Cypermethrin and Fenvalerate Residues in Stored Wheat and Milled Fractions

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Cypermethrin and fenvalerate were applied at 8 and 12 mg kg^{-1} to wheat of 13.3 and 15.0% moisture content. Treated wheat was stored at 25 and −5 °C for 60 weeks and sampled at six 12-week intervals. Residues were determined in wheat and milled fractions, viz., bran, middlings, and flour (endosperm). It was observed that highest amounts of insecticides were present in bran and least in endosperm. Both the insecticides degraded in treated wheat at slow rates. Half-lives of fenvalerate on grain ranged from 385.1 weeks on wheat of 13.3% moisture content stored at −5 °C to 69.3 weeks on wheat of 15% moisture content stored at 25 °C. Reduction of residues in flour through bread baking was low and 79–84% of cypermethrin and 87–88% of fenvalerate were present in bread made from flour (white and wholemeal) containing cypermethrin and fenvalerate residues.

INTRODUCTION

The development of malathion resistance in many stored product insects is threatening the usefulness of this commonly used grain protectant. The synthetic pyrethroids have shown their potential as alternate grain protectants in the few studies that have been conducted with these insecticides (Ardley and Desmarchelier, 1974; Bengston, 1978; Bengston et al., 1980; Desmarchelier et al., 1981; Bengston et al., 1983). Before a grain protectant can be tested extensively, it is necessary to study its degradation at the residue level under varying conditions.

When an insecticide is to be applied to grain, it is important to know its distribution in the intended milled fractions. Studies on cypermethrin and fenvalerate residues in the grain storage environment are very limited. Fenvalerate, along with permethrin, phenothrin, and deltamethrin have been reported to persist for very long periods on stored wheat (Nobel et al., 1982). Deltamethrin, applied to wheat of 12% moisture content, remained at the same level throughout a 15-month storage period at 25 °C (Hargreaves et al., 1982).

The aim of this study was to measure residues of cypermethrin and fenvalerate in stored wheat and its milled fractions. Insecticide residue degradation usually increases with increased moisture content and temperature (Rowlands, 1967). Therefore, the study was conducted with wheat at two moisture contents and two storage temperatures by using two levels of each of the insecticides.

MATERIALS AND METHODS

Grain Treatment and Storage. Hard red spring wheat, cultivar Neepawa, was adjusted to two moisture levels, 13.3 and 15.0%. Emulsifiable concentrate formulations of cypermethrin (40%) and fenvalerate (30%), supplied by Shell International Chemical Co., Canada, were diluted with water to contain 8.0 and 12.0 mg/mL. Two-kilogram batches of wheat were thinly spread in a tray lined with aluminum foil. Two milliliters of diluted insecticide emulsion was sprayed on wheat with a Paasche airbrush sprayer at a constant pressure of 0.52 kg/cm^2. Control samples were sprayed with 2 mL of distilled water. The treated lots were poured into 4.5-L glass jars and tumbled on a mechanical tumbler for 30 min to ensure uniform mixing of the insecticide and grain. Four such lots were treated for each insecticidal level. The lots from each treatment were mixed and divided into 350-g portions in glass jars. Samples for the 0 week analysis were taken immediately after treatment. The rest of the jars were stored in dark rooms maintained at 25 and −5 °C for subsequent sampling at 12, 24, 36, 48, and 60 weeks after treatment. At each sampling interval, one whole jar was taken from each treatment for analysis.

Grinding and Milling of Samples. Twenty-five grams of wheat from each sample was ground in a coffee grinder (GS Iona Model CG 8) and used for determination of the residues. For milling, 100 g of samples of wheat were milled on a micromill (Ottawa micromill No. 6012, Engineering Research Service, Agriculture Canada, Ottawa) to obtain bran consisting mainly of the outer layers of grain (pericarp, seed coat, and aleurone layer), middlings (germ, fine particles of bran, and coarse particles of flour), and flour (mainly endosperm). Triplicate samples from whole ground grain and milled fractions were used for analyses.

Analysis of Residues. Residues of cypermethrin and fenvalerate were determined by electron capture gas chromatography as described by Joia and Webster (1985). Five-gram samples were used for ground wheat, middlings, flour, and bread, whereas 3-g samples were used for bran in each analysis. For bread samples, 5-g of anhydrous sodium sulfate was added before extraction.

