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Photodegradation of the Carbamate Insecticide Ethiofencarb

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Abstract: In order to study the photoreactivity and possible photodegradation pathways of ethiofencarb (2-ethylthiomethylphenyl methylcarbamate) on plant surfaces, model experiments in the presence of cyclohexane, cyclohexene and isopropanol were performed. Both artificial light ($\lambda > 280$ nm) and natural sunlight were used. Half-lives of the ethiofencarb photodegradation were in the order cyclohexane < isopropanol < cyclohexene and ranged from 75 min to more than 20 h. Depending on the solvent and the light source chosen, different photoproducts were obtained. When ethiofencarb was irradiated in the presence of cyclohexane, photo-oxidation to the corresponding sulfoxide was the main degradation pathway, followed by a cyclization reaction. In the case of isopropanol as model solvent, numerous photoproducts were detected as a result of photo-oxidation, hydrolysis and the addition to ethiofencarb of the solvent molecule.

Key words: ethiofencarb, photodegradation, photo-oxidation, ethiofencarbsulfoxide, ethiofencarbsulfone.

1 INTRODUCTION

Ethiofencarb (2-ethylthiomethylphenyl methylcarbamate) is an insecticide widely used in agriculture for aphid control. Because of its systemic mode of action, both foliar and ground application are possible. When sprayed onto plants, ethiofencarb is first of all in contact with the plant cuticle and then exposed to the sunlight. Consequently photodegradation, controlled by the constituents of the plant cuticle, is one of the possible degradation pathways of ethiofencarb on plant surfaces. Little is known of the photochemistry of ethiofencarb. Jensen-Korte *et al.* investigated the influence of humic substances on the photodegradation rate of ethiofencarb in water.[1] No photodegradation products were reported. Studies on the uptake of ethiofencarb by roots, translocation in plants, and degradation in the ground and in water have been published.[2,3] In connection with these investigations, the corresponding sulfoxide and sulfone of ethiofencarb were mentioned as degradation products.

In order to study the photoreactivity and possible photodegradation pathways of ethiofencarb on plant surfaces, model experiments in the presence of cyclohexane, cyclohexene and isopropanol were performed. In this way the characteristic functional groups of the plant cuticle constituents namely alkanes, the secondary hydroxy group of hydroxy fatty acids, steroids and terpenes and their influence on photodegradation could be simulated.

2 MATERIALS AND METHODS

Ethiofencarb was isolated from 'Croneton'® GR (Bayer, Germany, active ingredient: 100 g kg^{-1}) by Soxhlet extraction with dichloromethane. It was further purified to analytical grade by column chromatography on silica gel (500 × 25 mm column packed with LiChroprep Si 60, 25–40 μm (Merck, Germany), eluent light petroleum distillate + diethyl ether (60 + 40 by volume), yielding colourless crystals (m.p. 34°C; purity HPLC > 99·5%).

As reference compound for high performance liquid chromatography analyses, the corresponding sulfone (3) of ethiofencarb was synthesized by oxidation of ethiofencarb with hydrogen peroxide in the presence of tungsten trioxide according to Schultz *et al.*[4] Furthermore 2-ethylthiomethylphenol (**4**), 2-ethylsulfinylmethylphenol (**5**) and 2-ethylsulfonylmethylphenol (**6**) were prepared from ethiofencarb, ethiofencarbsulfoxide

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and ethiofencarbsulfone, respectively (100 mg), by hydrolysis with methanolic potassium hydroxide (1 M; 10 ml) and partition in dichloromethane at pH 1 (3 × 5 ml).

The solvents used were of analytical grade (Merck, Germany), cyclohexane and cyclohexene were rectified over phosphorus pentoxide.

2.1 Photolysis equipment and photolysis procedure

For kinetic degradation investigations, solutions of ethiofencarb (1 g litre^{-1}) in isopropanol, cyclohexane and cyclohexene, respectively, were irradiated in a quartz tube for up to 16 h at room temperature, using 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 a glass filter WG 295, cut-off $\lambda < 280$ nm (Schott Glaswerke, Germany). In addition, a glass filter WG 320, cut-off $\lambda < 302$ nm, was used.

Irradiation experiments in the presence of cyclohexane and isopropanol in the sunlight were performed in Karlsruhe from 20 to 26 May 1992 and from 21 June to 6 July 1992, respectively (clear sky, 22–26°C).

2.2 HPLC analyses

Ethiofencarb degradation rate analyses were carried out on a high performance liquid chromatography (HPLC) system (Knauer, Germany) equipped with an autosampler (GAT, Germany). A Kromasil (Eka Nobel, Sweden) C8, 10 μm, reversed-phase column (4·6 cm i.d. × 25 cm) and a variable wavelength UV detector set at 220 nm was used. For purity checking and spectral information, a Shimadzu (Kyoto, Japan) photodiode array detector (SPDM6a) was connected to the above-mentioned system.

