THE UNIVERSITY OF CALGARY

PHOTOLYSIS OF SYNTHETIC PYRETHROIDS

by

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Photolysis of Synthetic Pyrethroids," submitted by Donald Langer in partial fulfilment of the requirements for the degree of Master of Science.

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ABSTRACT

This thesis presents a review of the history and development of synthetic pyrethroids which reveals a progression from highly toxic but photolabile and biodegradable compounds to persistent pesticides with both selective and broad-spectrum applications.

A survey of toxicologies of economic insecticides shows toxic action within clearly definable parameters. Differences occurred with respect to persistence, lethality, and selectivity.

The photodegradation of resmethrin in aqueous media ("snow-melt" and distilled water) generated many of the products that have been isolated in other solution and solid-phase photodegradation studies. Photoproducts included: benzyl alcohol, benzaldehyde, phenylacetic acid, and chrysanthemic acid. Resmethrin was found to be the single, largest compound isolated from photolyzed samples and was observed to persist for substantial periods of time ($T_{0.5}$ > 14 days).

A student project entailing preliminary investigations of the photodegradability of pyrethroids using thin-layer chromatographic analytical techniques indicated some promise.

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CHAPTER 1

INTRODUCTION

In recent years, new approaches to the teaching of science in schools have been developed in order to address many of the current issues of the day, and to place scientific knowledge into a highly interactive context. Traditionally, scientific knowledge constituted a large body of reference information concerned with results and conclusions derived from rather remote historical experiments. The links between the accepted passive body of facts and the active behaviour of matter all around us were seldom explicitly described, and only the more gifted students were capable of forging these links of relevance. The relevance of past, present, and future scientific exploration is no longer left to the student to infer, but the scientific discovery is made by the student within its own physical and societal context.

The role of the teacher is, therefore, to provide the student with a scientific problem that will enable the student to develop ideas, first hand, concerning the physical or chemical behaviour of a system that is of relevance to everyday living and that does impinge on society in a very obvious and, in some cases, controversial manner. Such an exercise places considerable demands on the teacher. A full appreciation of the societal and scientific context of the study must first be developed by the teacher. The primary research information will require refinement and simplification. The student will require general orientation in the broad topic area. A portion of this will then be investi-

gated in more detail in the practical laboratory projects. Frequently the development of new laboratory exercises by a teacher requires primary experimental research on his or her part.

This thesis is concerned with all these phases necessary to develop and implement a project for high school students. The first part concerns an experimental study of the photochemical behaviour of a synthetic pyrethroid insecticide, resmethrin. This section is essentially an environmental chemistry project that focuses attention on the organoanalytical aspects of trace residue analysis of products from a photochemical degradation under simulated environmental conditions.

The second part is directed toward chemical education and begins with a discussion of the structure, toxicity, and mode of action of commercially available and commonly used insecticides other than pyrethroids. This material is the crucial contextual material that must be provided by the teacher so that the significance of the student pyrethroid study can be appreciated in a comparative mode. This material is presented here rather than simply being cited because for this project to be implemented by other teachers, a ready source of the background information in appropriate form is essential. Unavailability of such information is usually sufficient to deter even the most enthusiastic of teachers.

The second section then describes the application of the experimental results and conclusions in a student research study of the same and related systems. Details of the project design and content, the evaluation tools and the students' results are discussed. It is not possible to present the results of all the evaluation phases of the implementa-

tion of the student project, since confidentiality must be assured. Thus parts of the evaluation are anecdotal, however some indication of the students' perception can be gleaned from this feedback.

The use of toxic substances in the environment is now common practice. It is of crucial importance that students develop a comprehensive appreciation of the benefits and risks associated with the use of modern synthetic chemicals.

Chapter 2

PART 1. PYRETHRINS AND PYRETHROIDS:

A Review of the Systematic Use of Pesticides

Mankind has shared the earth and its resources with a great variety of organisms, and has competed directly with them for space, food, and shelter. Many members of the insect class have always been staunch adversaries, referred to generally as "pests", and man has gone to extraordinary means to regulate their numbers. The use of chemical pesticides has remained the principal mode of man's efforts to decimate insect populations.

The history of the systematic use of pesticides has been a long one and its precise origins have been lost in antiquity. Earliest records of pesticide use go back as far as 1000 B.C., where Homer spoke of sulphur as a fumigant for pest control (O'Brien, 1967). Records have shown that by A.D. 900 the Chinese used arsenic to control garden insects (O'Brien, 1967). Pyrethrum, an insecticidal extract from plants of the Chrysanthemum genus of the Asteraceae family, has been accepted as one of the oldest insecticides known. It was used for louse control in Iran in 400 B.C. (Moore, 1964) and may have been introduced into Europe from the Far East by Marco Polo (1254-1324) (Brooks, 1974a). Records of its use as an insecticide in the Caucasus had been noted by A.D. 1800 (Shepard, 1951).

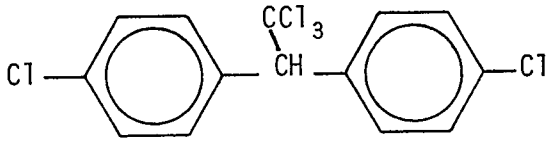
Certainly a wide variety of naturally occurring pesticides as extracts from plants or insects or the two in combination have been

utilized by both primitive and modern man to secure and consolidate his ecological niche. Excluding insect-derived pesticides, juvenile hormones, and bacterial and fungal insecticides, in excess of 2000 literature references have been listed on the subject of minor insecticides of plant origin (Crosby, 1971).

Naturally occurring pesticides have been garnered largely from four natural plant sources (Jacobson & Crosby, 1971). The first of these was "Pyrethrum," a powdered, concentrated extract from the flowers of Chrysanthemum cinerariaefolium. Pyrethrins I and II comprised the principal active ingredients in this formulation. The second was the rotenoids extracted from plant members of the Leguminosae family. Principal formulations included "Rotenone" and "Derris." A third group consisted of nicotine and other tobacco alkaloids. Nicotine was a major toxic component in these pesticides. The last and least appreciated group included the unsaturated isobutylamides which had been isolated from plants of the Asteraceae and Rutaceae families. These pesticides comprised a group of unsaturated, straight chain, C_{10-20} acid isobutylamides. Pellitorine, which was extracted from the root of Anacyclus pyrethrum DC, was but one member of this group.

Few economically important pesticides were recognized, however, until the discovery of the insecticidal activity of dichlorodiphenyltrichloroethane (DDT) in 1939. DDT was first synthesized by Zeidler in 1874 and it was not until 1939 that the pesticidal properties of the p,p' isomer were discovered by Muller (Brooks, 1974a). The successful

marketing of synthetic pesticide formulations had its beginnings in the patent formulations of DDT (Fig. 1) that were introduced in the U.S.A. and Europe in 1942, and the growth of this industry has had significant moral, social, ecological, and economic implications for the civilized world.



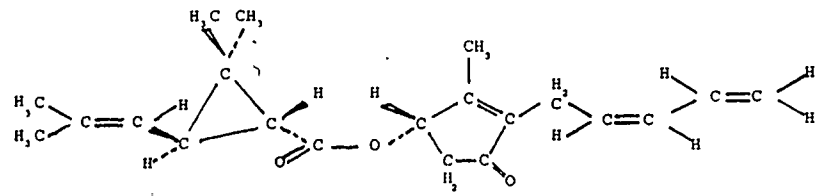
DDT
$C_{14}H_9Cl_5$

Figure 1. Dichlorodiphenyltrichloroethane

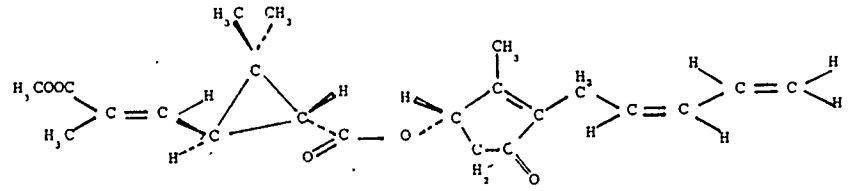
Natural Pyrethrins

The natural pyrethrins are extracted from the flowers of the plant genus Chrysanthemum (Fig. 2). More than one species has been used (Nakajima, 1983), but cinerariaefolium, which had its origin in Yugoslavia, has remained first in commercial significance. Six keto-esters: pyrethrins I, II, jasmolins I, II and cinerins I, II are the active insecticidal constituents of C. cinerariaefolium (Katsuda, 1982). Of these, the most active are pyrethrins I, II. A manifest killing superiority has been attributed to pyrethrin I, while knockdown efficacy has been ascribed to pyrethrin II.

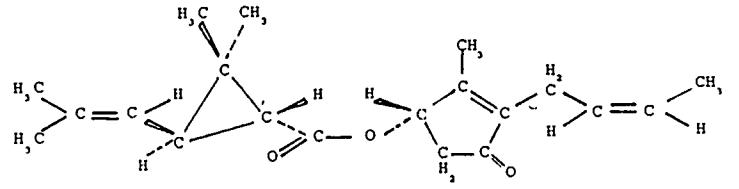
It is not certain when an awareness of the insecticidal activity of the pyrethrins became prevalent but speculation (Leahey, 1979) has indicated their commercial use originated in Persia more than 100 years ago. Katsuda (1982) stated that the growing of pyrethrum plants was first



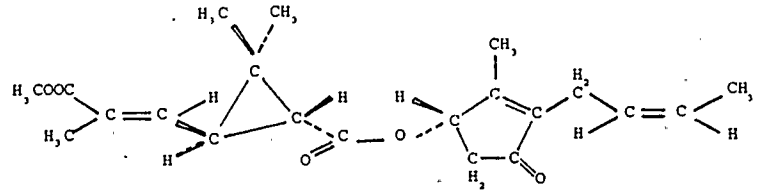
Pyrethrin I



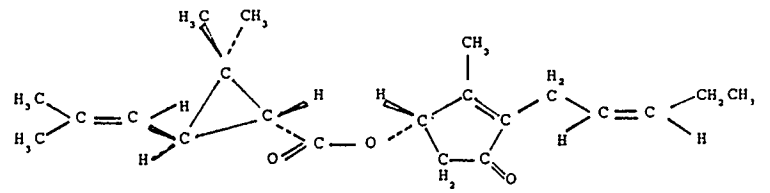
Pyrethrin II



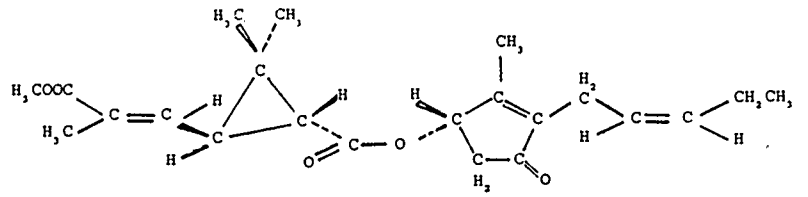
Cinerin I



Cinerin II



Jasmolin I



Jasmolin II

Figure 2. Natural Pyrethrins

introduced to Japan in 1885. The first of these were of German origin, while the seedstocks of the Japanese industry were obtained from the U.S.A. The use of pyrethrum as an insecticide in Europe was recorded early in the last century (Nakajima, 1982). C. cinerariaefolium was cultivated in Dalmatia in the early 1840s.

Pyrethrum, a term used to refer to the constituents of the flower extract of C. cinerariaefolium, was first reported in 1694 (Katsuda, 1982) but it was not until about 1910 (Leahey, 1979) that systematic efforts were initiated to isolate and characterize its active constituents.

Research has been confined largely to the most abundant homologs pyrethrin I and II and much of the important research has been completed. In spite of the synthesis of a host of new synthetic analogues, research reports relating to these original pesticides have persisted in the literature.

The original application of pyrethrum for insect control was in the form of a powder constituted from the milling of dry flowers. Solvent extraction in kerosene characteristically gave a yield of 20-25% active ingredient (Crosby, 1971). This method was improved upon with the development of a mosquito stick of 30 cm in length which would burn for about one hour and emit volatile pyrethrins that would effectively control mosquito infestations (Katsuda, 1982). A further refinement of this technique was provided with the introduction of the mosquito coil in about 1895, with a burning time of 7 to 8 hours (Nakajima, 1982).

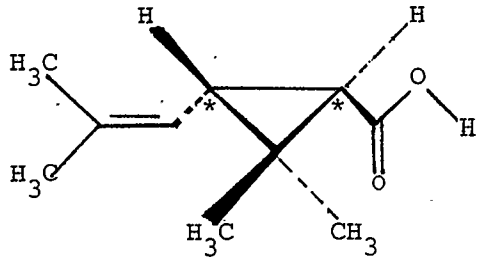
There has been some decline in pyrethrum production in certain countries as a direct consequence of the development of synthetic

pyrethroids, but Japan had a production peak of 13,000 tons per year in 1938 (Katsuda, 1982) which comprised about 70% of the world's production. Principal producing countries today are Kenya, Uganda, and Tanzania (Katsuda, 1982), with per annum output in excess of 20,000 tons.

Natural pyrethrins, however, have had two inherent disadvantages: they were especially susceptible to photolytic degradation and were susceptible to degradation by biological systems. The synthetic analogues of pyrethrins are known as pyrethroids. Early publications, however, made no clear distinction between natural and synthetic species, referring to them collectively as pyrethroids (Quraishi, 1977).

Synthetic Pyrethroids

It was the marked insecticidal activity of the natural pyrethrins that gave impetus to the development of synthetic analogues. The first of many such syntheses began in 1947 with the successful preparation of allethrin by La Forge and co-workers (La Forge, 1982). It had been ascertained that the unusually high activity and selectivity of pyrethrins could be attributed directly to the structural and stereochemical features of these molecules. (A more detailed discussion is given later.) Between 1910 and 1969 the structures and the exact spatial configurations of the active components of pyrethrum were mapped and ample data were collected to embark upon systematic research (Leahey, 1979).



Trans-orientation

Figure 3. Trans-Chrysanthemic acid

At least two distinct avenues of modification have been explored in the synthetic field. One area of development has involved coupling of a variety of groups for the alcohol functionality with chrysanthemic acid (Fig. 3) to produce synthetic analogues of pyrethrin I. The first of these was allethrin in which an allyl side chain was substituted on the rethrolone group in place of the pentadienyl group (Katsuda, 1982). A variety of alternative functionalities was investigated and patents for promising syntheses were registered. The substitution of an imidomethyl group has resulted in the commercially successful compound phthalthrin (Kato, Ueda, & Fujimoto, 1965). Benzyl esters of chrysanthemic acid have produced a variety of compounds ranging from simple substituted benzyl esters in the form of dimethrin (Barthel & Alexander, 1958), through benzylbenzyl esters (Katsuda, 1982), to phenoxy benzyl esters, e,g. phenothrin (Fujimoto, Itaya, Okuno, Kadota, & Yamaguchi, 1973), and α-cyano phenoxy benzyl esters, e.g. cyphenothrin (Matsuo, Itaya, Mizutani, & Ohno, et al., 1976). In addition, various alkoxyalkyl substituted benzyl esters have been synthesized and investigated by Nakanishi, Mukai, Inamatsu, Tsuda, and Abe (1970).

Furylmethyl ester syntheses with chrysanthemic acid have produced commercially significant products. These included 5-allyl and 5-propargyl furylmethyl esters (Katsuda & Ohgami, 1967) (e.g. furamethrin) and 5-benzyl-3-furylmethyl esters (e.g. resmethrin) (Elliott, Farnham, Janes, Needham, & Pearson, 1967).

Still another rethrolone substitute was investigated in the form of straight chain alkenyl and indanyl groups. Research in this area has generated compounds butathrin, cyphenothrin, and others (Katsuda, 1982).

These synthetic analogues all shared a common heritage. They were esters of chrysanthemic acid and, in varying degrees, carried the same structural inadequacies of the acid portion of their predecessor pyrethrin I. All but the structurally most stable of these derivatives were subject to extensive photo and biochemical degradation and their use was limited to household and some agricultural applications in which photo and biochemical degradation have minimal impact or where a nominal exposure time was required to destroy pest infestations.

A second avenue of exploration has centred upon structural modification of the chrysanthemic acid portion of pyrethronyl esters and the coupling of non-cyclopropane acids with a variety of configurations in the alcohol moiety. The former was carried out by Staudinger et al. in 1924 (in Katsuda, 1982) while research in the latter has persisted to the present day.

Structure-activity studies of derivatives of modifications in the chrysanthemic acid moiety have provided a number of useful generalizations. Functionalities that have appeared essential to effective insecticide activity have included the gem-dimethyl group (Matsui & Kitahara,

1967) and a cis orientation of the methyl group on C_3 relative to the ester linkage (Sugiyama, Kobayashi, & Yamashita, 1975). Substituents which enhanced their insecticidal activity have included: increasing the number of methyl substituents on the cyclopropane ring (Matsui & Kitahara, 1967); substitution of halogens in place of methyl in the isobutenyl side chain of chrysanthemic acid (Bentley, Cheetham, Huff, Pascoe, & Sayle, 1980; Elliot, Farnham, Janes, Needham, & Pulman, 1974; Farkas, Kouriim, & Sorm, 1958); and the substitution of a thiolactone ring in place of the pair of methyl groups on C_3 of the cyclopropane ring (Lhoste & Rauch, 1976) (see Fig. 3).

By far the most novel research synthesis has comprised that of modification of the ester linkage of pyrethroids and the synthesis of pyrethroid-like compounds in which vinylogous and other groups have heen substituted for the cyclopropane group and coupled with various pyrethroid alcohol moieties. Oxime linkage substitution for the ester linkage (Bull, Davies, Searle, & Henry, 1980; Yamamoto & Casida, 1966) was representative of the former and the synthesis of 2-(2-indenyl)-3-methylbutanoates illustrated the latter (Henrick, Garcia, Staal, Cerf, et al., 1980). Recent syntheses of acid-modified pyrethroids have been represented by those derived from halo-4-alkenoic acids (Ayad & Wheeler, 1984) and 3-methyl-2-2(3,4-dihydronaphthyl) butanoic acids esters (Wheeler, 1984).

Chapter 3

PYRETHROID TOXICOLOGY

Introduction

Researchers are in agreement that a variety of factors interact to determine the net toxicological effects of pesticides upon both target and non-target species (Baillie, 1984; Hollingworth, 1976; O'Brien, 1967; Quraishi, 1977). These include penetration and distribution, metabolism, target-site interactions and resistance, and resistance factors. The significance of individual factors may vary greatly from phylum to phylum and may even show significant differences among specific strains within one species. The critical combination of these factors renders one class, species, or even strain highly susceptible to a particular toxicant, while others may be highly tolerant and may even appear to be immune.

Most effective contact toxicants are lipid soluble and penetrate the integument by means that have not been fully investigated (Quraishi, 1977). The more or less apolar extracellular cuticle is in dynamic equilibrium with the metabolic pool, and once penetration has occurred the toxicant is transported to the site of action in non-vertebrates by way of the hemolymph (Quraishi, 1977). There is no evidence to suggest that significant differences exist between the major phyla with respect to permeability that might induce consistent selective toxicity (O'Brien, 1967).

The metabolism of xenobiotics begins on contact with the cuticle, and persists while the toxicant is transported through the organism (Quraishi, 1977). Biochemical action on pesticides detoxifies these

chemicals by means of a variety of reactions which include oxidation, hydroxylation, hydrolysis, conjugation, and other specific reactions. Degradation products are often more polar and easier to excrete. Some metabolic reactions (bioactivation) actually increase the toxicity of some agents (Quraishi, 1977; Schooley & Quistad, 1982). Chemicals that are made toxic or have enhanced toxicity due to bioactivation are commonly referred to as propesticides. While similar degradative means exist within a variety of phyla, the efficiency with which this process is effected varies greatly between those that are effective detoxifiers and those that are intolerant of pesticides (Kao, Motoyama, & Dauterman, 1985; Omura, Harada, & Yoshioka, 1982).

A good deal of research has been undertaken with respect to target-site interactions and resistance, and, although knowledge of some of these features has recently been enhanced, much remains to be revealed. Toxic pesticides owe their effectiveness to their ability to disrupt the essential activity of the nervous system either centrally or peripherally or both. While prolonged exposure to toxicants may induce other fatal physiological consequences, it is the immediate disruption of normal nervous system functions, even for a short period of time, that delivers the fatal blow to the victim (O'Brien, 1967). Most organisms have highly efficient metabolic and excretory functions that would enable them to dispose of toxicants before they were able to effect fatal action upon other body systems.

The nervous systems of different phyla vary a good deal when they are compared in terms of evolved complexity. The central nervous system (CNS) of mammals consists of the brain and spinal cord while in the more

primitive insect a chain of ventral ganglia acts as the integrating and determining system. The peripheral nervous systems across phyla also vary a great deal. Although all organisms possess the means for processing both afferent and efferent information, the mechanisms and efficiencies of their operation show a great deal of diversity. Mammals and other complex vertebrates have an effective blood-brain barrier both centrally and peripherally which permits selective transport of molecules from the blood. In mammals, the myelin sheath plays an important role in this activity (O'Brien, 1967). Insects and other arthropods do not possess myelinated nerve fibres, but they do have an effective blood-brain barrier. Glial cells invest neurons to form what is believed to be an insulating protective sheath in the arthropod nervous system (Chapman, 1982).

A variety of central and peripheral neurotransmitters and putative neurotransmitters have been isolated and characterized for a number of phyla. The precise reasons for the existence of so many neurotransmitter chemicals and the accurate descriptions of their individual functions have not yet been fully explained. Some generalizations can be made. Much remains to be discovered, and while the distribution of neurotransmitters may not be precisely constant across phyla, research shows that acetylcholine is an important CNS neurotransmitter in a broad range of organisms. The types of receptors for this transmitter may, however, vary for specific phyla (Chapman, 1982; Eldefrawi & Eldefrawi, 1983). Parent (1981a; 1981b) reviewed literature which reported serotonin (5-Hydroxytryptamine (5HT)) present as a CNS neurotransmitter in a wide range of phyla. Insects and vertebrates have many peripheral

neurotransmitters; those that are found in both include acetylcholine, dopamine, γ-aminobutyric acid, glutamate, and the previously mentioned 5-hydroxytryptamine (Clarke & Donnellan, 1982; Eldefrawi & Eldefrawi, 1983). L-glutamate is a proposed excitatory neuromuscular agent and γ-aminobutyric acid, an inhibitory neuromuscular agent in insects (Miller, 1978). In vertebrates, cholinergic and adrenergic junctions figure prominently in peripheral nervous transmissions. Differences in the kinds and sensitivities of neurotransmitters and their receptors in conjunction with anatomical differences contribute significantly to the range of toxicities of various pesticides toward individual species.

Resistance, the development of immunity, includes avoidance by virtue of irritation and other non-specific factors, but pertains in particular to the development of genetic resistance. Genetic resistance is often induced and controlled by a single gene allele, in which case the development of resistance is strong. When resistance is due to a combination of genes, its development takes much longer (Quraishi, 1977; Plapp, 1984). Resistance mechanisms are acquired genetically and may include a change in the enzyme rate of detoxification or reduction in the sensitivity of the site of action (Oppenoorth, 1984).