Processing of Flour. In a separate experiment, cypermethrin and fenvalerate were applied to 2-kg lots of wheat. Treated wheat was stored at 25 °C for 4 weeks. Samples were milled as described earlier to obtain white flour. Wholemeal flour was obtained by mixing the fractions obtained from milling. White bread and wholemeal bread was baked following "Remix Baking Test". The recipe used was as follows: flour 100 g, water variable, yeast 3.0 g, sugar 2.5 g, salt 1.0 g, malt syrup 0.3 g, ammonium dihydrogen phosphate 0.1 g, potassium bromate 1.5 mg. The procedure used was fermentation for 165 min at 30 °C, proof time 55 min at 30 °C, and baking for 25 min at 227 °C. The residues in flour and bread were determined following the procedure described earlier.

Calculation of Half-Lives. Half-lives of cypermethrin and fenvalerate on grain were calculated through regression analysis assuming the loss of pyrethroids follows "pseudo-first-order" kinetics, as has been shown for fenitrothion (Desmarchelier, 1978) and for deltamethrin,

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Table I. Cypermethrin and Fenvalerate Residues (mg kg^{-1}) Found on Wheat and Milled Fractions Immediately after Treatment at 8 and 12 mg kg^{-1} [a]

moisture content of wheat, %	insecticide	dosage, mg kg^{-1}	residues, mg kg^{-1}			
			whole grain[b]	bran	middlings	flour
13.3	cypermethrin	8	7.9 ± 0.6	25.5 ± 0.3	13.0 ± 0.7	0.9 ± 0.1
		12	12.7 ± 1.1	39.8 ± 1.0	21.8 ± 0.3	1.5 ± 0.2
15.0		8	7.5 ± 0.1	30.7 ± 2.1	12.1 ± 0.2	1.0 ± 0.0
		12	11.8 ± 0.1	45.3 ± 1.1	15.7 ± 0.2	1.5 ± 0.1
13.3	fenvalerate	8	8.2 ± 0.3	28.2 ± 0.6	15.1 ± 1.2	1.5 ± 0.1
		12	12.8 ± 0.7	39.7 ± 2.7	23.2 ± 3.2	2.1 ± 0.1
15.0		8	8.1 ± 0.2	27.1 ± 2.0	11.1 ± 0.7	1.1 ± 0.0
		12	12.8 ± 0.6	43.6 ± 2.1	16.0 ± 0.5	1.6 ± 0.1

[a] Mean of three replications + SD. [b] Ground wheat.

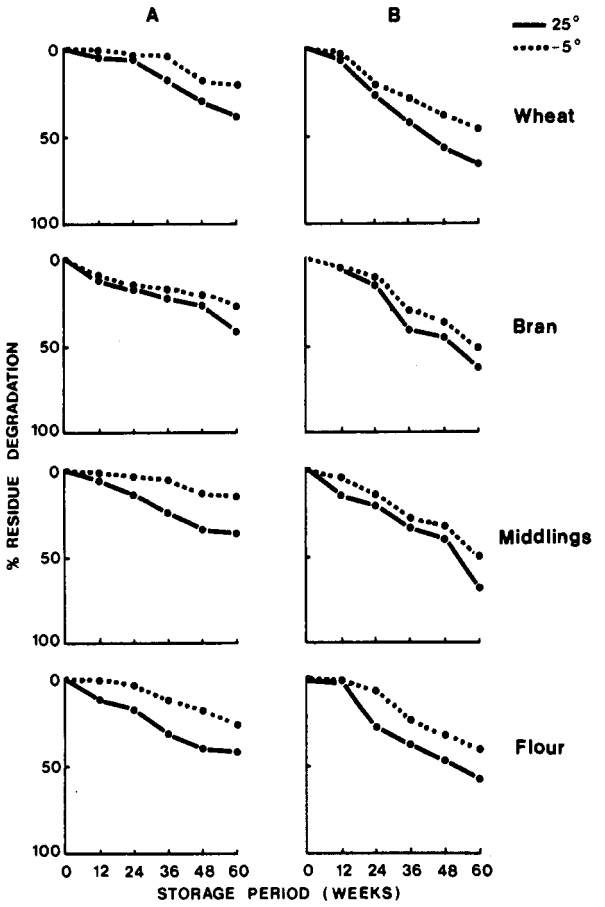

Figure 1. Percent residue degradation of cypermethrin (applied at approximately 8 mg kg^{-1}) in wheat and milled fractions during 60-week storage of wheat of 13.3 (A) and 15.0% (B) moisture content.

