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Original Article

Photodegradation of Fenothiocarb on Silica Gel Plate Exposed to Sunlight

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The photodegradation of ^{14}C-fenothiocarb [*S*-(4-phenoxy-U-^{14}C)butyl *N*,*N*-dimethylthiocarbamate] on a silica gel plate exposed to sunlight was studied. Radioactivity on the plate dissipated slowly with time. After 72 hr exposure (Sept. to Oct.), 34% of fenothiocarb remained, and its half-life was estimated as approximately 45 hr. Twelve photodegradation products were detected by two-dimensional thin-layer chromatography. Among twelve, products identified were *S*-4-phenoxybutyl *N*-formyl-*N*-methylthiocarbamate, *S*-4-phenoxybutyl *N*-methylthiocarbamate, bis(4-phenoxybutyl)thiolsulfinate, bis(4-phenoxybutyl)thiolsulfonate, fenothiocarb sulfoxide and 4-phenoxybutylsulfonic acid. A primary photochemical reaction seems to be the oxidation of sulfur to form fenothiocarb sulfoxide, followed by the cleavage of ester linkage and the oxidation or the dimerization of 4-phenoxybutylsulfenic acid intermediate. Moreover, the oxidation of *N*-methyl moiety of fenothiocarb is suggested as the second photochemical reaction of fenothiocarb.

INTRODUCTION

Fenothiocarb (*S*-4-phenoxybutyl *N*,*N*-dimethylthiocarbamate) is a thiocarbamate-type acaricide which has highly ovicidal and larvicidal activities to citrus red mite *Panonychus citri* MCGREGOR.[1,2] Its biotransformation in soils,[3,4] orange trees,[5] and citrus red mites[6] has been studied. In the present study, the photodegradation of fenothiocarb on the silica gel plate exposed to sunlight was investigated using ^{14}C-fenothiocarb.

MATERIALS AND METHODS

1. Chemicals

^{14}C-Fenothiocarb labeled uniformly at the phenyl ring was synthesized from [U-^{14}C]-phenol[4] for this study. The specific activity was 3.04 mCi/mmol and the radiochemical purity was more than 99% by thin-layer chromatography (TLC). Table 1 shows *Rf* values of the authentic compounds used for the identification of photodegradation products of fenothiocarb. These compounds were synthesized in our laboratory, or supplied by KI Research Institute Co., Ltd. Their chemical structures were confirmed by IR, PMR and MS spectrometry. The spots of unlabeled compounds were visualized under UV ray (254 nm).

2. Exposure to Sunlight of ^{14}C-Fenothiocarb on Silica Gel Plates

^{14}C-Fenothiocarb (11.99 μg, 0.144 μCi) in a 100 μl acetone solution was spotted to the origin (2 cm from the corner, Fig. 1) of silica gel plates (20×20 cm in size and 0.25 mm thick, 60F_{254}, Merck), and exposed to sunlight for 72 hr from the middle of September to the end of October, corresponding to the season for application of fenothiocarb to the citrus red mites. The plates were exposed to

Table 1 Chemical names, designations, TLC solvent systems and *Rf* values for authentic compounds and ^{14}C-photodegradation products.

Chemical names	Designations	*Rf* values in indicated solvent systems[a] A	B	C	D	E	F
bis(4-Phenoxybutyl)thiolsulfonate	(4-PB)$_2$-SO$_2$-S-	0.70	0.52	—	—	—	—
S-4-Phenoxybutyl *N*-formyl-*N*-methylthiocarbamate	*N*-CHO-FC	0.69	0.47	0.49	0.89	0.97	0.85
S-4-Phenoxybutyl *N*,*N*-dimetylthiocarbamate	FC	0.64	0.36	0.39	0.85	0.95	0.81
bis(4-Phenoxybutyl)thiolsulfinate	(4-PB)$_2$-S(O)-S-	0.63	0.24	0.28	0.85	0.95	0.86
S-4-Phenoxybutyl *N*-methylthiocarbamate	Desmethyl-FC	0.58	0.28	0.33	0.86	0.96	0.84
S-4-Phenoxybutyl *N*,*N*-dimethylthiocarbamate sulfoxide	FC sulfoxide	0.19	0.01	0.01	0.36	0.53	0.38
4-Phenoxybutylsulfonic acid	4-PB-SO$_3$H	Origin	Origin	Origin	0.20	0.17	0.35
	Unknown X	0.43	0.07	—	—	—	—
Unidentified photoproducts	Unknowns Y	Origin	Origin	—	—	0.57–0.73	—
	Unknown Z	Origin	Origin	—	—	Origin	—

