and of that 1.6% was PB-acid and 19.3% was 4'-OH-PB-acid. All three PB complexes readily cleaved with HCl to yield PB-acid while complexes 2 and 3 also yielded 4'-OH-PB acid along with two or three additional products.

Ohkawa et al. (1980) found that in greenhouse-grown bean plants, fenvalerate metabolism included ester cleavage, hydrolyses of the CN group to $-CONH_2$ and -COOH groups, hydroxylation at the 2'- and 4'-phenoxy positions, oxidation of the 3-phenoxybenzyl alcohol (PB-alc), derived by hydrolysis, to PB-acid, and conjugation of the resulting carboxylic acids and alcohols with sugars. They detected only one Cl-Vacid conjugate in beans while we have found several in cotton callus tissue. Part of the diversity of the cotton Cl-Vacid conjugates may be due to species differences, and it is interesting to note that some of the [*chlorophenyl*-^{14}C-]fenvalerate metabolites recovered in preliminary work with soybean callus tissue incubated with fenvalerate also do not cochromatograph with those recovered from cotton. Treatment of the soybean metabolites with β-glucosidase and acid hydrolysis yielded Cl-Vacid.

Both bean and cotton plants metabolize the benzyl part of the molecule in a similar manner. In beans, [*benzyl*-^{14}C]fenvalerate was metabolized to free PB-alc, PB-acid, 2'-HO-PB acid, 4'-HO-PB acid, and α-cyanophenoxybenzyl alcohol along with their conjugates (Ohkawa et al., 1980). The alcohol moiety of deltamethrin was metabolized by cotton leaves to 3-phenoxybenzaldehyde, the corresponding alcohol and acid, 4'-HO-PB acid, in addition to conjugates of PB-alc, PB-acid, and α-cyanophenoxybenzyl alcohol (Ruzo and Casida, 1979). In this short-term treatment (5 h) of cotton leaf disks with deltamethrin, good uptake was achieved but little metabolism took place (Ruzo and Casida, 1979).

The metabolism of cypermethrin in cotton plants produced conjugates of the acid moiety that have been tentatively identified as glycosylxylose and glucosylarabinose esters (Wright et al., 1980). In excised cotton leaves [^{14}C]-3-phenoxybenzoic acid was converted to the glucose ester and disaccharide conjugates (More et al., 1978).

In greenhouse-grown bean plants, about 45% of the applied label was recovered as fenvalerate 60 days after treatment with labeled fenvalerate (Ohkawa et al., 1980). Fenvalerate had a half-life of approximately 2 weeks under green-house conditions (Ohkawa et al., 1980), while under field conditions it had a half-life of 2 days in cotton (Holmstead et al., (1978). Decarboxylfenvalerate, $CONH_2$-fenvalerate, and COOH-fenvalerate recovered from bean plants were considered to be produced in whole or part via photochemical and/or physiochemical reaction (Ohkawa et al., 1980). In a study of photodecomposition on cotton under field conditions, decarboxylfenvalerate, Cl-Vacid, PB-acid, PB-alc, PB-aldehyde, and 3-phenoxybenzyl cyanide were detected (Holmstead et al., 1978). In 4 days axenic cotton callus tissue metabolized 30% of the fenvalerate to numerous conjugates, and after 8 days 40% of the fenvalerate was metabolized. No attempt was made to optimize the metabolism, and direct addition to liquid media may increase the rate of degradation.

The fate of fenvalerate in cotton callus tissue is similar to the metabolism of fenvalerate in bean plants as well as the metabolism of the alcohol moiety of deltamethrin and cypermethrin in cotton plants. Therefore, cotton callus tissue is an excellent source of fenvalerate plant metabolites since sterile conditions can be maintained over a longer period than for leaf disks.

ACKNOWLEDGMENT

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Registry No. Fenvalerate, 51630-58-1.