In light of the foregoing, it is apparent that research in the area of pesticide toxicology has become rather sophisticated and holds potential for considerable reward. One final point of clarification is in order. Many pesticides have been developed and certified for use in specific regions and, from time to time, certain of these have been banned for specific environmental, ecological, and health reasons. At present, no international regulatory agency exists apart from the World

Health Organization. This agency monitors the world use of pesticides and provides guidelines for their safe use only. Thus, it is the domain of each individual country to regulate the certification and use of pesticides. As a consequence, the variety of pesticides licensed for use differs substantially in many parts of the world. In the province of Alberta, the Department of Environment (Pollution Control Division) monitors and regulates the use of pesticides. In turn, Agriculture Canada (Plant Products and Plant Health Division) certifies chemicals for pest control and sets down regulations which provide guidelines for provincial implementation (personal communication, 1986).

Pyrethroid Symptomology

O'Brien (1967) described allethrin poisoning of insects as excessive excitability followed by paralysis. Individual variation in symptoms he attributed to differences in relative peripheral and central effects. Aldridge (1982) observed two modes of action in rats depending on the group of pyrethroid sampled. A "T-syndrome" consisting of aggressive sparring with sensory sensitivity, which progressed into tremoring and eventual prostration, was contrasted with a "CS-syndrome" which featured pawing and burrowing, salivation, tremoring, and clonic seizures. Narashi (1982) and Lund (1984) recorded similar poisoning symptoms which featured tremoring, convulsions, and paralysis.

Toxicity

The pyrethrins and early pyrethroids are thought to be quite selective as pesticides while some of the more recent formulations are con-

sidered to be rather broad spectrum pesticides (Aldridge, 1982). Pyrethroids are of low toxicity to mammals with oral LD-50 values (the dose required to kill 50% of test animals) ranging between 425 ppm and greater than 20,000 ppm (Kenaga & End, 1974). They are highly toxic to insects and are extremely effective with selective applications. Topical application of a mix of pyrethrin I and I-I provided an LD-50 value when administered at 40 ppm to the Japanese beetle and 1 ppm to the Aedes aegypti mosquito (O'Brien, 1967). Pyrethroids are of low toxicity to birds (Aldridge, 1982) and are readily metabolized by ester cleavage and oxidation reactions (Leahey, 1979). McEwen and Stephenson (1979) published useful data on the LD-50 values of a wide range of pesticides for 8 bird species.

Unfortunately, like many other pesticides, pyrethroids are extremely toxic to fish and to aquatic microorganisms. In an article reviewing the risks of synthetic pyrethroids to fish, Khan (1982) cited data from several studies indicating LC-50 (the concentration required to kill 50% of test animals) values in 96-hour test experiments in the low ppb and ppt range for fish and aquatic invertebrates. One such study by Coats and O'Donnell-Jeffrey (1979) reported 24-hour LC-50 values for 4 pyrethroids ranging between 8.6 ppb and 61 ppb when administered to rainbow trout.

Generalizations about pyrethroids allow that they are rather innocuous pesticides in that their metabolites are generally non-toxic and, as a class, they are largely non-mutagenic and non-carcinogenic and have marginal reproductive and teratogenic potential (Aldridge, 1982). In addition, cis-isomers are generally more toxic than are trans-isomers.

Mode of Action

While a variety of theories has been proposed with respect to the mode of action of pyrethroids (Gray, 1985; Lawrence, Gee, & Yamamura, 1985; Matsumura, 1982; Narahashi, 1985; Nicholson, Wilson, Potter, & Black, 1982; Osborne & Smallcombe, 1982; Soderlund, 1985, Vijverberg & de Weille, 1985), the model which best summates the available data and incorporates them into a plausible theory, that reflects the views of a good number of researchers in a very credible fashion, is that offered by Lund (1984). This model proposes that the primary action of pyrethroids on the nervous system is not unlike that of DDT and that the range of observed symptoms induced by a variety of pyrethroids is that which differs only in degree and not kind. Lund's model suggests that pyrethroids are nerve membrane sodium channel intoxicants that interact with sodium channels in the open configuration and modify their kinetics such that their inactivation under depolarizing conditions is retarded and their return to the resting state under polarizing conditions is inhibited. According to Lund, the dysfunction of less than 1.0% of Na^+ channels can induce poisoning symptoms which are characterized by repetitive firing and trains of action potentials and development with acute poisoning into reduction of action potential amplitude and conduction block.

Degradation

The degradation of pyrethroids by metabolic means has been investigated substantially in some species and only sparingly or not at all in others. There is agreement that, for a broad range of vertebrates, the

enzyme systems charged with the inactivation of xenobiotics differ not in kind but only in efficiency (Foureman & Bend, 1982). Metabolizing enzyme systems include hydrolytic, reductive, and conjugative enzymes and cytochrome P-450 dependent mono-oxygenases (Foureman & Bend, 1982). Mammals are noted to be resistant to pyrethroids due to their ability to metabolize these compounds efficiently by means of ester hydrolysis and hydroxylation reactions (Aldridge, 1982). Other vertebrates, fish in particular, and microbiological organisms detoxify pyrethroids by similar means but are much more susceptible because of their inefficient means of degrading these foreign compounds. Insect susceptibility is due to their inability to degrade pyrethroids efficiently, since the means available to them -- which include hydrolysis and oxidation -- are similar in nature to that of vertebrates (Aldridge, 1982; Ishaaya & Casida, 1982).

The photochemical degradation of pyrethroids is effected by two principal means. The natural pyrethrins and early photolabile pyrethroids are subject to extensive oxidative inactivation reactions and consequently have a very limited persistence in the environment. By contrast, more recent photostable pyrethroids undergo photochemical reactions which include isomerization, dehalogenation, decarboxylation, and ester cleavage, and undergo oxidative photochemical reactions only as secondary reactions (Miyamoto & Mikami, 1982; Ruzo, 1982). These photostable pyrethroids are much more stable than their antecedents and may present an environmental threat due to their increased persistence in the environment (Briggs, Elliott, & Janes, 1982; Elliott & Janes, 1983; Kimmel, Casida, & Ruzo, 1982).

Summary

In summary, the foregoing has shown that economically significant pesticides act within a fairly narrow and clearly definable range in terms of symptoms and action modes, and vary significantly primarily with respect to toxicity and degradation characteristics.

Previous photochemical research conducted on resmethrin is presented in Chapter 4, along with an outline of the materials and research methodologies employed used in this particular study.

Chapter 4

RESMETHRIN PHOTOCHEMISTRY

Physical and Chemical Properties

Resmethrin, 5-(phenylmethyl)-3-furylmethyl 2,2-dimethyl-3(2-methyl-1-propenyl)cyclopropanecarboxylate is an odorless, yellow, crystalline solid with a boiling point of 180°C and a melting point just above room temperature (Papadopoulou-Mourkidou, 1983).

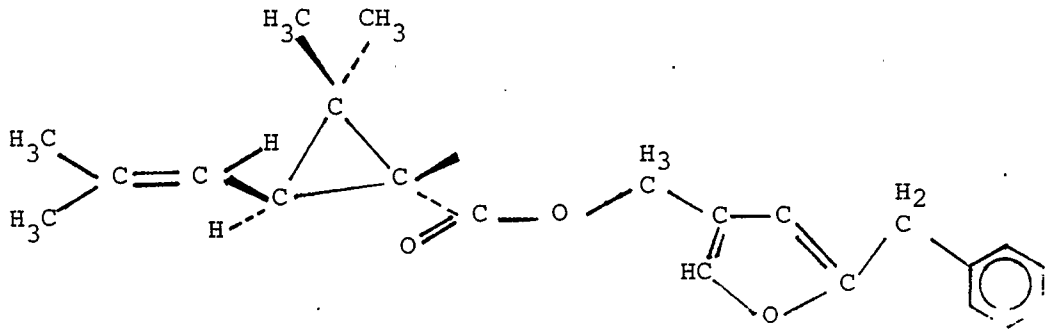


Figure 4. Trans-Resmethrin

This compound, ($C_{22}H_{26}O_3$), with a molar mass of 338 g, has the distinction of being the first synthetic pyrethroid to demonstrate equal or greater killing activity toward many insect species than its natural precursors, and shows a somewhat lower level of toxicity toward mammalian species (Elliott, 1977). Despite its enhanced capabilities in both toxicity and specificity, resmethrin retains the inherent lack of photostability that has characterized the natural pyrethrins (Fig. 4).

The photochemical activity of the pyrethrins, pyrethroids, and related compounds has been the subject of continued extensive research. While a variety of conditions has been examined, the majority of labora-

tory and field studies have involved non-aqueous media. Ruzo (1982:311) defended the lack of research in aqueous media with a single statement:

> Their lipophilicity does not easily allow for photo--chemical investigations in aqueous solutions, nor may this type of study be recommended since it is most likely that their immediate environment will be a solid particle or hydrophobic layers.

Miyamoto and Mikami (1982) attested to the lack of research data on the behaviour of pyrethroids in aquatic environments. They reminded their colleagues of the significance of studies on accumulation and degradation in aquatic environments in that natural drainage and reservoir systems could easily be contaminated with pyrethroid residues and their degradation products, and thus present a significant environment hazard. They argued further that the accumulation of these data might provide useful insights into the development of new types of pyrethroids with lower levels of toxicity to particularly sensitive non-target species.

The statements of these two environment-conscious pesticide researchers provided the impetus for this review of the research conducted on the photochemical reactions of resmethrin in aqueous media which, in turn, provided the foundation for this photochemical study of resmethrin in an aqueous medium.

In all, no more than six papers have commented significantly on the photochemistry of resmethrin. Of these, only one (Ueda, Gaughan, & Casida, 1974) offered extensive, detailed research data on resmethrin

photochemistry. One other (Ruzo, Casida, & Holden, 1985) provided the results of a single photochemical study of resmethrin in conjunction with discussions of reactions of 5-benzyl-3-furylmethyl derivatives. The remainder either reviewed the accumulated information on photochemical degradation of resmethrin and other synthetic pyrethroids or provided data on the photochemical activity of chrysanthemic acids, and 5-benzyl-3-furylmethyl alcohols and their derivatives.

The single, extensive study of resmethrin photochemistry was conducted by Ueda, Gaughan, and Casida and the results in their research were published in 1974 in the Journal of Agricultural Food Chemistry. The authors of this paper reported that the photolysis of resmethrin yielded, amongst others: the alcohol, aldehyde, and acid of benzene; nonisomerized chrysanthemic acid and phenyl acetic acid; the chrysanthemates of 2-benzyloxy-5-oxo-2,5-dihydro-3-furyl-methanal, 5-hydroxy-3-oxo-4-phenyl-1-cyclopentenylmethanol, and 5-benzyl-5-hydroxy-2-oxo-2,5-dihydro-3-furylmethanol; the isomeric epoxychrysanthemates with both modified and unmodified alcohol moieties; and a number of unidentified ester photoproducts.

The characterized products were extracted photoproducts of the studies next described. In one study, oxygen-aerated (+)-cis-resmethrin as a mixture with Rose Bengal in methanol was irradiated with a 40-watt G.E. showcase lamp for a period of 3 hours. The principal abundant photoproduct was 5-benzyl-2-hydroperoxy-5-methoxy-2,5-dihydro-3-furylmethyl cis-chrysanthemate. In a second experiment, unlabelled (+)-trans and (+)-cis-resmethrin, 4.0 and 3.0 g respectively, were applied at 1.7 mg/cm^2 to silica gel 60 chromatoplates and exposed to solar irradiation

for a period of 10 hours. Significant characterized extracts included unphotolyzed resmethrin and chrysanthemic acid. Minor products included benzaldehyde, phenylacetic acid, two oxidized esters, and benzyl alcohol and benzoic acid. The remaining products were poorly resolved and not characterizable. A third photostudy of resmethrin utilized [^{14}C] resmethrin. Radioactive (+) and (-)-trans-resmethrin deposits on silica gel 60 chromatoplates were irradiated for 90 minutes with a sunlamp. Of the 11 photoproducts identified, 7 were esters and the others were trans-chrysanthemic acid, benzyl alcohol, benzoic acid, and phenylacetic acid. Time comparison studies of acid-labelled trans-resmethrin, trans-tetramethrin, and a s-bioallethrin were conducted on silica gel chromatoplates irradiated with a sunlamp for 30 to 90 minutes and with sunlight for 15 minutes. Resmethrin was found to be the most photolabile of the three. A fifth study included sunlight and sunlamp irradiation of [^{14}C] trans-resmethrin on filter paper, glass plates and silica gel, and as a solution in water. Recovered products included: trans-resmethrin, (+) and (-) trans-epoxyresmethrin, cyclopentenolone (5-hydroxy-3-oxo-4-phenyl-1-cyclopentenylmethyl trans-chrysanthemate), hydroxy lactone (5-benzyl-5-hydroxy-2-oxo-2,5-dihydro-3-furylmethyl trans-chrysanthemate), benzyloxy lactone (2-benzyloxy-5-oxo-2,5-dihydro-3-furylmethyl trans-chrysanthemate), and trans-chrysanthemic acid. A sixth study incorporated the use of uv screening agents, antioxidants, and light filters. Only the use of light filters significantly altered the product yield, both in rate and ratio, for the photodecomposition of trans-resmethrin on silica gel plates.

The single, remaining, authentic aqueous photo-chemical research was published by Ruzo, Casida, and Holden in 1985. Photo-oxidations of resmethrin were conducted as 0.2 molar solutions in oxygen-saturated $CDCl_3$ at 360 nm. Samples were irradiated with a Rayonet photo-reactor, using RPR 3500 lamps for a period of 2 hours. The authors reported that keto aldehydes were not detected and confirmed the previously reported benzylidene lactone chrysanthemate (Ueda et al., 1974). They concluded that furan epoxidation and ring cleavage reactions appeared to contribute to the photochemical and metabolic breakdown of resmethrin and related compounds.

From this review it became apparent that photolysis of resmethrin in distilled water, rainwater or standing ground water had been seriously neglected. It was therefore resolved to undertake the study of the photodegradation of resmethrin in a medium that, to some extent, simulated natural conditions. Photolyses were also to be conducted in distilled water, for comparative purposes.

In order to develop an effective experimental protocol for the photolysis, extraction and analysis phases of the experimental portion of the study previously reported experiments were repeated and the results obtained compared with these in the literature.

Experimental Materials and Methods

Chemicals

All chemicals used as general reference compounds for comparison with suspected photoproducts were of reagent grade and were used without further purification. Solvents and other reagents used for clean-up and

extractions were mostly of reagent grade. Reference compounds resmethrin and permethrin, and resmethrin used in the photochemical studies discussed in this work were generously provided by M. Elliott and N. F. Janes of the Rothamsted Experimental Station, Harpenden, Hertfordshire, England.

Resmethrin Cleanup

Technical grade resmethrin (30%/70% cis-trans) was purified by column chromatography. Samples (5.00 g) of technical grade resmethrin were dissolved in 20 ml of (30°-60°) petroleum ether and introduced onto the column which had been prepared with 40 g of silica gel per gram of resmethrin and was wetted with (30°-60°) petroleum ether. The resmethrin was eluted with 200 ml portions of 50:50 petroleum ether:toluene. Twelve fractions were collected and evaporated to near dryness. Each fraction was then dissolved in a small amount of petroleum ether and transferred to a sample vial for analysis by gas chromatography.

Photolysis

Resmethrin in hexanes (extended irradiation P3 and P4). Two experiments were performed in which 1.00 g of resmethrin was dissolved in 295 ml of hexane in a pyrex Erlenmeyer flask fitted with a water-cooled condenser. One was irradiated for a period of 8 days while the other was irradiated for a period of 8.5 days in a Rayonet Reactor equipped with RPR 3000 light filaments.

Resmethrin in methanol (3 hr. P5-A/B). Duplicate experiments were performed in which 1.00 g of resmethrin was dissolved in 300 ml of methanol in a pyrex Erlenmeyer flask fitted with a water-cooled condenser. The

solutions were irradiated for a period of 3 hr. in a Rayonet Reactor equipped with RPR 3000 light filaments.

Resmethrin in water (3 hr. P6-A/B). Duplicate experiments were performed in which 10 mg of resmethrin dissolved in 3 ml of ethyl acetate was evaporated to dryness on a pyrex petri dish and immersed in 5.0 ml of distilled water at a pH = 5.8. The samples were irradiated for 3 hr. in a Rayonet Reactor equipped with RPR 3000 light filaments.

Resmethrin in hexanes (3 hr. P7-A/B). Duplicate experiments were performed in which 0.10 g of resmethrin were dissolved in 30.0 ml of hexane in a pyrex Erlenmeyer flask fitted with a water-cooled condenser. The samples were irradiated for a period of 3 hr. in a Rayonet Reactor equipped with RPR 3000 light filaments (peak output λ = 290-320 nm, which lies within the solar spectrum).

Resmethrin in distilled water (P8-A/B). Duplicate experiments were performed in which 280 mg of purified resmethrin dissolved in 14 ml of ethyl acetate was transferred in 0.50 ml aliquots into two sets of 14 numbered pyrex test tubes from which the solvent was then evaporated. Distilled water (5 ml) with a pH = 5.8 was added to each test tube. The remainder of the experiment was conducted as per the resmethrin in the "snow-melt" experiment.

Resmethrin in "snow-melt" water (P9-A/B). Duplicate experiments were performed in which 140 mg of purified resmethrin dissolved in 7 ml of ethyl acetate was transferred in 0.50 ml aliquots into 14 numbered pyrex test tubes from which the solvent was then evaporated. Filtered "snow-melt" water (5 ml) (which had been obtained earlier from the Ghost River valley on the Forestry Trunk Road, 5 miles north of 1A Highway, in

Alberta) with a pH = 7.3 was added to each test tube. The test tubes were stoppered with corks and sealed with para-wax film and placed at an angle (so that the liquid phase did not contact the cork stoppers) in white styrofoam test tube trays. These samples were then placed on the roof of Science B Building at the University of Calgary in bright sunlight exposure and samples were selected for analysis according to a predetermined schedule.

Extractions and Quantitation

Resmethrin water extraction.

Resmethrin photo product residues were saturated in their aqueous media with reagent grade NaCl and then extracted with dichloromethane (3×10ml) in a separatory funnel (Ueda et al., 1974). The extract was dried by passing it through anhydrous Na_2SO_4. These were then evaporated to near dryness and transferred in about 2 ml of ethyl acetate to sample bottles for analysis.

Resmethrin extraction from methanol and hexane.

Products of photolysis were isolated from the solvent systems by evaporation to near dryness. The residues were dissolved in a small volume (3 ml) of ethyl acetate and transferred to sample vials.

Extraction efficiency experiment.

Resmethrin (0.090 g) was dissolved in 3 ml of ethyl acetate and evaporated to dryness on a pyrex petri dish. Five ml of distilled water was added to the petri dish and the system was saturated with reagent grade NaCl. The resmethrin was extracted by partition into CH_2Cl_2 (3×10ml) in a separatory funnel and dried by passing it through anhy-

drous Na_2SO_4. The solvent was removed with a combination of rotary and vacuum evaporations. Extraction efficiency was calculated as the percentage of resmethrin reisolated.

Spiking experiment.

Quantitation was effected by the addition of resmethrin to selected samples. Integrated gas chromatograms were acquired for each sample prior to and after spiking with a measured mass of purified resmethrin. These data were then used to calculate the integrator counts per mg value for that sample, for resmethrin and thence the absolute quantities of components in product mixtures.

Physical Data

A mixture of the cis/trans-isomers of resmethrin has a melting point just above room temperature (Papadopoulou-Mourkidou, 1983). The compound is highly lipophilic and has a water solubility of less than 1 ppm (Khan, 1982). The logarithm of octanol-water partition coefficient is 6.2 (Elliott, 1976). Resmethrin is photochemically active and absorbs substantially in the 240-320 nm range (ε max = 12.51 cm^{-1} $mole^{-1}$ litre, λ = 270 nm). Resmethrin mass spectral data include (EI):m/e (relative intensity) 338 (2) (M), 171 (60), 143 (51), 128 (40), 123 (100), 91 (17), 81 (25), 43 (22), 41 (25).

Instrumentation

Gas chromatography/mass spectroscopy (gc/ms).

Gc/ms coupled analyses were performed with a Shimadzu G.C. gas chromatograph connected to a VG Micromass 7070F mass spectrometer. Two

analytical capillary columns were used: (1) a J. & W. Scientific DB-1 column, an OV-101 equivalent bonded phase, low polarity alkylated silicone liquid phase, 20 m × 0.25 mm i.d. column with a 25 μm coating; (2) an S.G.E. BP-1 column with an identical bonded liquid phase as above, 25 m × 0.22 mm i.d. with a 25 μm coating. A split injector system (ratio 50:1) was used with He flow rate of 0.5 ml/min. through the column. A temperature program of 5°/min. at 60°C with a temperature gradient of 5°/min. (or 15°/min.) to 250°C which was maintained for an additional 5 min. to resolve experimental components.

Gas chromatography.

Quantitation of products was performed on a Varian model 3700 gas chromatograph utilizing flame ionization detection and a Varian 4290 integrator. The carrier gas was helium. Analyses were performed on two columns: (1) an SE-30 vitreous silica capillary column, 12 m × 0.33 mm i.d., with a temperature program of 5 min. at 50°C followed by a temperature gradient of 15° per min. to 220°C which was maintained for an additional 20 min.; (2) a second OV-101 column but of 30 m × 0.25 mm i.d. with a 0.25 μm coating, utilizing the same temperature program as set up for the earlier mentioned OV-101 column.

Infrared analysis.

Infrared analyses were performed on a Perkin-Elmer 467 Grating Infrared spectrophotometer.

Ultraviolet analysis. Ultraviolet spectra were obtained on a Unicam SP 1800 ultraviolet spectrophotometer equipped with a Unicam AR 25 Linear Recorder.

Proton and carbon-13 magnetic resonance analysis.

^{1}H and ^{13}C NMR spectra were obtained on a Varian XL 200 NMR spectrometer. The solvent used was $CDCl_3$ which also provided the lock signal with TMS as internal standard.

Derivatization

Esterification. Methyl ester synthesis was effected by a recommended procedure (Morrison & Smith, 1964). Reagent (3 ml) (BF_3, BCl_3) was added to 100 - 200 mg of sample in a 20 mm × 150 mm test tube and boiled for 2 min. The product was poured into 20 ml of distilled water and then transferred to a separatory funnel containing 30 ml of petroleum ether (30° - 60°). The mixture was agitated vigorously and the layers were allowed to separate. The petroleum ether fraction was extracted and dried over anhydrous Na_2SO_4. The sample was evaporated to near dryness and transferred in 2 ml of ethyl acetate to a sample vial.

Trimethylsilyl derivatives. Trimethylsilyl ethers were synthesized by a standard method (Sweeley, Bentley, Makita, & Wells, 1963). Samples (10 mg) were added to a solution containing 1.0 ml of pyridine, 0.2 ml of hexamethyldisilazane, and 0.1 ml of trimethylchlorosilane. The mixture was shaken vigorously for a minimum of 30 sec. and was transferred to a sample vial after standing at room temperature for a minimum of 5 minutes.

The results of these experiments and some suggested interpretations of the research described here are given in Chapter 5.