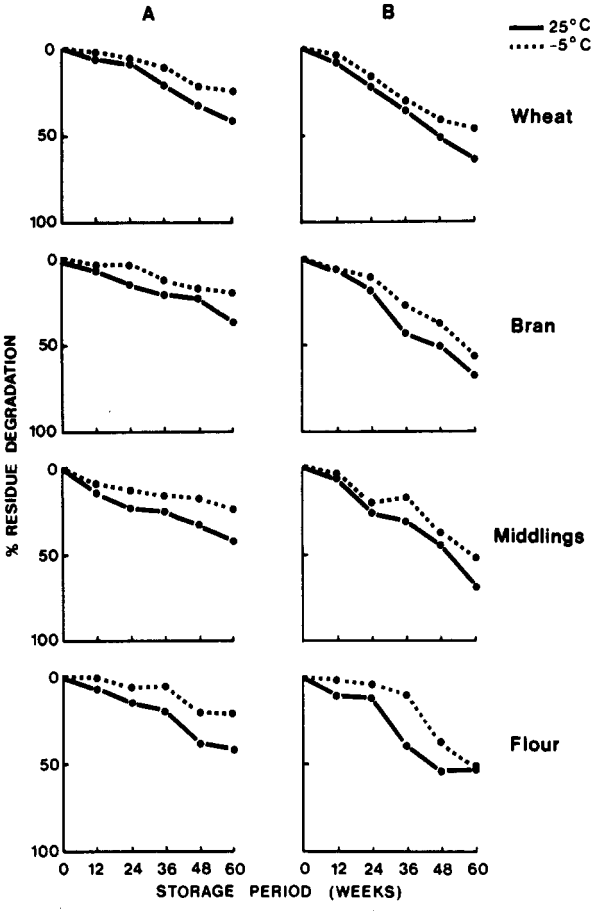

Figure 2. Percent residue degradation of cypermethrin (applied at approximately 12 mg kg^{-1}) in wheat and milled fractions during 60-week storage of wheat of 13.3 (A) and 15.0% (B) moisture content.

fenvalerate, phenothrin, and permethrin (Noble et al., 1982). Thus

$$\ln (C/C_0) = k't$$

in which C is the concentration at time t, C_0 is the concentration at time zero, and k' is the pseudo-first-order rate constant; k' depends upon the water activity (A_w).

$$k' = kA_w$$

in which k is the first-order rate constant and

$$t_{1/2} = -\left(\frac{1}{K'}\right) \ln 0.5$$

where $t_{1/2}$ is the half-life at water activity A_w.

RESULTS

Residues of Cypermethrin. Table I shows that the residues of cypermethrin on wheat of 13.3 and 15.0% moisture content immediately after treatment were close to the intended levels. Cypermethrin residues on wheat of 13.3% and 15.0% moisture content at various intervals at 25 and −5 °C are shown in Figure 1 for wheat treated at 8 mg kg^{-1} and those on wheat treated at 12 mg kg^{-1} are presented in Figure 2. On wheat of 13.3% moisture content, the residues decreased from an initial level of 7.9 mg kg^{-1} at 0 week to 4.8 mg kg^{-1} after 60 weeks at 25 °C, and to 6.3 mg kg^{-1} at −5 °C. From an initial level of 12.7 mg kg^{-1}, the residues declined to 7.4 and 9.7 mg kg^{-1} when wheat was stored at 25 and −5 °C, respectively, for the same interval of 60 weeks.