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Metabolism of Deltamethrin by Cow and Chicken Liver Enzyme Preparations

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Deltamethrin is metabolized by an enzyme or enzymes in various fractions of liver homogenates from cow and chicken. Studies that employed acid- and benzyl-labeled insecticide showed the main metabolic pathway to be due to cleavage of the ester bond. The enzyme(s) responsible for ester bond cleavage was (were) located equally in both the soluble and microsomal fractions of a chicken liver homogenate. In cow liver homogenate, enzymatic activity was higher in the microsomal fraction. The metabolites identified were 3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acid, 3-phenoxybenzaldehyde, 3-phenoxybenzyl alcohol, 3-phenoxybenzoic acid, 3-(4-hydroxyphenoxy)benzyl alcohol, and 3-(4-hydroxyphenoxy)benzoic acid. GC and HPLC methods for analyses of various compounds are detailed.

Synthetic pyrethroids are the new generation of pesticides that are being developed as good substitutes for unwarranted organochlorine and toxic organophosphorus insecticides. One of the important members of this family is deltamethrin, which is also known by other names, e.g., RU-22974, NRDC-161, OMS-198, Decamethrin, Decis, and K-Orthin.

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Deltamethrin, one of the most potent insecticides known, has a structure (*S*)-α-cyano-3-phenoxybenzyl (1*R*,3*R*)-*cis*-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate. Although it is being developed for control of insect pests of crops, livestock, and man, very little is known about its metabolism in poultry and farm animals. The metabolic fate of deltamethrin in the mouse liver microsomal system (Shono et al., 1979) and in rats (Ruzo et al., 1978) has been reported. The current studies were undertaken to determine the fate of deltamethrin in chicken and cow liver enzyme preparations.

MATERIALS AND METHODS

Chemicals. Deltamethrin (^{14}C labeled and unlabeled) was a gift from Roussel-Uclaf-Procida through its subsidiary Hoescht of Canada, Ltd. The position of labeling, radiochemical purity (as determined by TLC), and specific activity were as follows: acid labeled (*gem*-dimethyl-^{14}C, 98%, 56 mCi/mmol) and benzyl labeled (benzylic ^{14}C, 96%, 58.17 mCi/mmol). A portion of ^{14}C-labeled material was individually mixed with purified deltamethrin and dissolved in toluene or acetone to give the following concentrations: acid labeled (100 μL = 48.4 μg, 4.64×10^5 dpm) and benzyl labeled (100 μL = 48.3 μg, 5.43×10^5 dpm). Base-catalyzed hydrolysis of deltamethrin followed by purification by TLC gave pure 3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylic acid (Br_2CA). 3-Phenoxybenzaldehyde (3-PBald), 3-phenoxybenzoic acid (3-PBacid), 3-penoxybenzyl alcohol (3-PBalc) were purchased from Aldrich Chemical Co., New York. 3-(4-Hydroxyphenoxy)benzoic acid (4′-HO-3-PBacid) and 3-(4-hydroxyphenoxy)benzyl alcohol (4′-HO-3-PBalc) were prepared following the procedures of Unai and Casida (1977). Sigma Chemical Co. (Missouri) was the supplier of the NADPH-generating system.

Enzyme Preparation. Fresh livers [chicken (three to four) and cow] were washed in distilled water and placed on crushed ice. Liver homogenate was prepared in 0.134 M sodium–potassium phosphate buffer, pH 7.4 (8 g/40 mL) in a glass–Teflon homogenizer for 5 min. The homogenate was centrifuged at 1740*g* for 5 min at 4 °C. The pellet was discarded and the supernatant was centrifuged at 11950*g* for 10 min at 4 °C. The supernatant (soluble plus microsomes) used in the incubation is referred to as crude. A portion of the supernatant was further centrifuged at 105000*g* for 30 min at 4 °C to obtain the soluble fraction. The pellet (microsomes) was washed by resuspending in buffer and centrifuging at 105000*g* for further 30 min. The resultant pellet, i.e., the microsomal preparation, was resuspended in the original volume of the phosphate buffer.

