).

RESULTS AND DISCUSSION

UV irradiation (λ > 280 nm) resulted in the fastest photodegradation of vinclozolin in 2-propanol and *n*-propanol as model media, where it completely degraded within 1 h. The reactivity was significantly lower in the other solvents used, possibly because of their H-donor properties. After 5 h of irradiation, the degradation was 13.6% in cyclohexane, 21.5% in cyclohexene, 14.9% in methanol, 13.4% in TBME, and 61.4% in ethanol (Figure 3). Comparative irradiations of the fungicide in 2-propanol with UV filters cutting off different parts of the UV-B spectrum showed the expected faster degradation at higher frequencies (Figure 4).

Photolysis of vinclozolin in 2-propanol, *n*-propanol, ethanol, and cyclohexane yielded the photoaddition products **1**–**5**, **8**, **9**, and **14**–**16**, respectively (Figures 1 and 5). After 2 h of irradiation in 2-propanol, 62, 28, 0.4, and 2.0% of degraded vinclozolin was converted to the addition products **1**, **2**, **3**, and **4**, respectively.

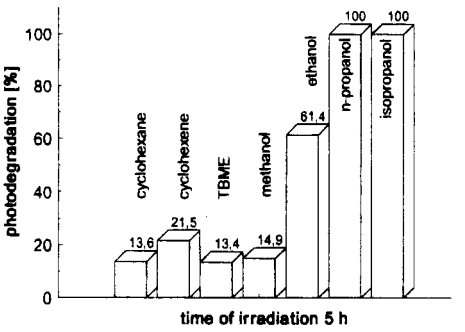

Figure 3. Photodegradation (λ > 280 nm) of vinclozolin after 5 h of irradiation in various organic solvents (50 mg/50 mL).

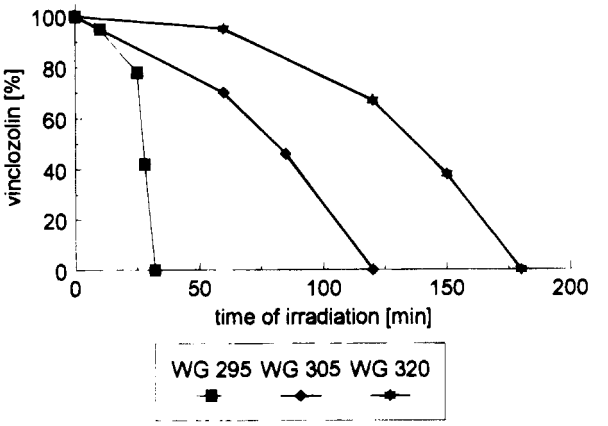

Figure 4. Photodegradation of vinclozolin in 2-propanol using different UV filters.

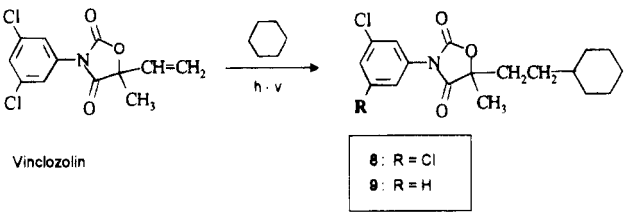

Figure 5. Photodegradation of vinclozolin in the presence of cyclohexane.

Product **5** was detected as a trace compound and could not be quantified individually.

In 2-propanol, photoaddition is surprisingly spontaneous and almost exclusive to the vinyl group of vinclozolin. There are indications for a radical reaction type in which an excited carbonyl group of vinclozolin acts as a sensitizer (Figure 6). It is unlikely that the isolated vinyl chromophore will absorb light with wavelengths >280 nm and be directly excited. The direct formation of a 2-propanol or an *n*-propanol radical also seems unlikely. On the other hand, carbonyls like aldehydes and ketones readily abstract hydrogen in *n*-triplet conditions (Becker, 1983). As shown in Figure 6, the successive photoproducts in 2-propanol may be derived. Homolytic or charge transfer induced cleavage of a C—Cl bond of **1**, the main photoproduct in 2-propanol, yields the radical **1a**. Now, there are two possible reactions. The more likely is that **1a** will be saturated by a hydrogen transfer from the solvent 2-propanol yielding **2** as the monodechloro product of **1**, which was isolated as a further main product. Alternatively, **1a** can combine with a hydroxyisopropyl radical leading to **3** as substitution product to a minor extent.

