during the field study and as interpreter is acknowledged.

Registry No. Captan, 133-06-2; benomyl, 17804-35-2.

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COMMUNICATIONS

Involvement of Oxygen in the Photoreactions of Cypermethrin and Other Halogenated Pyrethroids

Photolysis of cypermethrin and fenpyrithrin in alcohols, aqueous acetonitrile, and sodium dodecyl sulfate micelles results in isomerization and ester and oxidative cleavage reactions. The nature of the products obtained is dependent on the availability of oxygen and on the solvent used. Similar products are obtained from these pyrethroids and from deltamethrin in alcohol solvents. Oxygen is incorporated into both acid and alcohol moieties upon cleavage. Fenpyrithrin is more photoreactive than cypermethrin in degassed and oxygenated methanol solutions.

Pyrethroid insecticides photodecompose readily in a variety of systems yielding complex mixtures (Ruzo, 1982a; Miyamoto, 1981). The dihalovinylcyclopropanecarboxylates primarily undergo isomerization, reductive dehalogenation, decarboxylation, and especially ester cleavage processes (Ruzo, 1982b), while the chrysanthemates are extensively oxidized (Ruzo, 1982c). Due to their lipophilicity pyrethroids in the environment are generally bound to solid particles (Graham-Bryce, 1980) or combined with organic matter, e.g., on surface slicks of lakes. This report uses two pyrethroids not previously emphasized, cypermethrin (1, Y = C) and fenpyrithrin (1, Y = N) (Figure 1), to consider the origin of 3-phenoxybenzoyl cyanide obtained from deltamethrin (Ruzo et al., 1977) and fenvalerate (Holmstead et al., 1978b), reasons why the characterized mass balance is in general lower for the acid than the alcohol moiety, and the reaction rates and product distribution of *cis*-cypermethrin photolyzed in aqueous acetonitrile vs. micellar solutions.

MATERIALS AND METHODS

Chemicals. Structures and designations of the compounds used are shown in Figure 1. Sources for the pyrethroids and other chemicals are as follows: *cis*- and *trans*-cypermethrin were gifts of Roussel-Uclaf (Paris, France); *cis*- and *trans*-fenpyrithrin were supplied by Dow Chemical Co. (Walnut Creek, CA). Other pyrethroids and degradation products were obtained from sources previously reported (Ruzo and Casida, 1982; Ruzo et al., 1977). Sodium dodecyl sulfate ($NaDodSO_4$, Sigma) was recrystallized from ethanol, while tri-*tert*-butylphenol (TTBP, Aldrich) and dimethylfuran (DMF, Aldrich) were used as received.

Analyses. Thin-layer chromatography (TLC) was carried out as previously reported (Ruzo and Casida, 1982). Gas chromatography–chemical ionization mass spectrometry (GLC–CI-MS) utilized a Finnigan 3200 instrument equipped with 5% OV-101 or OV-25 columns operated with temperature programming (120–240 °C, 6 °C/min) and methane (0.8 torr) as the carrier and ionization gas.

Nuclear magnetic resonance (NMR) was conducted at 250 MHz in benzene-d_6. Fourier-transform infrared spectroscopy (FT-IR) was carried out on KBr micropellets by courtesy of Shell Development Co., Modesto, CA. Ultraviolet spectroscopy utilized a Perkin-Elmer 576 ST spectrophotometer.

Photolysis Procedures. The pyrethroids were irradiated at $\lambda > 290$ nm (Pyrex) in a Rayonette Reactor (The Southern New England Ultraviolet Co., Middletown, CT) equipped with RPR 3000 lamps. Pyrethroid concentra-

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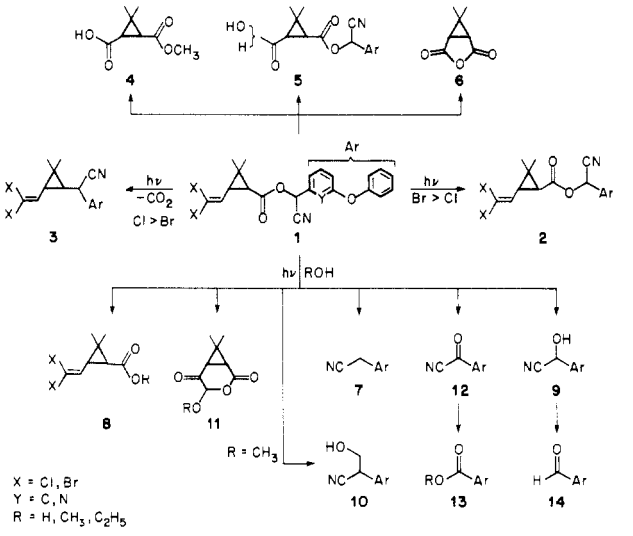


Figure 1. Solution photodecomposition of the α-cyano-3-phenoxybenzyl pyrethroids cypermethrin (X = Cl, Y = C), fenpyrithrin (X = Cl, Y = N), and deltamethrin (X = Br, Y = C).