In Vitro Incubation. Incubations were carried out in glass-stoppered Erlenmeyer flasks at 37 °C for 2 h. The incubation mixture consisted of acid- or benzyl-labeled deltamethrin (9.7×10^{-8} mol), enzyme preparation (15 mL, equivalent to 3 g wet weight of liver), and where necessary the NADPH-generating system (5 μmol). The NADPH-generating system was prepared just prior to use. The incubations, carried out in duplicate, were terminated by addition of acetonitrile (20 mL) and mixed thoroughly for 1 min.

Extraction of Radioactivity. The incubation mixture was filtered and the precipitate was washed with acetonitrile (3 × 20 mL). The combined extracts, evaporated to 15 mL, were transferred to a centrifuge tube (40 mL), and the flask was washed with $CHCl_3$ (3 × 2 mL). The aqueous phase was extracted with $CHCl_3$ (3 × 15 mL), after centrifugation for 5 min at 2000 rpm to break any emulsion. The combined chloroform extract was passed through anhydrous Na_2SO_4 and evaporated to near dryness. The oily residue was transferred to a centrifuge tube (40 mL) with hexane (3 × 4 mL) and extracted with acetonitrile (3 × 20 mL). The acetonitrile fraction was evaporated to dryness, and the residue was taken up in acetone and, after volume adjustment, the radioactivity measured, in duplicate. Hexane and aqueous phases contained in total ≤2% of the original radioactivity.

Isolation of Radioactive Metabolites. The acetone extracts were reduced in volume (ca. 0.1 mL), applied to TLC plate(s), and developed in $CHCl_3$–acetic acid (99.0:1.0 v/v), and the plates were exposed to X-ray films (autoradiograph). The radioactive regions were scraped off the plate(s) and extracted with appropriate solvent, and the radiocarbon content was measured. A summation of the radioactivity content of various regions of a TLC plate gave the total extractable radioactivity, which was taken as 100%, and the percentage of a metabolite in an incubation mixture was then calculated. The recovery of applied radioactivity from the TLC plates was, in general, excellent (95–97%).

Identification of Metabolites. Metabolites extracted from incubation mixtures were identified by a combination of TLC, GC, and HPLC techniques. The identity of a compound was established by cochromatography with unlabeled standards in various TLC solvent systems and by cochromatography with authentic standards on GC, after derivatization where necessary. Unchanged deltamethrin was authenticated by GC analysis on a 3% SE-30 and a 5% OV-210 column at various temperatures. Br_2CA and 3-PBacid were analyzed by GC as their methyl and 2-chloroethyl esters. In order to obtain the ECD-sensitive derivative, 3-PBalc was treated with BCl_3–2-chloroethanol, the structures of which were established independently. Deltamethrin, 3-PBalc, 3-PBacid, 4′-HO-3-PBalc, and 4′-HO-3-PBacid were also identified by HPLC.

Measurement of Radioactivity. The radioactivity of various phases was determined, in duplicate, in a Packard Model 3320 Tri-Carb liquid scintillation counter by using an external standard and quench correction. Organic extracts were assayed in a scintillation cocktail, Bioscint (ICN, Canada), whereas the radioactivity in aqueous phase was measured in Aquasol (NEN), a xylene-based scintillation cocktail.

Thin-Layer Chromatography (TLC). Silca gel linear K (LK6DF) preadsorbent (0.25 mm thick) TLC plates (Whatman) were spotted with acetone (extracts concentrated to 0.1 mL with a slow stream of nitrogen) and developed in a chloroform–acetic acid (99:1 v/v). The R_f values of deltamethrin, Br_2CA, 3-PBald, 3-PBacid, 3-PBalc, 4′-HO-3-PBacid, and 4′-HO-3-PBalc were 0.86, 0.53, 0.80, 0.37, 0.46, 0.08, and 0.05, respectively. The metabolites were detected by (i) viewing under UV light (254 nm) and (ii) autoradiography. The R_f values of deltamethrin, 3-PBald, in toluene–hexane (80:20 v/v) were 0.57 and 0.42, respectively. Br_2CA was not easily visible under UV light. Large quantities of Br_2CA were needed to make the spot visible.