Via the same mechanisms, both **2** and **3** were further dechlorinated, yielding **4** and **5**. Product **5** may also be

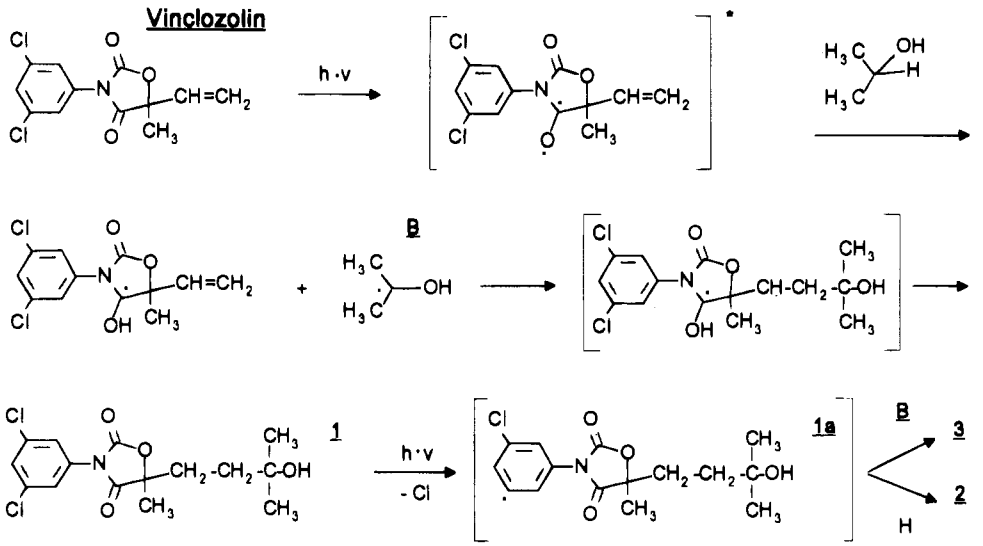

Figure 6. Formation of 2-propanol radicals in the presence of vinclozolin acting as a sensitizer.

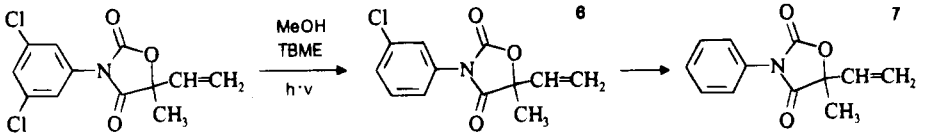

Figure 7. Photodegradation pathway of vinclozolin in the presence of MeOH or TBME.

seen as a combination product of a radical formed by homolytic cleavage of the C—Cl bond of **2** with an intermediate hydroxyisopropyl radical **B** (Figures 1 and 6).

Thus, the main reaction consists of the addition of 2-propanol to the vinclozolin vinyl group followed by successive dehalogenations. To a minor extent, a substitution of the phenyl-Cl by a hydroxyisopropyl moiety occurs followed by dechlorination. On the basis of the identification of **14** (Figure 1) as the main product (90% of degraded vinclozolin) after 5 h of irradiation in the presence of *n*-propanol, it must be assumed that vinclozolin will be degraded by the aforementioned pathway.

During irradiation of vinclozolin dissolved in cyclohexane, a single dehalogenation leading to **6** (7.0% of degraded vinclozolin after 5 h) was first observed. However, in contrast to what we expected, the most important pathway was the photoaddition of the vinclozolin vinyl group to the cyclohexane solvent, resulting in **8** (Figure 5) as the main product (75% of degraded vinclozolin) after 5 h. Subsequent dehalogenation yielded the singly dechlorinated trace compound **9** (Figure 5). Another possibility of forming **9** is the addition of cyclohexane to the initial photoproduct **6** (Figure 1), which was the predominant reaction on irradiation of the isolated **6** in cyclohexane.

Finally, even after 5 h of irradiation with an UV-filter with cutoff at 295 nm, **6** was not detectable, but photoaddition still occurred. This result indicates that dehalogenation reactions mainly take place at higher frequencies.

When vinclozolin was irradiated in ethanol solutions, competition between photoaddition and photodehalogenation was observed. The first detectable reaction is a dehalogenation step leading to **6**, as was observed in the cyclohexane experiments. Further reactions consist of the addition of ethanol to the vinclozolin vinyl group, followed by successive dehalogenations, leading to photoproducts **15** and **16** (Figure 1). After 5 h of irradiation in ethanol, 51, 7.5, and 15.3% of degraded vinclozolin was converted to the photoproducts **6**, **15**, and **16**, respectively.