[a] Composition of TLC solvent systems (v/v, %): A, acetone–dichloromethane (1 : 7); B, ethyl acetate–benzene (1 : 9); C, ethyl acetate–*n*-hexane (2 : 3); D, acetic acid–methanol–ethyl acetate (1 : 1 : 10); E, formic acid–water–ethyl acetate (1 : 1 : 14); F, acetic acid–water–*n*-butanol (1 : 1 : 6).

sunlight only on sunny days. After exposure, the plates were covered with glass plates and stored in a cold room (5°C) in the dark to minimize the loss of fenothiocarb and its degradation products. The photodegradation products were analyzed 9, 18, 36 and 72 hr after exposure to sunlight. The plates exposed to sunlight with definite intervals were developed with the authentic compounds in two-dimensions using solvent systems A (vertical) and B (horizontal). The plates below *Rf* value 0.25 (solvent system A) were cut off and developed again horizontally with solvent system E to separate polar photodegradation products (Fig. 1).

3. *Radioassay*

Photodegradation products on plates were detected by autoradiography using Fuji X-ray film. The radioactive spots on the plates were scraped off into vials containing 1 ml methanol–water (1 : 1) and 10 ml scintillator (Scintisol® EX-H, Dojindo Laboratories). Radioactivity measurement was conducted by a liquid scintillation spectrometer (Aloka 673).

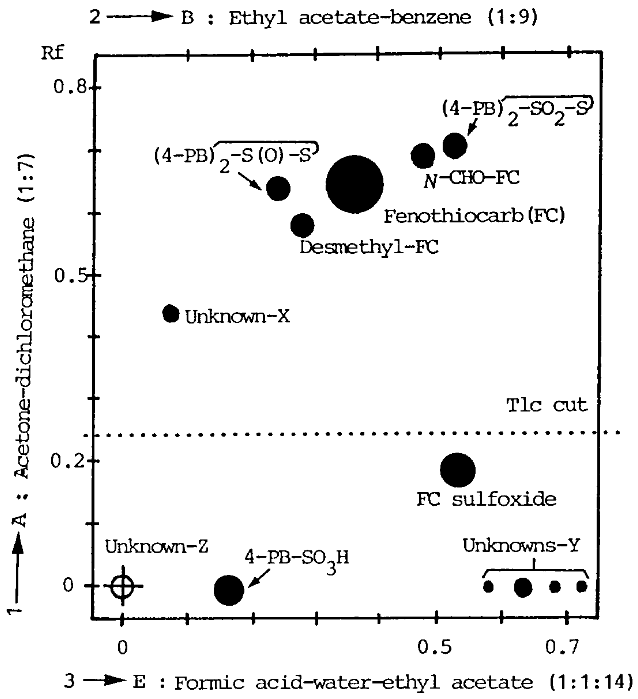

Fig. 1 Thin-layer chromatogram of photodegradation products by sunlight.

Table 2 Degradation of ^{14}C-fenothiocarb on a silica gel plate exposed to sunlight.

^{14}C-Compounds	% of the applied radiocarbon (hr)			
	9	18	36	72
Fenothiocarb (FC)	86.02	76.84	58.30	34.22
N-CHO-FC	0.21	0.30	0.51	0.63
Desmethyl-FC	0.32	0.47	0.38	0.49
(4-PB)$_2$-SO$_2$-S-	0.36	0.47	0.52	1.09
(4-PB)$_2$-S(O)-S-	0.85	1.04	0.98	1.13
FC sulfoxide	1.16	1.75	4.02	3.55
4-PB-SO$_3$H	3.97	7.84	13.96	25.54
Unknown X (non-polar)	0.43	0.65	0.87	1.27
Unknowns Y (polar)	0.88	1.51	2.53	3.93
Unknown Z (TLC origin)	1.02	1.90	2.93	5.08
Recovered radiocarbon	95.22	92.77	85.00	76.93

RESULTS

1. *Photodegradation of Fenothiocarb by Sunlight*

Table 2 shows the time-course of dissipation for fenothiocarb and its photodegradation products. About 77% of the applied radioactivity was recovered after 72 hr exposure to sunlight, and about 34% of the applied radioactivity remained as fenothiocarb. The half-life of disappearance, estimated by the graphical method, was 45 hr, and the appearance of photodegradation products changed with exposure time.

2. *Photodegradation Products of Fenothiocarb*

As shown in Fig. 1, thirteen spots were detected by two-dimensional TLC. Seven of them were separated by solvent systems A and B, and other 5 spots with high polarity were separated by solvent system E. Fenothiocarb was found as a main component of the radioactivity, and *S*-4-phenoxybutyl *N*-formyl-*N*-methylthiocarbamate, *S*-4-phenoxybutyl *N*-methylthiocarbamate, bis(4-phenoxybutyl)thiolsulfinate, bis(4-phenoxybutyl)thiolsulfonate, fenothiocarb sulfoxide and 4-phenoxybutylsulfonic acid were tentatively identified as photodegradation products. The latter two compounds were dominant photodegradation products. The spot located at the origin was probably of polymerized products, the amount of which increased with time.