Chapter 5

OBSERVATIONS AND INTERPRETATIONS

This section describes the preparation of the materials used in the study, experiments performed to establish the quantitative nature of the extraction procedure, and the results of the photolysis reactions themselves, including kinetic analysis. In discussing the analysis of products from photolysis, the results from the extended photolysis in aqueous media are discussed first, since these experiments provided appreciable quantities of photoproducts that could be analyzed by gc/ms. Thus gc and spectral parameters were obtained from these samples, and subsequently these data were used to positively identify photoproducts in the case of the photolyses P3-P7.

Resmethrin Clean-up

In this research, column clean-up of technical grade resmethrin (30%-70% cis/trans) produced substrate of >95% purity without appreciable alteration of the cis/trans ratio. Calculations based upon gas-chromatogram integration values yielded a cis/trans ratio ranging between 25.4/74.6 and 33.7/66.3 with a mean of 30.6/69.4%. A gas chromatogram and mass spectrum of the resmethrin used for the experiments in this research are shown in Figures 5 and 6, and proton and Carbon 13 NMR spectra (with assignments) of the same sample are found in Figures 7 and 8.

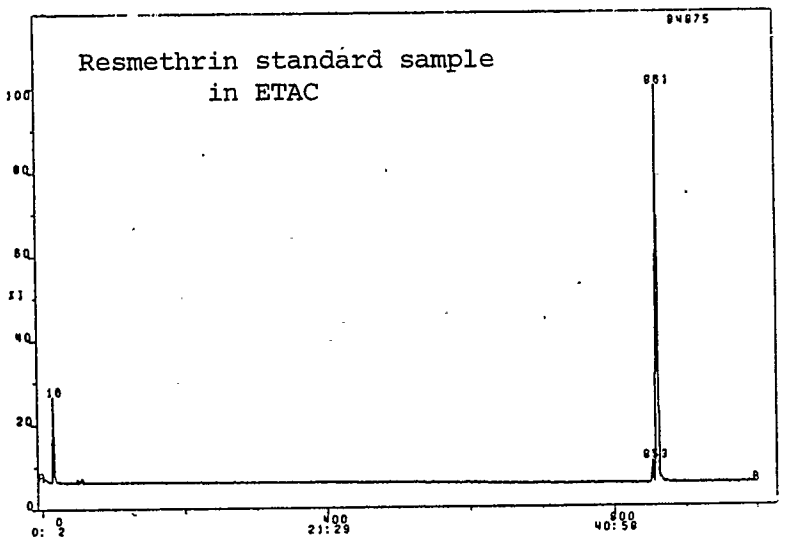


Figure 5. Standard resmethrin total ion current gas chromatogram.

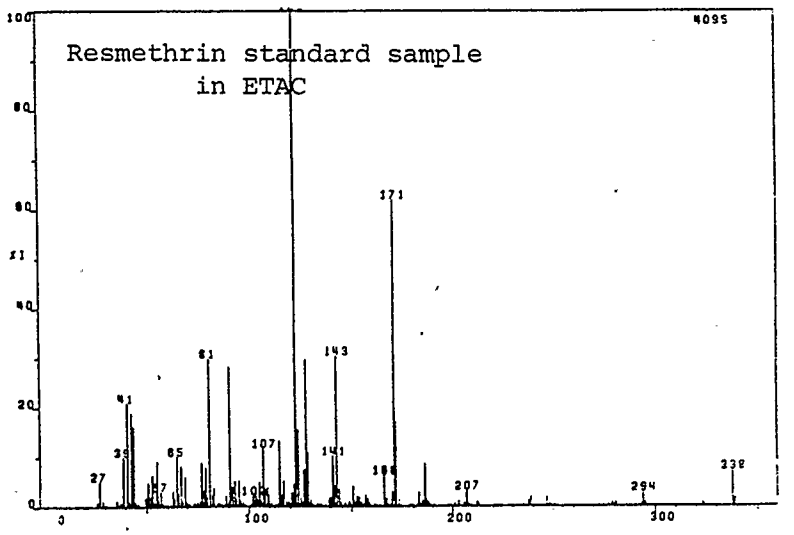
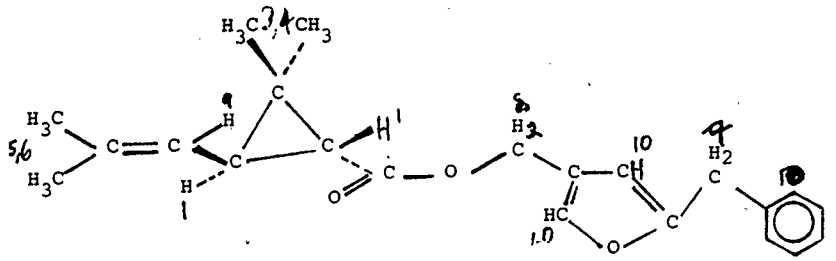


Figure 6. Standard resmethrin mass spectrum.

Proton Chemical Shift Assignments

Chemical	Shift (δ)	Group
1.	1.24	cyclopropyl
2.	1.43	cyclopropyl
3.	1.12	methyls on cyclopropane
4.	1.25	
5.	1.69	methyl on double bond
6.	1.70	
7.	3.94	methylene on phenyl ring
8.	4.91	methylene on oxygen
9.	6.04	Double bond proton
10.	7.20-7.35	Benzene ring (5 protons)
		Furan ring (2 protons)



Trans-resmethrin

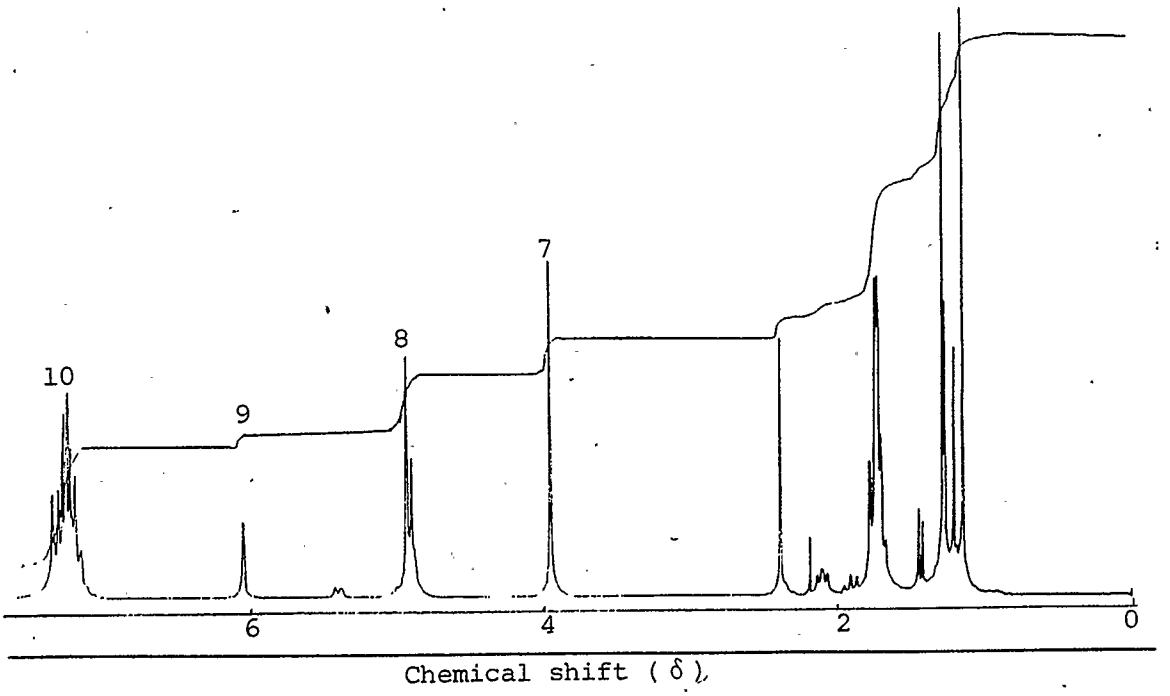
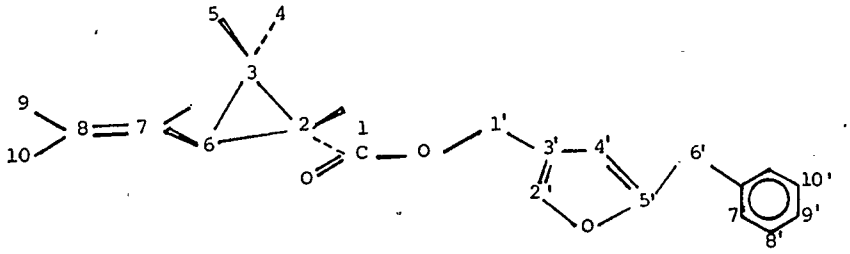


Figure 7. Resmethrin proton NMR

Carbon Chemical Shift Assignments

Carbon No.	Alcohol PPM	Carbon No.	Acid PPM
1'	57.7	1	172.4
2'	140.25	2	34.7
3'	121.41	3	38.72
4'	107.28	4	20.4
5'	155.51	5	22.15
6'	34.55	6	32.82
7'	137.77	7	121.07
8'	128.52	8	135.49
9'	128.72	9	18.45
10'	126.55	10	25.53



Trans-resmethrin

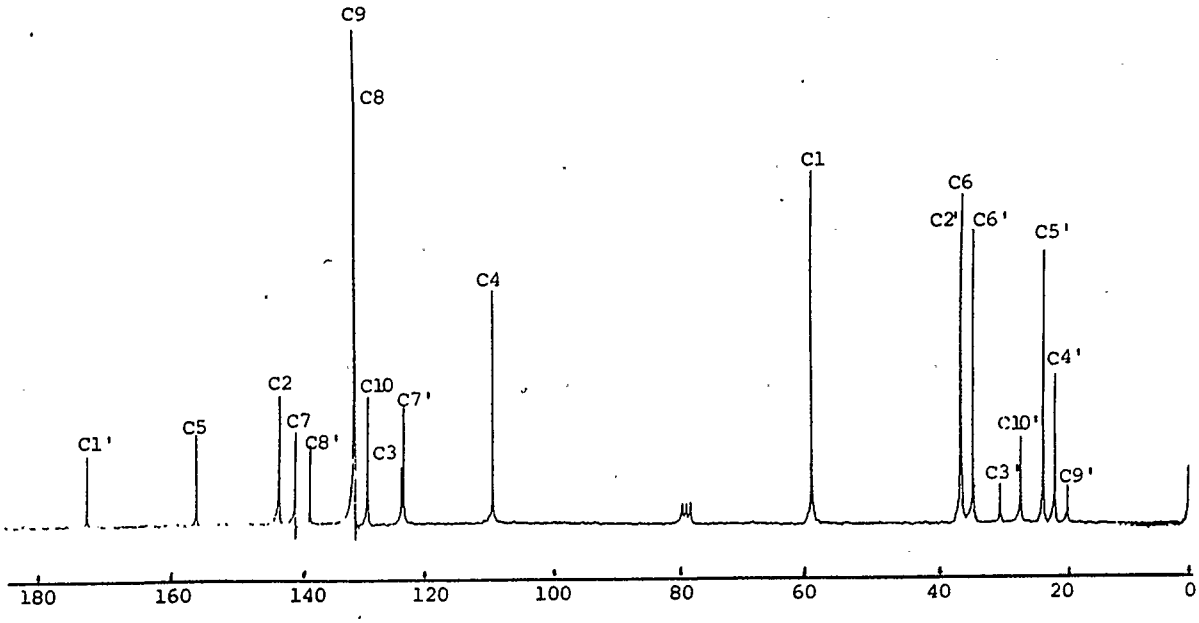


Figure 8. Resmethrin Carbon-13 NMR spectrum

Resmethrin P9-A		Resmethrin P9-B	
X (Days)	Y (Log % resmethrin)	X (Days)	Y (Log % resmethrin)
1	1.896	1	1.915
2	1.892	2	1.921
3	1.916	3	1.916
4	1.932	4	1.899
5	1.912	5	1.901
6	1.915	6	1.879
7	1.866	7	1.871
8	1.866	8	1.830
11	1.916	11	1.876
14	1.904	14	1.664
17	1.866	17	1.862
20	1.874	20	1.837
23	1.624	23	1.866
26	0.964	26	1.855
Slope = -2.14292E-02 Y-Intercept = 2.02808		Slope = -3.30262E-03 Y-Intercept = 1.89843	

Slope equation $$m = \frac{\Sigma X_i Y_i - \Sigma X_i \Sigma Y_i / n}{\Sigma X_i^2 - \Sigma X_i^2 / n}$$

Resmethrin P8-A		Resmethrin P8-B	
X (Days)	Y (Log % resmethrin)	X (Days)	Y (Log % resmethrin)
1	1.943	1	1.957
2	1.957	2	1.412
3	1.959	3	1.525
4	1.953	4	1.783
5	1.954	5	1.739
6	1.951	6	1.698
7	1.933	7	1.915
8	1.942	8	0.000
10	1.927	10	1.862
12	0.874	12	1.893
14	1.855	14	1.397
16	1.920	16	1.609
18	1.851	18	0.000
19	1.444	19	0.000
Slope = -2.14472E-02 Y-Intercept = 2.01028		Slope = -6.89952E-02 Y-Intercept = 1.95817	

Extraction Efficiency

Extraction efficiency based upon a single trial was qualitative. Indeed a slight increase was recorded. This was due to the presence of traces of extracting solvent.

Spiking Experiment

Calculations of absolute quantities of components in product mixtures, based upon data acquired from the spiking of selected samples from photolysis experiments, provided an alterative check of the efficiency of extraction of photolysis products from aqueous media. In addition, these data (as already indicated) afforded quantitation of components in product mixtures of the selected samples. Determination of the mass of products extracted for three of the samples spiked established extraction values of 10.66, 13.02, and 15.10 mg. The yield in excess of the 10 mg input was explained, in part, by the observation that several of the compounds accounted for in the mass integration had been derived from accumulation of impurities in the clean-up solvent system used. Thus, additional confirmation had been acquired for the almost quantitative extraction of photoproducts from the system.

Reaction Kinetics

The rate equation for a first-order reaction is

$$\text{Rate} = -d[A]/dt = k[A]$$

where -d[A] is the change in concentration of A, dt is the change in time, and k is the "rate constant". This equation can be converted into the expression

$$\log (a-x) = (-k/2.303)t + \log (a)$$

where initial concentration of A = a, and concentration of A that has reacted at time t = x. This is the form of the equation for a straight line

$$y = mx + b.$$

From this equation, the slope of the line is -k/2.303 and from this the rate constant can be determined.

$$k = - \frac{\text{slope}}{2.303}$$

Data from P8 and P9 were fitted to this equation using a linear least squares procedure. The first-order rate constants and the half-life for the reaction under these experimental conditions were calculated from the slope. The equation used for the least squares procedure, the input data, and the slope and Y intercept values, are given in Tables 1 and 2. Values of X represent the number of days that the sample was photolysed and Y values represent the logarithm for the percentage of resmethrin for measureable residues. Values for the Y intercept are one measure of the goodness of fit and show approximately 100% resmethrin was present at day 0 (80-109%).

Since resmethrin, like all pyrethroids, has a low solubility in water (0.2 ppm) (Briggs et al., 1982), the system is best described as a large chemical reservoir (10 mg) which maintains the concentration of resmethrin in the solution phase at a constant and saturated level throughout the photolysis. On this basis it may seem appropriate to view the reaction in the solution phase as a zero order reaction. How-

ever, since photolysis most probably occurred in the solid and solution phases and the analysis of photoproducts was performed upon the residue from the entire system, both solution and pure state, the reaction is viewed as a pseudo first-order reaction and the "rate constant" was calculated accordingly.

Calculations of the rate constant from the data for the four trials rendered a rate constant range of 0.00761 to 0.159 $days^{-1}$, with trials P8-A and P9-A giving values of 0.0494 and 0.0494 $days^{-1}$, respectively. Substitution of these rate constant values into the equation

$$T_{0.5} = 2.303 \log (2/k)$$

allows the time required to photo-decompose 50% of the parent compound, the half-life, to be calculated. Photo-decomposition rates (P8-A and P9-A) give a half-life for the resmethrin of 14 days. Only one of the four calculations produced an interval of less than 14 days. A majority of the data indicated a lengthy persistence of the parent compound.

Resmethrin in "Snow-Melt" Water (P9-A/B)

Resmethrin samples, prepared by the method discussed earlier, were photolysed in bright sunlight in the manner previously described. Photolysed samples were collected in the schedule as outlined in Table 3 and were prepared for analysis by the method described under "Resmethrin Water Extraction." The hours of bright sunshine, and daily maximum, minimum, and mean temperatures for the duration of the experiment, are listed in Table 4. Photolysed samples, once extracted, were stored in closed vials, placed within light-shielding, cardboard boxes and kept under refrigeration. Individual samples were then selected for specific analyses.

Sample No.	Date Collected	Sample No.	Date Collected
S1	18/07/85	S8	25/07/85
S2	19/07/85	S9	28/07/85
S3	20/07/85	S10	31/07/85
S4	21/07/85	S11	03/98/85
S5	22/07/85	S12	06/08/85
S6	23/07/85	S13	09/08/85
S7	24/07/85	S14	12/08/85

	C-T E M P E R A T U R E S			Hours Bright
Date	Max.	Min.	Mean	Sunshine
JUL				
18	24.9	6.4	15.7	13.6
19	20.9	9.3	15.1	6.1
20	25.9	9.5	17.7	14.4
21	32.0	13.2	22.6	14.5
22	30.7	12.2	21.5	12.6
23	21.6	10.6	16.1	4.6
24	21.1	9.7	15.4	11.6
25	25.0	11.0	18.0	13.2
26	21.0	11.0	16.0	13.5
27	21.5	8.0	14.8	14.3
28	23.0	11.9	17.5	7.5
29	17.4	10.5	14.0	2.1
30	24.6	8.0	16.3	10.1
31	25.0	10.5	17.8	14.4
AUG				
1	28.0	9.0	18.5	7.4
2	27.7	12.0	19.9	6.0
3	28.4	11.6	20.0	13.0
4	29.1	12.8	21.0	10.2
5	24.0	10.6	17.3	9.0
6	24.0	8.1	16.1	11.2
7	25.8	10.7	18.3	1.8
8	13.1	4.5	8.8	3.9
9	20.0	2.2	11.1	4.2
10	11.3	6.7	9.0	1.4
11	20.0	3.4	11.7	7.1
12	13.2	7.2	10.2	3.3

Qualitative Analysis (Characterization)

To facilitate the identification of extracted products, reagent grade samples of suspected reference compounds (Fisher Scientific Company, or Aldrich Chemical Company) were run to produce retention times and mass spectra for comparison with resolved photoproducts. The resulting mass spectra are shown in Figures 14 through 18. Further verification was obtained by comparison with mass spectral data acquired from the U.S. National Institute of Health, Environment Protection Agency (NIH/EPA) Handbook and Eight Peak Index of Mass Spectra references.

Analysis of photolysed samples with an OV-101 equivalent gc column resolved a substantial number of components. Their photochemical development with time is traced here in the section dealing with the quantitative descriptions of this experiment. Examination of all data collected from the extracted samples of the duplicate experiments resulted in the selection of sample P9-12B (20 days of solar irradiation) as the best candidate for interpretive purposes. A gas-chromatogram of the sample is reproduced in Figure 14. The mass spectra of resolved peaks were interpreted and their identification is discussed below.

Scan numbers below #62 were examined and labelled as acetone (#17), ethyl acetate (#26), and other solvent components, and not photoproducts. Scan #62 had a retention time of 4:02 min., and both its retention time and mass spectrum (see Fig. 15a) corresponded closely with those of the reference sample. A spectrum with substantial peaks at m/e (mass per unit charge) 92 (molecular ion, "M^+") and 91 (M^+ -1 ions), and a base peak of 43 mass units, is characteristic of toluene. Since toluene was used as an eluting agent in the clean-up of the resmetherin,

