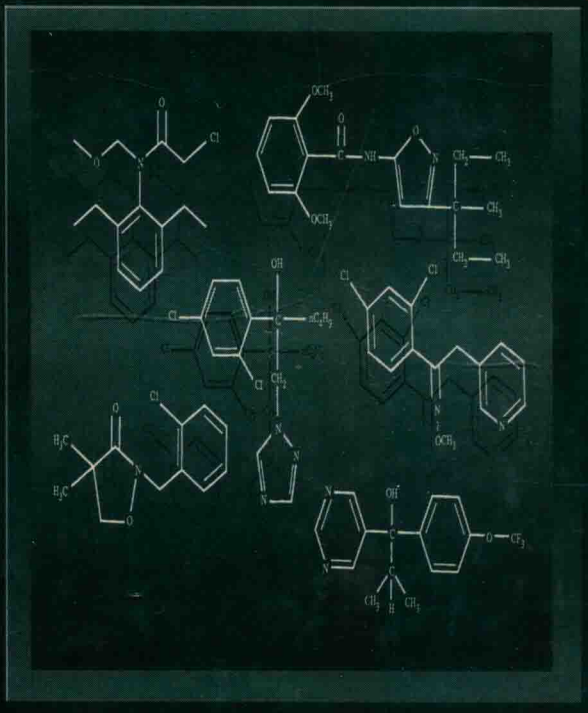
Comprehensive Analytical Profiles of Important Pesticides

A Volume in the Series

Modern Methods for Pesticide Analysis



Edited by
Joseph Sherma
Thomas Cairns

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A Volume in the Series
Modern Methods for Pesticide Analysis

Edited by
Joseph Sherma, Ph.D.
John D. and Frances H. Larkin Professor and Head
Department of Chemistry
Lafayette College
Easton, Pennsylvania

Thomas Cairns, Ph.D., D.Sc.
U.S. Food and Drug Administration
Los Angeles District Office
Los Angeles, California

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Comprehensive Analytical Profiles of Important Pesticides

PREFACE

This volume in the series, *Modern Methods for Pesticide Analysis,* provides detailed information on the properties and analytical methodology for nine prominent pesticides, comprising one insecticide, two fungicides, five herbicides, and one plant growth regulator. In addition, the analysis of various fumigants in food is also covered.

The format of the presentation follows that previously adopted in the earlier series, *Analytical Methods for Pesticides and Plant Growth Regulators,* edited by Gunter Zweig and Joseph Sherma for Academic Press. General properties of the pesticides are provided, in addition to a review of methods for formulation and residue analysis and experimental details for the recommended analytical methods. The general information includes formulations and uses, chemical and physical properties, toxicity data, and tolerance on various foods and feeds. In most cases, analytical information is given in sufficient detail so that the methods can be carried out without having to consult additional literature sources.

We know of no other easily accessible source of comprehensive, authoritative information on widely used pesticides such as is offered in this volume. We hope that such a comprehensive compilation will prove to be of great value to a multidisciplinary audience requiring access to concise reports illustrating the latest successful approaches to analyzing these important pesticides, including analytical chemists, laboratory managers, and residue chemists. In combination with the other volumes on current methodology and regulatory aspects, we hope this series will provide the pesticide analytical community with a continuing source of vital general and specific information.

The authors contributing to this volume are all recognized authorities in their fields from Europe and America. In most cases they are the principal scientists representing the chemical manufacturers of the specific pesticides discussed.

We invite readers to contact us with comments and possible errors, which inevitably seem to arise in spite of the best efforts of the authors, editors, and production staff of the publisher. We also would like to receive suggestions for topics that should be addressed in future volumes of the series, and encourage our correspondents to offer their services or nominate one of their colleagues to join our distinguished roster of contributors.

Joseph Sherma, Ph.D.
Thomas Cairns, Ph.D., D.Sc.