On wheat of 15.0% moisture content, the decline in cypermethrin residues was faster than at 13.3% moisture content (Figures 1 and 2). From an initial level of 7.5 mg kg^{-1}, the residues decreased to 2.5 mg kg^{-1} after 60 week storage at 25 °C and 4.1 mg kg^{-1} at −5 °C. From an initial treatment of 11.8 mg kg^{-1}, 4.2 mg kg^{-1} of cypermethrin was

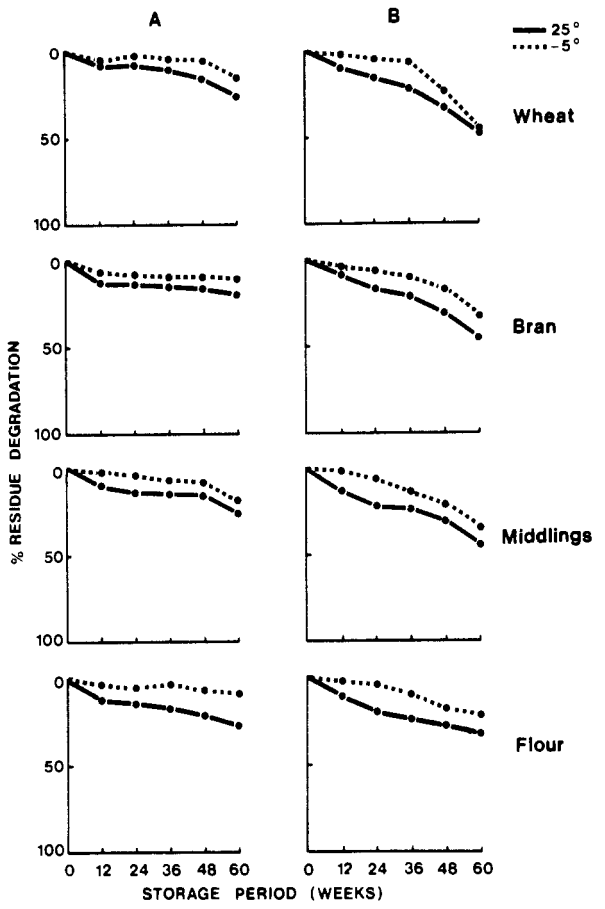

Figure 3. Percent residue degradation of fenvalerate (applied at approximately 8 mg kg^{-1}) in wheat and milled fractions during 60-week storage of wheat of 13.3 (A) and 15.0% (B) moisture content.

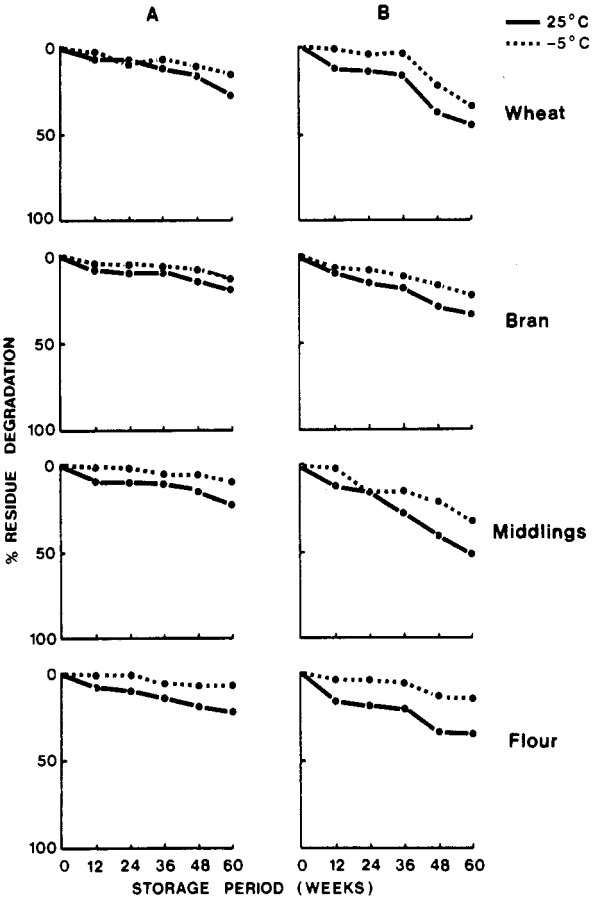

Figure 4. Percent residue degradation of fenvalerate (applied at approximately 12 mg kg^{-1}) in wheat and milled fractions during 60-week storage of wheat of 13.3 (A) and 15.0% (B) moisture content.

detected after storage for 60 weeks at 25 and 6.3 mg kg^{-1} at −5 °C.

Analysis of milled fractions of grain treated at 8 and 12 mg kg^{-1} showed maximum residues in bran followed by middlings and flour in that order (Table I and Figures 1 and 2). The residues decreased with time in all fractions, the rate being faster in 15% moisture content wheat than in 13.3% moisture content wheat samples and also more rapid at 25 than at −5 °C.