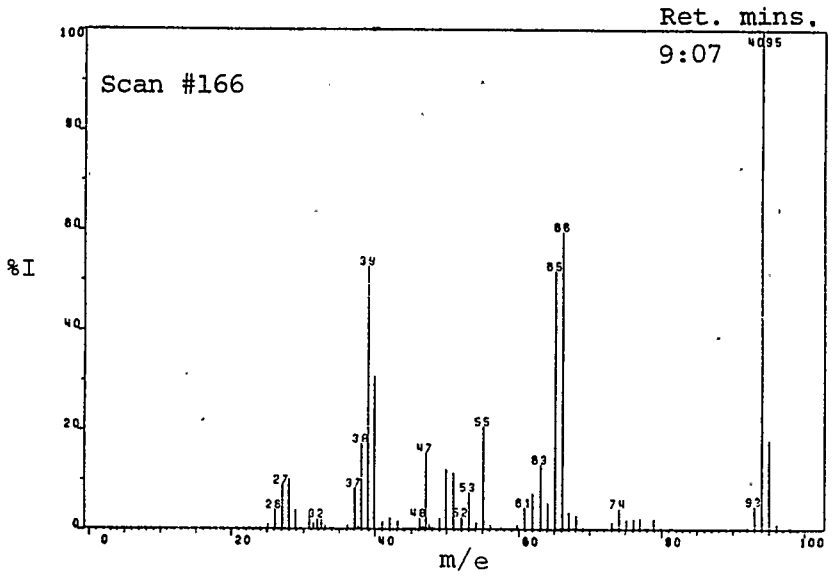


Figure 9a. Mass spectrum of authentic phenol

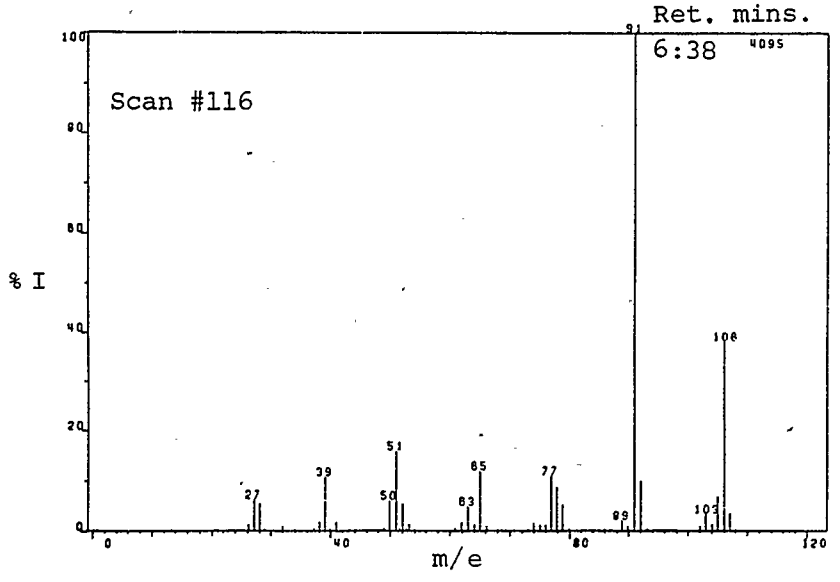


Figure 9b. Mass spectrum of authentic ethyl benzene

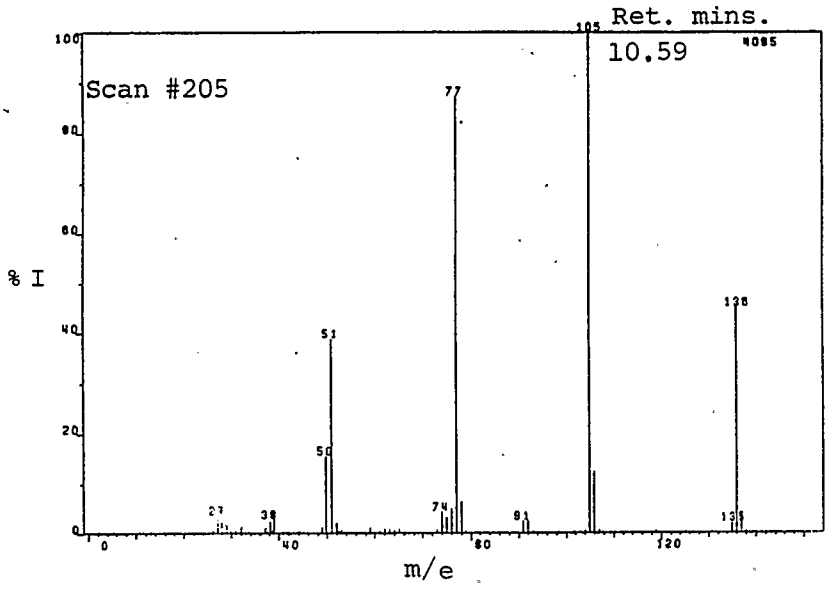


Figure 10a. Mass spectrum of authentic methyl benzoate

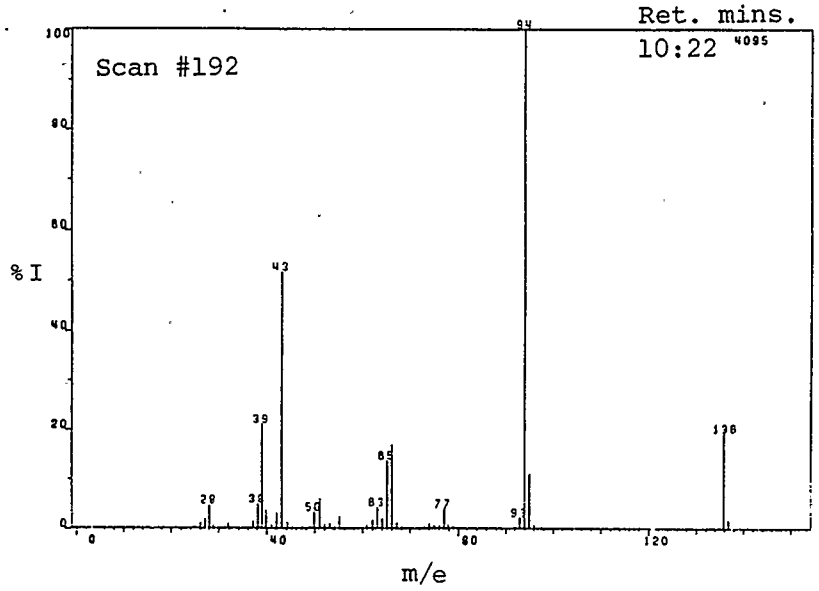


Figure 10b. Mass spectrum of authentic phenyl aetate

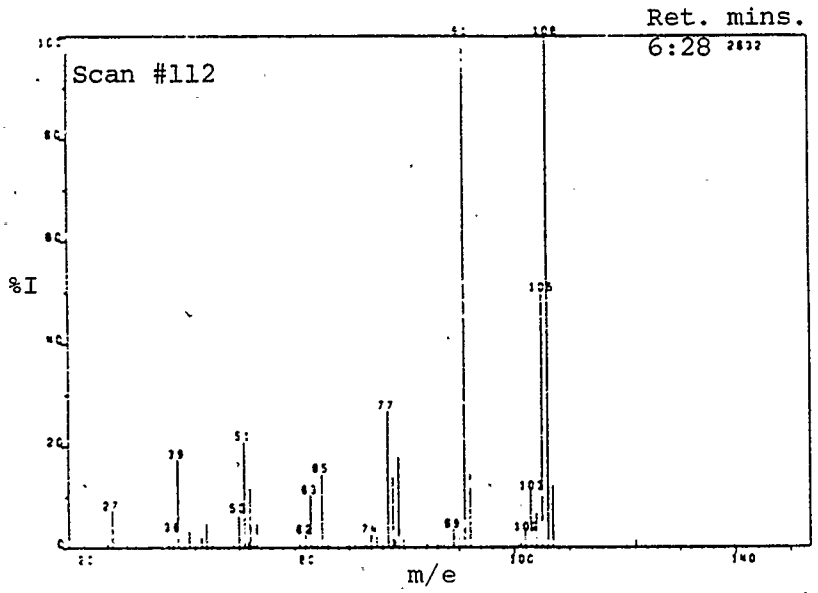


Figure 11a. Mass spectrum of authentic 1,3-xylene and 1,4-xylene

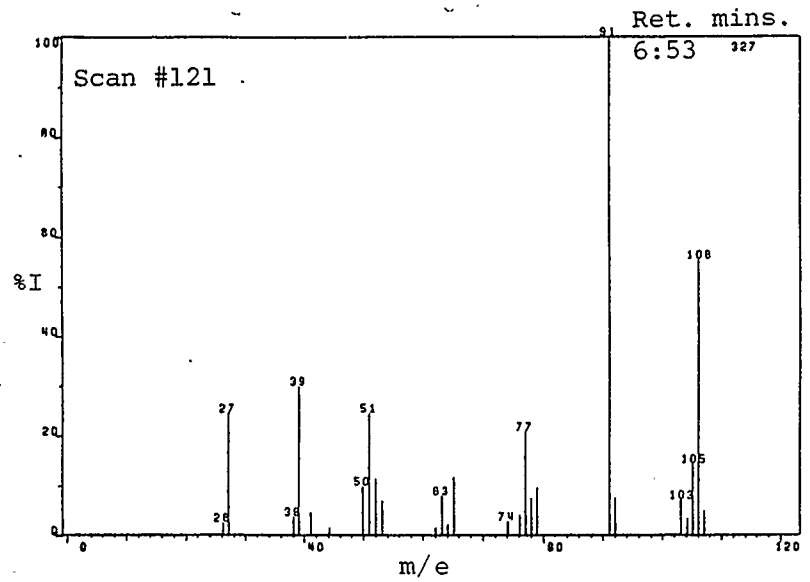


Figure 11b. Mass spectrum of authentic 1,2-xylene

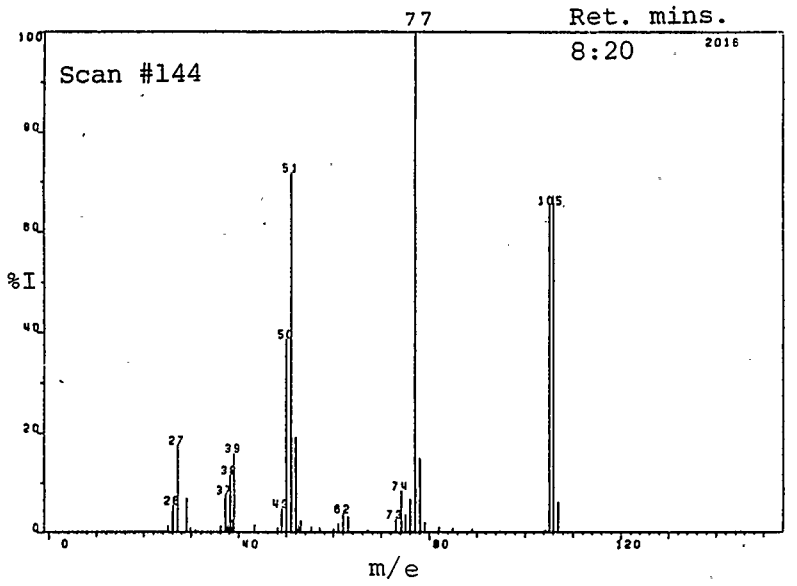


Figure 12a. Mass spectrum of authentic benzaldehyde

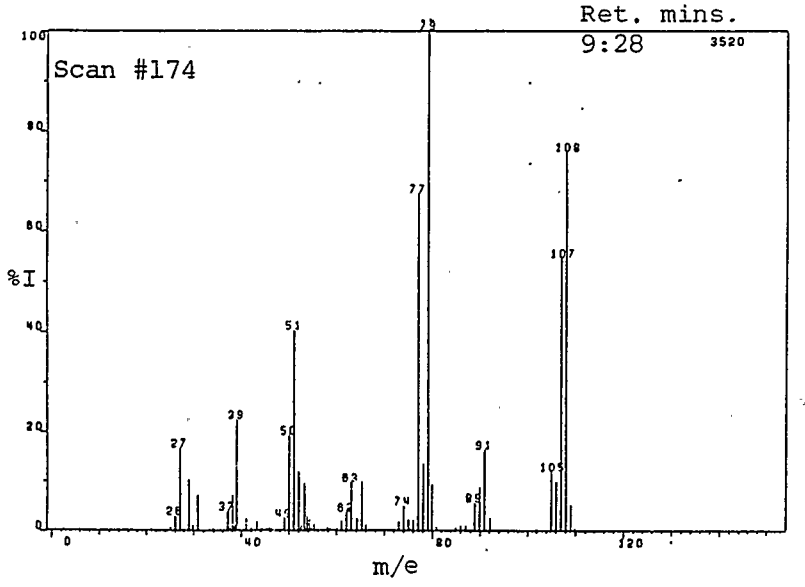


Figure 12b. Mass spectrum of authentic benzyl alcohol

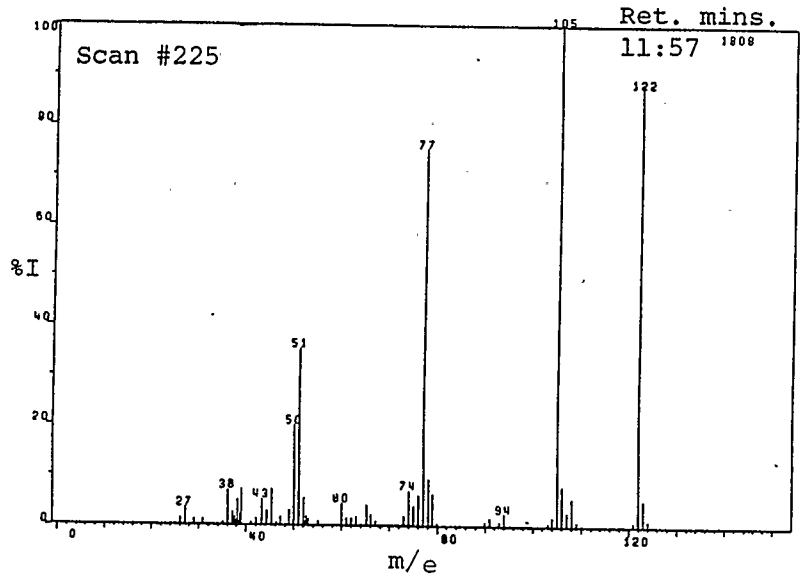


Figure 13a. Mass spectrum of authentic benzoic acid

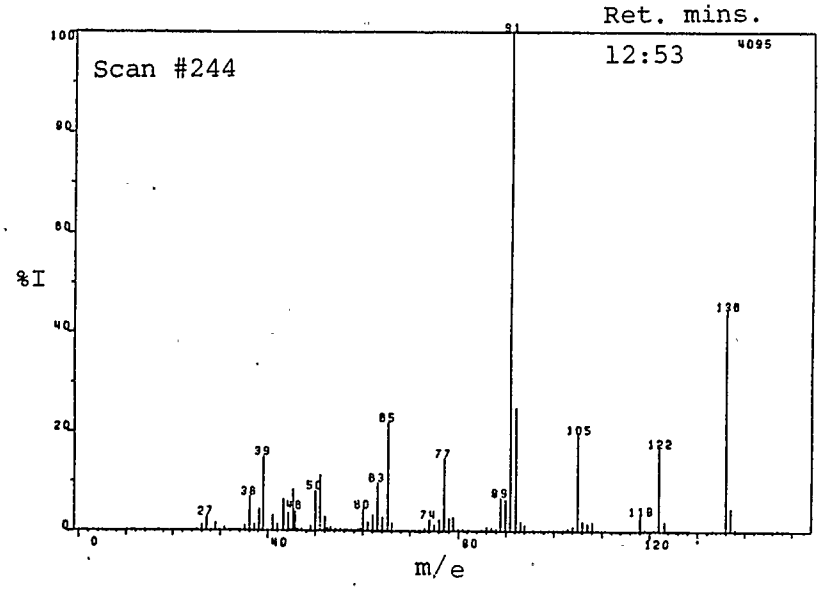


Figure 13b. Mass spectrum of authentic phenylacetic acid

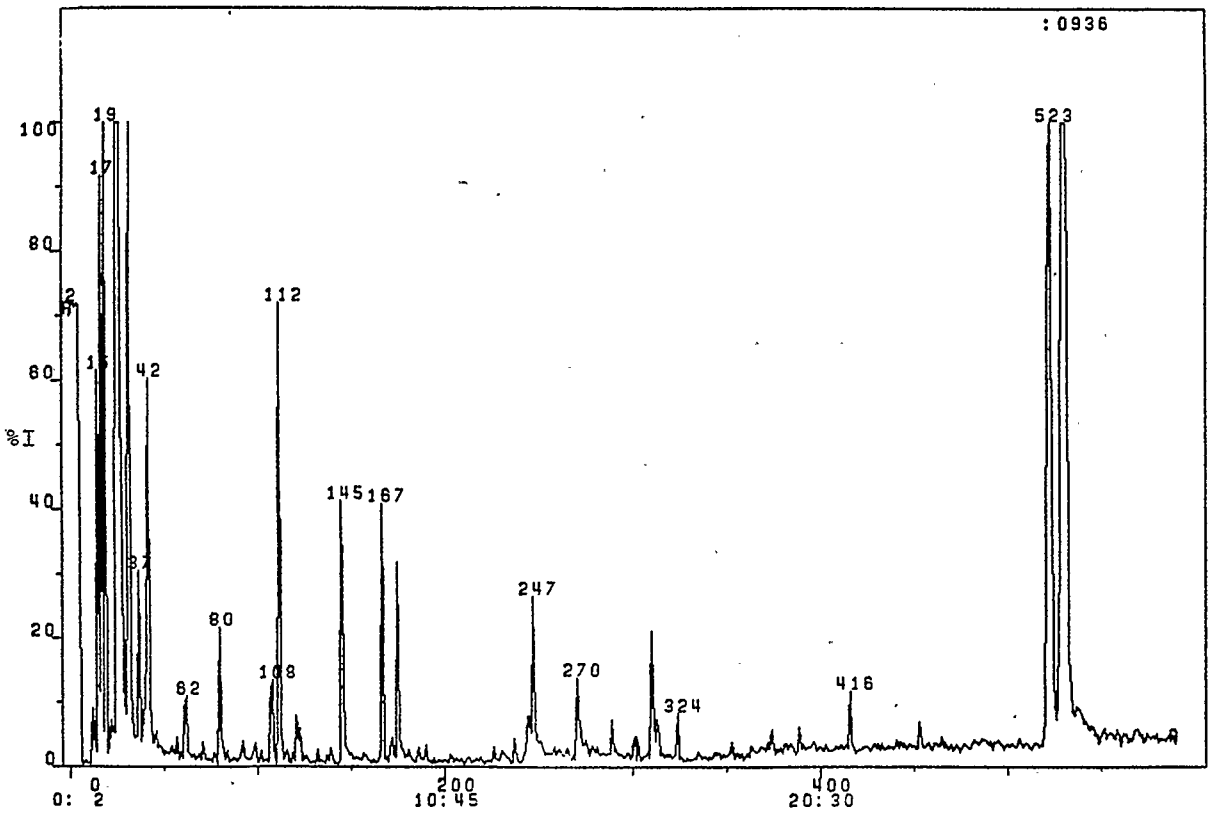


Figure 14. Total ion current gas chromatogram of P9-12B

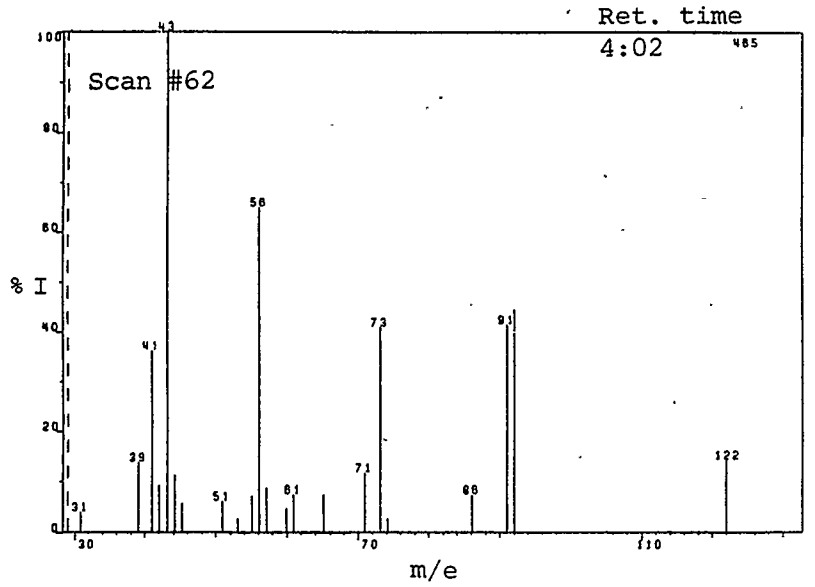


Figure 15a. Mass spectrum of toluene - Scan #62 from P9-12B

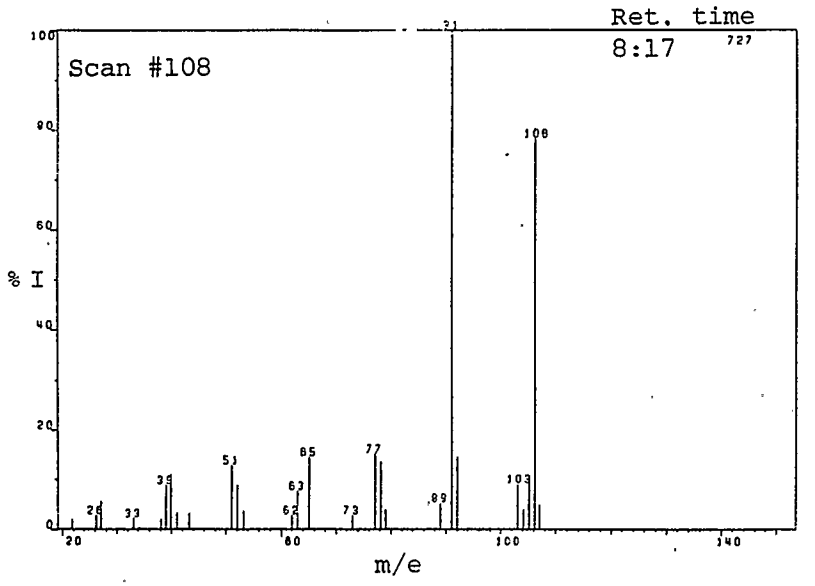


Figure 15b. Mass spectrum of ethylbenzene - Scan #108 from P9-12B

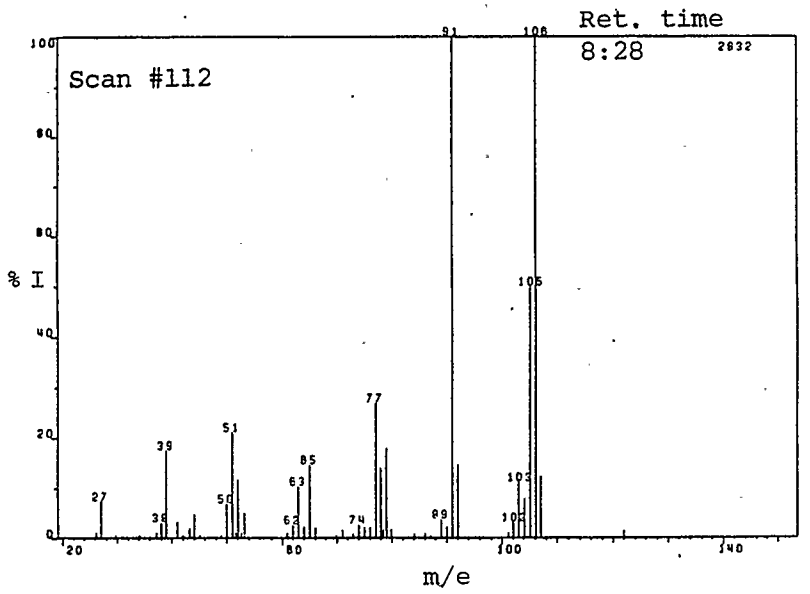


Figure 16a. Mass spectrum of 1,3- and 1,4-xylenes - Scan #112 from P9-12B

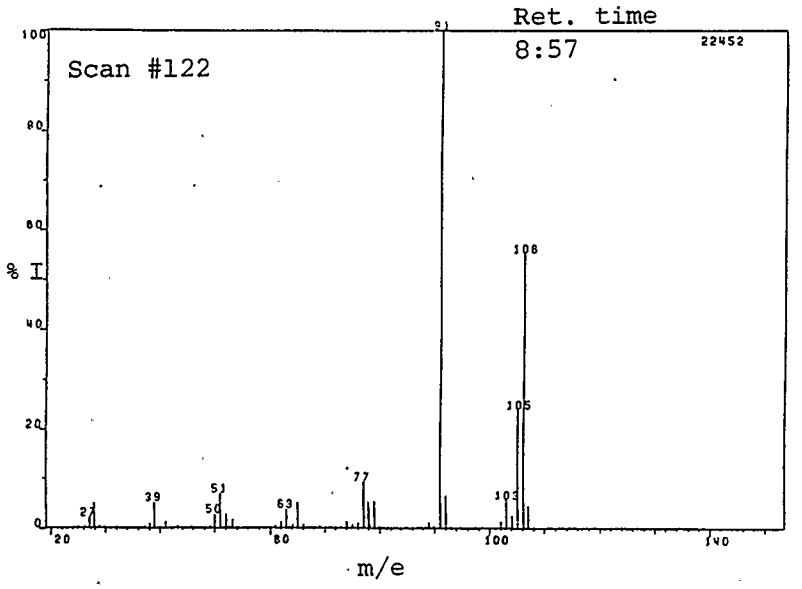


Figure 16b. Mass spectrum of 1,2-xylene - Scan #122 from P9-12B

the chromatography purification step was the most likely source of the toluene observed, rather than its being a photoproduct.

Scan #80 had a retention time of 4:55 min. This spectrum had an M^+ of m/e 112 and a base peak at m/e 43. Other prominent ions occurred at m/e 97, 56, 41, 61, 73, and 55. An on-line computer search of the NIH/EPA library of mass spectra indicated that this component corresponded quite closely to n-butyl acetate. However, the molecular weight of n-butyl acetate is 116 and the highest m/e peak of scan #80 is 112. It is suspected, therefore, that this component is a butadienyl acetate.