The following acetonitrile + water gradient at a flow rate of 1 ml min^{-1} was used: 12 min 15+, over the next 5 min change to 60 + 40, then change to 85 + 15 in 2 min and hold for 5 min. The following retention times (min) were obtained: Ethiofencarb (16·3), **8** (20·5), **4** (17·1), **9** (15·5), **10** (15·2), **7** (13·5), **6** (11·6), **3** (11·2), **5** (9·5), **2** (9·2). Quantifications were performed by external standard mode. For structures of these compounds, see Figs 2 and 3.

2.3 Product isolation

After irradiation the photolysis mixtures were evaporated to dryness, dissolved in dichloromethane + methanol (95 + 5 by volume) and chromatographed on silica gel plates 60 F254 (Merck, Germany) using multiple development technique with decreasing polarity of the solvent mixture:

1. diethyl ether + methanol (90 + 10 by volume),
2. diethyl ether,
3. light petroleum distillate + diethyl ether (30 + 70 by volume),
4. light petroleum distillate + diethyl ether (50 + 50 by volume).

The regions of silica gel containing the photoproducts were scraped from the plate and eluted with acetone. For isolation of the photoproduct **10**, the isopropanol photolysis mixture was diluted with water (150 ml) and freeze dried. The residue was dissolved in acetonitrile (1 ml) and chromatographed on modified silica gel (250 × 16 mm, Eurospher RP18, 15 μm (Knauer, Germany), eluent: acetonitrile + water (35 + 65 by volume) at a flow-rate of 17 ml min^{-1}). Retention time of **10**: 11.0 min. Further purification was unsuccessful due to degradation processes.

2.4 Spectrometric analysis

[^{1}H] and [^{13}C] nuclear magnetic resonance spectroscopy (NMR) was performed on a Bruker AM 250 and a Bruker AM 400 (Karlsruhe, Germany), respectively, in deuterochloroform solution, except where otherwise indicated. Spectra are reported in ppm downfield from tetramethylsilane as internal standard.

High resolution mass spectrometry (HRMS) was carried out with a Finnigan Mat 90 (Bremen, Germany). Field desorption mass spectra (FD–MS) were recorded by a Finnigan Mat 711.

IR spectra were recorded on a Perkin Elmer (Überlingen, Germany) IR spectrometer model PE 882 using potassium bromide pellets or, in the case of **5**, **8** and **9**, chloroform solutions.

2.5 Spectral data obtained on isolated photoproducts

Ethiofencarbsulfoxide (**2**): m.p.: 68–72°C; IR: 3362 (m), 3302 (s), 3062 (m), 2942 (m), 2884 (w), 1738 (s, —CO—NH—), 1636 (w), 1541 (s), 1488 (s), 1455 (m), 1423 (w), 1298 (m), 1260 (m), 1226 (s), 1185 (s), 1021, (s, —S=O), 931 (m), 935 (m), 763 (m) cm^{-1}, [^{1}H]NMR (250 MHz): δ = 7·13–7·32 (m, 4H, Ar—H), 5·27 (s, 1H, —NH—CH$_3$), 4·04–3·85 (dd, 2H, Ar—CH$_2$—SO), 2·83 (d, 3H, —NH—CH$_3$), 2·55 (dq, 2H, —SO—CH$_2$—CH$_3$, J = 1·5 Hz), 1·25 (trip, 3H, —SO—CH$_2$—CH$_3$, J = 1·5 Hz); [^{13}C]NMR (100 MHz): δ = 155·23 (sp^2), 150·4 (sp^2, —CO—), 132·1 (sp^2), 130·3 (sp^2), 126·6 (sp^2), 123·7 (sp^2), 123·4 (sp^2), 53·7 (sp^3, CH$_2$—SO), 45·0 (sp^3, SO—CH$_2$—CH$_3$), 28·5 (sp^3, —NH—CH$_3$), 17·2 (sp^3, —CH$_2$—CH$_3$); MS (70 eV); m/z = 184 (11·9%), 137 (1·3%), 108 (6·8%), 107 (100%), 79 (6·3%), 78 (8·3%), 77 (16·8%), 51 (2·2%); HRMS: of m/z = 184 ($C_9H_{12}O_2S$ = 2-(ethylsulfinylmethyl)-phenol), found: 184·0537, calculated: 184·0558.

