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A DIGEST OF INFORMATION ON ALLETHRIN

By

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Division of Insecticide Investigations

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CONTENTS

Page

Introduction 4
Nomenclature 4
Physical characteristics 5
Synthesis
  Synthesis of allethrin 6
  Synthesis of chrysanthemum monocarboxylic acid 7
  Synthesis of 2,5-dimethyl-2,4-hexadiene 8
  Alternate synthesis of 2,5-dimethyl-2,4-hexadiene 8
Analysis 9
Production 11
Patents 12
Specifications 12
Allethrin in aerosols 13
Stability of allethrin and its formulations 14
Use of synergists with allethrin
  MGK-264 15
  n-Propyl isome 15
  Sulfoxide 16
  Piperonyl butoxide 16
  m-Nitrobenzamides 17
  Comparative value of synergists for allethrin 17
Allethrin stereoisomers 20
Analogs of allethrin 22
Toxicology 23
Classification of insects against which allethrin has been tested 26
Orthoptera
  Blattidae 26
Thysanoptera
  Thripidae 27
Homoptera
  Aleyrodidae 27
  Aphidae 28
  Cicadellidae 29
  Coccidae 29
Heteroptera
  Coreidae 29
  Lygaeidae 30
  Miridae 30
  Pentatomidae 30
Anoplura
  Haematopinidae 30
  Pediculidae 30

Coleoptera
Anobiidae 31
Chrysomelidae 31
Coccinellida 32
Cucujidae 32
Curculionidae 32
Dermestidae 32
Scarabaeidae 33
Tenebrionidae 33
Lepidoptera
Hyponomeutidae 33
Papilionidae 33
Phalaenidae 34
Phycitidae 34
Pieridae 35
Pyraustidae 35
Sphingidae..... 35
Hymenoptera
Formicidae 36
Diptera
Culicidae 36
Drosophilidae 37
Hippoboscidae 37
Mycetophilidae 37
Muscidae 38
Tabanidae 40
Acarina
Argasidae..... 40
Ixodidae 41
Tetranychidae 41

This digest has been prepared in response to numerous requests for information concerning the Bureau of Entomology and Plant Quarantine's new synthetic insecticide, allethrin. This product, because of its high toxicity to insects and its non-toxicity to warm blooded animals, has excited great interest among entomologists, chemists, insecticide manufacturers, food processors and public health officials. Information on the chemistry, economic status, toxicology and insecticidal value of allethrin has been collected and is presented in the form of a digest in which reference is made to many anonymous articles, press releases and advertisements in order to present in detail the early history of the development of allethrin by the Bureau. These references would normally not be included in a bibliography issuing from the Bureau of Entomology and Plant Quarantine.

INTRODUCTION

The achievement of Schechter, LaForge and Green in synthesizing allethrin was first made public by Bishopp (47) in a statement dated March 11, 1949.

Although considerable work had been done by Swiss and British workers on the chemistry of the active principles of pyrethrum flowers, the final structures of pyrethrins I and II and cinerins I and II were determined mainly by LaForge and associates in 1947 as the result of 15 years of research. Cinerin I was chosen as the object of synthesis because of its simpler structure and greater stability. Workers in England had already devised an improved synthesis of chrysanthemum monocarboxylic acid, the acidic portion of the molecule. The problem therefore was reduced to the preparation of cinerolone, the ketoalcoholic part of cinerin I. In 1948 Schechter, LaForge and Green finally were able to devise a general synthesis for cyclopentenolones of the type of cinerolone and a stereoisomer of cinerolone was prepared. When esterified with chrysanthemum monocarboxylic acid it gave a product highly toxic to house flies. Other analogs were also prepared, but the ester which proved to be the best with regard to toxicity and knockdown effect on house flies and also from the standpoint of commercial production was the ester having an allyl side chain.

The United States Department of Agriculture (185) on March 18, 1949, issued a press release announcing this new pyrethrum-like chemical and on May 1 of the same year it issued a picture story (186) which depicted LaForge, Schechter, Green and Gersdorff performing operations having to do with the synthesis and biological testing of the new synthetic. The information in these departmental releases quickly appeared in the public press and in trade and technical journals (1-5) where the synthesis of allethrin was hailed as an achievement comparable with that of the synthesis of rubber.

NOMENCLATURE

The product now called allethrin was referred to as a "pyrethrin-like ester" and as a "homolog of cinerin I" in the original release by Bishopp. The release of March 18, 1949 referred to "pyrethrum-like chemicals" and the picture story of May 1, 1949 mentioned "synthetic pyrethrum-like material" and the "new pyrethrum synthetics". Items in technical and trade journals referred to Schechter and LaForge's achievement as the synthesis of an "isomer of cinerin I" and of a "homolog of cinerin I". In July 1949 an editorial in a trade journal (Anon. 6) spoke of "synthesizing pyrethrum" and a news item in the same issue (Anon. 7) was headlined "Penick synthesizes pyrethrum" although the article stated that the "allyl homolog of cinerin I" had been produced. Later articles referred to "synthetic pyrethrins", "so-called synthetic pyrethrum", and "synthetic pyrethrum".

This confusion in names was ended when the new name "allethrin" was coined by the Interdepartmental Committee on Pest Control (Rohwer 150) to designate the insecticidal chemical dl-2-allyl-4-hydroxy-3-methyl-2-cyclopenten-1-one esterified with a mixture of cis and trans dl-chrysanthemum monocarboxylic acids. Although not officially announced until May 15, 1950, "allethrin" was revealed as the new name for the allyl homolog of cinerin I on March 20, 1950 at a meeting at the Boyce Thompson Institute, Yonkers, New York, sponsored by the Carbide and Carbon Chemicals Division of the Union Carbide and Carbon Corporation for the purpose of announcing the first commercial synthesis of allyl cinerin (Anon. 17-19).