Residues of Fenvalerate. Amounts of fenvalerate present in grain immediately after treatment were in agreement with the intended dosage levels. Figures 3 and 4 show residues of fenvalerate in wheat of 13.3 and 15.0% moisture content, respectively, and its milled fractions at various posttreatment intervals. From an initial fenvalerate level of 8.2 mg kg^{-1} on wheat of 13.3% moisture content, the residues decreased to 6.1 mg kg^{-1} after 60 weeks at 25 °C and to 7.0 mg kg^{-1} at −5 °C. The level of 12.8 mg kg^{-1} fenvalerate decreased to 9.2 and 10.7 mg kg^{-1} after storage for 60 weeks at 25 and −5 °C, respectively.

The rate of decline in fenvalerate residues on 15.0% moisture content wheat was faster than on 13.3% moisture content wheat (Figure 4). Thus, from an initial level of 8.1 mg kg^{-1}, fenvalerate residues declined to 4.3 mg kg^{-1} after 60 weeks storage at 25 °C and to 4.5 mg kg^{-1} after storage for the same length of time at −5 °C. Similarly, the residues from a level of 12.81 mg kg^{-1} decreased to 6.9 and 8.4 mg kg^{-1}, after 60-weeks storage at 25 and −5 °C, respectively.

The distribution of fenvalerate residues in milled fractions followed the same pattern as that for cypermethrin. The maximum amounts were in bran followed by middlings and flour in that order (Table I, Figures 3 and 4). The percent degradation of fenvalerate residues decreased with time in wheat and each fraction, the rate being faster in 15.0% moisture content wheat than in 13.3% moisture content wheat samples and also faster at 25 than at −5 °C.

Table II. Cypermethrin and Fenvalerate Residue Levels[a] in White and Wholemeal Flour and Bread (Expressed on a Moisture-Free Basis)

	residue, mg kg^{-1}			
insecticides	white flour	white bread	wholemeal flour	wholemeal bread
cypermethrin	0.51	0.43 (84.3)[b]	3.50	2.78 (79.4)
fenvalerate	0.66	0.58 (87.9)	3.96	3.44 (86.9)

[a] Mean of three replications. [b] Percent residues remaining after baking.

Effect of Processing on Residues in Flour and Bread. The residues of cypermethrin and fenvalerate in white and wholemeal flour and bread are presented in Table II. There was a reduction of 16 and 21% in cypermethrin residues following baking of white and wholemeal bread, respectively. Fenvalerate residues decreased by 12 and 13%, respectively, during baking of white and wholemeal bread. No difference was observed in bread weight, volume, texture, and taste between treated and control breads.

Half-Lives of Cypermethrin and Fenvalerate. Half-lives of cypermethrin and fenvalerate on wheat calculated from regression analysis are presented in Table III. The longest half-life of fenvalerate (385 weeks) was on wheat of 13.3% moisture content stored at −5 °C and the shortest (69 weeks) was on wheat of 15.0% moisture con-

Table III. Pseudo-First-Order Rate Constants and Half-Lives of Cypermethrin and Fenvalerate on Treated Wheat of 13.3 or 15.0% Moisture Content Stored at 25 or -5 °C for 60 Weeks

			storage conditions			
insecticide	treatment level, mg kg^{-1}	temp, °C	moisture content, %	pseudo-first-order rate constants 10^3, week^{-1}	half-life, $t_{1/2}$ weeks	95% confidence limits on $t_{1/2}$
cypermethrin	8	-5	13.3	4.1	169	124-267
	12	-5	13.3	5.0	139	105-204
	8	25	13.3	8.5	82	65-108
	12	25	13.3	9.0	77	65-94
	8	-5	15.0	10.8	64	57-74
	12	-5	15.0	11.5	60	53-69
	8	25	15.0	19.1	36	33-41
	12	25	15.0	17.2	40	36-46
fenvalerate	8	-5	13.3	1.8	385	231-1155
	12	-5	13.3	2.5	277	182-578
	8	25	13.3	4.1	169	133-231
	12	25	13.3	4.7	148	115-204
	8	-5	15.0	8.9	78	59-114
	12	-5	15.0	6.8	102	77-157
	8	25	15.0	9.7	72	61-87
	12	25	15.0	10.0	69	57-88

tent stored at 25 °C. In general, the half-lives of cypermethrin were shorter than those of fenvalerate. The longest half-life of cypermethrin (169 weeks) was on wheat of 13.3% moisture content stored at -5 °C and the shortest (36 weeks) was on wheat of 15.0% moisture content stored at 25 °C.