CONTRIBUTORS

Dennis D. Arras
Monsanto Company
St. Louis, Missouri

Naresh C. Atreya
ICI Agrochemicals
Jealott's Hill Research Station
Bracknell, England

Audrey W. Chen, Ph.D.
FMC Corporation
Agricultural Chemical Group
Princeton, New Jersey

James L. Daft
Total Diet Laboratory
U.S. Food and Drug Administration
Department of Health and Human Services
Kansas City, Missouri

Geoffrey S. Davy, Ph.D.
ICI Agrochemicals
Jealott's Hill Research Station
Bracknell, England

Richard Demchak, Ph.D.
Merck Research Laboratories
Division of Merck & Co., Inc.
Three Bridges, New Jersey

Michael R. Duffin
ICI Agrochemicals
Jealott's Hill Research Station
Bracknell, England

Roland P. Hänni
Dr. R. Maag Ltd.
Dielsdorf, Switzerland

Kevin J. Harradine
ICI Agrochemicals
Jealott's Hill Research Station
Bracknell, England

Joan Lasota, Ph.D.
Merck Research Laboratories
Division of Merck & Co., Inc.
Three Bridges, New Jersey

Peter Massey
ICI Agrochemicals
Jealott's Hill Research Station
Bracknell, England

Euphemia Papadopoulou-Mourkidou, Ph.D.
Pesticide Laboratory
Aristotelian University
Thessaloniki, Greece

Bonnie S. Rutherford
Environmental Chemistry Laboratory
DowElanco
Greenfield, Indiana

Anton J. Schuler
Dr. R. Maag Ltd.
Dielsdorf, Switzerland

J. Michael Warner, Ph.D.
Monsanto Company
St. Louis, Missouri

Teresa Wehner, Ph.D.
Merck Research Laboratories
Division of Merck & Co., Inc.
Rahway, New Jersey

Sheldon D. West
Environmental Chemistry Laboratory
DowElanco
Greenfield, Indiana

Chris Wollerton
ICI Agrochemicals
Jealott's Hill Research Station
Bracknell, England

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Chapter 1

THE PYRETHROID INSECTICIDES

Euphemia Papadopoulou-Mourkidou

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I. INTRODUCTION

The agricultural uses of pyrethroids have increased steadily in the years since the introduction of the first photostable pyrethroid for field use in the late 1970s. They share approximately 25% of the total insecticide market for plant protection, and have made a substantial impact on control involving major pests of cotton, lepidopterous pests on fruit and vegetable crops, and aphids on cereals. Their uses have also expanded to other agricultural markets, including stored product pest control for which they are slowly replacing the traditionally used insecticides (Hirano, 1989; Elliott, 1989). Pyrethroids also play a wide-ranging and significant role in health care throughout the world. In the last 10 to 15 years, they have effectively replaced many areas traditionally covered by other groups of insecticides in public health, vector, and industrial pest control (Carter, 1989).

Pyrethroids are lipophilic compounds. However, unlike the organochlorines, they are readily degraded under field conditions by sunlight (photodegradation) and by most living organisms (biodegradation). The degree of photostability and biodegradability varies among the different members of the group, and their applications have been developed accordingly.

Reviews on the analysis of pyrethroids have been published by Miyamoto (1981) and Papadopoulou-Mourkidou (1983 and 1988b), and by Sharp et al. (1988), who cover only aspects of pyrethroid analysis related to residues in grains and grain products. Consistent with the reputation of pyrethroids developed thus far, the number of compounds successfully reaching the market is also increasing steadily, and their uses and applications are also expanding accordingly. Therefore, diverse methods of analysis, due to their applications in a wide variety of substrates, are also steadily increasing, and the present review is appropriate at this time to supplement and update our review on this matter written 4 years ago.

The common and chemical names of the pyrethroids discussed in the text are listed in Table 1.

II. ANALYSIS OF PYRETHROID TECHNICAL AND FORMULATED MATERIALS

A. HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC METHODS

High-performance liquid chromatography (HPLC) is a fast-growing separation technique suitable for the analysis of technical and formulated materials of pyrethroids, especially when isomeric forms have to be quantified. It has been demonstrated that HPLC is a superb technique for separating pyrethroids from their synthesis byproducts, formulation ingredients, and synergists, and for providing better resolution for their geometric and diastereomeric isomers compared to other separation techniques. On columns packed with chiral materials, the direct separation of their optical isomers is also feasible.