2-Ethylsulfonylmethylphenylmethylcarbamate (ethiofencarbsulfone) (**3**): m.p.: 121°C; IR 3360 (s), 3071 (w), 2993 (m), 2943 (m), 1741 (s), 1724 (s), 1683 (w), 1606 (w), 1538 (s), 1489 (s), 1452 (m), 1418 (m), 1300 (s, $-SO_2-$), 1283 (s), 1259 (m), 1127 (s), 1049 (m), 930 (m), 769 (m), 728 cm^{-1} (m); [^{1}H]NMR (250 MHz): δ = 7·22–7·68 (m, 4H, Ar—H), 5·24 (s, 1H, $-\underline{NH}-CH_3$), 4·27 (s, 2H, $Ar-\underline{CH_2}-SO_2$), 2·84–2·92 (m, 5H, $-NH-\underline{CH_3}$, interfered by $-SO_2-\underline{CH_2}-CH_3$, J = 7·5 Hz), 1·33 (t, 3H, $-SO_2-CH_2-\underline{CH_3}$, J = 7·5 Hz); [^{13}C]NMR (100 MHz): δ = 155·1 (sp^2), 150·4 (sp^2, $-\underline{C}O-$), 132·7 (sp^2), 130·9 (sp^2), 126·6 (sp^2), 123·7 (sp^2), 121·4 (sp^2), 53·9 (sp^3, $Ar-\underline{CH_2}-S$), 46·4 (sp^3, $-\underline{CH_2}-CH_3$), 28·5 (sp^3, $-NH-\underline{CH_3}$), 6·7 (sp^3, $-CH_2-\underline{CH_3}$); MS (FD, 11 kV): m/z = 257 (17·1%, M^+), 200 (100%), 199 (15·2%); HRMS: $C_{11}H_{15}NO_4S$, found: 257·0778, calculated: 257·0722.

2-Ethylthiomethylphenol (**4**): IR: 3306 (m), 3011 (m), 2977 (m), 2932 (m), 1609 (w), 1582 (m), 1485 (s), 1452 (w), 1420 (w), 1375 (w), 1349 (w), 1261 (m), 1230 (s), 1150 (m), 1087 (m), 1037 (w), 976 (w), 879 (w), 862 (m) cm^{-1} [^{1}H]NMR (250 MHz): δ = 7·23–7·16 (m, 1H, Ar—H), 7·1–7·06 (m, 1H, Ar—H), 6·91–6·82 (m, 2H, Ar—H), 6·7 (s, 1H, $-O\underline{H}$), 3·82 (s, 2H, $Ar-\underline{CH_2}-S$), 2·42 (q, 2H, $-S-\underline{CH_2}-CH_3$, J = 7·3 Hz), 1·23 (t, 3H, $-S-CH_2-\underline{CH_3}$, J = 7·3 Hz); MS (70 eV): m/z = 168 (M^+, 39·3%), 107 (100%), 79 (5·3%), 78 (9·6%), 77 (15·4%), HRMS: $C_9H_{12}OS$, found: 168·0595, calculated: 168·0609.

2-Ethylsulfinylmethylphenol (**5**): IR: 3070 (s), 2976 (w), 2936 (w), 2876 (w), 1601 (m), 1506 (w), 1489 (w), 1460 (s), 1378 (m), 1312 (m), 1275 (s), 1253 (s), 1006 (s), 756 (s) cm^{-1}; [^{1}H]NMR (250 MHz): δ = 9·30 (s, 1H, Ar—O$\underline{H}$), 7·27–7·20 (m, 1H, Ar—H), 7·06–6·90 (m, 2H, Ar—H), 6·88–6·84 (m, 1H, Ar—H), 4·36 and 3·89 (dd, 2H, $Ar-\underline{CH_2}-$), 2·69 (dq, 2H, $-\underline{CH_2}-CH_3$, J = 7·5 Hz), 1·31 (t, 3H, $-CH_2-\underline{CH_3}$, J = 7·3 Hz); [^{13}C]NMR (250 MHz): δ = 156·9 (sp^2), 132·1 (sp^2), 130·6 (sp^2), 120·6 (sp^2), 119·1 (sp^2), 118·0 (sp^2), 53·1 (sp^3, $Ar-\underline{CH_2}-SO$), 43·9 (sp^3, $-\underline{CH_2}-CH_3$), 7·1 (sp^3, $-CH_2-\underline{CH_3}$): MS (70 eV): m/z = 184 (7·4%, M^+), 107 (100%), 79 (4·7%), 78 (6·1%), 77 (12·0%); HRMS: $C_9H_{12}O_2S$, found: 184·0578, calculated: 184·0558.

2-Ethylsulfonylmethylphenol (**6**): m.p.: 90–91°C; IR: 3327 (s), 3053 (w), 3031 (w), 2994 (w), 2974 (w), 2943 (w), 2925 (w), 1597 (m), 1504 (m), 1458 (s), 1405 (w), 1366 (m), 1315 (w), 1275 (s, $-SO_2-$), 1257 (s), 1122 (s, $-SO_2-$), 1175 (w), 1045 (m), 792 (s), 760 (s), 724 (m) cm^{-1}; [^{1}H]NMR (250 MHz): δ = 7·47–7·20 (m, 2H, Ar—H), 7·01–6·95 (m, 2H, Ar—H), 6·85 (s, 1H, $-\underline{OH}$, 4·35 (s, 2H, $Ar-\underline{CH_2}-$), 2·98 (q, 2H, $-\underline{CH_2}-CH_3$, J = 7·5 Hz), 1·39 (t, 3H, $-CH_2-\underline{CH_3}$, J = 7·5 Hz); [^{13}C]NMR (250 MHz): δ = 155·28 (sp^2), 132·25 (sp^2), 131·03 (sp^2), 121·79 (sp^2), 118·52 (sp^2), 115·51 (sp^2), 54·95 (sp^3, $Ar-\underline{CH_2}-SO_2$), 45·58 (sp^3, $-\underline{CH_2}-CH_3$), 6·31 (sp^3, $-CH_2-\underline{CH_3}$); MS (70 eV): m/z = 200 (9·3%, M^+), 107 (100%), 79 (3·2%), 78 (7·8%), 77 (16·1%); HRMS: $C_9H_{12}O_3S$, found: 200·0523, calculated: 200·0507.