Gas Chromatography (GC). Extracts after appropriate dilution and derivatization where necessary were analyzed on a Perkin-Elmer Sigma 1 gas chromatography equipped with a ^{63}Ni electron-capture detector. The column was 3% SE-30 on 80–100-mesh Chromosorb WHP. The compounds were analyzed under different operating conditions (Table I).

Gas Chromatography–Mass Spectrometry. The GC–MS analyses were carried out on a Finnigan Model 3100 mass spectrometer connected to a Finnigan Model

Table I. Gas Chromatographic Conditions[a] for Identification of Deltamethrin and Its Metabolites

compound	temperature, °C injector	temperature, °C oven	retention time, min
deltamethrin	275	240	3.4
	250[b]	245	17.3
1*R* (cis) isomer	250[b]	245	15.5
methyl ester of Br_2CA	225	115	2.8
2-chloroethyl ester of Br_2CA	275	150	3.2
3-PBacid	275	150	10.9
α-chloro-3-Ptoluene	275	150	2.5
α-(2-chloroethoxy)-3-Ptoluene	275	150-250	5.5[c]

[a] The column was a 3% SE-30 on Chromosorb WHP, and the detector temperature was maintained at 400 °C; the flow rate of the carrier gas (5% methane in argon) was 40 mL/min. [b] On a 5% OV-210 column (1.82 m × 4 mm i.d.). [c] On a 3% SE-30 column (1.5 m × 4 mm i.d.) programmed from 150 to 250 °C at 8 °C/min.

9500 gas chromotograph by means of a jet separator. The mass spectrometer was interfaced with a Model 6100 computer-controlled data acquisition system. A 3% SE-30 on a 80–100-mesh Chromosorb WHP column (1.52 m × 4 mm i.d.) was used at various operating temperatures. The mass spectra were recorded at 70 eV.

High-Performance Liquid Chromatography (HPLC). The HPLC instrument used was a Model 6000 equipped with Model U6K loop injector and a Model 450 variable-wavelength UV detector (Waters Associates, Ontario). Deltamethrin was analyzed on a 300 × 3.9 mm (i.d.) μPorasil column by using an isocratic mobile phase of hexane (995 mL) and acetonitrile (5 mL) at a flow rate 2.0 mL/min. The detector sensitivity and wavelength were set at 0.02 a.u.f.s. and 225 nm, respectively. Under these operating conditions deltamethrin and the 1*R* cis isomer had retention times of 10.0 and 8.6 min, respectively. The polar metabolites 3-PBacid, 3-PBalc, 4′-HO-3-PBacid, and 4′-HO-3-PBalc were analyzed on a Waters Associates radial compression module, Model RCM-100, with a Radial-PAK cartridge (100 × 5 mm i.d., C-18, Water Associates), by using a mixture of acetonitrile and 0.05 M NaH_2PO_4 (30:70 v/v) as a solvent system (flow rate of 1.9 mL/min). The detector wavelength and sensitivity were maintained at 215 nm and 0.02 a.u.f.s., respectively. Under the operating conditions employed, the retention times for 3-PBalc, 3-PBacid, 4′-HO-3-PBalc, and 4′-HO-3-PBacid were 13.0, 7.6, 3.0, and 1.9 min, respectively.

RESULTS AND DISCUSSION

When deltamethrin was incubated with various fractions of cow and chicken liver homogenates, it was degraded into a number of products. In all cases, the main degradation and initial route was the cleavage of the ester bond. In general, the rate of metabolism of deltamethrin appeared to be a little faster in the chicken liver system, as compared to that of cow liver, as evidenced by the amount of unmetabolized deltamethrin recovered at the end of incubation. Very little degradation of deltamethrin occurred when incubated with buffer and deactivated enzyme (boiled) systems (Table II).