Scan #108 (Fig. 15b) with a retention time of 6:17 min. gave a spectrum that suggested a mono alkylbenzene compound. A very large molecular ion at mass 106, peaks at 91 and 77, and the general appearance of this spectrum led to its identity as ethylbenzene.

This and other compounds were suspected as been derived from accumulation of impurities found within the toluene that had been used for the initial cleanup. To test this hypothesis 500 ml of toluene were reduced by careful fractional distillation to a volume of less than 10 ml and this residue was examined for the presence of residual products. Examination of gas-chromatogram and gc/mass spectral data for this residue indicated that ethylbenzene had accumulated from concentration of the solvent toluene.

Scan #112 (Fig. 16a) had a retention time (6:28 min.) that compared closely to that of xylene. Both 1,3 and 1,4-xylene isomers of reference samples were eluted from the column in this time range and could not themselves be resolved. Mass peaks at 106 (M^+), 105, and a base peak (B^+) at 91 afforded sufficient evidence for comparison and confirmation

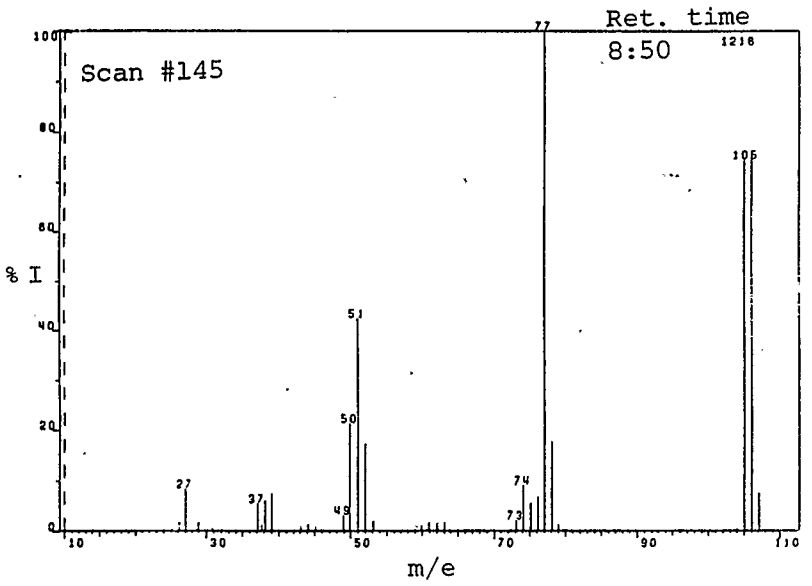


Figure 17a. Mass spectrum of Benzaldehyde - Scan #145 from P9-12B

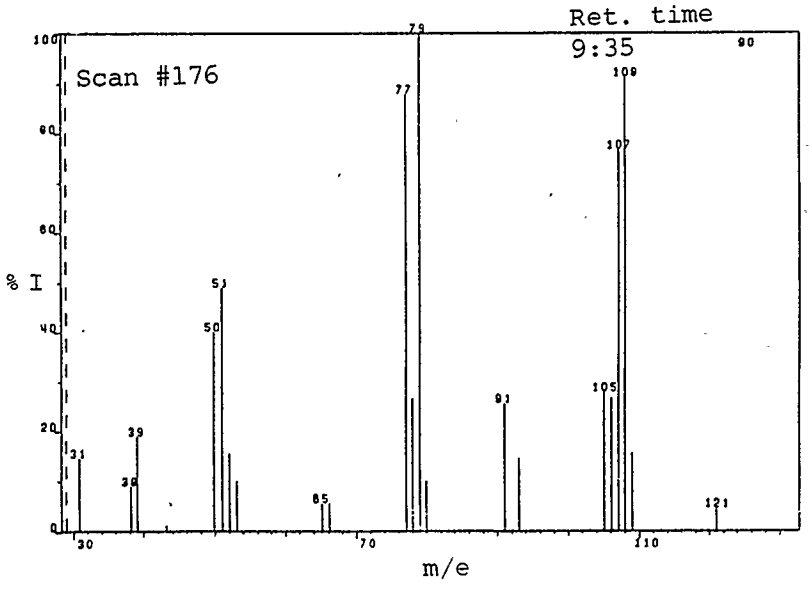


Figure 17b. Mass spectrum of Benzyl alochol - Scan #176 from P9-12B

of identity. Retention time did not enable identification of the two isomers (they were not resolved) nor did comparison of their respective mass spectra allow for easy identification. However, these two isomers were resolved when eluted from an SE-30 column, with 1,3-xylene preceding the 1,4-isomer. These two compounds were identified as concentration residues of the clean-up procedure.

Scan #122 (Fig. 16b) was eluted from the column with a retention time of 6:57 min. and was suspected as the third xylene isomer. Retention time comparison coupled with mass spectral data of an authentic reference sample confirmed its identity as 1,2-xylene (cf. Fig. 16b with the reference in Fig. 11a). This compound, too, was found as a very minor constituent of the toluene that had been used in the initial clean-up.

Scan #145 (Fig. 17a) had a retention time of 8:50 min. This time compared favourably with that of authentic benzaldehyde. Comparison of their mass spectra which evidenced large peaks at m/e 106 and 105 (M^+ and $M^+ -1$) and a B^+ at m/e 77 confirmed the identity of benzaldehyde.

Scan #167 had a retention time of 9:09 min. With a molecular ion at mass 136 and a base peak at mass 93, phenyl acetate, methyl benzoate, and benzyl formate were possible identities. Authentic samples of the first two were injected to furnish retention times and spectral data for comparison. Comparison of these data revealed that the compound was neither phenyl acetate nor methyl benzoate. Literature spectra of benzyl formate excluded this as the component. The on-line NIH/EPA library search indicate this component bore some resemblance to myrcene (7-methyl-3-methylene-1,6-octadiene); thus, the component is probably a

triene derived from chrysanthemic acid.

With a retention time of 9:35 min., Scan #176 (Fig. 17b) had a mass spectrum consistent with the character of an aromatic alcohol. Comparison of this spectrum with that of a reference sample confirmed its identity as benzyl alcohol (M^+ = 108, M^+ -1 = 107, B^+ = 77).

The next substantial peak, with a retention time of 13:03 min. and a Scan #247 (Fig. 18), proved to be chrysanthemic acid when compared with a reference spectrum taken from the NIH/EPA handbook of standard references.

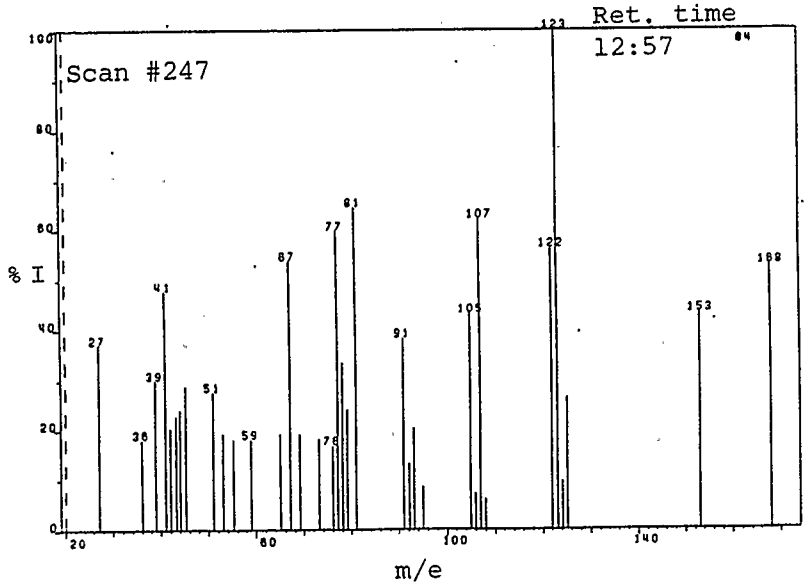


Figure 18. Mass spectrum of chrysanthemic acid - Scan #247 from P9-12B

Although an authentic sample was not available, comparison of the sample spectrum with that of the standard reference spectrum left no doubt of its identity. A substantial molecular ion at mass 168 (~ 30%) and a base peak of 123 mass units are but two identifying features. Other characteristic peaks occurred at m/e 107, 41, 81, 153, 91, 39, and 79. The sample gas-chromatogram at this scan number showed a near

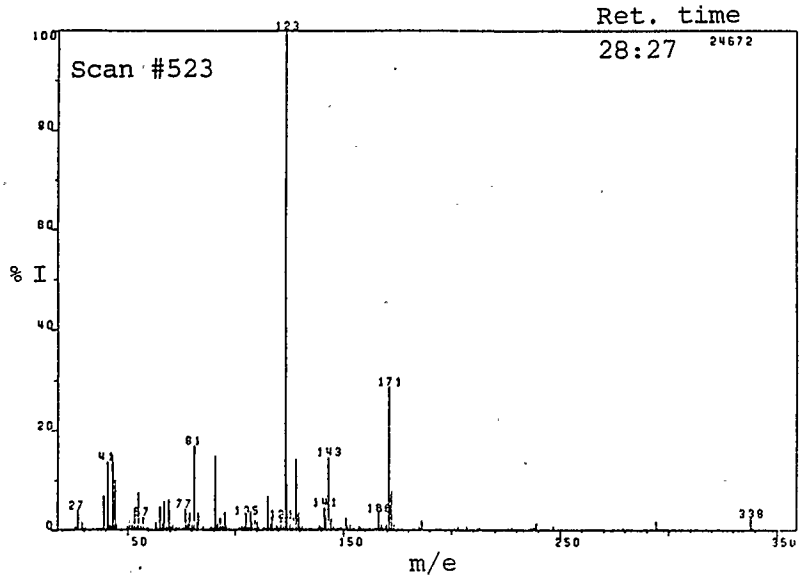


Figure 19a. Mass spectrum of cis-resmethrin - Scan #523 from P9-12B

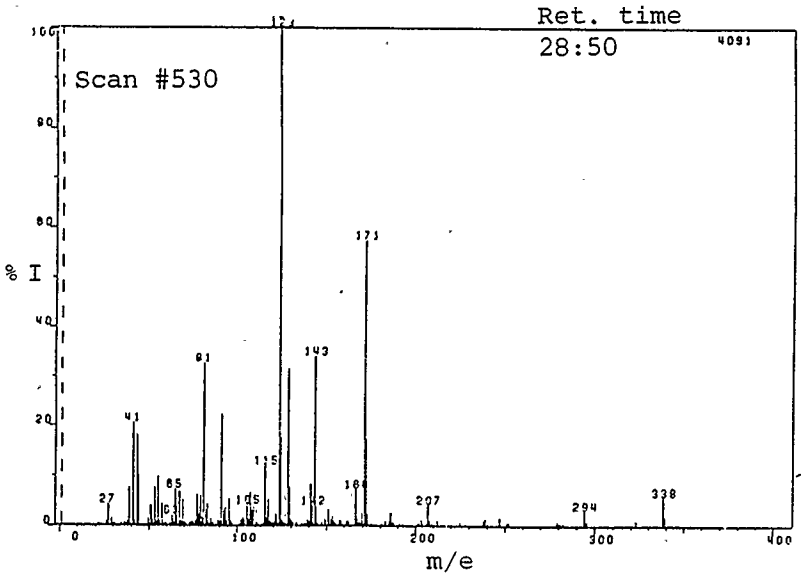


Figure 19b. Mass spectrum of trans-resmethrin - Scan #530 from P9-12B

resolution of two distinct peaks which very likely were the two geometric isomers of the acid. These compounds would have been formed with the initial ester cleavage of the parent compounds.

At a retention time of 14:10 min. and Scan #270, a compound was eluted with a base peak at m/e 67 and an M^+ at m/e 158. Other prominent peaks were formed at m/e 91 and 39. These ions could be consistent with a benzyl substituted furan and, of course, this partial structure is present in resmethrin. A note of caution is that the unusual $C_3H_3^+$ ion at m/e 39 is also characteristic of substituted cyclopropane derivatives as well as substituted furans.

Scan #313 with a retention time of 16:16 min. had a spectrum very similar to that of Scan #270, with prominent peaks occurring at m/e 67, 186, 39, and 91. The molecular ion at m/e 186 appeared to lose an ethylene fragment to give the m/e 158 ion of Scan #270. Thus, it would appear that these two are closely related substances, differing by an ethylene moiety.

Scans #324, #348, #380, and #416 contained similar series of ions at m/e 91, 129, 202, 207, and 281, and these were identified as compounds that had bled from the stationary phase of the column and no attempt was made to identify them.

Scan #523 and #530 (Figs. 19a and 19b) both had a molecular ion with a mass of 338, a B^+ at m/e 123, and other prominent peaks at m/e 171, 143, and 81. These immediately suggested the parent ester resmethrin. Comparison of the sample retention times and mass spectra with those of the original reference material resulted in a positive identification of resmethrin.

Quantitative Analysis (Abundance Trace)

To produce a view of the time course of evolution of the system's significant components being photolysed, integrated gas-chromatograms were run (in the manner described earlier) for each sample collected in the experiment. After careful examination, 15 gas chromatogram peaks, which represented both the most prominent and consistent components of the samples in the experiment, were selected for analysis. Retention times and relative percentage compositions are given in Tables 5a and 5b and Tables 6a and 6b.

Selected compounds were identified by comparing their retention times with those of reference compounds that were run under identical conditions on the same columns, and by comparing their retention times and order of elution when run on the two analysing instruments.

The first peak selected had a retention time of 1:17 min. (F-1) and was identified as toluene. A probable source of this compound has already been indicated. Peaks at 1:61, 1:72, and 1:99 min. (F-2, F-3, and F-4) were identified as ethylbenzene, 1,4-xylene, and 1,3-xylene, respectively. Again, these compounds were perceived to be distillation residues of the solvent system and may very well not have been resmethrin photoproducts.

An eluate with a retention time of 2:86 min. (F-5) was identified as benzaldehyde. This compound was present in all samples and its relative abundance increased consistently with the increasing time. F-6, with a retention time of 5:30 min., was distinguished as being benzyl alcohol. As with benzaldehyde, the relative concentration of this product increased with time. F-7 had a retention time of 9:52 min. and was

Table 5a: Resmethrin P9-A sample fractions

sample	S1#	S2#	S3#	S4#	S5#	S6#	S7#	S8#	S9#	S10#	S11#	S12#	S13#	S14#
F-1	1.77	2.02	1.31	0.92	1.25	1.28	1.71	1.74	0.86	0.19	1.20	1.24	6.57	6.26
F-2	2.88	3.03	2.05	1.47	1.88	1.94	2.54	2.56	1.28	1.63	1.89	1.85	2.57	2.62
F-3	9.36	9.68	6.64	4.74	6.12	6.29	8.21	8.25	4.10	5.26	6.08	5.97	9.85	9.21
F-4	1.55	1.34	1.05	0.77	0.93	0.98	1.39	1.21	0.57	0.90	1.04	0.93	4.84	4.36
F-5	1.28	0.95	0.97	1.07	1.08	0.83	0.92	0.45	0.00	1.54	2.30	1.40	3.42	11.87
F-6	0.42	0.00	0.82	0.71	1.23	0.56	0.64	0.57	0.78	1.70	3.13	1.81	4.48	13.58
F-7	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.38	0.90	2.01	2.95	7.43	8.77	0.00
F-8	2.03	1.81	2.35	2.67	2.69	2.70	4.24	1.72	2.88	2.69	4.40	0.00	9.91	18.16
F-9	0.50	0.00	0.55	0.57	0.76	0.59	0.74	0.79	0.94	0.97	1.60	1.75	4.39	11.15
F-10	0.00	0.00	0.00	0.36	0.58	0.34	0.36	0.41	0.84	0.64	1.43	1.77	3.07	9.82
F-11	0.26	1.78	0.35	0.00	0.34	0.25	0.26	0.17	2.03	0.20	0.00	0.00	0.00	3.74
F-12	0.81	1.28	0.78	0.80	0.80	1.26	1.02	1.06	0.67	0.75	0.48	0.96	0.00	0.00
F-13	0.43	0.00	0.57	0.53	0.76	0.73	1.03	2.49	1.83	1.42	0.00	0.00	0.00	0.00
F-14	26.20	25.85	27.58	28.61	27.26	27.58	25.52	24.28	25.99	26.58	23.84	24.13	13.51	3.01
F-15	52.53	52.25	54.99	56.80	54.31	54.68	51.43	52.98	56.33	53.53	49.66	50.76	28.61	6.20

Table 5b: Resmethrin P9-B fraction percentages

SAMPLE	S1#	S2#	S3#	S4#	S5#	S6#	S7#	S8#	S9#	S10#	S11#	S12#	S13#	S14#
F-1	1.37	1.25	1.21	1.43	1.56	1.76	1.68	2.19	0.81	0.51	0.94	1.17	0.00	1.31
F-2	2.43	2.21	2.05	2.41	2.40	2.90	2.51	3.38	2.11	1.37	2.56	1.79	1.61	1.88
F-3	7.86	7.09	6.62	7.82	7.86	9.42	8.26	11.04	6.61	4.12	7.82	5.81	7.14	6.25
F-4	1.41	1.24	1.14	1.32	1.22	1.59	1.31	1.86	1.53	0.89	1.58	0.93	0.68	0.90
F-5	0.95	0.74	0.73	1.69	0.54	1.37	2.00	1.91	1.37	1.04	3.13	2.97	2.57	2.66
F-6	0.34	0.30	0.33	0.63	0.40	0.73	0.82	3.26	2.52	0.00	1.32	4.00	1.61	3.08
F-7	0.00	1.65	1.68	2.54	4.33	3.25	1.98	4.14	2.08	5.62	2.04	4.08	3.52	3.01
F-8	1.94	0.00	0.00	0.00	0.00	0.00	2.94	0.00	2.71	1.36	3.12	3.88	4.40	3.60
F-9	0.49	0.43	0.42	0.57	0.48	0.69	0.99	1.08	1.17	14.28	1.18	2.19	1.39	1.60
F-10	0.00	0.00	0.00	0.25	0.00	0.36	0.60	0.74	1.10	21.36	0.81	2.40	1.22	1.72
F-11	0.00	0.29	0.21	0.49	0.00	0.38	0.00	0.72	0.21	2.15	0.21	0.22	0.28	0.17
F-12	0.74	0.91	2.76	0.86	1.03	0.97	0.93	1.06	1.39	0.47	1.34	0.88	0.94	1.17
F-13	0.20	0.54	0.38	0.54	0.61	0.87	1.61	1.05	1.31	0.72	1.17	0.91	1.25	1.11
F-14	24.80	25.20	24.81	23.88	23.91	25.35	24.83	22.63	25.12	15.11	24.22	22.55	21.59	21.15
F-15	57.47	58.14	57.67	55.47	55.66	50.37	49.53	44.92	49.97	30.98	48.56	46.22	51.79	50.40

Table 6a: Resmethrin P9-A fraction retention times

sample	S1#	S2#	S3#	S4#	S5#	S6#	S7#	S8#	S9#	S10#	S11#	S12#	S13#	S14#
F-1	1.13	1.13	1.17	1.17	1.17	1.18	1.19	1.22	1.12	1.26	1.13	1.12	1.18	1.17
F-2	1.56	1.56	1.61	1.61	1.61	1.62	1.63	1.67	1.55	1.74	1.56	1.55	1.43	1.37
F-3	1.66	1.66	1.77	1.71	1.71	1.72	1.73	1.77	1.65	1.85	1.66	1.65	1.61	1.60
F-4	1.93	1.93	1.99	2.0	1.99	2.0	2.01	2.05	1.93	2.15	1.93	1.93	1.99	1.98
F-5	2.77	2.79	2.87	2.87	2.87	2.88	2.89	2.92		3.07	2.78	2.79	2.86	2.84
F-6	5.2		5.32	5.32	5.32	5.32	5.34	5.34	5.25	5.62	5.2	5.23	5.3	5.27
F-7								9.53	9.47	9.71	9.52	9.53	9.52	
F-8	9.57	9.57	9.57	9.57	9.53	9.57	9.59	9.63	9.54		9.57		9.56	9.54
F-9	10.45		10.44	10.44	10.44	10.44	10.44	10.45	10.45	10.65	10.45	10.45	10.44	10.45
F-10				12.19	12.19	12.19	12.19	12.21	12.2	12.41	12.2	12.2	12.19	12.22
F-11	16.90	16.89	16.90		16.89	16.90	16.89	16.90	16.90	17.00				16.90
F-12	18.85	18.82	18.83	18.83	18.82	18.83	18.83	18.87	18.83	19.04	18.93	18.94		
F-13	19.42		19.41	19.40	19.39	19.38	19.40	19.43	19.40	19.64				
F-14	18.47	18.44	18.48	18.49	18.46	18.48	18.46	18.51	18.46	18.67	17.86	17.85	18.41	18.42
F-15	18.69	18.64	18.70	18.70	18.66	18.69	18.68	18.74	18.65	18.88	17.96	17.95	18.59	18.60

Table 6b: Resmethrin P9-B fraction retention times

SAMPLE	S1#	S2#	S3#	S4#	S5#	S6#	S7#	S8#	S9#	S10#	S11#	S12#	S13#	S14#
F-1	1.17	1.17	1.18	1.17	1.17	1.17	1.17	1.18	1.18	1.21	1.19	1.20		1.18
F-2	1.61	1.61	1.61	1.60	1.61	1.61	1.61	1.61	1.62	1.68	1.61	1.64	1.60	1.62
F-3	1.72	1.71	1.72	1.71	1.71	1.71	1.71	1.71	1.72	1.78	1.73	1.74	1.70	1.72
F-4	1.99	1.99	1.99	1.99	1.99	1.99	1.99	1.99	1.99	2.10	2.00	2.02	1.98	2.00
F-5	2.86	2.87	2.88	2.85	2.88	2.86	2.86	2.85	2.86	2.98	2.86	2.87	2.85	2.85
F-6	5.29	5.34	5.33	5.32	5.35	5.31	5.29	5.28	5.27		5.28	5.29	5.29	5.27
F-7		9.52	9.54	9.55	9.52	9.54	9.50	9.51	9.52	9.62	9.52	9.54	9.51	9.52
F-8	9.60						9.57		9.62		9.63	9.60	9.61	9.64
F-9	10.42	10.43	10.43	10.44	10.43	10.44	10.42	10.43	10.44	10.54	10.44	10.45	10.43	10.44
F-10				12.18		12.18	12.18	12.18	12.20	12.39	12.20	12.23	12.19	12.21
F-11		16.88	16.88	16.89		16.89		16.87	16.87	17.01	16.88	16.87	16.89	16.87
F-12	18.85	18.80	18.82	18.81	18.80	18.79	18.79	18.78	18.81	19.01	18.81	18.81	18.78	18.81
F-13	19.40	19.36	19.39	19.37	19.37	19.37	19.37	19.36	19.38	19.62	19.38	19.37	19.36	19.37
F-14	18.49	18.43	18.46	18.46	18.44	18.44	18.42	18.42	18.45	18.63	18.46	18.44	18.43	18.45
F-15	18.76	18.66	18.68	18.66	18.64	18.64	18.63	18.62	18.68	18.84	18.68	18.68	18.64	18.67

denoted as phenyl acetic acid on this basis. The concentration tended to increase with time in an inconsistent manner. With a retention time of 10:42 min., F-9 was identified as chrysanthemic acid. The relative concentration of this product increased gradually in the first 9 samples and then levelled off for the remaining samples in P9-B. Samples of P9-A differed only in that relative concentrations did not level off with the same consistency for the last 5 samples. The observed concentration changes for these four products were consistent with that which was expected, in that chrysanthemic acid is a primary photoproduct resulting from the hydrolysis of the parent compound, and benzaldehyde, benzyl alcohol, and phenylacetic acid are products resulting from extensive oxidation of the alcohol moiety of the ester (Ueda et al., 1974). Histograms for these four products are shown in Figures 20a and 20b and Figures 21a and 21b.