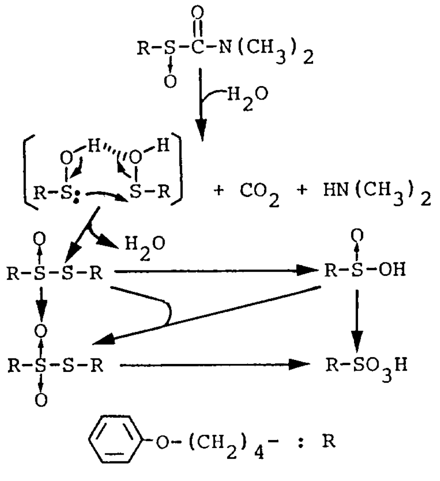

Fig. 2 Reactions of fenothiocarb sulfoxide *via* 4-phenoxybutylsulfenic acid intermediate.

DISCUSSION

As shown in Table 2, major photodegradation products, fenothiocarb sulfoxide and 4-phenoxybutylsulfonic acid gradually increased during 36 hr exposure. The appearance of the two products was parallel during 36 hr exposure to sunlight, suggesting the possibility of a sequential degradation of fenothiocarb *via* fenothiocarb sulfoxide. Thiocarbamate sulfoxides are well known photoproducts[7-9] and also primary metabolites[10,11] of thiocarbamates in biological systems. The presence of bis(4-phenoxybutyl)thiolsulfinate and its sulfone in the photodegradation products might result from the dimerization of 4-phenoxybutylsulfenic acid as shown in Fig. 2. Fenothio-

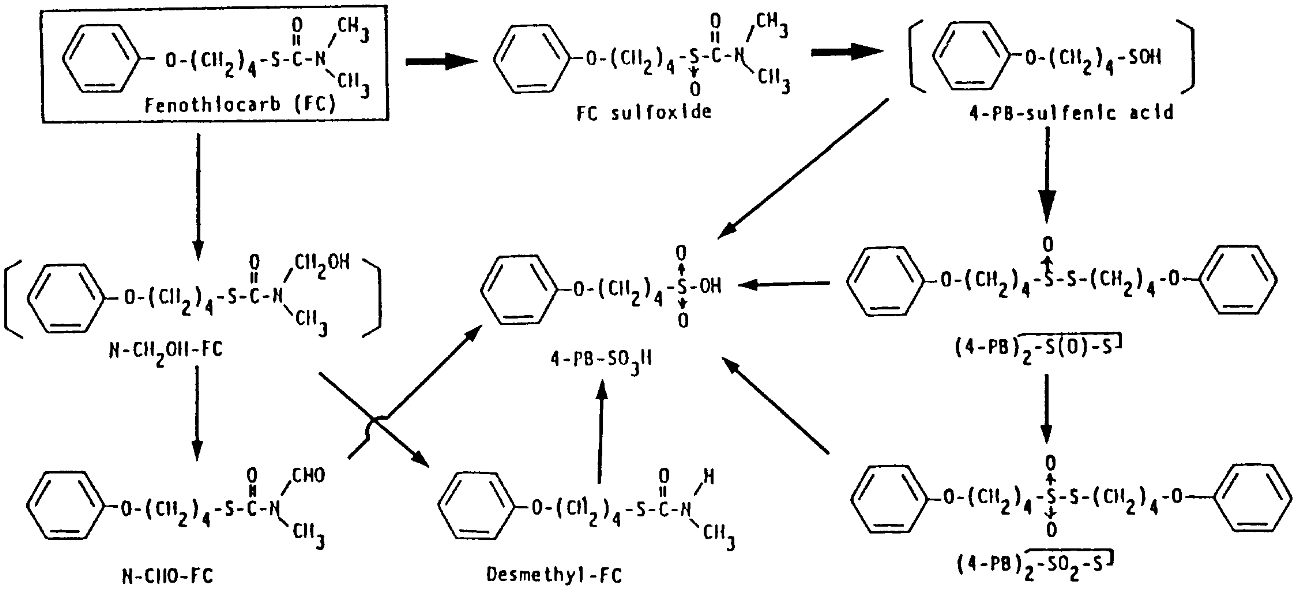

Fig. 3 Proposed photodegradation pathways of fenothiocarb on silica gel plate exposed to sunlight.