Table II records the radiocarbon distribution in the incubation mixtures. These values are based on the amount of extractable radioactivity. It is noteworthy that a considerable loss (19–20%) of radioactivity was observed when ^{14}C-acid- or [^{14}C]benzyl-labeled deltamethrin were carried through the entire procedures. In most cases, the amount of ^{14}C extracted from the incubation mixtures ranged between 76 and 82% of the applied radioactivity. However, on occasions, especially when the enzyme preparation contained excessive fat, the loss was as high as 40%. This may be due to poor partitioning of the ^{14}C compound(s) between the fat and the extracting solvent. In a few cases, it was shown by a combination of exhaustive extraction and cleanup procedures that a major portion of the ^{14}C in the fat was associated with unmetabolized deltamethrin.

The data in Table II show the extent of metabolism of deltamethrin by liver enzyme preparations from cow and chicken: The extent of metabolism was greater in the microsomal fraction than in the soluble fraction of cow liver homogenate. However, no such difference was apparent in the various enzyme fractions of a chicken liver, which is in agreement with an in vitro study of fenvalerate with chicken liver systems (Akhtar, 1983).

Incubation of deltamethrin with various cow liver enzyme fractions, e.g., soluble and normal microsome (esterase) and microsome plus NADPH [esterase plus oxidase; see Shono et al. (1979)], yielded compounds mainly due to ester cleavage. The extent of cleavage of the ester bond was somewhat greater in the microsomal systems. Although greater degradation of deltamethrin was observed in the microsomal plus NADPH system, there was no increase in the amount of the oxidation products. Thus, the ester bond cleavage may result from both esteratic and oxidative mechanisms. Shono et al. (1979) have previously postulated an oxidative cleavage of *cis*-permethrin and

Table II. Metabolites of Acid- and Benzyl-Labeled Deltamethrin in Various Incubation Systems

	% of extracted ^{14}C[a]									
	cow						chicken			
compounds	buffer	boiled	crude[b]	sol	micro	micro + NADPH	boiled	sol	micro	micro + NADPH
acid labeled deltamethrin[c]	98.5	97.6	86.2	92.8	69.5	74.6	97.3	76.6	76.4	
Br_2CA	1.2	1.6	12.6	5.6	29.2	23.5	2.2	15.9	18.5	
unidentified	0.3	0.8	1.2	1.6	1.3	1.9	0.5	7.5	5.1	
benzyl labeled deltamethrin	96.3		71.0	82.1	71.0	64.3	96.2	66.3	64.5	64.1
3-PBald[d]	tr		13.1	12.8	7.3	4.2	tr	13.2	6.9	6.3
3-PBalc	tr		7.4	0.2	8.4	15.2	tr	1.7	11.5	15.4
3-PBacid	tr		7.2	3.5	11.8	15.4	tr	10.5	12.0	12.9
4′-HO-3-PBalc, 4′-HO-3-PBacid, unidentified	3.7		1.3	1.4	1.5	0.9	3.8	8.3	5.1	1.3

[a] Average of duplicate incubations. [b] Crude refers to soluble plus microsomes. [c] No epimerization occurred during the studies. [d] See Figure 2 and Materials and Methods for structures and abbreviations.