3,4-Dihydro-3-methyl-1,3-benzoxazine-2,4-dione (**7**): m.p.: 140°C; IR: 3082 (w), 2930 (w), 2856 (w), 1769 (s), 1694 (s), 1627 (m), 1617 (s), 1600 (m), 1471 (s), 1423 (s), 1370 (s), 1311 (s), 1271 (w), 1226 (m), 1120 (m), 1019 (m), 796 (w), 767 (s), 749 (s), 686 (m) cm^{-1}; [^{1}H]NMR (250 MHz, hexadeuteroacetone): δ = 8·05–7·01 (m, 1H, Ar—H), 7·85–7·78 (m, 1H, Ar—H), 7·48–7·34 (m, 2H, Ar—H), 3·39 (s, 3H, $-N-\underline{CH_3}$); MS (70 eV): m/z = 177 (M^+, 62·8%), 162 (38·0%), 120 (100%), 92 (59·0%), 65 (2·9%), 64 (16·8%), 63 (17·3%); HRMS: $C_9H_7NO_3$, found: 177·0390, calculated: 177·0426.

2-[Bis(ethylthio)methyl]phenylmethylcarbamate (**8**): IR: 3464 (m), 3021 (m), 2927 (m), 1741 (s), 1599 (w), 1510 (m), 1477 (m), 1444 (m), 1341 (w), 1260 (w), 1230 (w) cm^{-1}; [^{1}H]NMR (250 MHz): δ = 7·71–7·67 (m, 1H, Ar-H), 7·31–7·10 (m, 3H, Ar—H), 5·19 (s, 1H, $Ar-\underline{CH}-S$), 5·05 (s, 1H, $-\underline{NH}-CH_3$), 2·91 (d, 3H, $-NH-\underline{CH_3}$), 2·55 (m, 4H, $-(S-\underline{CH_2}-CH_3)_2$), 1·21 (t, 6H, $-(S-CH_2\underline{CH_3})_2$); MS (70 eV); m/z = 285 (M^+, 1·1%), 224 (44·7%), 168 (9·5%), 167 (100%), 148 (3·5%), 139 (4·4%), 137 (25·8%), 133 (4·3%), 107 (6·6%), 77 (2·4%), 58 (2·9%); HRMS: $C_{13}H_{19}NO_2S_2$, found: 285·0886, calculated: 285·0857.

2-(Isopropoxycarbonyl)phenylmethylcarbamate (**9**): IR: 3464 (m), 3025 (m), 2984 (w), 1737 (s), 1705 (m), 1605 (w), 1514 (m), 1478 (m), 1447 (m), 1418 (w), 1372 (w), 1351 (w), 1296 (w), 1259 (m), 1198 (m), 1107 (m), 1079 (w), 929 (w), 794 (w) cm^{-1}; [^{1}H]NMR (250 MHz): δ = 7·97–7·94 (m, 1H,Ar—H), 7·52–7·48 (m, 1H, Ar—H), 7·31–7·13 (m, 2H, Ar—H), 5·22 (sept., 1H, J = 6·3 Hz, $-CH(CH_3)_2$, 5·05 (s, 1H, —N—H), 2·91 (d, 3H, $-NH-C\underline{H_3}$), 1·34 (d, 6H, J = 6·2 Hz, $-CH(C\underline{H_3})_2$); MS (70 eV): m/z = 194 (0·3%), 181 (3·1%), 180 (32·1%), 178 (8·0%), 139 (2·9%), 138 (41·1%), 120 (100%), 92 (14·0%), 65 (5·6%), 64 (2·3%), 63 (1·5%), 58 (3·5%), 43 (3·0%).

2-(1-Ethylthio-2-methyl-2-hydroxypropyl)phenylmethylcarbamate (**10**): [^{1}H]NMR (250 MHz): δ = 7·24–7·12 (m, 3H, Ar—H), 7·10–7·07 (m, 1H, Ar—H), 5·09 (s, 1H, $-\underline{NH}-CH_3$), 4·27 (s, 1H, $Ar-\underline{CH}-S$), 2·90 (d, 3H, $-NH-\underline{CH_3}$), 2·68 (s, 1H, $C-O\underline{H}$), 2·38 (dq, 2H, $-S-\underline{CH_2}-CH_3$), 1·18 (s, 6H, $-CH(C\underline{H_3})_3$, 1·15 (t, 3H, $-S-CH_2C\underline{H_3}$); MS (70 eV): m/z = 283 (M^+, 0·1%), 265 (1·6%), 225 (20·4%), 169 (7·5%), 168 (67·4%), 167 (21·1%), 149 (9·7%), 147 (8·8%), 139 (34·7%), 123 (34·2%), 108 (22·3), 107 (100%), 106 (4·5%), 105 (3·6%), 103 (2·4%), 95 (5·5%), 91 (4·6%), 78 (3·4%), 77 (9·2%), 59 (16·0%), 58 (6·3%), 45 (6·5%), 43 (11·5%); HRMS: $C_{14}H_{21}NO_3S$, found: 283·1263, calculated: 283·1242.