DISCUSSION

Analyses of grain and milled fractions at various intervals showed that there was a slow decline in the residues of cypermethrin and fenvalerate. Limited studies on related pyrethroids have shown that these insecticides are highly persistent in stored grain. Hargreaves et al. (1982) have reported that deltamethrin applied to wheat of 12.0% moisture content remained at the same level throughout a 15-month storage period at 25 °C. At the somewhat higher moisture content levels in the present work, cypermethrin and fenvalerate do undergo significant reduction.

In the present studies, reduction of fenvalerate residues was slower than for those of cypermethrin. There had been no reported work on the comparative degradation of these two insecticides on stored grain. However, fenvalerate had been found to be the most persistent insecticide on stored wheat, among deltamethrin, fenvalerate, permethrin, and phenothrin (Noble et al., 1982). These authors reported that fenvalerate had a half-life of 210 and 182 weeks on wheat of 12.0 and 15.0% moisture content, respectively, stored at 25 °C. Bengston et al. (1983) also confirmed that fenvalerate is more persistent than deltamethrin, permethrin, and phenothrin. Longer residual life of fenvalerate than cypermethrin may be explained on the basis of their hydrolysis rate constants. In aqueous systems at pH 6, hydrolysis rate constants of 1.10×10^{-1} per day for cypermethrin and 2.33×10^{-2} for fenvalerate have been reported (Grayson, 1975).

In the present studies, the reduction in residues was faster at higher temperature and moisture content of wheat as expected (Rowlands, 1967). Desmarchelier (1980) observed that residues of bioresmethrin and phenothrin on wheat depended on temperature and equilibrium relative humidity.

Reports on the distribution of pyrethroids in milled fractions of treated wheat are limited. However, a number of studies on organophosphate insecticides have shown bran to contain maximum residues after milling of treated wheat. Thus, maximum residues in bran and minimum in flour (endosperm) were obtained from wheat treated with malathion, bromophos, iodophenphos and primiphos-methyl (Mensah et al., 1979), methyl phoxim (Alnaji and Kadoum, 1979), and malathion and fenitrothion (Abdel-Kader, 1981). Bengston et al. (1983) found 0.70, 3.3, and 0.08 mg kg^{-1} fenvalerate in wheat, bran, and flour (endosperm), respectively, 10 months after an application of 1 mg kg^{-1} fenvalerate to wheat.

A slow decline in residues of cypermethrin and fenvalerate observed in the present studies is similar to that observed for phenothrin, deltamethrin, permethrin, and fenvalerate (Bengston et al., 1983; Hargreaves et al., 1982; Noble et al., 1982; Nambu et al., 1981). However, the results differ from those of Ardley and Halls (1979) who could not detect phenothrin residues in bran or bread made about 3 weeks after an application of 8 mg kg^{-1} phenothrin to wheat.

Bengston et al. (1983) reported no loss in residues of deltamethrin, fenvalerate, phenothrin, and permethrin during baking of white or wholemeal bread. The reductions of 12 to 13% in fenvalerate and 15 to 21% in cypermethrin residues, found in the present studies, may be due to a higher baking temperature and longer baking time used in the present studies. The present results agree with 13-30% reduction in phenothrin residues observed by Nambu et al. (1981). However, the reduction is much less than observed for methyl phoxim (79-100%) or malathion (80-100%) reported by Alnaji and Kadoum (1981).

The long persistence of these pyrethroids on grain is a desirable property for long-term storage, especially under hot and humid climates. Under these conditions, stored product insects multiply quickly and organophosphate insecticides degrade rapidly. Frequent repeat applications add to cost and also expose insects to low levels of fast degrading insecticides causing selection pressure for resistance. Fumigation is effective but only for a short period.

Pyrethroids are attractive as grain protectants under such conditions. Although, initial cost may be high, they would be more economical in the long-term because of their greater longevity. Further studies should be conducted involving more species, other cereal products, and varying storage conditions.