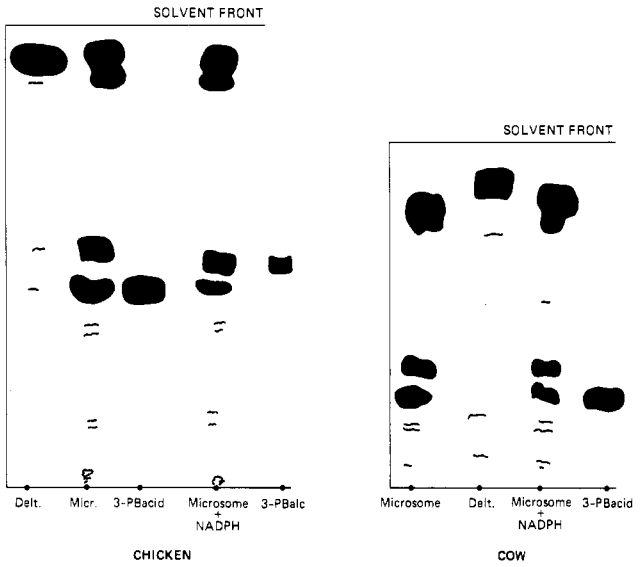

Figure 1. Autoradiograph of extractable ^{14}C products from in vitro incubations of benzyl-labeled deltamethrin with cow and chicken liver microsomes and microsomes plus NADPH.

deltamethrin since they found large amounts of 3-PBalc, 3-PBald, 3-PBacid, etc. in incubation extracts of these compounds with mouse liver microsomal systems in which esterase activity was inhibited by the addition of tetraethyl pyrophosphate (TEPP).

The extent of degradation of deltamethrin in chicken liver systems is not influenced by the enzyme fractions. In all systems including esterase plus oxidase, the metabolites were mainly due to the cleavage of the ester bond. This suggests that the hydrolytic cleavage of the ester is the predominant route in the chicken liver and the oxidative cleavage may not be an important metabolic pathway. These data also tend to suggest that the esterase (pyrethroid carboxylesterase) is distributed almost evenly in the microsomal and soluble fractions. In studies with rat liver homogenates, Suzuki and Miyamoto (1978) found the pyrethroid esterase primarily in the microsomal fraction.

The nature of metabolites in the incubation extracts was determined by a combination of techniques. The extracts from each incubation, after measurement of radioactivity, were analyzed directly by TLC followed by autoradiography. Comparisons with authentic standards chromatographed on the same TLC plate afforded the preliminary identification for most compounds (Figure 1). In order to fully authenticate the identity of a radioactive zone, the extracts from each zone were further analyzed by GC and HPLC before and after derivatization, where necessary. GC–MS analyses were also carried out on selected samples. The percentage of compounds found, on the basis of radioactivity measurement, in the incubation extracts are given in Table II.

Radioactive zones due to unmetabolized compound were found in the incubation extracts of both acid and benzyl labeled deltamethrin. The extracts of acid-labeled deltamethrin exhibited only one radioactive zone (R_f 0.83), whereas in the extracts of benzyl-labeled compound, two poorly resolved radioactive zones (R_f 0.83 and 0.78) were found. In order to fully resolve the two radioactive regions, the zones were extracted together and rechromatographed in a toluene–hexane (80:20 v/v) solvent system that resolved the two zones. The compound with a high R_f value (0.83) was identified as unmetabolized deltamethrin; GC and HPLC data were identical with those of pure deltamethrin. Under the incubation conditions employed, no epimerization of deltamethrin to its 1*R* cis isomer took place. Similar results were reported by Shono et al. (1979), who also did not observe epimerization in a mouse liver microsomal system. On the other hand, methanolic solution of deltamethrin was epimerized (≃45%) when allowed to stand at room temperature for 8 h. Other workers (Ruzo et al., 1978) have also observed facile epimerization of deltamethrin in methanol.

The compound with R_f 0.78 was identified as 3-PBald by comparison with the TLC retention time. In addition, the extracts when allowed to stand at room temperature were converted into a compound that behaved like 3-PBacid. Since the air-oxidized compound cochromatographed with a standard 3-PBacid on a C-18 HPLC column, its structure was confirmed as 3-PBald.