TABLE 1
Nomenclature of Pyrethroids Mentioned in the Text

Common name	Chemical designation
Allethrin	(*RS*)-3-Allyl-2-methyl-4-oxocyclopent-2-enyl (1*RS*)-*cis,trans*-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate
α-Cypermethrin	(*R*)(1*S*)*cis* + (*S*)(1*R*)*cis* isomers of cypermethrin
Bioallethrin	(*R*)(1*R*)*trans* + (*S*)(1*R*)*trans* isomers of allethrin
Bioresmethrin	(1*R*)*trans* isomer of resmethrin
Biphenthrin	2-Methylbiphenyl-3-ylmethyl(Z)-(1*RS*,3*RS*)-3-(2-chloro-3,3,3-trifluoroprop-1-enyl)-2,2-dimethylcyclopropanecarboxylate
Cismethrin	(1*RS*)*cis* isomers of resmethrin
Cyfluthrin	(*RS*)-α-Cyano-4-fluoro-3-phenoxybenzyl (1*RS*)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
Cyhalothrin	(*RS*)-α-Cyano-3-phenoxybenzyl (Z)-(1*RS*)-*cis*-3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylate
Cypermethrin	(*RS*)-α-Cyano-3-phenoxybenzyl (1*RS*)-*cis,trans*-3-(2,2-dichlorovinyl-2,2-dimethylcyclopropanecarboxylate
Deltamethrin (Decamethrin)	(*S*)-α-Cyano-3-phenoxybenzyl (1*R*)*cis*-3-(2,2-dibromovinyl)-2,2-dimethylcyclopropanecarboxylate
Esfenvalerate	(SS) isomer of fenvalerate
Fenpropathrin	(*RS*)-α-Cyano-3-phenoxybenzyl 2,2,3,3-tetramethylcyclopropanecarboxylate
Fenvalerate	(*RS*)-α-Cyano-3-phenoxybenzyl (*RS*)-2-(4-chlorophenyl)-3-methylbutyrate
Flucythrinate	(*RS*)-α-Cyano-3-phenoxybenzyl (*S*)-2-(4-difluoromethoxyphenyl)-3-methylbutyrate
Fluvalinate	(RS)-α-Cyano-3-phenoxybenzyl *N*-(2-chloro-α,α,α-trifluoro-*p*-tolyl)-D-valinate
λ-Cyhalothrin	(*R*)(1*S*)*cis* + (*S*)(1*R*)*cis* isomers of cyhalothrin
Permethrin	3-Phenoxybenzyl (1*RS*)-*cis,trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
Phenothrin	3-Phenoxybenzyl (1*RS*)-*cis,trans*-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate
Resmethrin	5-Benzyl-3-furylmethyl (1*RS*)-*cis,trans*-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate
Terallethrin	(*RS*)-3-Allyl-2-methyl-4-oxocyclopent-2-enyl 2,2,3,3-tetramethylcyclopropanecarboxylate
Tetramethrin (Phthalthrin)	3,4,5,6-Tetrahydrophthalimidomethyl (1*RS*)-*cis,trans*-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropanecarboxylate

Both normal and reversed-phase systems have been applied for the analysis of pyrethroids. Normal phase systems consisting of silica gel columns eluted with mixtures of acetonitrile with halogenated solvents (carbon tetrachloride, dichloromethane, chloroform, 1,2-dichloroethane), cyclohexane, heptane, or hexane, or mixtures of hexane with diisopropyl ether or dioxane have been used for the analysis of the pyrethroids that were developed early including allethrin, cypermethrin, deltamethrin, fenvalerate, permethrin, d-phenothrin, tetramethrin, and resmethrin. These data have been discussed in the previous review article by Papadopoulou-Mourkidou (1988b).