3 RESULTS AND DISCUSSION

On UV irradiation ($\lambda > 280$ nm) in the presence of the model solvents cyclohexane, cyclohexene and isopropanol, ethiofencarb was rapidly photodegraded. The half-lives were extremely dependent on the solvent chosen, as shown in Fig. 1. In the presence of cyclohexane, ethiofencarb was photodegraded by 50% within 75 min, in isopropanolic solution the half-life was 330 min, whereas in cyclohexene ethiofencarb was hardly affected by irradiation within this time. The photodegradation of ethiofencarb was therefore faster in cyclohexane than in isopropanol, the reverse of the degradation rates in these two solvents established for other carbamate insecticides, propoxur and pirimicarb.[5,6] Furthermore, when the photodegradation of the three carbamate insecticides is compared to their UV spectra (Table 1) it is interesting that there is no correlation between the molar absorptivities at 280 nm and photodegradation half-lives. The experiments with ethiofencarb make this result especially clear. If photodegradation and half-lives only depended on their UV spectra, photodegradation of propoxur should have been more efficient than that of ethiofencarb due to its greater molar absorptivity at 280 nm.

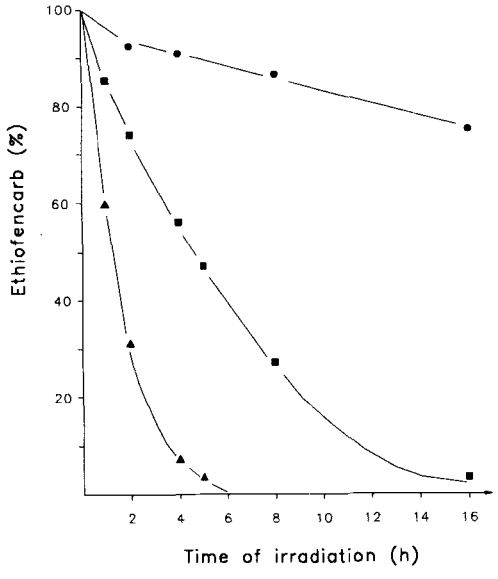

Fig. 1. Photodegradation ($\lambda > 280$ nm) of ethiofencarb in (●) cyclohexene, (■) isopropanol and (▲) cyclohexane (1 mg ml^{-1}).

TABLE 1
Molar Absorptivity of Ethiofencarb, Pirimicarb and Propoxur at 280 nm and Half-Lives on Irradiation ($\lambda > 280$ nm) in Cyclohexane, Cyclohexene and Isopropanol (1 mg ml^{-1})

	Pirimicarb	*Ethiofencarb*	*Propoxur*
Molar absorptivity at 280 nm (mol litre^{-1} cm^{-1})	2200	60	1200
Half-life in isopropanol	60 min	330 min	12 h
Half-life in cyclohexane	85 min	75 min	39 h
Half-life in cyclohexene	140 min	28 h	32 h

In addition, the effect of different wavelengths using UV filters and, in comparison, natural sunlight on photodegradation was studied. On irradiation of ethiofencarb at $\lambda > 302$ nm in the presence of cyclohexane, the half-life was curiously almost unaffected and was still about 75 min, whereas photodegradation of ethiofencarb in isopropanolic solution decreased. After 27 h ethiofencarb was decomposed by 76%, comparable degradation resulted within 8 h at $\lambda > 280$ nm. In natural sunlight, half-lives of photodegradation in the presence of cyclohexane and isopropanol were 44 h and 103 h, respectively.

As to photoproducts, great differences were established depending on the solvent used. On irradiation of ethiofencarb in the presence of cyclohexane, a white precipitate was observed soon after the irradiation was started. The precipitate was the main product after 5 h and was found to be 2-ethylsulfinylmethyl phenylmethylcarbamate (Fig. 2, **2**, ethiofencarbsulfoxide). Based on degraded ethiofencarb, 47% was oxidized to **2**. Two further minor photoproducts were detected by HPLC analyses. By means of mass spectrometry and NMR spectroscopy, these products were identified as 2-ethyl-