Table I. UV Characteristics of Cypermethrin and Fenpyrithrin in Protic Solvents

	methanol		aqueous acetonitrile		$NaDodSO_4$	
	λ, nm	ε, M^{-1} cm^{-1}	λ, nm	ε, M^{-1} cm^{-1}	λ, nm	ε, M^{-1} cm^{-1}
cypermethrin	208	32 000	200	56 000	196	68 000
	279	1 700	279	2 500	277	1 500
fenpyrithrin	212	21 000	197	55 000	197	49 000
	277	5 100	277	5 700	277	4 700

tions were as follows: 10^{-3} M in methanol and ethanol; 10^{-5} M in 1:1 acetonitrile–water or in 10^{-2} M $NaDodSO_4$ in water. The solutions were either saturated with argon after degassing (freeze–pump–thaw) or continuously flushed with oxygen during irradiation. Additives (TTBP or DMF) were 10^{-2} M in the alcohol solutions. Singlet oxygen was generated in methanol by Rose Bengal sensitization.

Photolysates were inspected at ~10 and 70% conversion by GLC–CI-MS and TLC before and after methylation (diazomethane) or acetylation (acetic anhydride, pyridine). Reactivity comparisons were done at early irradiation times. Product yields were estimated by comparison of GLC areas with standards of similar retention times.

RESULTS AND DISCUSSION

Ultraviolet Spectroscopy. The effect of the solution media on the UV spectra of cypermethrin (**1C**) and fenpyrithrin (**1N**) is shown in Table I. The λ_{max} (π–π^*) is shifted to shorter wavelength in water relative to methanol for both compounds and the extinction coefficient is increased. The position of the shoulder band (n–π^*) at >270 nm is not affected significantly but its absorptivity is somewhat greater in aqueous acetonitrile than in $NaDodSO_4$ or methanol solution. The extinction coefficients at 300 nm for cypermethrin (830 M^{-1} cm^{-1}) and fenpyrithrin (13 000 M^{-1} cm^{-1}) reflect the influence of the n–π^* interaction due to the heteroatom.

Reactivity. Cypermethrin (**1C**) reacts at similar rates (0.2 mM h^{-1}) whether the methanol solution was saturated with argon or oxygen. Fenpyrithrin (**1N**) reacts nearly 4-fold faster than cypermethrin in argon-saturated solution but only 2-fold faster in oxygenated methanol. No significant rate differences were obtained with the cis and trans isomers. The higher reactivity of fenpyrithrin is probably caused by greater absorptivity and the observed oxygen quenching may indicate longer lived excited states. When cypermethrin photodecomposition rates are examined in oxygenated aqueous acetonitrile compared with those in the $NaDodSO_4$ solution, no significant difference is observed from those in methanol, and the same cis/trans ratios are obtained. However, the products arising from ester cleavage are quite different. These results suggest that oxygen is more likely to intervene in the reactive intermediate when the substrate is accessible than when it is enclosed in the micellar hydrophobic chains.

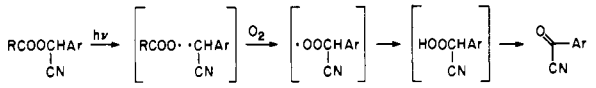
Photoproducts. As with other pyrethroids, cypermethrin and fenpyrithrin undergo efficient cis/trans isomerization (**2**) and ester cleavage reactions (Figure 1) including that leading to decarboxylation. Relative to deltamethrin there is negligible reductive dehalogenation observed. Decarboxylation is a more important process for the dichlorovinyl compounds (~10%) than for deltamethrin [~4% (Ruzo et al., 1977)], presumably because of the greater reactivity of the latter in other types of processes. Decarboxylated materials (**3**) are obtained as isomeric mixtures of four products, i.e., from the cis and trans isomers. The yield of these is substantially decreased in oxygenated solution. This observation is consistent with the radical pair mechanism established by ESR (Mikami and Miyamoto, 1982). In analogy with permethrin (Ruzo and Casida, 1982) some oxidative cleavage of the halogenated side chain is observed with **1C** and **1N** (combined yields of compounds **4**–**6** is ~10%).

We have previously reported a variety of products arising from deltamethrin (Ruzo et al., 1977) and permethrin (Holmstead et al., 1978a) detected at high conversion (>50% reaction) of the pyrethroid. However, the identified photoproducts originating from the acid moiety fell short of accounting for reacted material. In order to determine the fate of this group, the reaction was carried out to <10% conversion with oxygenated and argon-saturated solutions of *cis*- and *trans*-cypermethrin and -fenpyrithrin.