Recently, the analysis of deltamethrin and cyfluthrin, the latter a relatively new pyrethroid, was also reported on silica gel columns eluted with 5 and 2.5% (v/v) dioxane in hexane, respectively (Hanks, 1990; Slahck, 1990). With this system, the four diastereomers of cyfluthrin were resolved, and these were also separated from all known impurities and decomposition products contained in technical and formulated (emulsifiable concentrate and a wettable powder) materials (Slahck, 1990). The system proposed for the analysis of deltamethrin in technical and formulated materials was collaboratively evaluated for the analysis of five formulated materials of deltamethrin and recommended as an official first action CIPAC-AOAC method (Hanks, 1990). However, in the proposed method for the analysis of deltamethrin in ultralow volume (ULV) formulations, a CN-bonded silica column was recommended, as this material is more resistant to polar solvents and water contained in ULV formulations, which may inactivate the silica gel column (Hanks, 1990).

CN-bonded phases eluted with mixtures of diethylether with hexane or dioxane with isooctane have been used for the analysis of cypermethrin, deltamethrin, and fenvalerate (Papadopoulou-Mourkidou, 1988b). The CN-bonded phases appear to be efficient in separating diastereomers and geometrical isomers of pyrethroids. They are also reported as being more suitable for gradient elution due to their rapid equilibration with the mobile phase, and for the quantitative analysis of pyrethroids due to their higher reproducibility (Cayley and Simpson, 1986).

An HPLC system involving a CN-bonded phase column eluted with tetrahydrofuran in hexane was reported as being better for the separation of allethrin *cis/trans* isomers than a NO_2-bonded phase column system, while the NO_2-bonded phase column eluted with 2-propanol in hexane was reported more efficient in separating the diastereomers of (*RS*)-bioallethrin (Ando et al., 1986). Under these conditions, *cis*-allethrin was eluted as a single peak. However, when the NO_2-bonded phase was eluted with tetrahydrofuran, the diastereomers of (*RS*)-bioallethrin were separated from C_3-cyclopropyl and propynyl analogs of (*RS*)-bioallethrin derived from the UV irradiation of (*RS*)-bioallethrin. Thus, the latter system is suggested as a reliable method to quantitate allethrin photoreaction products (Ando et al., 1986).

NH_2-bonded phases were also evaluated for the analysis of pyrethroids (Chapman, 1983; Cayley and Simpson, 1986). The NH_2-bonded phase column should be protonated with acetic acid because otherwise, poor chromatographic behavior is observed for cypermethrin, cyfluthrin, fenvalerate, and flucythrinate when analyzed on NH_2-bonded phases in the free base form eluted with 0.1% propanol in hexane (Chapman, 1983). However, the separation of isomers for these pyrethroids on the protonated NH_2-bonded column was inferior to that obtained by Cayley and Simpson (1986) when a CN-bonded phase column was used instead.

Reversed-phase C_{18}-bonded columns eluted with methanol-water or acetonitrile-water have been reported for the analysis of cyhalothrin, fenpro-

pathrin, fenvalerate, fluvalinate, kadethrin, permethrin, and resmethrin. C_8-bonded columns eluted with acetonitrile in acidified water were applied for the analysis of deltamethrin and fenvalerate, while a phenyl-bonded column eluted with methanol-water was applied for the analysis of d-phenothrin. These data have been included in a previous review article by Papadopoulou-Mourkidou (1988b) on pyrethroid analysis.

HPLC was also proven as a superb, rapid, and convenient technique for the direct analysis of pyrethroid optical isomers. It appears that separation of isomeric forms down to the optical antipodes is becoming a necessity for pyrethroids as well as other groups of agrochemicals, since isomers and antipodes usually exhibit different biological activities, while in a number of cases inactive isomers, present in racemic mixtures, antagonize the effects of the active isomers (Vijverberg and Oortgiesen, 1988). Currently, we see individual antipodes or selected mixtures of isomers commercialized as agrochemicals (e.g., esfenvalerate, λ-cyhalothrin, d-phenothrin, α-cypermethrin, etc.), thus further reducing any adverse effects of pyrethroids to the environment.