Registry No. Cypermethrin, 52315-07-8; fenvalerate, 51630-58-1.

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Pyrethroid Chemistry: Reactive α,β-Unsaturated Keto Aldehydes from Peracid Oxidation, Oxidative Photodecomposition, and Metabolism of 5-Benzyl-3-furylmethyl Derivatives

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Oxidation of 5-benzyl-3-furylmethyl 2,2,3,3-tetramethylcyclopropanecarboxylate or the analogous methyl ether with 1.5 equiv of *m*-chloroperoxybenzoic acid proceeds by 4,5-addition, furan ring opening, and rearrangement to form the (*Z*)-2-[(acyloxy)methyl]- or (*Z*)-2-(methoxymethyl)-4-keto-5-phenyl-2-pentenal, respectively, together with small amounts of the corresponding carboxylic acids. The 2-methoxymethyl keto aldehyde also forms in small yield on oxidative photodecomposition and microsomal metabolism. In biomimetic systems, both this methoxymethyl α,β-unsaturated keto aldehyde and peracid-oxidized 5-benzyl-3-furylmethyl *cis*-chrysanthemate (resmethrin) form covalent derivatives with bovine serum albumin and the methoxymethyl keto aldehyde also forms a thioether derivative with 3,4-dichlorobenzenethiol. Oxidative furan ring opening of 5-benzyl-3-furylmethyl derivatives, including pyrethroids, may therefore contribute to their photochemical and metabolic lability and to tissue binding and persisting fragments in mammals. The α,β-unsaturated keto aldehyde products are not detected as mutagens in several types of *Salmonella typhimurium* assays.

The pyrethroid insecticides resmethrin (**1A**, Figure 1) (Elliott et al., 1967), kadethrin (Martel and Buendia, 1974), and tetramethylcyclopropanecarboxylate **1B** (Figure 1) (Berteau and Casida, 1969) are esters of 5-benzyl-3-furylmethyl alcohol. **1A** and kadethrin undergo a variety of photoreactions including extensive oxidative opening of the furan ring probably via an ozonide-type cyclic peroxide (Ueda et al., 1974; Ohsawa and Casida, 1979). Metabolism of **1a** and kadethrin in rats and/or hepatic microsomal oxidase systems involves hydrolysis of the cyclopropanecarboxylate linkage and hydroxylation at the 4′- and α-methylene positions of the alcohol moiety in both cases, hydroxylation of the isobutenyl methyl groups in resmethrin, and oxidative cleavage of the thiolactone ring in kadethrin (Miyamoto et al., 1971; Ueda et al., 1975a,b; Ohsawa and Casida, 1980). An additional minor pathway proposed for metabolism of **1A** involves hydroxylation at C-4 of the furan (Miyamoto et al., 1971). **1A** also yields bound metabolites on activation in hepatic microsomal oxidase systems (Ueda et al., 1975b) and in the liver of treated rats (Ueda et al., 1975a; Graillot and Hoellinger, 1982; Hoellinger et al., 1983) with higher binding for the alcohol than the acid moiety. It has recently been reported that **1a** (1(*R*),trans and 1(*R*),cis isomers) and 5-benzyl-3-furylmethyl alcohol bind covalently to protein after oxidative in vitro metabolism (Hoellinger et al., 1985). The reactive intermediate in **1A** metabolism is tentatively proposed to be 5-benzyl-3-furylcarboxaldehyde (Ueda et al., 1975b).

Substituted-furans undergo epoxidation on photolysis (Karminski-Zamola et al., 1982) and oxidative ring opening on peracid treatment (Kobayashi et al., 1983; Ravindranath et al., 1984) and on metabolism involving cytochrome P-450 monooxygenases (Ravindranath et al., 1984). The keto aldehydes from microsomal oxidation of methylfurans are proposed to contribute to their toxicity and tissue binding (Ravindranath et al., 1984).

This study examines the chemical, photochemical, and microsomal oxidative reactions of the 5-benzyl-3-furylmethyl moiety and the possible toxicological significance of the resulting products.

MATERIALS AND METHODS

Analytical Procedures. Nuclear magnetic resonance (NMR) spectroscopy was carried out with a Bruker WM 300 instrument at 300 MHz (^{1}H), 75.5 MHz (^{13}C), or 47 MHz (^{2}H). ^{2}H spectra were obtained in the unlocked mode

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