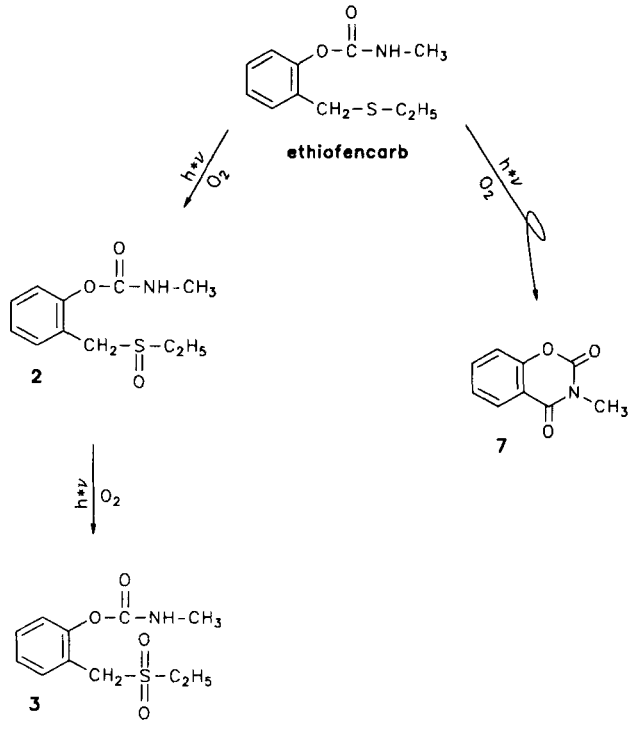

Fig. 2. Photodegradation pathways of ethiofencarb in the presence of cyclohexane (1 mg ml^{-1}, WG 295): **2** ethiofencarbsulfoxide; **3** ethiofencarbsulfone; **7** 3,4-dihydro-3-methyl-1,3-benzoxazine-2,4-dione.

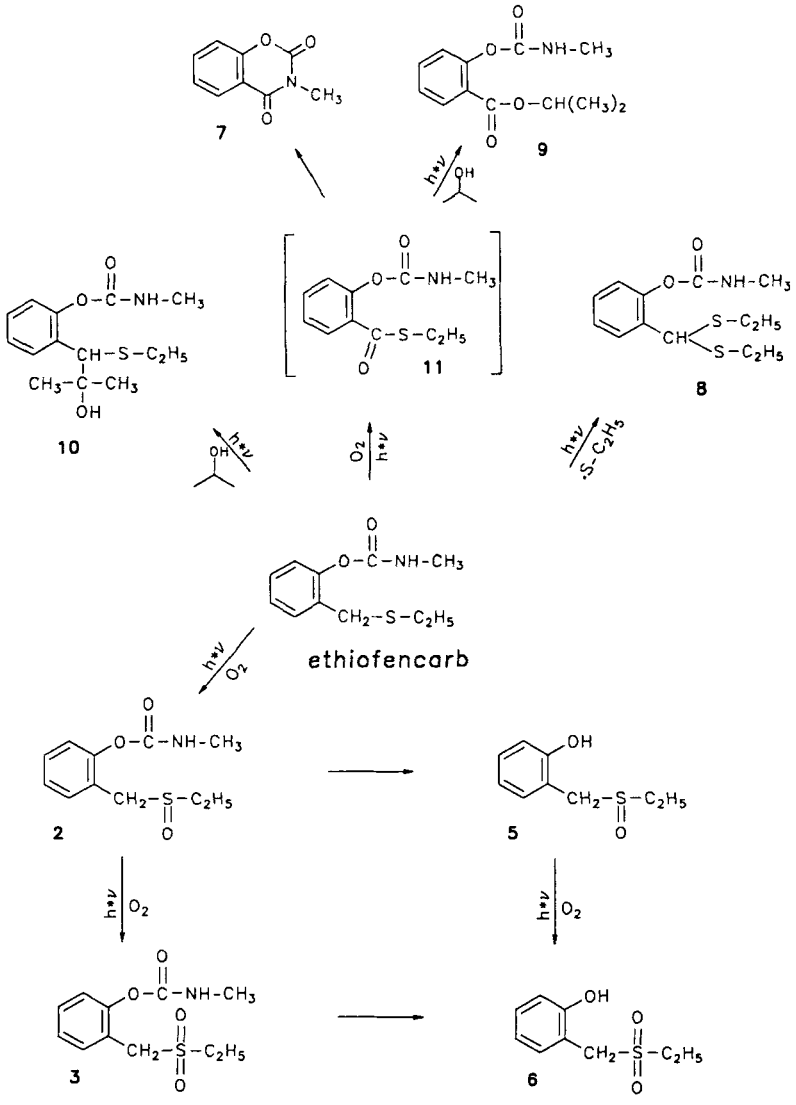

Fig. 3. Photodegradation pathways of ethiofencarb in the presence of isopropanol (1 mg ml^{-1}, WG 295): **2** ethiofencarbsulfoxide; **3** ethiofencarbsulfone; **5** 2-(ethylsulfinylmethyl)phenol; **6** 2-(ethylsulfonylmethyl)phenol; **7** 3,4-dihydro-3-methyl-1,3-benzoxazine-2,4-dione; **8** 2-[bis(ethylthio)methyl]phenylmethylcarbamate; **9** 2-(isopropoxycarbonyl)phenylmethylcarbamate; **10** 2-(1-ethylthio-2-methyl-2-hydroxypropyl)phenylmethylcarbamate; **11** 2-(ethylthiocarbonyl)phenyl methylcarbamate.

sulfonylmethylphenyl methylcarbamate (**3**, ethiofencarbsulfone) and 3,4-dihydro-3-methyl-1,3-benzoxazine-2,4-dione (**7**, see Fig. 2). Looking at the structure of photoproduct **7**, it seems likely that the methylene group situated at the phenyl ring of ethiofencarb is first oxidized, followed by nucleophilic substitution of the thioethyl moiety by the carbamate-N, forming the cyclization product. As long as ethiofencarb was detectable by HPLC the formation of **7** did not exceed 3·5% of the degraded ethiofencarb. After 5 h, when ethiofencarb was nearly completely degraded, the photoproduct ethiofencarbsulfoxide **2** began to decompose and the concentration of **7** increased to about 7% within one hour. During the entire irradiation period ethiofencarbsulfone was only detected as a trace component.