Fractions at retention times of 9:60, 12:18, 16:88, 18:85, and 19:40 min. (F-8, F-10, F-11, F-12, and F-13) could not be characterized merely on the basis of gas chromatography. Fraction #8 increased in concentration from Samples 1 through 14 in both P9-A and P9-B. This was most apparent in P9-A where it increased from 2.03% to 16.62% of the total concentration of the 15 components that were monitored. Fractions #10 and #11 were present only in small quantities in samples of both P9-A and P9-B, while concentrations of fractions #12 and #13 varied irregularly from sample to sample in both P9-A and P9-B and were small or negligible in a number of samples from p9-A.

Peaks with retention times of 18:49 and 18:76 min, (F-14 and F-15) were identified as the cis- and trans-isomers of resmethrin. The rela-

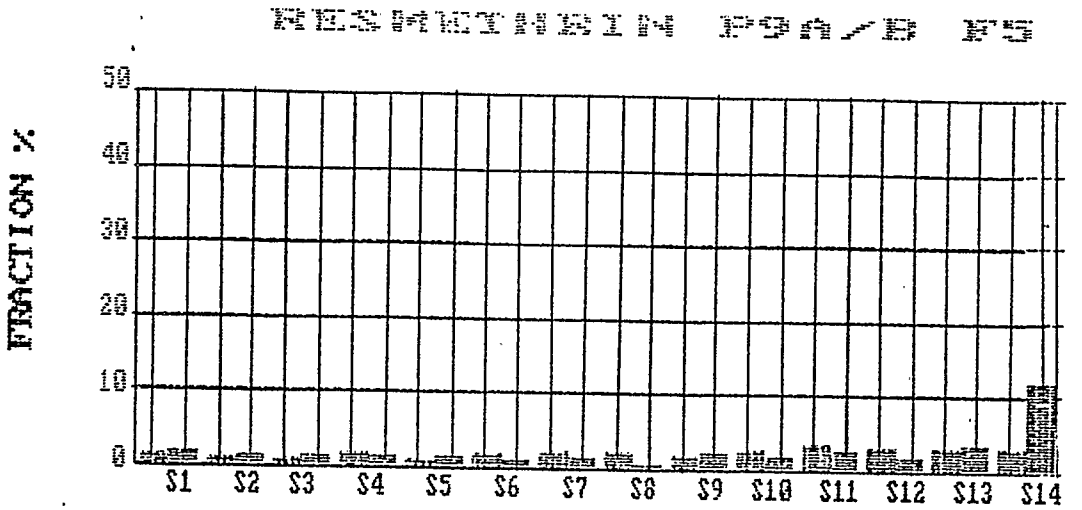


Figure 20a. Benzaldehyde histogram

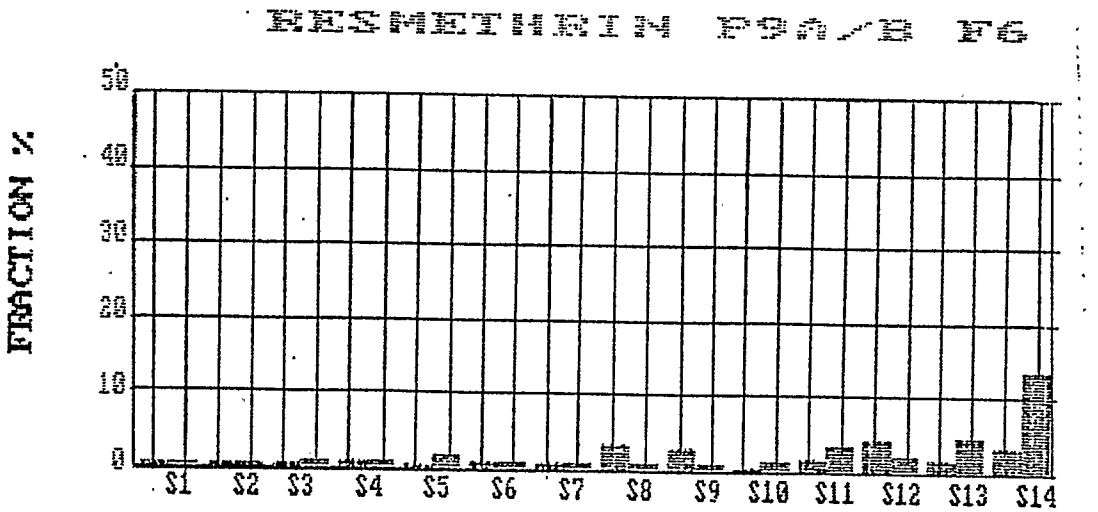


Figure 20b. Benzyl alcohol histogram

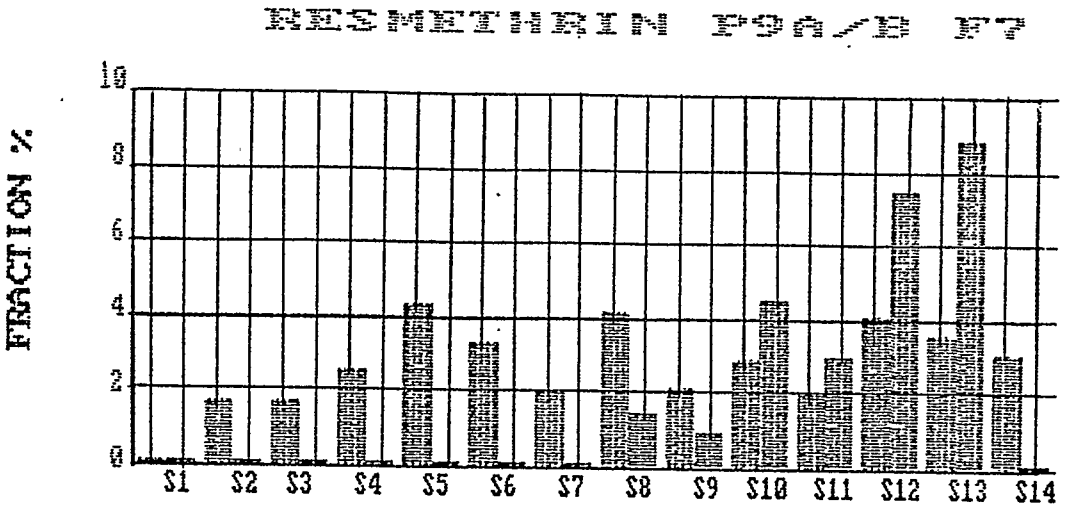


Figure 21a. Phenylacetic acid histogram

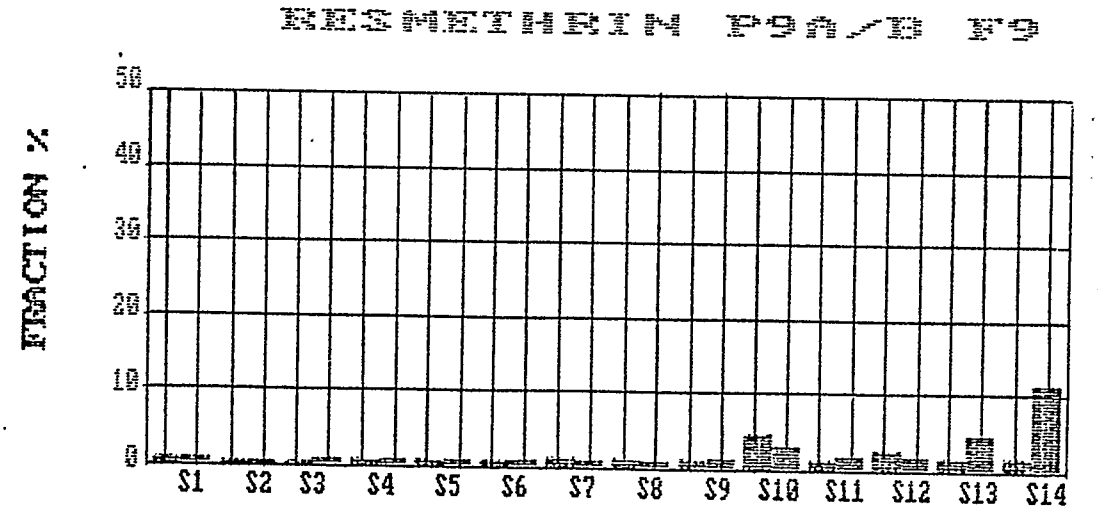


Figure 21b. Chrysanthemic acid histogram

tive concentrations of these two isomers decreased with time in both P9-A and P9-B trials and the ratio of the concentrations of cis- to trans-isomer remained constant. Both of these observations were consistent with expected results in that the amount of resmethrin present would necessarily decrease as its primary photoproducts are generated and resmethrin is not known to undergo cis-trans isomerization when photolysed (Ueda et al., 1974). It was particularly notable that, despite the extent of exposure to solar irradiation, resmethrin remained by far the single most abundant species in virtually all samples. Under these conditions, contrary to what has previously been published, resmethrin was quite persistent and could present a significant environmental hazard to sensitive species. Histograms of cis/trans isomer ratios and concentrations have heen reproduced in Figure 22 and Figures 23a and 23b.

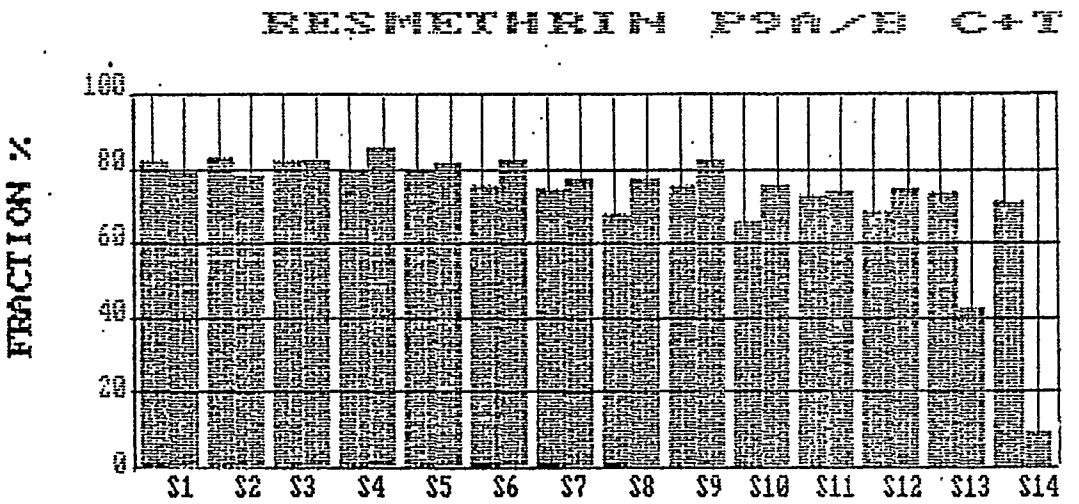


Figure 22. Cis/trans resmethrin histogram

Resmethrin in Distilled Water (P8-A/B)

Samples were prepared in the same manner as in the photolysis of resmethrin in "snow-melt" water and were photolysed in sunlight. Photo-

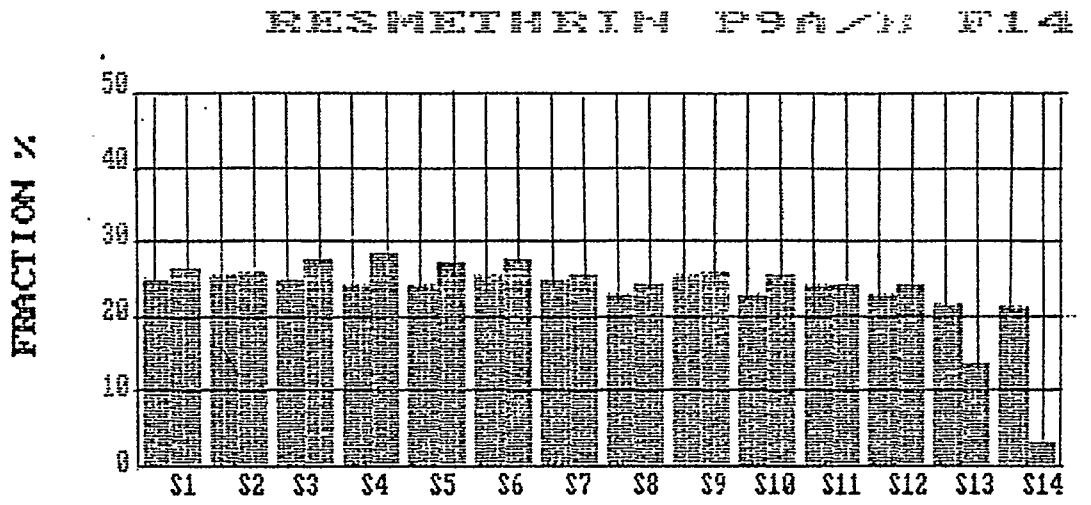


Figure 23a. Cis-resmethrin histogram

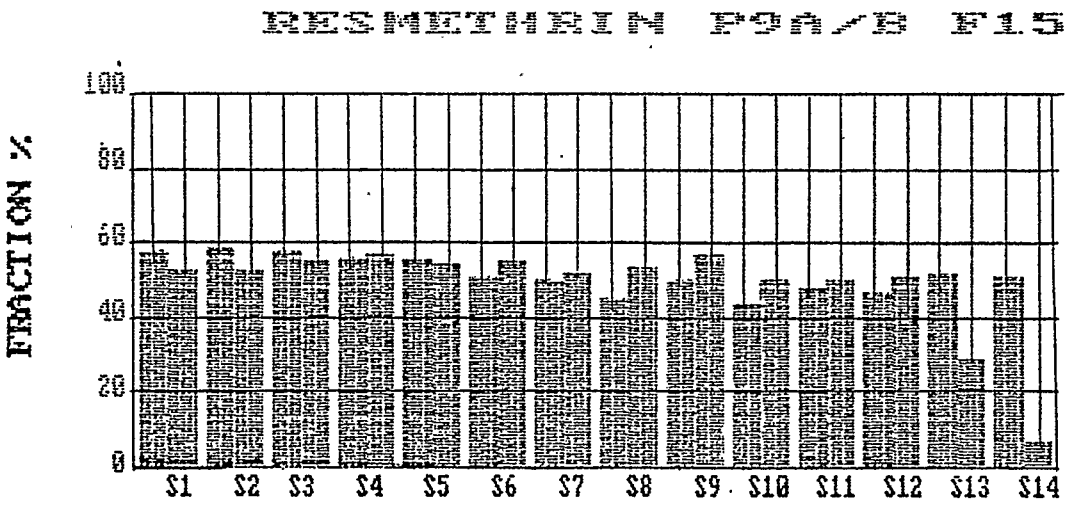


Figure 24b. Trans-resmethrin histogram

Table 7: Schedule of sample collections of resmethrin solar photolysis in distilled water (P8-A/B)

Sample No.	Date Collected	Sample No.	Date Collected
S1	31/07/85	S8	07/08/85
S2	01/08/85	S9	09/08/85
S3	02/08/85	S10	11/08/85
S4	03/08/85	S11	13/08/85
S5	04/08/85	S12	15/08/85
S6	05/08/85	S13	17/08/85
S7	06/08/85	S14	18/08/85

Table 8: Weather conditions during resmethrin solar photolysis in distilled water (P8-A/B)

	C-TEMPERATURES			Hours Bright Sunshine
Date	Max.	Min.	Mean	
JUL				
31	25.0	10.5	17.8	14.4
AUG				
1	28.0	9.0	18.5	7.4
2	27.7	12.0	19.9	6.0
3	28.4	11.6	20.0	13.0
4	29.1	12.8	21.0	10.2
5	24.0	10.6	17.3	9.0
6	24.0	8.1	16.1	11.2
7	25.8	10.7	18.3	1.8
8	13.1	4.5	8.8	3.9
9	20.0	2.2	11.1	4.2
10	11.3	6.7	9.0	1.4
11	20.0	3.4	11.7	7.1
12	13.2	7.2	10.2	3.3
13	18.1	2.2	10.2	10.0
14	20.6	8.9	14.8	2.2
15	12.1	5.6	8.9	0.0
16	17.5	7.2	12.4	10.1
17	22.6	6.2	14.4	13.5
18	24.7	7.9	16.3	13.6

lysed samples were collected as scheduled in Table 7 and were prepared for analysis as done previously for P6-A, P6-B, P9-A, and P9-B. The hours of bright sunshine, and daily maximum, minimum, and mean temperatures for the term of the experiment, are listed in Table 8. Once extracted, photolysed samples were stored with the same precautions as those used for all previous experiments.

This experiment was set up and performed in duplicate only after the two trials of Experiment P9 (resmethrin solar photolysis in "snowmelt") were under way. It was not an integral part of the major area of study (i.e. photolysis in a representative environmental water sample) and was performed primarily as a comparison to the major study. The collated data for the retention times and relative percentages of the 16 most significant peaks over the course of the experiment are presented in Tables 9, 10, 11, and 12.

Initial examinations of these data, and comparisons among P8-A and P8-B and the two P9 experiments, indicated that neither the product identities nor their time course evolution showed complete correlation. Specifically, P9-A showed a gradual, steady decrease from 78% to 74% (cis + trans) resmethrin after 20 days followed by a rapid loss to 41% at 23 days and 9% at 26 days. P9-B showed a decrease form 81% to 72% after 6 days with only one sample not fitting this trend, namely S10 at 15 days. P8-A showed a similar gradual loss of resmethrin from 87% to 70% after 19 days except one sample, S10, which showed only 7%. P8-B, however, is a very inconsistent data set, with a decrease from 90% down to 20%, but with many fluctuations. One other disturbing observation is that the cis/trans ratio does not stay constant, and this suggests in-

Table 9: Resmethrin P8-A fraction retention times

Sample	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
F-1	8.92	8.94	8.94	8.94	8.94	8.95	/	8.93	/	8.97	8.98	8.88	8.88	8.91
F-2	1.63	/	/	/	1.59	/	/	/	/	/	1.63	1.58	1.61	1.61
F-3	1.73	1.72	1.72	1.73	1.72	1.74	1.74	1.72	1.67	1.74	1.63	1.68	1.71	1.71
F-4	/	1.82	1.83	1.84	1.84	1.85	1.85	1.83	1.78	1.85	1.73	1.82	/	/
F-5	/	/	/	/	/	/	/	/	/	/	2.827	1.983	1.77	2.979
F-A	/	3.87	3.89	3.89	3.88	3.88	3.89	3.88	3.81	3.89	/	3.89	/	/
F-6	4.58	/	/	/	/	/	/	/	/	/	/	/	/	/
F-7	5.31	5.29	/	/	/	/	/	/	/	/	/	5.21	5.29	5.29
F-8	/	/	5.67	5.68	5.61	5.61	5.62	5.65	/	5.61	5.29	/	/	/
F-8	/	/	/	/	/	/	/	/	/	/	9.54	9.53	9.53	/
F-9	9.63	9.68	9.72	9.71	9.66	9.67	9.71	9.72	9.69	9.66	9.66	9.66	9.67	9.62
F-10	/	10.66	10.66	10.66	10.65	10.66	/	10.67	10.61	10.67	/	/	/	/
F-11	/	15.97	15.97	15.97	15.96	15.96	15.96	15.98	15.99	15.97	15.84	15.83	15.83	15.93
F-12	18.54	18.28	18.48	18.46	18.49	18.81	18.77	18.77	18.76	18.78	18.45	18.48	18.44	/
F-13	18.79	18.48	18.7	18.69	18.76	19.14	19.81	19.81	18.98	18.88	18.71	18.74	18.68	18.79
F-C	19.32	19.28	19.33	19.32	19.36	/	/	/	/	/	/	/	/	/
F-D	19.82	/	/	/	/	19.84	19.79	19.77	19.77	/	/	/	19.74	/

Table 10: Resmethrin P8-B fraction retention times

Sample	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13	S14
F-1	8.88	8.85	8.88	8.87	8.85	8.89	8.88	8.91	8.90	8.92	8.88	8.87	8.91	8.88
F-2	1.61	1.55	1.60	1.59	1.54	1.62	1.60	1.61	1.63	1.61	1.61	1.58	1.61	1.60
F-3	1.71	1.65	1.71	1.69	1.64	1.73	1.70	1.71	1.73	1.71	1.71	1.68	1.71	1.70
F-4	2.0	1.93	1.98	1.98	1.92	2.01	1.98	1.99	2.01	1.99	1.99	1.95	1.99	1.97
F-5	2.87	2.77	2.85	2.85	2.76	2.88	2.84	2.85	2.87	2.86	2.86	2.80	2.86	2.85
F-6	/	/	4.48	4.49	4.38	4.52	4.47	4.50	4.52	4.51	4.51	4.43	4.51	4.45
F-7	/	5.18	5.27	5.27	5.18	5.30	5.30	5.29	5.31	5.31	5.29	5.23	5.28	5.24
F-8	9.57	9.53	9.54	9.53	9.53	/	9.57	9.53	9.53	9.53	9.53	9.55	9.53	9.55
F-9	/	9.64	9.71	9.63	/	9.63	/	/	9.62	9.59	9.69	9.73	9.76	9.69
F-10	/	10.45	10.46	10.46	10.45	10.45	10.45	10.45	10.44	10.45	10.45	10.45	10.45	10.46
F-E	/	12.13	12.15	12.15	12.20	12.20	12.19	12.20	12.21	12.20	12.20	12.20	12.23	12.23
F-F	/	13.54	13.55	13.54	13.54	13.53	13.54	13.53	/	/	13.53	13.53	12.89	12.90
F-11	/	/	/	/	15.83	15.82	15.84	15.82	15.83	15.83	15.82	15.84	15.83	15.82
F-G	/	/	/	/	/	/	/	/	/	/	17.75	17.75	17.75	17.76
F-12	18.48	18.44	18.44	18.44	18.44	18.43	18.47	/	18.47	18.44	18.42	18.43	/	/
F-13	18.72	18.62	18.63	18.66	18.62	18.62	18.69	/	18.69	18.68	18.61	18.64	/	/