Only one radioactive zone was found, near the expected region of Br_2CA (R_f 0.53), in the extracts of acid-labeled deltamethrin incubation. The extracts of the region after ^{14}C measurement were treated with BCl_3–2-chloroethanol and analyzed by GC. The chromatogram of the reaction mixture exhibited a major peak that cochromatographed with the authentic 2-chloroethyl ester of Br_2CA. Smaller peaks due to the 2-chloroethyl ester of 3-PBacid and α-chloro-3-phenoxytoluene (α-chloro-3-Ptoluene) were also observed (see below for a detailed discussion). The GC–MS of the 2-chloroethyl ester of Br_2CA showed molecular ions at *m/z* 358, 360, 362, and 364 due to various isotopes of bromine and chlorine atoms. The pattern was identical with that reported by McLafferty (1980) for a molecule containing two bromine and one chlorine atoms. The mass spectrum also had peaks at 279, 281, and 283 ($M^+ - OCH_2 - CH_2Cl$) and 251, 253, and 255 ($M^+ - COOCH_2CH_2Cl$).

Incubation extracts of benzyl-labeled deltamethrin exhibited, in addition to 3-PBald, two distinct radioactive regions at R_f 0.48 and 0.33. The identity of the compound with R_f 0.33 was established as 3-PBacid by comparison with its HPLC retention time and analytical data of its 2-chloroethyl ester with those of a standard 2-chloroethyl ester of 3-PBacid. The mass spectrum of the ester of this region was identical with that recorded for a pure 2-chloroethyl ester of 3-PBacid (Akhtar,1983).

The radioactive zone at R_f 0.48 cochromatographed with standard 3-PBalc when analyzed on a C-18 HPLC column. Further structural confirmation was obtained by its reaction with BCl_3–2-chloroethanol. The reaction afforded two products: α-chloro-3-phenoxytoluene (α-Cl-3-Ptoluene, 70%, R_f 0.55, toluene–hexane, 80:20 v/v) and α-(2-chloroethoxy)-3-phenoxytoluene [α-(2-chloroethoxy)-3-Ptoluene, 20%, R_f 0.12, toluene–hexane, 80:20 v/v]. The mass spectrum of α-Cl-3-Ptoluene had peaks at *m/z* 220 (M^+ for ^{37}Cl), 218 (M^+ for ^{35}Cl), and 183 ($M^+ - Cl$), whereas α-(2-chloroethoxy)-3-Ptoluene exhibited peaks at *m/z* 264 (M^+ for ^{37}Cl), 262 (M^+ for ^{35}Cl), 184, 91, and 77. A reaction between pure 3-PBalc and BCl_3–2-chloroethanol under the same reaction conditions also afforded the same two products. This appears to be a covenient method for converting benzyl alcohols into benzyl chlorides—an ECD-sensitive derivative.

Radioactive regions near the origin were found in all the incubation extracts. However, the ^{14}C content of these regions was small. For example, 0.9–1.9% of the extractable radioactivity from cow liver systems was found in this region. A higher value of 1.3–8.3% of the extractable radioactivity from chicken liver systems was located in this region. Analyses of the combined extracts of radioactive regions near the origin of benzyl-labeled deltamethrin showed the presence of 4′-HO-3-PBacid and 4′-HO-3-PBacid. The combined extracts of acid-labeled

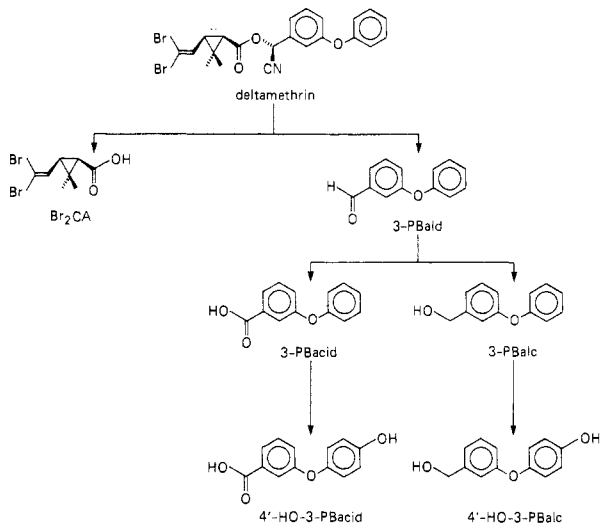

Figure 2. Metabolic pathways of deltamethrin in enzyme preparations from liver of cow and chicken.