Chiral HPLC has shown an enormously rapid development in recent years, leading to the commercial availability of more than 30 different chiral stationary phases (Vermeulen and Testa, 1988). However, the number of chiral phases found appropriate for pyrethroid antipode analysis is still very limited. Three main types of chiral phase have been found useful in separating pyrethroid optical isomers (Figure 1). The first chiral phase evaluated for the analysis of pyrethroids was the so-called Pirkle type 1-A phase, consisting of (*R*)-*N*-(2,5-dinitrobenzoyl)phenylglycine chiral liquid phase ionically bonded to 3-aminopropylsilanized silica gel (Phase I_a, Figure 1) (Chapman, 1983; Cayley and Simpson, 1986). The respective chemically bonded (*R*)-*N*-(2,5-dinitrobenzoyl)phenylglycine phase to 3-aminopropylsilanized silica gel (Phase I_b) was evaluated by Papadopoulou-Mourkidou (1985) and Doi et al. (1985). Recently, a modified Pirkle type 1-A chiral material containing (*R*)-*N*-(3,5-dinitrobenzoyl)-1-naphthylglycine ionically bonded to 3-aminopropylsilanized silica gel (Phase I_c) has also been evaluated for pyrethroid analysis (Oi et al., 1989). Phase I_c, as the other materials of the Phase I type of chiral phases, has one chiral center; however, the substitution of a phenyl ring by a naphthyl ring appears to increase the enantioselectivity of this material toward the pyrethroid antipodes (Oi, et al., 1990).

Chiral phases of type II are novel chiral materials derived from (*S*)- or (*R*)-1-(α-naphthyl)ethylamine with (*S*)-valine chemically bonded to 3-aminopropylsilanized silica gel (Oi et al., 1986, 1989). These chiral phases will be referred to in the present discussion as Phases II_a and II_b, respectively (Figure 1). Similarly, two other related chiral materials derived from (*S*)- or (*R*)-1-(α-naphthyl)ethylamine and (*S*)-*tert*-leucine (Oi et al., 1990) will be referred to as Phases II_c and II_d, respectively. Chemically, the Phase II type of materials are urea derivatives containing two chiral centers as substituents to the two urea nitrogens, respectively (Figure 1).