In order to study whether the cyclic product **7** was a degradation product of the main photoproduct, ethiofencarbsulfoxide (**2**) was also irradiated ($\lambda > 280$ nm) in the presence of cyclohexane. Within 2 h, **2** was almost completely degraded, forming strongly polar unidentified photoproducts. Compounds **3** and **7** were detected as trace components. Consequently, the ethiofencarbsulfoxide primarily formed during the irradiation of ethiofencarb is not in the long term photostable, and is not a special precursor of **7**.

On irradiation of ethiofencarb in the presence of cyclohexane at $\lambda > 302$ nm as well as in natural sunlight, the same photoproducts were obtained as at $\lambda > 280$ nm, but their concentrations were different. With the decreasing energy of the light source, the photoproducts become more stable. In sunlight, the ethiofencarb degradation was 95% after seven days, when 65·7% was oxidized to the corresponding sulfoxide (**2**) and 12·7% of the cyclic photoproduct **7** was

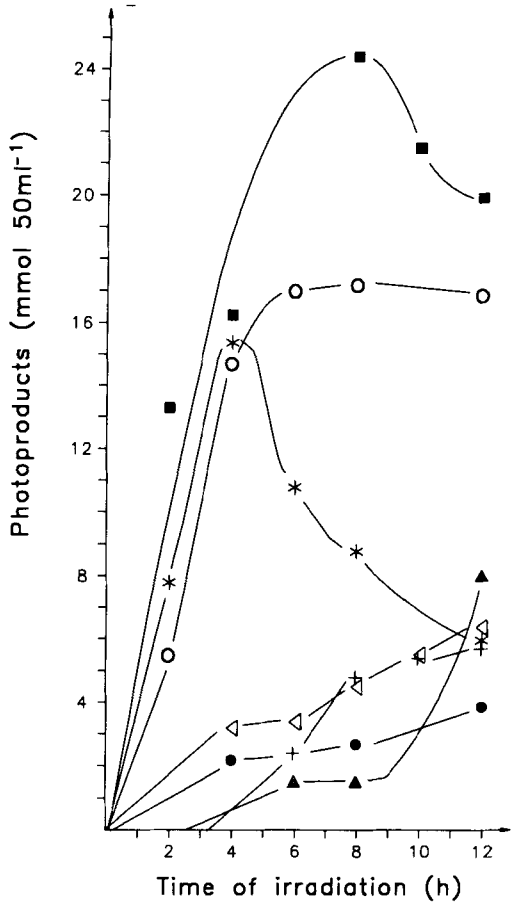

Fig. 4. Concentration of photoproducts produced during the irradiation of ethiofencarb in isopropanol (4·44 mmol ml^{-1}, WG 295). (■) **2**; (○) **10**; (*) **8**; (▲) **9**; (△) **6**; (+) **3**; (●) **5**.

formed, both percentages based on the degraded ethiofencarb. This was the highest yield of these photoproducts during our investigations. Again the corresponding sulfone (**3**) was detected as a trace component.

In contrast to the experiments with cyclohexane as solvent, irradiation of ethiofencarb in isopropanol yielded a complex mixture of photoproducts. Most of the products could be identified. By means of co-chromatography with known products and synthesized standards, ethiofencarbsulfoxide (**2**), ethiofencarbsulfone (**3**) and their corresponding phenols **5** and **6** were established as part of the mixture (Fig. 3). For the first time in our investigations the cleavage of the carbamate moiety was detected to a greater extent, but not starting from the parent compound ethiofencarb. After an irradiation time of 8 h ethiofencarbsulfoxide (**2**) reached its maximum concentration at 16% of the photodegraded ethiofencarb. The concentrations of ethiofencarbsulfone (**3**) and the phenols **5** and **6** did not exceed 3·5% based on degraded ethiofencarb.