deltamethrin contained unchanged insecticide, Br_2CA, and other unidentified products. However, the amounts of unchanged deltamethrin and Br_2CA were higher in chicken liver systems than those from cow liver. This may be, in part, due to the higher fat content of the chicken liver.

The data presented above provide evidence for the metabolic pathway of deltamethrin in in vitro incubation with various enzymatic fractions of a cow and chicken liver homogenates. The preferred metabolic pathway for deltamethrin is the cleavage of the ester bond to yield to Br_2CA and 3-PBald (after fast elimination of HCN from 3-PBald cyanohydrin). 3-PBald can undergo both oxidation and reduction to afford 3-PBacid and 3-PBalc, respectively. In the present study 3-PBacid and 3-PBalc were produced in almost equal quantities, suggesting efficient oxidase and reductase in liver systems. Shono et al. (1979) also found sufficient quantities of 3-PBacid and 3-PBalc when they incubated deltamethrin with mouse liver microsomes (oxidase or oxidase plus esterase). However, the amount of 3-PBacid produced was always high (4.7–6.5 times that of 3-PBalc).

Although all the polar metabolites were not identified in the present study, the amounts of these metabolites were very small. Thus, it appears that hydroxylation of the ring(s) and the methyl group(s) is not an efficient metabolic pathway. Based on the metabolites identified, a metabolic pathway for deltamethrin in the liver homogenates of cow and chicken is proposed in Figure 2.

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Registry No. Deltamethrin, 52918-63-5; Br_2CA, 53179-78-5; 3-PBald, 39515-51-0; 3-PBalc, 13826-35-2; 3-PBacid, 3739-38-6; 4'-HO-3-PBalc, 63987-19-9; 4'-HO-3-PBacid, 35065-12-4.

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Possible Factors of Leaf-Feeding Resistance in Corn to the Southwestern Corn Borer

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This report describes results of studies to chemically describe differences between leaf feeding resistant and susceptible corn genotypes to the southwestern corn borer, *Dietraea grandiosella* (Dyar), a major pest of corn (*Zea mays* L.) in parts of the southwestern and southeastern United States. The compound 6-methoxybenzoxazolinone was present in very low concentrations (20 $\mu g/g$) in the corn lines tested and was relatively nontoxic for this insect. Crude fiber and residue content, the latter obtained by 70% aqueous methanol extraction of inner whorl tissue, were consistently higher in resistant lines and were negatively correlated with insect weight ($r = -0.84^{**}$, 15 df) and with insect damage ($r = -0.57^{**}$, 20 df). The hemicellulose content of the fiber from resistant whorls (24.0%) was higher than in susceptible whorls (17.6%), while the cellulose content was unchanged. The susceptible lines were at least 25% higher in several constituents, notably crude protein, lipid, total sugars, ash, and polyphenol oxidase activity. These factors explain at least in part the bases of resistance and susceptibility in the cultivars studied.

The southwestern corn borer [*Diatraea grandiosella* (Dyar)] (SWCB) is a native of Mexico and was first reported in New Mexico in 1913. Since that time, the borer has spread northward and eastward (Henderson et al., 1966). The northern limits (Kansas) are restricted by its inability to survive winter temperatures (Chippendale, 1974). Presently, the SWCB infests corn eastward to the Alabama–Georgia border.

The damage to corn plants is caused by larvae. Normally, corn plants are in the whorl stage of growth when moths that have emerged from the overwintering generation lay their egges on the corn leaves. After the eggs hatch, the young larvae move into the whorl where they

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