carb sulfoxide was readily hydrolyzed to form 4-phenoxybutylsulfenic acid and *N*,*N*-dimethylcarbamic acid, the latter of which was probably decomposed to dimethylamine and carbon dioxide.[12] The sulfenic acid is a very reactive intermediate forming thiolsulfinate by the dehydration reaction.[12-14] A part of the 4-phenoxybutylsulfenic acid is probably oxidized to form 4-phenoxybutylsulfinic acid. It was possible that these reactive intermediates reacted through a scrambling process[13] to form bis(4-phenoxybutyl)thiolsulfonate, 4-phenoxybutylsulfonic acid or polymerized products. These reactions are involved in the thermal and photochemical degradation processes of carbamoyl sulfoxides[12] and alkyl thiolsulfinates.[13]

S-4-Phenoxybutyl *N*-formyl-*N*-methylthiocarbamate and *S*-4-phenoxybutyl *N*-methylthiocarbamate were found as minor photodegradation products, indicating that the *N*-methyl moiety of fenothiocarb was another site of oxidative photodegradation. The *N*-alkyl oxidation and *N*-dealkylation are well known processes of photodegradation for substituted urea[15-17] or substituted benzylthiocarbamate[8,9] herbicides.

Photodegradation pathways of fenothiocarb on silica gel plates exposed to sunlight can be proposed as shown in Fig. 3.

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REFERENCES

1) H. Ogawa, T. Hirano, Y. Moriichi, T. Miyaki, H. Koyasu, H. Shimizu, K. Fujimori & M. Tamaru: Abstr. 16th Int. Congr. Entomol., p. 420, 1980
2) H. Ogawa, T. Miyaki, M. Tamaru & K. Fujimori: *Appl. Entomol. Zool.* **16**, 335 (1981)
3) T. Unai & C. Tomizawa: Abstr. 5th Int. Congr. Pestic. Chem. (IUPAC), Vd-10, 1982
4) T. Unai & C. Tomizawa: *J. Pesticide Sci.* **11**, 335 (1986)
5) T. Unai & M. Tamaru & C. Tomizawa: *J. Pesticide Sci.* **11**, 347 (1986)
6) T. Unai & C. Tomizawa: *Appl. Entomol. Zool.* **21**, 283 (1986)
7) J. E. Casida, E. C. Kimmel, H. Ohkawa & R. Ohkawa: *Pestic. Biochem. Physiol.* **5**, 1 (1975)
8) K. Ishikawa, Y. Nakamura & S. Kuwatsuka: *J. Pesticide Sci.* **2**, 17 (1977)
9) W. M. Draper & D. G. Crosby: *J. Agric. Food Chem.* **29**, 699 (1981)
10) J. E. Casida, R. A. Gray & H. Tilles: *Science* **184**, 573 (1974)
11) R. Santi & F. Gozzo: *J. Agric. Food Chem.* **24**, 1229 (1976)

12) F. Gozzo, M. Masoero, R. Santi, G. Galluzzi & D. H. R. Barton: *Chem. Ind.* **1975**, 221

13) E. Block & J. O'Connor: *J. Am. Chem. Soc.* **96**, 3929 (1974)

14) D. H. R. Barton, D. P. Manly & D. A. Widdowson: *J. Chem. Soc. Perkin I*, **1975**, 1568

15) F. S. Tanaka, R. G. Wien & R. G. Zaylskie: *J. Agric. Food Chem.* **25**, 1068 (1977)

16) F. S. Tanaka, R. G. Wien & E. R. Mansager: *J. Agric. Food Chem.* **27**, 774 (1979)

17) F. S. Tanaka, R. G. Wien & E. R. Mansager: *Pestic. Sci.* **13**, 287 (1982)

要約

Fenothiocarbの太陽光によるシリカゲル板上での光分解

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^{14}C-フェノチオカルブの太陽光による分解を検討した．フェノチオカルブをシリカゲル板上で72時間太陽光に照射した場合，親化合物は34% 残存し，半減期は約45時間と推定された．12個の光分解物が検出され，同定された化合物は，*S*-4-phenoxybutyl *N*-formyl-*N*-methylthiocarbamate, *S*-4-phenoxybutyl *N*-methylthiocarbamate, bis(4-phenoxybutyl)thiolsulfinate, bis(4-phenoxybutyl) thiolsulfonate, fenothiocarb sulfoxide および 4-phenoxybutylsulfonic acid であった．フェノチオカルブの第一の分解部位は分子中のイオウ原子の酸化反応によるスルホキシドの生成で，次いで本化合物から形成される 4-phenoxybutylsulfenic acid 中間体の酸化や2量化反応が起こることが想定された．第二の分解部位は *N*-methyl 基の酸化反応と考えられた．