Table 11: Resmethrin P8-A fraction percentages

SAMPLE	S1#	S2#	S3#	S4#	S5#	S6#	S7#	S8#	S9#	S10#	S11#	S12#	S13#	S14#
F-1	1.38	1.98	0.21	0.24	0.44	0.49	0.00	0.24	0.00	3.47	1.34	0.78	1.59	0.94
F-2	1.03	0.00	0.00	0.00	0.08	0.00	0.00	0.00	0.00	0.00	2.26	1.92	2.66	4.80
F-3	3.32	1.02	1.20	1.32	1.29	1.27	1.07	1.26	1.51	7.00	2.26	6.51	9.33	15.59
F-4	0.00	3.31	3.85	4.28	4.29	4.12	3.43	4.01	4.85	22.10	7.29	0.12	0.00	0.00
F-5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	4.64	1.14	2.70	9.34
F-6	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
F-A	0.00	0.19	0.43	0.89	0.91	1.09	1.05	1.16	0.97	22.34	0.00	0.11	0.00	0.00
F-7	0.00	1.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.45	3.37	5.21
F-B	0.00	0.00	0.25	0.26	0.71	0.94	0.48	0.55	0.00	21.58	3.93	0.00	0.00	0.00
F-8	0.34	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.39	1.71	3.34	0.00
F-9	6.30	1.17	1.97	1.70	0.84	0.78	5.04	2.87	5.60	9.13	3.93	2.71	5.26	34.28
F-10	0.00	0.20	0.22	0.22	0.12	0.21	0.00	0.30	0.52	4.12	0.00	0.00	0.00	0.00
F-11	0.00	0.23	0.27	0.26	0.16	0.78	1.81	0.37	0.83	2.77	0.35	0.24	0.36	2.05
F-C	0.00	0.24	0.63	1.00	1.18	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
F-D	0.00	0.00	0.00	0.00	0.00	0.99	1.33	1.70	1.20	0.00	0.00	0.00	0.36	0.00
F-12	22.04	22.77	22.76	22.66	22.86	22.80	21.15	22.06	21.97	2.02	5.37	19.53	17.47	0.00
F-13	65.59	67.76	68.20	67.16	67.15	66.53	64.64	65.48	63.45	5.47	66.23	63.77	53.55	27.78

Table 12: Resmethrin P8-B fraction percentages

SAMPLE	S1#	S2#	S3#	S4#	S5#	S6#	S7#	S8#	S9#	S10#	S11#	S12#	S13#	S14#
F-1	1.39	0.82	2.90	1.54	1.37	1.09	0.39	3.02	2.38	0.26	9.04	1.75	1.02	1.01
F-2	1.08	2.86	4.30	2.29	2.24	3.45	1.73	7.22	2.53	1.62	2.81	3.77	2.07	3.83
F-3	3.43	9.16	13.22	7.34	7.31	11.01	5.54	22.96	8.01	5.16	9.21	12.33	6.70	12.46
F-4	0.70	1.30	2.73	1.16	1.28	1.70	0.87	3.79	1.47	0.85	1.33	1.81	0.97	1.77
F-5	0.58	6.90	8.65	5.84	8.49	2.66	0.84	16.07	3.02	1.74	8.67	3.25	14.69	5.44
F-6	0.00	0.00	1.25	1.28	1.17	1.52	0.61	2.04	1.73	0.72	2.69	2.88	0.47	2.52
F-7	0.00	9.83	9.63	6.63	5.83	7.10	0.52	27.12	1.74	2.18	10.81	4.52	12.47	12.50
F-8	2.18	4.93	4.77	3.03	9.82	0.00	5.73	5.44	1.85	2.21	5.58	5.46	5.00	7.59
F-9	0.00	31.57	16.16	7.74	0.00	18.32	0.00	0.00	2.83	2.83	15.45	18.52	25.56	18.56
F-10	0.00	1.79	1.49	1.58	2.71	1.41	0.33	6.11	0.67	0.91	2.73	1.52	4.57	9.85
F-E	0.00	2.72	0.58	0.37	1.96	0.71	0.52	3.13	0.86	0.75	1.53	1.02	4.13	9.85
F-F	0.00	2.28	0.78	0.46	1.48	0.63	0.26	1.40	0.00	0.00	0.91	0.46	6.94	1.70
F-11	0.00	0.00	0.00	0.00	1.52	0.54	0.44	1.69	0.23	0.53	1.11	0.70	0.89	1.52
F-G	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	3.18	1.35	14.52	11.42
F-12	23.07	6.49	8.31	4.83	6.17	9.14	19.54	0.00	18.26	7.53	3.18	7.45	0.00	0.00
F-13	67.58	19.36	25.21	55.91	48.66	40.72	62.66	0.00	54.44	72.68	21.78	33.20	0.00	0.00

complete sample extraction and also lack of gas chromatographic resolution of the cis and trans isomers such that integration of the separated isomers was not possible. Thus the combined amount of resmethrin is a more reliable estimate of the quantity of resmethrin remaining.

It is perhaps pertinent to point out that the design of the experiment, which is essentially 14 separate experiments, is the most exciting and vigorous way to conduct this photolysis investigation. The more commonly adopted method of sampling a single reaction solution at different time periods does not test the reproducibility of the data in such a vigorous manner.

The discrepancies in these data initiated a careful comparison of the conditions of the two experiments which provided probable cause for differences. These included: a substantial difference in pH (5.8 to 7.3), the probable absence of any organic organisms in the distilled water (while algae and probably other organics were present in the "snow-melt"), and significant differences in the amount and intensity of solar irradiation in the two experiments. Perhaps the most significant factor in creating these last differences between P8-A and P8-B, and between the "snow-melt" experiment, was an observation noted when the experiment was performed. Nearly all of the samples in P8-B floated to the surface of the immersing fluid, whereas in P8-A and in both trials of P9, the resmethrin samples remained submerged and were attached as a droplet to the bottom surface of the sample tubes.

It is quite apparent from the rate of reaction that photolysis occurs in both solid and solution phases. The surface area of the solid will have a large influence on the quantity of solar irradiation absorb-

ed, and this could easily give rise to the discrepancies noted in P8-B.

Retention time and mass spectral data acquired from extracted samples of this experiment, when compared with those of reference compounds, indicated that, despite these differences, many of the photoproducts generated in the previous experiments were also created here. Specifically, good evidence was found for the presence of benzaldehyde, benzyl alcohol, chrysanthemic acid, both cis- and trans-resmethrin, and the distillation concentrates of solvent impurities identified in the other studies.

Rayonet Photolysis of Resmethrin in Hexanes (P3, P4, 8 days)

Two trials, in which 1.00 g of resmethrin was dissolved in 295 ml of hexane in a pyrex Erlenmeyer flask fitted with a water-cooled condenser, were conducted. One sample was irradiated for a period of 8 days while the other was irradiated for a period of 8.5 days in a Rayonet Reactor. The samples were then extracted and stored in the manner described earlier.

Gas chromatograms of methyl ester and silyl ether derivatives of photoproduct residues were used in conjunction with gc and gc/ms spectral data of photoproducts to detect products generated by the photolysis. Positive identifications were made for benzaldehyde, benzyl alcohol, benzoic acid, chrysanthemic acid, and the parent compound, resmethrin. Compounds that originated in solvents used in experimental procedures, which included toluene and xylenes, were also detected in these samples. A number of other photoproducts, for which identification was not possible, were generated in this experiment in which the resmethrin

was photolysed for an extended period of time. It should be noted here that this was the only instance in which benzoic acid was found. In previous photolysis studies of resmethrin in oxygen-enriched environments, benzoic acid was detected as a recurrent product.

Rayonet Photolysis of Resmethrin in Methanol (3 hr. P5-A/B)

Two trials were performed in which 1.00 g of resmethrin was dissolved in 300 ml of methanol in a pyrex Erlenmeyer flask fitted with a water-cooled condenser. Samples were photolysed for a period of 3 hr. in a Rayonet Reactor as described earlier.

Gas chromatography/mass spectroscopy data were used, in conjunction with gc chromatograms of photolysis residues and their silyl ether and methyl ester derivatives, to identify photoproducts. These analyses isolated and identified chrysanthemic acid and the parent compound resmethrin. Benzaldehyde, benzyl alcohol, phenylacetic and benzoic acids were absent as photoproducts. As in many of the other experiments, a number of other products were isolated only in small amounts and were not characterizable.

Rayonet Photolysis of Resmethrin in Distilled Water (3 hr. P6-A/B)

Duplicate experiments were performed in which 10 mg of resmethrin dissolved in 3 ml of ethyl acetate were evaporated to dryness on a pyrex petri dish and immersed in 5.0 ml of water at a pH of 5.8. Samples were irradiated for 3 hr. in a Rayonet Reactor and then extracted by the procedure described earlier.

Interpretation of the gc/ms spectra for photoproduct residues and examination of gc chromatograms of photoproduct residues and their silyl

ethers and methyl esters established the identification of a number of compounds. These included toluene, 1,3- and 1,4-xylene, benzaldehyde, phenyl acetate, benzyl alcohol, chrysanthemic acid, and the parent compound resmethrin. The first three compounds, as discussed earlier, were likely solvent residues while the latter four were resmethrin photoproducts.

Rayonet Photolysis of Resmethrin in Hexanes (3 hr. P7-A/B

Duplicate experiments were conducted in which 0.100 g of resmethrin were dissolved in 30.0 ml of hexanes in an Erlenmeyer flask fitted with a water-cooled condenser and photolysed in a Rayonet Reactor for a period of 3 hr. (details described earlier). These and other experiments were performed to compare the kinds of products generated by photolysing resmethrin in various solution media, and their results were compared with published information.

Careful examination of the data derived from gas chromatography of extracted residues and products generated by silyl ether and methyl ester syntheses, when combined with information derived from gas chromatography/mass spectroscopy (gc/ms) analysis of photolysis residues, served to identify several of the rather limited number of compounds generated. Positive identification was made for all four compounds. These included ethyl acetate (sample solvent), xylenes (from clean-up procedures), and the cis- and trans-isomers of the original resmethrin substrate. The generation of no detectable quantities of photoproducts was not entirely unexpected in that hexane is rather stable solvent and the limited photolysis of resmethrin in this medium, without additional oxygen or photosensitizers, would provide little opportunity for reaction.

PART 2. PESTICIDE CHEMISTRY IN HIGH SCHOOL PROJECTS

This section of the thesis deals specifically with the application of the results from the extended experimental studies in the senior high school curriculum in Alberta. The optional portions of the prescribed curriculum allow for the development of project work, both bibliographic and experimental in nature, wherein some of the issues generated at the interface between science and society can be confronted and explored in some detail.

To this point the discussion has concentrated on pyrethroid chemistry alone. It is now necessary to widen the discussion of pesticides to encompass the major commonly used classes. Pyrethroids, far more expensive and less-widely used than other classes, may now be studied and evaluated from a benefit/risk point of view on a comparative basis.

This section therefore comprises two parts; first, a more general introduction to the other major classes of insecticides, namely the chlorinated hydrocarbons including lindane, cyclodienes, and DDT, the carbamates, and finally the organophosphates. The second part is a detailed description of a student project supervised by this researcher. The project was an experiment to determine the practicality of engaging qualified matriculation students in introductory research investigations of pyrethroid pesticides. The outcomes sought included the acquisition of knowledge of pesticides and their toxicologies, skills in sampling and analytical techniques, and an enhanced appreciation of the social and economic implications of the use of pesticides.

Chlorinated Hydrocarbons

Lindane (Hexachlorocyclohexanes)

Classification

Lindane has been defined as a mixture of 5 of the 8 theoretical stereoisomers of 1,2,3,4,5,6-hexachlorocyclohexane (O'Brien, 1967), along with other closely related compounds (Nakajima, 1983).

Symptomology

For mammals, symptoms of intoxication have been noted to progress through increased respiration rate, tremors, salivation, and convulsions, resulting ultimately in respiratory failure or cardiac arrest (Quraishi, 1977). For insects, clinical observation has shown violent quivering of the body, particularly the extremities, with accompanied abnormal fluttering (Nakajima, 1983).

Nakajima (1983) studied behaviours induced by the principal stereoisomers and reported numerous variations, i.e.: the physiological effect of the α-isomer (65-70% fraction of technical preparations) was that of a weak stimulant while the γ-isomer (a 12-13% fraction) acted as a strong stimulant. The β-isomer (a 5-6% constituent) was an inert or at best weak depressant, and the δ-isomer (at 6-8%) acted as a strong depressant (see Fig. 24). The ε-isomer (a 3-5% component) had no particular physiological effects.

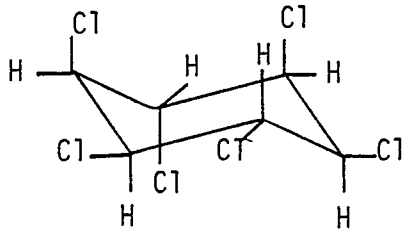


Figure 24. γ-Hexachlorocyclohexane

Toxicity

Lindane has been classified as a broad-spectrum insecticide. O'Brien (1967) reported that for most insects the γ-isomer is the principal active ingredient with a toxic factor of between 100 and 1000 times greater than that of any of the other individual isomers. Typical doses that are lethal to 50% of a test population (LD-50) were recorded as low as 2 ppm for the male house-fly and as high as 32.5 ppm for the milkweed bug. In contrast, lindane was of low oral toxicity to mammals, with LD-50 ranging from 86 ppm for mice to LD-50 in the range of 200 ppm for rabbits. In dramatic comparison, LD-50 values in 96 hours for 7 different species of fish ranged from 38 ppb to 152 ppb.

It should be noted at this time that researchers generally agree that the toxic effects of pesticides in mammals have specific physiological bases, these being respiratory failure and/or cardiac arrest. Unfortunately, the physiological factors directly responsible for the death of insects have not been specifically identified.

Mode of Action

O'Brien (1967) reviewed the evidence available at the time and concluded that lindane was probably an axonic poison not unlike DDT. Quraishi (1977) supported O'Brien's contention, describing lindane as a CNS stimulant in mammals. Nakajima (1983) and Matsumura and Ghiasuddin (1983) have proposed further details of the action of this neurotoxin. Both authors have provided evidence in support of the hypothesis that lindane causes CNS excitation by stimulating transmitter release. Lindane does not initiate neurotoxic action by acting as an anticholinesterase but rather increases the release of acetylcholine from the

presynaptic membrane. This results in the accumulation of an excess of acetylcholine in the synaptic region of CNS neurons (Nakajima, 1983). The proposed progenitor of enhanced acetylcholine release is the lindane-induced inhibition of Na^+-K^+-ATPase activity.

The peripheral neurotoxic activity of lindane in insects, as demonstrated in its action on the coxal muscle of the American cockroach, has been proposed to be an inhibition of γ-aminobutyric acid (GABA) stimulated Cl^- uptake (Matsumura & Ghiasuddin, 1983). The disruption of chloride uptake triggers a concentration gradient-induced release of acetylcholine which, in turn, amplifies nervous activity.

Degradation

The critical step in the biotransformation of hexachlorocyclohexane is the cleavage of C-H bonds (Nakajima, 1983). Biodegradation of lindane has been investigated in a number of organic systems (Nakajima, 1983; Portig, 1982) with qualitative if not quantitative consistencies in characterized metabolites. Degradative sequences have been characterized as oxygenation, dehydrochlorination, dehydrogenation, and glutathione conjugation (Nakajima, 1983). The metabolites and experimentally determined biodegradative sites and agents were discussed in some detail for representative species by the above mentioned authors.

The degradation of lindane by non-biological means has received relatively little attention in the review literature. Technical hexachlorocyclohexane (HCH) begins to melt at 65°C and various isomers and impurities melt at values above this. The β-isomer melts only at temperatures over 200°C. Lindane is volatile and exceptionally stable at elevated temperatures, making it an effective fumigant (Brooks, 1974a).

Its chemical stability makes it resistant to photolytic and oxidative degradation. However, it is readily converted into inactive isomers of trichlorobenzene in the presence of bases (Brooks, 1974a). The presence of pentachlorocyclohexene and tetrachlorocyclohexadiene have been detected as degraded products when lindane is stored for extended periods in the presence of light, moisture, and traces of bases (Brooks, 1974a). The volatization of soil degradation products has been suggested as a major means of purging this pesticide from soil.

Cyclodienes

Classification

O'Brien (1967) has defined cyclodienes as chlorinated adducts of hexachlorocyclopentadiene with a variety of double bonded compounds including Diels-Alder reaction products of the above. Examples might include chlordane, aldrin, and endrin (Fig. 25).

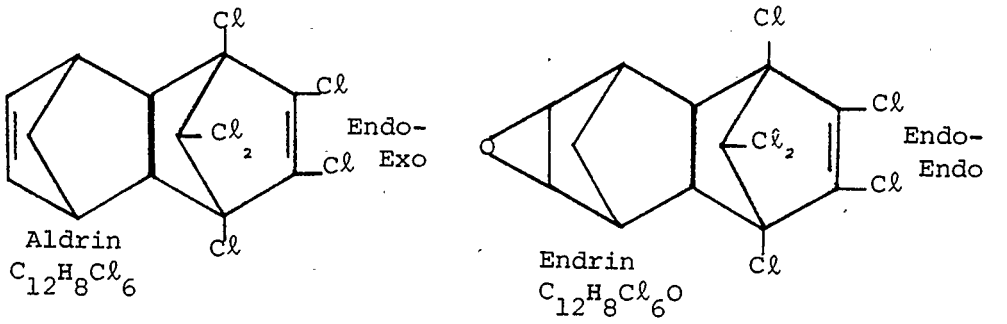


Figure 25. Cyclodienes

Symptomology

Vertebrate symptoms of intoxication have been seen to include lowering of blood pressure, excessive excitability, and convulsions in cats, while salivation, slowing of heartbeat, and increased blood pressure have been observed in dogs (O'Brien, 1967). Brooks (1974b) described acute mammal intoxication as having generalized similar effects. These symptoms include hypersensitivity, generalized tremors, and tonic-clonic convulsions, followed by respiratory failure ending in death.

O'Brien (1967) described insect poisoning as being caused by CNS disruptions giving rise to tremoring. Brooks (1974b) concluded that the symptoms of insect poisoning are similar for all members of this chemical class and are much like that of lindane, albeit somewhat slower in development. Poisoning symptoms of the common housefly demonstrate the progression: a period of normal activity is followed by quiescence which erupts into wing tremors of increasing frequency, then wingbeating spasms. Subsequent sudden, violent uncoordinated flight progresses into a convulsive phase which subsides and is followed by ataxic movements which lead to prostrate rhythmic contractions and extensions, and eventual death.

Toxicity

Cyclodienes are broad-spectrum insecticides. Many of this class are persistent and are highly toxic, both as a contact and stomach poison, for many insects (Brooks, 1974a). For the common house-fly, typical LD-50 values range from 1.6 ppm for endrin to 7 ppm for α-chlordane (O'Brien, 1967). Lethal concentration (LC)-50 for fish varies noticeably. Brooks (1974b) reviewed evidence indicating aldrin and

dieldrin LC-50 levels ranging from 0.067 ppm to 0.009 ppm for carp and sunfish, respectively. The toxicity of cyclodienes varies a great deal in mammalian vertebrates. Endrin is toxic to rats at 11 ppm while concentrations of 700 ppm of α-chlordane are needed to achieve equivalent mortality rates (O'Brien, 1967). Human oral ingestion has induced convulsions in a child at 10 ppm and death at 6 g in a woman for chlordane (Brooks, 1974b). The toxicity of other cyclodienes is estimated to be similar.

Mode of Action

O'Brien (1967) proposed that cyclodienes were likely to be axonic poisons. Matsumura (1982) concluded from his research that cyclodienes suppress the λ-aminobutyric acid stimulated uptake of Cl^-. Disruption of the function of the abundant chloride sensitive sites in the presynaptic plasma membranes, by antagonizing the natural inhibitory action of the GABA transmitter, stimulates neurotransmitter release at excitatory synapses. Tanaka, Scott, and Matsumura (1984) supported these findings with their arthropod research.

Degradation

According to Brooks (1974b), the biotransformation of cyclodienes is achieved primarily through oxidative processes. In mammals, mixed function oxidases activity in microsomal tissue (smooth endoplasmic reticulum liver cell tissue) is a significant biotransformation site. As well, microsomal oxidation is a principal degradation mechanism in insects. Epoxidation is a major oxidative avenue in both mammals and insects. Other operative oxidative mechanisms include hydroxylation and oxidative dechlorination. He also found that removal of chlorine, dehy-

drochlorination, and skeletal rearrangements are additional inactivation mechanisms.

Photochemical degradation of cyclodienes may be effected by rearrangement and photolytic oxidative and dechlorination reactions. Cyclodienes are also subject to acidic oxidation, basic epoxidation, and dehydrochlorination and other non-specific inactivation reactions (Brooks, 1974a).

DDT

Classification

DDT is 2,2-bis(p-chlorophenyl)-1,1,1-trichloroethane (O'Brien, 1967) and is the major component of technical formulations (Brooks, 1974a).

Symptomology

Narahashi (1979) described the onset of intoxication of insects and other invertebrates as the development of a state of ataxia with hyperexcitability and convulsions which progresses into paralysis and eventual death. Intoxication to the point of mortality is a protracted event. Narahashi (1982) described the symptoms of DDT poisoning in equivalent terms. He reported that DDT has a considerably lesser effect on higher animals than have other insecticides.

Toxicity

DDT exhibits a wide range of levels of toxicity with insects and its effectiveness as an intoxicant varies greatly with the mode of application. Topical application to the differential grasshopper requires a dose of 9380 ppm while the American cockroach experiences an

equivalent LD-50 with a 93 ppm application. Toxicity among representative mammals shows a similar broad range of values. Acute oral doses range between 87 ppm and 500 ppm while acute levels of dermal application range from 1931 ppm to 3263 ppm (Kenaga & End, 1974). LD-50 values for quails, starlings, and ducks range from 300 ppm to greater than 2000 ppm. Typical lethal concentrations for fish are very low and range from 0.005 ppm for adult fish to as little as 0.001 ppm for fry (O'Brien, 1967).

Mode of Action

DDT is most certainly a neurotoxin interacting with axonic transmission mechanisms as opposed to disruptive activity at the synapse. While some researchers have claimed that there is no definite model for mode of action (Narahashi, 1979), the observed neurological descriptions of intoxication are consistent. DDT is generally envisaged to bind at the lipid and protein interface region of Na^+ channel gates when they are in their open configuration. Gates thus bound exhibit different kinetics which then affect activation and inactivation and these in turn regulate action potential amplitude and frequency and afterpotential prolongation. These effects produce the classical neurotoxic symptoms of repetitive firing, prolonged depolarization, and suppression of Na^+ conductance (Narahashi, 1982; Osborne & Smallcombe, 1982; Van den Bercken & Vijverberg, 1982).

Degradation

DDT is biodegraded in one of five principal routes (Quraishi, 1977). In vertebrates, three oxidative routes for DDT have been characterized: (1) dicholorodiphenylethanoic acid (DDA); (2) dichlorodiphenyl-

trichloroethanol (kelthane); and (3) dichlorobenzophenone. Reductive dechlorination of DDT generates dichlorodiphenyldichloroethane (DDD) whereas dehydrochlorination of DDT produces dichlorodiphenyldichloroethene (DDE). Researchers have detected the majority of these products in a range of organisms extending from higher mammals down to simple yeasts, bacteria, and aquatic microorganisms (Quraishi, 1977).

As with some other chlorinated insecticides, DDT is environmentally persistent and is not readily degraded by abiotic means. DDT is a global contaminant probably due to atmospheric volatization and rainfall precipitation (Mellanby, 1976). Mellanby (1976) has suggested that, due to DDT's persistence and global transport, its concentration levels will likely continue to increase for at least another three decades, in which time levels may exist that could have significant environmental effects.