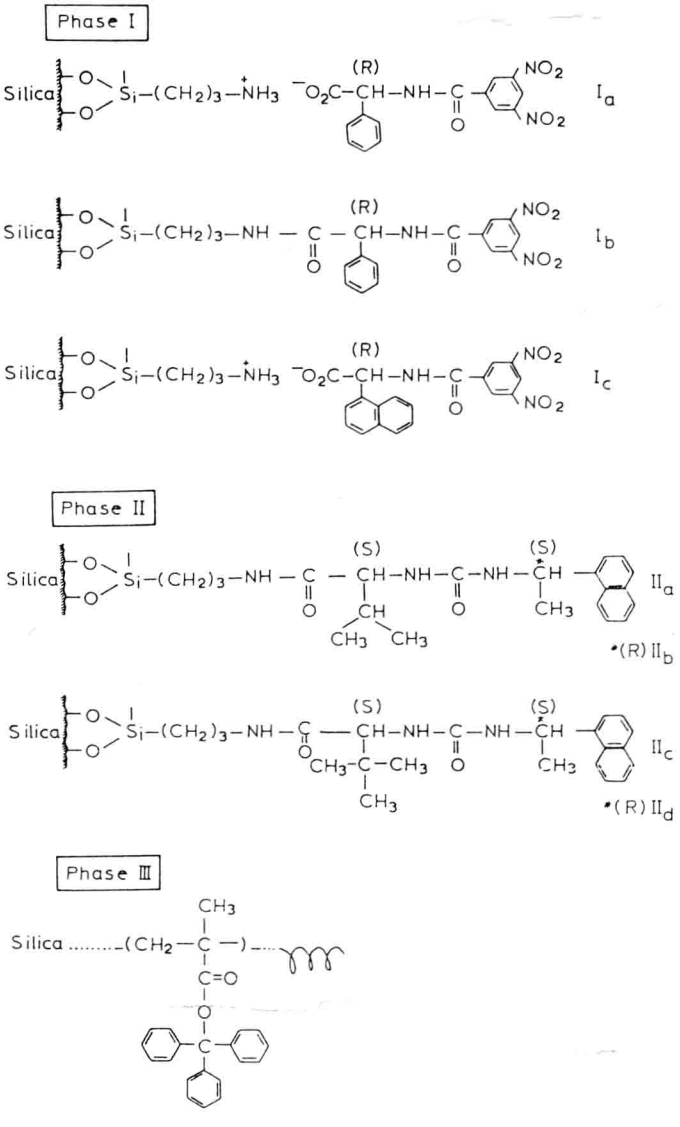

FIGURE 1. HPLC chiral column materials evaluated for the analysis of pyrethroid antipodes.

Okamoto and Hatada (1986) reported the synthesis of a new, optically active material derived from the polymerization of triphenylmethyl methacrylate [(+)-poly(triphenylmethyl methacrylate), PTrMA], which attains its chirality by helicity. This chiral phase material is referred to as Phase III (Figure 1). A soluble form of Phase III coated on macroporous silica gel (ChiralPack $OT_{(+)}$) was also evaluated recently for the separation of pyrethroid enantiomers.

In order to facilitate the discussion on the HPLC data reported thus far on the direct analysis of pyrethroids on chiral column materials and to assist in the evaluation of the data with respect to the enantioselectivity of the different chromatographic systems toward certain antipodes, expressed as the separation factor (a), Table 2 has been prepared. Phases I_a and I_b eluted with mixtures of 2-propanol in hexane have been evaluated for the analysis of many pyrethroids (Chapman, 1983; Papadopopoulou-Mourkidou, 1985; Cayley and Simpson, 1986). However, from the data reported thus far, these systems appear to be more selective in separating geometrical and diastereomeric pairs of isomers rather than enantiomeric isomers, except for type III pyrethroids, adopting the classification proposed by Cayley and Simpson (1986), i.e., fenvalerate, fluvalinate, and flucythrinate, which were satisfactorily resolved into their respective enantiomers (Table 2). However, the separation factors (a) between enantiomers were still in the 1.04 to 1.15 range for fenvalerate and fluvalinate, and 1.35 for flucythrinate. Oi et al. (1990) achieved a better separation between fenvalerate isomers (separation factors ranging from 1.11 to 1.34) on Phase I_b eluted with hexane-1,2-dichloroethane-methanol mixtures, while by substituting the Phase I_b-containing column with the modified Pirkle type 1-A phase-containing column, Phase I_c, the separation factors between fenvalerate isomers were further increased to the 1.34 to 1.45 range without the concomitant increase of the respective capacity factors and the need for decrease or change of the mobile phase strength (Table 2).

The analysis of fenvalerate optical isomers on the Pirkle type 1-A covalent column (Phase I_b) eluted with 0.2% 2-propanol in hexane, in association with a UV diode array detection system, was investigated by Papadopoulou-Mourkidou (1988a; 1989a; 1989b). The retention times of the eluted isomers were decreased as the column temperature was increased from 2° to 35°C. The separation factors between enantiomers decreased, while those between diastereomers remained unchanged as the column temperature increased. However, the resolution between all pairs of adjacent peaks was best when the column was thermostatted at 15°C. The HPLC column temperature is indeed an important parameter in controlling and optimizing separation processes; this has been ignored as indicated by the reported literature, in which the column temperature is only occasionally stated and usually is assumed to be ambient temperature. Another aspect associated with column temperature variations during the HPLC analysis is the appearance of artifacts, baseline drifts, and lack of solute retention time reproducibilities.

Doi et al. (1985), using a longer column (50 cm, rather than a 25-cm column used in all other chiral applications) packed with Phase I_b and hexane-1,2-dichloroethane or hexane-1,2-dichloroethane-ethanol mobile phases, achieved baseline separation between the enantiomers of chysanthemate pyrethroids (phenothrin, resmethrin, and tetramethrin) (Table 2). The modified Pirkle type 1-A material (Phase I_c), however, still appears to be more enantioselective for chrysanthemate pyrethroid enantiomers, as indicated by the separation factors obtained for fenpropathrin, permethrin, phenothrin, res-