Pure photodehalogenation leading to the photoproducts **6** and **7** was observed on irradiation of vinclozolin in TBME (28% and 59.4% of degraded vinclozolin) and methanol (76% and 16% of degraded vinclozolin) after 17 h (Figure 7). Product **6** was also detected during irradiation of vinclozolin in methanol (Clark and Watkins, 1984). The dehalogenation products **6** and **7** have been synthesized individually, too, to obtain pure reference material (Walker, 1994).

Because of the surprising photoaddition of cyclohexane, we focused our attention on the irradiation of vinclozolin in benzene. According to the results just mentioned, an addition of benzene to the vinyl group of vinclozolin could also be expected. However, in accordance with the reported results of Clark and Watkins, the main reaction type was a substitution of a phenyl-Cl by a solvent molecule leading to **13** (Figure 8), which was isolated with >70% of the entire yield. Besides **13**, biphenyl (**17**) was detected as a minor product.

When vinclozolin was irradiated in cyclohexene, the main reaction was a substitution of Cl by solvent molecules, thus leading to cyclohexyl- and cyclohexenyl-substituted products **10**—**12**, respectively (Figure 9).

Products **11** and **12** were structurally characterized by GC/MS analysis, but they could not be isolated from irradiated cyclohexene solution because of a couple of cyclohexene byproducts that formed. Photoaddition of cyclohexene to the vinclozolin vinyl group was not observed at all. Alicyclic carbonyls are known to undergo photoadditions with olefinic structures forming oxetanes or photoreductions leading to carbinols (Schwack, 1990). However, corresponding products

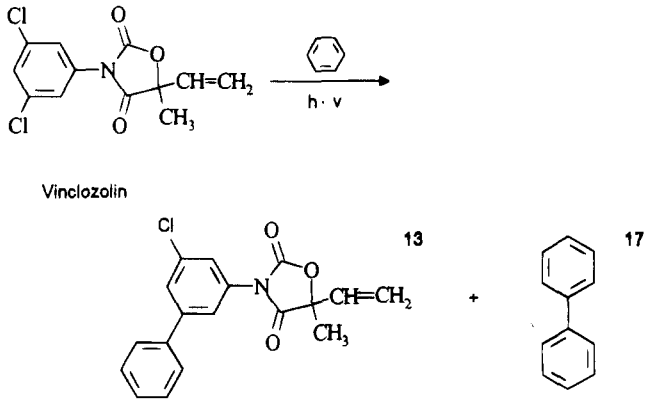

Figure 8. Photodegradation of vinclozolin in the presence of benzene.

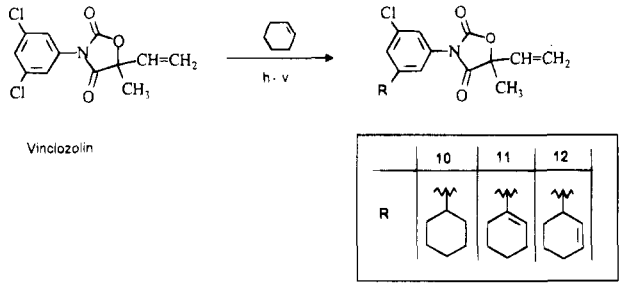

Figure 9. Photodegradation of vinclozolin in the presence of cyclohexene.

could not be detected during irradiation of vinclozolin in the presence of cyclohexene. The comparatively low photodegradation is a further indication that this type of reaction did not occur.

In conclusion, our investigations show the high potential of vinclozolin to undergo photoinduced reactions with various types of chemical structures in different model environments. Formation of the photoaddition products **1**–**5** and **8**–**16** (in 2-propanol, *n*-propanol, ethanol, benzene, cyclohexane, and cyclohexene) containing the solvent moiety indicates the possible formation of *bound residues* in plant cuticles where solvent molecules are replaced by constituents of plant waxes and the cutin polymer in such reaction pathways. Experiments in model solvents are only the first step to investigate the photochemistry of vinclozolin on plant surfaces (Walker, 1994; Armbruster, Walker and Schwack, 1994). A detailed report of the results obtained on other cuticle model systems and on fruit surfaces will be the subject of a forthcoming publication.

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