Carbamates

Classification

O'Brien (1967) defined carbamates as esters of derivatives of carbamic acid, NH_2-COOH. He described two subgroups of carbamate pesticides: N-methyl and N,N-dimethyl. The N-methyl usually more potent than their N,N-dimethyl analogues. Two formulations representative of this class of insecticides are shown in Figure 26.

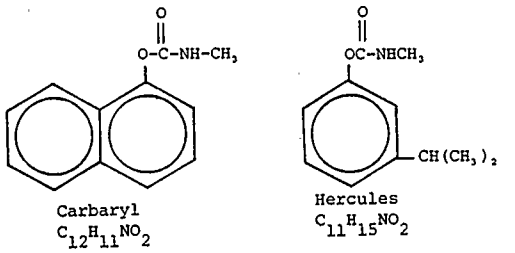


Figure 26. Carbamates

Symptomology

Notable poisoning symptoms include lachrymation (tearing), salivation, myosis (pupil constriction), and convulsions terminated by death (O'Brien, 1967). Kuhr and Dorough (1976) described mammal intoxication symptoms as being specifically: salivation, vomiting, bréathing difficulty, CNS depression, muscular tremoring, and cyanosis (purplish skin discolouration due to oxygen deficiency). Hyperactivity, ataxia (loss of coordination), clonic and tonic convulsions, paralysis, and death are graphic descriptions of insect poisoning.

Toxicity

Carbamates are not considered to be broad spectrum pesticides. Some are thought to be the most specific of all insecticidal chemicals (Quraishi, 1977). Kuhr and Dorough (1976) found bird LD-50 levels of toxicity to range from 0.4 ppm to 72,000 ppm administered orally to a variety of species. When they tested 8 different carbamates, typical LD-50 levels in fish species ranged between 0.8 ppm and 20 ppm. These data were based on testing 12 and 18 fish species, respectively, the first with zectran and the second with carbaryl. Since organic chlorides are often 10^2 to 10^3 times as toxic, carbamates are not considered to be highly toxic to these aquatic species. Mammal acute oral LD-50 concentrations ranged between 5 ppm and greater than 4000 ppm with typical LD-50 levels ranging in the 100+ ppm region (Kenaga & End, 1974). Carbamates are only slightly toxic to some species of insects and highly toxic to others, and where one carbamate is highly toxic another may not be. For example, the LD-50 of carbaryl is <500 ppm when administered to the house-fly while aldicarb has an LD-50 level of just 6 ppm for the

same species (Kuhr & Dorough, 1976).

Mode of Action

Carbamates are considered to be anticholinesterase intoxicants. The mechanism by which carbamates inactivate acetylcholinesterase is perceived as being a reversible sequence where the carbamate initially complexes with the acetylcholinesterase molecule and then carbamylizes the esterase by reacting chemically at the active serine hydroxyl group site of the esterase (see Fig. 27). The reaction is reversed by hydrolyzing (decarbamylizing) the product to generate the original enzyme (O'Brien, 1967).

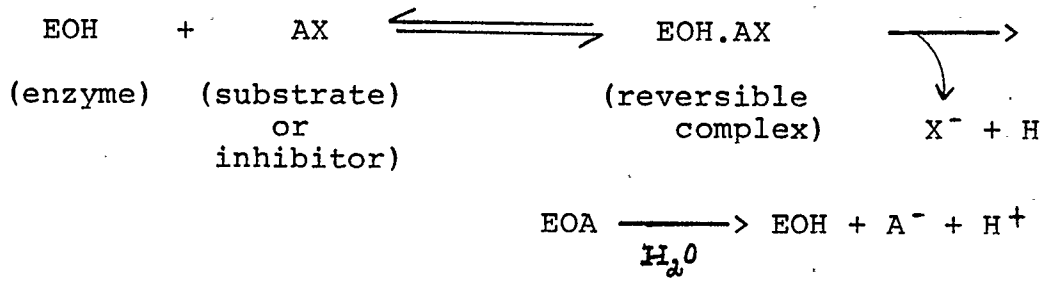


Figure 27. Carbamate mode of action

Since the carbamylation reaction is more readily reversed than is the phosphorylation reaction of phosphates, carbamate acetylcholinesterase poisoning is generally more treatable from the detoxification perspec-

tive (Fukuto, 1979).

Degradation

While dimethylcarbamates are observed to persist somewhat longer, methylcarbamates are destroyed rapidly, persisting for as little as a few days and at most a few weeks in aquatic environments (Kuhr & Dorough, 1976). Degradation is a combination of photochemical, hydrolytic, and microbiological metabolic reactions. In an attempt to summarize the data relating to photochemical degradation of carbamates, Kuhr & Dorough (1976) concluded that, while wavelength, intensity, pH, exposure medium, and duration greatly influence the effectiveness of photodecomposition reactions, the variance in data reported provided little by way of conclusive evidence with respect to the significance of photochemical reactions as effective environmental degraders of carbamates. A large variety of products is generated photochemically depending upon the carbamate photolyzed, and numerous products have not been characterized (Kuhr & Dorough, 1976; O'Brien, 1967).

Biodegration of carbamates occurs quite rapidly in a number of organisms. Mammals metabolize carbamates quickly with hydrolysis appearing as a major degradative pathway. While many metabolic products remain unidentified, hydroxylated derivatives and simple and conjugated hydrolysis products are evident (O'Brien, 1967). Detailed and useful information of metabolic studies of specific carbamates has been published by Kuhr and Dorough (1976).

Organophosphates

Classification

O'Brien (1967) defined organophosphates as a generic term covering all toxic organic compounds that contain phosphorus. These mostly include esters of a phosphorous acid or an anhydride of a phosphorous acid combined with some other acid. While millions of phosphate compounds have been synthesized, something in the order of 100 organophosphorous compounds have had or currently have pesticide applications (Eto, 1974). Parathion and malathion exemplify this pesticide class (Fig. 28).

Symptomology

Excitability, tremors, paralysis, and death, the immediate cause of which is unknown, are evident features of insect organophosphate intoxication (O'Brien, 1967).

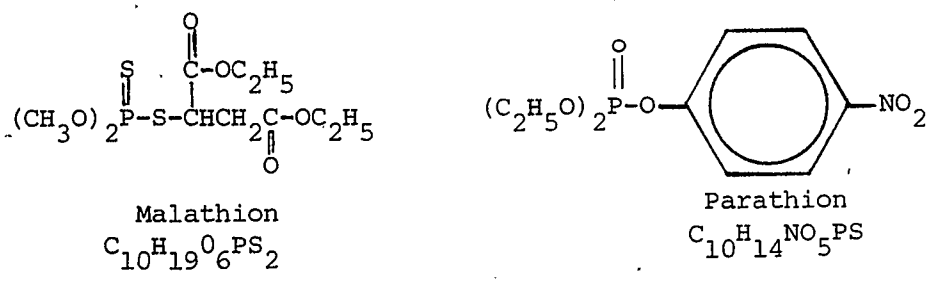


Figure 28. Organophosphates

This poisoning is evidenced by parasympathetic stimulation and neuromuscular activity causing defecation, urination, lachrymation, pupil contraction, and heartbeat depression. Neuromuscular action begins with excitatory muscle twitching followed by inhibitory paralysis. Vertebrate mortality is due to asphyxiation caused by respiratory failure,

either centrally or peripherally induced (O'Brien, 1967).

Toxicity

Like carbamates, organophosphates are post-synaptic poisons. Parathion and other related organophosphates are broad spectrum pesticides (Jones, Sudershan, & O' Brien, 1979). While some organophosphates are highly toxic to mammals, many are not and may be used as animal systemics. Many members of this chemical class are very short-lived and are readily hydrolyzed to non-toxic products (Quraishi, 1977). Oral ingestion LD-50 values in the mouse for a broad range of organophosphorous insecticides ranged from a low of 2 ppm to a high of 870 ppm in a study reported by Eto (1974). Non-selective pesticides consistently had low LD-50 values while selective pesticides had much higher average values. The common house-fly reported in the same study showed LD-50 values as small as 0.007 ppm for schradan and as large as 302 ppm for cyanophos. Organophosphates are considered to be extremely toxic to fish. Results of a study by Hollingworth (1976) showed LC-50 for 8 species of fish with a range of 4 ppb up to 4270 ppb in a 96-hour study with azinphos-methyl. He also reported results of a study comparing the toxicity of chlorfenvinphos with different species of mammals and birds. The data showed a range of between 16.4 ppm and 148 ppm for 3 species of birds.

Mode of Action

Organophosphates are post-synaptic neurotoxins. Their action is much like that of carbamates as they are also considered to be anticholinesterases. They block the action of acetylcholinesterase by phosphorylating the hydroxyl group on the serine segment of the acetylcholinesterase molecule. Thus, phosphorylated acetylcholinesterase is prohibi-

ted from hydrolyzing acetylcholine in the synaptic cleft and transmission is disrupted, first, by creating excessive firing activity and, finally, by blockage due to overload (Fest & Schmidt, 1973). The greater the irreversibility of the phosphorylation the greater the poisoning potential of the organophosphate.

Degradation

Biodegradation of organophosphates varies with the organism involved and the phosphate being degraded. Two enzyme systems, the microsomal oxidative and non-oxidative enzyme systems, including the esterases, are the principal degrading mechanisms (Quraishi, 1977). The microsomal fraction of the liver is frequently the centre of the microsomal oxidative system in mammals while the fat body performs comparable functions in insects. Hydrolysis is the single most important deactivation reaction for most organophosphates (O'Brien, 1967). Other such reactions include oxidation, desulphuration, hydroxylation, and dealkylation (Eto, 1974). Many organophosphates are considered to be short residual or rapidly decomposing compounds. They are characteristically degraded into non-toxic, water-soluble compounds which are readily expelled from organic systems, both plant and animal (Eto, 1974).

Photochemical reactions of organophosphates depend on a variety of factors including frequency, intensity, irradiation time, pH, state of chemicals, and the presence of other agents such as water, air, and photosensitizers (Eto, 1974). Photo-oxidation and photo-isomerization of UV irradiated organophosphorothionates generate even more potent enzyme inhibitors. Other such degradations include oxidation, cis-trans and rearrangement isomerizations, hydrolysis, and solvent interaction degradation products (Eto, 1974).

Chapter 6

STUDENTS' RESEARCH PROJECT

Participant Selection

Three students at the senior high school level were selected from applications. They were chosen on the basis that they had completed the core material of the Chemistry 30 curriculum with a minimum standing of 80% and had expressed a definite interest in participating in a research project.

Project Implementation

The three student participants met with their supervisor (this researcher) for a minimum of three hours per week over a period of two months. In that interval, the objectives, as defined in general terms in the project outline included at the end of this chapter, were clearly delineated. For each objective, projects involving literature review (see Student Project References following thesis References Cited), numerical and design problem-solving, and/or laboratory experimentations were assigned. All laboratory experiments, problem assignments, and readings were jointly discussed and reviewed. Particular emphasis was given to providing a maximum positive learning experience through frequent, individual attention to student concerns and through student participation in the definition of the limits of the learning objectives. Positive reinforcement was effected by means of prompt evaluation of tests and assignments and by utilizing a variety of evaluation tools.

Evaluation

Informal student evaluation was made by the supervisor based upon quality and quantity of student participation in group and individual discussions and through observing skill performance and its improvement in the interval of participation in the program. Formal evaluation was effected in three ways: (1) two formal examinations combining multiple-choice and short-answer questions were administered at intervals in the program; (2) one take-home assignment requiring the construction of an experimental design solution to a hypothetical problem was given near the end of the program; and (3) grades were assigned to the four experiments performed in the course of the program.

Program Results

Test results and informal evaluations indicated that student project participants acquired an above-average comprehension of and appreciation for the concepts and principles as defined by the learning objectives. Even though the results are not recorded here for reasons of confidentiality, suffice it to say that grades earned in this project were approximately of the same standing as grades from other portions of the Chemistry 30 course and from the Alberta Department of Education Departmental Exams.

Experimental design evaluations indicated that students had acquired effective skills for problem analysis and definition, for solution synthesis, and for the interpretation and evaluation of results. Observations of experiment performance and grading of experiment laboratory reports demonstrated that all participants had enhanced their under-

standing and skill in laboratory procedures and their ability to interpret results. A joint critique submitted by the students confirmed a perceived appreciation of the interdisciplinary content of scientific research and viewed participation in the project as having been informative and rewarding.

Experimental Results

Introduction to Thin-Layer Techniques

Students demonstrated the acquisition of skills in solvent system preparation, known and unknown sample preparation, sample spotting techniques, chamber preparation, thin-layer development, calculation of Rf values, interpretation of laboratory results, and laboratory safety in experimentation.

Thin-Layer Chromatography of Commercial Synthetic Pyrethroids

Students reviewed and practised skills acquired in the previous experiment and demonstrated that commercially available preparations varied in terms of both their composition and resolvability, based upon sampling techniques used, solvent systems used, and Rf values recorded.

Thin-Layer Chromatography of Permethrin and Resmethrin

The student experimenters acquired additional skill and practice in thin-layer techniques and resolved the active components of commercial pyrethroid preparations and compared these with reference standards and Rf values for related systems provided by literature references. Both colour agent and UV visualization techniques were utilized. Average results based upon 24-drop applications are shown in Table 13.

Table 13: Commercial and reference pyrethroids - Thin Layer Chromatography

Compound[a]	Solvent System	Average Rf Value
Permethrin (commercial)	9:1:1[b]	(5 trials) 0.52-0.56
Permethrin (reference)	9:1:1[b]	(3 trials) 0.53-0.58
Resmethrin (commercial)	9:1:1[b]	(5 trials) 0.57
Resmethrin (reference)	9:1:1[b]	(3 trials) 0.57
Permethrin (commercial)	85:15[c]	(3 trials) 0.69-0.71
Permethrin (reference)	85:15[c]	(3 trials) 0.71
Resmethrin (commercial)	85:15[c]	(3 trials) 0.71-0.74
Resmethrin (reference)	85:15[c]	(3 trials) 0.67

(a) Commercial permethrin = C.I.L. (Ambush); commercial resmethrin = Chipman Inc. (Kerigard): permethrin reference = NRDC 143 (permethrin) c/t 40/60%; resmethrin reference = NRDC 104 (resmethrin) c/t 30/70%, technical 85%. (b) 9:1:1 = n-Hexane:Toluene:Acetone Vol:Vol ratio. (c) 85:15 = Toluene:Ethyl Acetate vol:vol ratio. (d) All developments were performed at room temperature (22°C-25°C). Thin layer plates = Whatman LK6F Linear-K silica gel, size: 20×20 cm; thickness: 250 μm.

The Rf values for reference and commercial samples (Table 13) showed good correlation on individual plates for each solvent system but revealed some variation among different plates. Additional trials are needed to ensure reproducibility and limits of these data.

Solar Photolysis of Resmethrin and Permethrin on a Thin-Layer Medium

The students resolved the components of commercial and reference standard resmethrin and permethrin on thin-layer plates, exposed them to solar irradiation for a period of 18 hours, and developed the products at right angles to the first development. Average results based on 20-drop applications of permethrin and 40-drop applications of resmethrin are shown in Table 14 for the first development, and in Table 15 for the second development.

Again, correlations (see Table 14) between reference and commercial Rf values were good for both compounds tested. As with the previous set of data, variation among different plates did occur and additional trials are needed to determine the experimental limits of the data presented.

The Rf values for the photolyzed permethrin in Table 15 did not differ sufficiently from those of the initial development to confirm the existence of photoproducts. Additional investigation is required here to produce any substantial conclusions. The second development for resmethrin produced no movement, indicating that the deposit could not be resmethrin and was polar photoproducts. Resmethrin was not found within the limits of detection. Additional investigation is required to determine the feasibility of the resolution of photoproducts from this commercial product and to investigate the nature of the photoproducts formed.

Table 14: Two directional development of thin layer chromatographic plates. (a) Initial development of commercial and reference pyrethroids

Compound[a]	Solvent System[b]	Average Rf Values[c]
Permethrin (commercial)	9:1:1	(3 trials) 0.44-0.50
Permethrin (reference)	9:1:1	(3 trials) 0.44-0.52
Resmethrin (commercial)	9:1:1	(3 trials) 0.55-0.66
Resmethrin (reference)	9:1:1	(3 trials) 0.53-0.64

(a) Commercial permethrin = C.I.L. (Ambush); Commercial resmethrin = Chipman Inc. (Kerigard); Reference permethrin = NRDC 143 (Permethrin) c/t 40/60%; Reference resmethrin = NRDC 104 (Resmethrin) c/t 30/70%, technical 85%. (b) 9:1:1 = n-Hexane:Toluene:Acetone (Vol:Vol ratio). (c) All developments were performed at room temperature (22°-25°C). Thin layer plates = Whatman LK6F linear -K silica gel, size: 20×20 cm, thickness: 250 μm.

Table 14: (b) Right-angle development after 18 hours of solar photolysis

Compound[a]	Solvent System[b]	Average Rf Values[c]
Permethrin (commercial)	9:1:1	(3 trials) 0.50-0.57
Permethrin (reference)	9:1:1	(3 trials) 0.48-0.56
Resmethrin (commercial)	9:1:1	(3 trials) No movement on plate
Resmethrin (reference)	9:1:1	(3 trials) No movement on plate

(a) Commercial permethin = C.I.L. (Ambusy); Commercial resmethrin = Chipman Inc. (Kerigard); Reference permethrin = NRDC 143 (Permethrin) c/t 40/60%; Reference resmethrin = NRDC 104 (Resmethrin) c/t 30/70%, technical 85%. (b) 9:1:1 = n-Hexane:Toluene:Acetone (Vol:Vol ratio). (c) All developments were performed at room temperature (22°-25°C). Thin-layer plates = Whatman LK6F linear-K silica gel, size: 20×20 cm, thickness: 250 μm.

The outline of all components of the Student Project, including all the reading and laboratory exercises, and the learning objectives and their evaluation of outcomes is shown below.

STUDENT PROJECT: PHOTOSTUDY OF PYRETHROIDS (THIN-LAYER MEDIUM)

I. History of Pesticide Use

A. Learning Objective: To state the time frame of the use of natural and synthetic pesticides and to name the general sources of significant natural pesticides.

B. Learning Activity: 1. Read collected materials provided by instructor
2. Group discussion

C. Evaluation: Formal examination

II. Basic Insect Neurology

A. Learning Objective: To state by illustration and explanation the general mechanisms of nervous system transmission and the means by which toxicants interact with this system.

B. Learning Activity: 1. Read and make notes on assigned readings
2. Review discussion

C. Evaluation: Formal examination

III. Pesticide Toxicology

A. Learning Objective: For organophosphates, carbamates, chlorinated hydrocarbons and pyrethroids:

1. Define the pesticide group
2. State the current theory for mode of action
3. State the general and specific levels of toxicity (i.e. LD-50) values and classification as broad or specific toxins)

4. Appreciate difference between persistent and non-persistent pesticides

B. Learning Activity: 1. Read and makes notes on assigned materials

2. Group review

C. Evaluation: Formal examination

IV. Introductory Quantum Mechanics

A. Learning Objective: To state the basic principles of quantum mechanics as they relate to light and simple orbital theory.

B. Learning Activity: 1. Read and make notes on assigned reading materials

2. Do assigned problems

3. Review lecture and discussion

C. Evaluation: Formal examination

V. Introduction to Photochemistry

A. Learning Objectives: 1. To distinguish between chemical and photochemical reactions.

2. To define and use terms
- absorption spectrum
- emission spectrum
- chromophore
- auxochrome
- fluorescence
- phosphorescence
- sensitizer
- quencher

B. Learning Activity: 1. Complete reading assignment, make notes, and answer assigned problems

2. Group discussion and review

C. Evaluation: Formal examination

VI. Introduction to Thin-Layer Chromatography

A. Learning Objectives:
1. To define the principle of chromatographic separation of components of mixtures.
2. To demonstrate proficiency in thin-layer chromatographic techniques
   - developer preparation
   - sample preparation
   - chamber set-up
   - spotting technique
   - development
   - visualization (colour agents and ultraviolet light)
   - calculation of Rf values
   - characterization by comparison with authentic standards and literature reference

B. Learning Activity:
1. Thin-layer chromatography of known compounds and a mixture of the same
2. Thin-layer chromatography of commercial synthetic pyrethroids
3. Thin-layer chromatography of permethrin and resmethrin
4. Solar photolysis of resmethrin and permethrin on a thin-layer medium using bidirectional development

C. Evaluation:
1. Teacher evaluation of experimental work
2. Formal examination

Chapter 7

CONCLUSIONS AND SUGGESTIONS FOR FURTHER RESEARCH

A review of the information derived from the data collected during the experimental investigations of the photolytic degradation of resmethrin in water has resulted in a number of interesting observations. No previous studies have been conducted in this area in that no attempt had been made to duplicate prevailing environmental conditions. Not only has there been little research of resmethrin photodegradation in water, but neither has such research attempted to duplicate the pH, the dissolved oxygen content, nor the organic constituent composition shown in nature. It has been well established that the degradation of chemicals in distilled water is not of the same character as that in water with organic components and that neither effectively replicates degradation in the field.

An attempt was made in the present experiment to represent something of the conditions that would prevail in a field study by simulating these conditions in terms of pH, oxygen content, and organic content with the expectation that the findings would have more representative application for predicting reactions in the field.

As discussed earlier, many of the products isolated in this study corresponded with those found by other investigators. These included chrysanthemic acid, the degraded products of the alcohol fragment of resmethrin (benzyl alcohol, benzaldehyde, and in one instance, benzoic acid), and a number of partly identified photoproducts. Products notably absent were the highly oxygenated derivatives, namely, peroxides and epoxides that had been reported in earlier studies. This was not

entirely unexpected, because previous research had utilized sensitization and oxygenation techniques to generate many of these products.

A compound that was found in virtually all photolysed samples, and was the single largest component detected in each sample, was resmethrin. Contrary to previous reports, resmethrin, under the conditions investigated here, can be expected to persist for an extended period of time when immersed in aqueous solutions. Thus, resmethrin could pose a potential threat to sensitive species if it were allowed to contaminate water resources. Resmethrin has been found to be highly toxic to fish, crustacea, and aquatic microorganisms at the parts per billion level.

Research results to date have provided only a limited amount of information with respect to the fate of resmethrin when photolyzed in aqueous media. Further study is needed in which experiments are designed to enable the generation and labelling of larger quantities of aqueous photoproducts so that trace photoproducts can be identified. Experiments could be designed in which greater precision and accuracy might be maintained with respect to the determination of the time course of the evolution of aqueous photoproducts. An area in special need of investigation is that of true field testing of the environmental fate of resmethrin in natural water systems. Finally, more research is required in the area of thin-layer chromatographic studies of commercial pesticides to establish their feasibility for routine pyrethroid investigations, for both field work and instructional purposes (e.g., student projects),

As has been the case with a number of other well-accepted and widely used chemicals, renewed investigations with technically improved

means have provided new and useful information for the assessment of the balance between benefits and potential risks involved in the use of chemicals. Although biological control of pests has been an area of vigorous research, the use of chemicals to regulate pest populations remains the single most effective method for their control; therefore, to establish their environmental fate is crucial.

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