In the absence of oxygen the major ester cleavage products (Figure 1) are 3-phenoxybenzyl cyanide (**7**, ~75%) and the dichlorovinyl cyclopropanecarboxylic acid (**8**, R = H, ~70%). The methyl ester (**8**, R = Me), cyanohydrin (**9**), and alcohol adduct (**10**) are also observed. However, the product distribution changes quite drastically when oxygen is introduced. In this case the major acid moiety product is the ketolactone (**11**, 50–60%) (Figure 1). Analogous compounds are obtained in methanol, ethanol, and acetonitrile–water solutions but not in the presence of micelles. The product **11** (R = Me) is obtained on methylation (CH_2N_2) of the aqueous photolysate (**11**, R = H). **11** (R = Me) is tentatively characterized by spectroscopy: CI-MS *m/z* (rel intensity) 213 [$(M + 29)^+$, 11], 185 [$(M + 1)^+$, 80], 153 [$(M - OCH_3)^+$, 100], 141 (10), 139 (10), 127 (20), 125 (20), 109 [$(M - OCH_3 - CO_2)^+$, 35]; NMR δ 0.40 (CH_3, s), 0.68 (CH_3, s), 1.47 (CH–CH, br s), 3.26 (CH_3O, s), 4.17 (HCO, s); IR 1700 (CO), 1743 (COO), 2850 (OCH_3), 1163 cm^{-1} (C–O–C).

The mechanism for formation of **11** must involve reaction of the original carboxylate radical with oxygen since the presence of hydrogen donors (TTBP or micelles) and an oxygen trap (DMF) inhibit its formation and yield instead the acid **8** (R = H). Several further steps are then required, presumably via cyclization and nucleophilic attack by solvent. In any case, **11** is unstable and is not detected after prolonged irradiation. An identical product is obtained from deltamethrin and permethrin. On irradiation the trans isomers of cypermethrin and fenpyrithrin do not produce **11** in oxygenated methanol, yielding caronic acid derivative **4** instead.

Photolysis of rigidly deoxygenated alcohol solutions does not produce the benzoyl cyanide 12, establishing that the oxygen source is external and negating our previously proposed mechanism (Ruzo et al., 1977). However, 12 and its degradation products (13) are observed even in the presence of trace amounts of oxygen. Thus, a likely pathway for formation of 12 involves a hydroperoxide as



shown in the scheme above. The phenoxybenzoyl cyanide can then react with solvent to give the corresponding acid (13, R = H) or ester (13, R = Me) (Ruzo et al., 1977; Holmstead et al., 1978b).

The products resulting presumably from photonucleophilic reaction with solvent, i.e., 8 and cyanohydrin 9, form equally in the presence or absence of oxygen. The cyanohydrin could be observed directly in this study upon derivatization with acetic anhydride: CI-MS m/z (rel intensity) 268 (M + 1, 4), 241 (M – CN, 42), 208 (M – AcO, 100). 9 decomposes further to the aldehyde (14).

Micellar solutions yield simple product mixtures containing the dihalovinyl acid (8, R = H) and 3-phenoxybenzaldehyde and acid (13, R = H and 14). It appears that in close proximity to an abundant hydrogen source the carboxylate radical abstracts hydrogen readily to give the acid 8 (R = H), while the corresponding cyanobenzyl radical is longer lived and can undergo secondary reaction with oxygen to give the sequence outlined in the scheme. The 3-phenoxybenzaldehyde and part of the acid 8 (R = H) obtained must arise from nucleophilic cleavage of the ester and subsequent decomposition of the cyanohydrin (Ruzo et al., 1977).

Oxidation products are also formed by reactions in the vinyl side chain. These caronic acid derivatives (4–6) do not arise from dioxetanes formed on singlet oxygen addition since cypermethrin is unreactive to dye-generated $^1O_2$. They are more likely to form by reaction with ozone generated in solution (Ruzo and Casida, 1982).

The present results illustrate the lability of the dihalovinyl group of pyrethroids under oxidative conditions and clarify the reasons for depletion of the acid moiety and for the formation of 12, a product common to all α-cyano-3-phenoxybenzyl pyrethroid esters studied (Ruzo, 1982a).

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Inhibition of Sugar–Amine Browning by Aspartic and Glutamic Acids

The browning of lysine–glucose and lysine–fructose model systems (pH 8.0, 60 °C, 58 h) was decreased by adding L-aspartic acid or L-glutamic acid. Specially prepared potato chips darkened less when they were dipped in aspartic or glutamic acid solutions before frying.

Since Maillard (1912) first observed the darkening accompanying the reaction of sugars with amino acids, numerous publications appeared discussing the so-called nonenzymatic browning of foods (Hodge, 1953; Ellis, 1959; Shallenberger and Birch, 1975). It is now known that, besides the carbonyl–amine reaction, several other nonenzymatic reactions can lead to food browning and that some of the browning reactions may also affect the flavor and the nutritional value of foods.

In this communication, we report on the observation that L-aspartic acid and L-glutamic acid may significantly diminish the browning resulting from the interaction of an amino acid, lysine, strongly involved in food darkening, with two common food sugars, glucose and fructose. This observation was made during a larger study in which amino acids, single or in pairs, were allowed to react with glucose and fructose.

EXPERIMENTAL SECTION

The following eight groups of reaction systems were prepared by dissolving the appropriate quantities of reagents in 0.2 M phosphate buffer, pH 8.0: (a) 0.4 M D-glucose, 0.04 M L-lysine, and L-aspartic acid at seven concentrations in the range 0.00–0.04 M; (b) 0.4 M D-

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