Identification of the other photoproducts was complicated by their instability during isolation, and the difficulty of obtaining pure substances. Freeze-drying of the irradiation mixtures was a gentle isolation method to minimize these problems. Eventually three further photodegradation products could be identified. Figure 3 presents the photodegradation pathway of ethiofencarb in the presence of isopropanol. Beside photo-oxidation and hydrolysis the solvent molecule was involved in photodegradation of ethiofencarb forming the addition products **9** and **10**. The cyclic photoproduct **7** found in irradiation mixtures of ethiofencarb in cyclohexane was detected as well, though as a trace component. One can conclude that starting from 2-ethylthiocarbonylphenyl methylcarbamate (**11**, Fig. 3) the carbamate-N was competing with isopropanol for the nucleophilic substitution of the thioethyl moiety. The reaction with isopropanol was faster by far, because up to 4·4% of photoproduct **9** (based on degraded ethiofencarb) was formed. Compound **11** could not be isolated or identified in the irradiation mixtures. Ethiofencarbsulfoxide

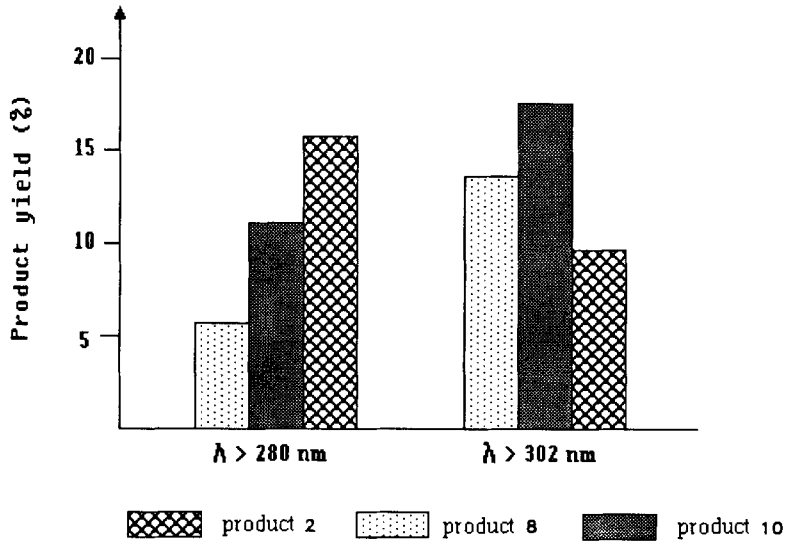

Fig. 5. Yields (based on the degraded ethiofencarb) of the photoproducts **2**, **8** and **10**, on irradiation of ethiofencarb in isopropanol, using filters WG 295 ($\lambda > 280$ nm) and WG 320 ($\lambda > 302$ nm).

(**2**) and the second photoaddition product, **10**, were main products. Up to 14% of degraded ethiofencarb was converted to product **10**.

Furthermore 2-[bis(ethylthio)methyl]phenylmethylcarbamate (**8**, Fig. 3) was isolated from the isopropanolic irradiation mixture. The concentration of **8** (up to 8·9% analysed by HPLC) was almost of the same order as that of the main products **2** and **10** and could not be disregarded. However this curious product **8** was formed, the structural analyses clearly proved that there is a second thioethyl substituent on the methine group and that nothing else is changed in comparison to the ethiofencarb molecule.

It is important to note that after an irradiation time of about 6 h the main photoproducts **2**, **8** and **10** were further photodegraded, as shown in Fig. 4. At this time ethiofencarb was degraded by about 50%.

On irradiation of ethiofencarb in the presence of isopropanol at $\lambda > 302$ nm, great changes in the ratio of the main products (Fig. 5) were established. Photooxidation reactions decreased and the photoaddition product **10** became the main product. Surprisingly the product spectrum resulting from irradiation of ethiofencarb in the presence of isopropanol in natural sunlight was completely different from that in the artificial light. Using sunlight, nearly 100% of the degraded ethiofencarb was oxidized to ethiofencarbsulfoxide (**2**). After seven days of irradiation the photoproducts **3**, **6**, **7** and **10** were detected, but only to a small extent. The reason for this could not be clarified. These results were in sharp conflict with our investigations with the carbamate insecticide pirimicarb and the behaviour of ethiofencarb when irradiated in the presence of cyclohexane, where the data obtained from different light sources correlated well.

4 CONCLUSIONS

The photochemical behaviour of ethiofencarb was extensively explored using different solvents as our first model stage.[7] The predominant reactions are photooxidation to yield the corresponding sulfoxide **2**. To a lower extent, the new cyclization product **7** is a result of oxidation of the benzylic position. Under the same conditions, the carbamate group is rather photostable.

The formation of photoproducts **9** and **10** containing the bound isopropanol moiety from the isopropanol solvent is an indication of the possible formation of bound residues in plant cuticles if hydroxy fatty acids or waxy alcohols were to replace isopropanol in such reaction pathways.

As expected, ethiofencarb also undergoes photooxidation reactions in sunlight, but the half-lives of the photoproducts are longer than when a UV lamp is used. The change in product distribution, which, especially in isopropanol was partly due to the change of the source of irradiation, cannot only be attributed to the decrease in the energy of irradiation. Therefore, it is equally important to check the relevance of the solvent experiments before extrapolating these studies to the reaction processes on leaf and fruit surfaces. In experiments on apple fruits, for example, ethiofencarbsulfoxide was the main product in each case.[8] A detailed report of the results on plant surfaces and further cuticle model systems[7] will be the subject of a forthcoming publication.

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