Before the name allethrin was announced Starr et al. (172) suggested that the allyl homolog of cinerin I be called "devinylpyrethrin I", or in abbreviated form "DVPy I". In England allethrin has been called "allylrethrin" (Blackith 49) and Harper's (96) nomenclature "synthetic dl-allylrethronyl dl-cis-trans-chrysanthemate" has been used by Galley (75) and by Elliott et al. (66).

Although Rohwer's announcement applied the name allethrin to the "substantially pure" chemical those in the insecticide industry have urged that it mean 100 percent material (Moore 131).

Certain trade names have been applied by S. B. Penick and Company to allethrin, for example, Allexcel 20 (143) and Pyresyn (19, 144).

According to Frear (74) Allexcel 20 contains 1 percent of allethrin, 5 percent of n-propyl isome, 10 percent of butoxyethanol, and 84 percent of oil. Allexcel 80 emulsifiable contains 3 percent of allethrin, 28.4 percent of n-propyl isome, 20.3 percent of methylated naphthalene, and 12.1 percent of oil. Pyresyn technical contains 75 percent of allethrin and 25 percent of related compounds.

PHYSICAL CHARACTERISTICS

Commercial allethrin has the following physical properties.--McNamee (120, 121), Moore (131).

Appearance	Clear, brownish
Color on Gardner scale	15
Specific gravity at 20/20	1.005-1.015
Refractive index at 30° C.	1.5010-1.5035
Refractive index at 20° C.	1.5040
Acidity calculated as chrysanthemum monocarboxylic acid	< 3 percent
Odor	Mild, unobjectionable
Freon insoluble	< 0.1 percent

SYNTHESIS

The synthesis of allethrin is accomplished in 13 steps, 6 steps in making allethrolone, 6 steps in making chrysanthemum monocarboxylic acid chloride, and a final step in combining these two components.

The reactions involved are shown below.

Synthesis of Allethrin

$CH_3COCH_2COOC_2H_5$ (Ethyl acetoacetate)

+ $CH_2 = CHCH_2Cl$ (Allyl chloride)

+ $NaOC_2H_5$ (Sodium ethylate)

↓

$CH_3COCHCOOC_2H_5$ (alpha-Allyl acetoacetic ester)

$CH_2CH = CH_2$

+ Alkali

↓

$CH_2= CHCH_2CH_2COCH_3$ (Allyl acetone)

+ $(C_2H_5O)_2CO$ (Ethyl carbonate)

+ $NaOCH_3$ (Sodium methylate)

↓

$CH_2 = CHCH_2CH_2COCH_2COOC_2H_5$ (gamma-Allyl acetoacetic ester)

+ Alkali

↓

$CH_2 = CHCH_2CH_2COCH_2COOK$ (salt of gamma-Allyl acetoacetic acid)

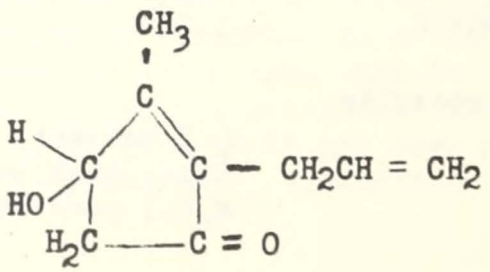
+ CH_3COCHO (Pyruvaldehyde)

↓

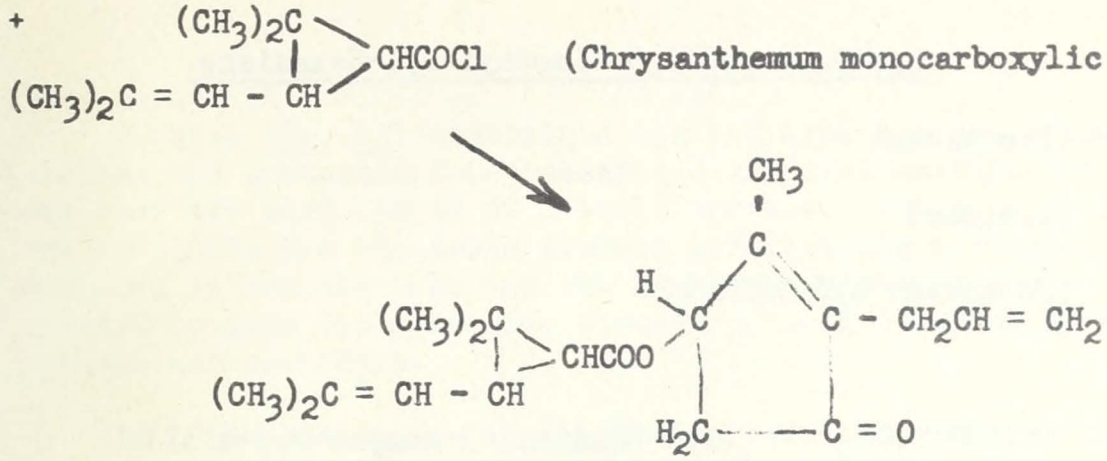
$CH_3COCHOHCH_2COCH_2CH_2CH = CH_2$ (3-Hydroxy-8-nonene-2,5-dione)

+ Alkali

→



(Allethrolone)



Allethrin

Synthesis of Chrysanthemum Monocarboxylic Acid

$C_2H_5OOCCH_2NH_2.HCl$ (Glycine ethyl ester hydrochloride)

+ Acid + $NaNO_2$ (Sodium nitrite)

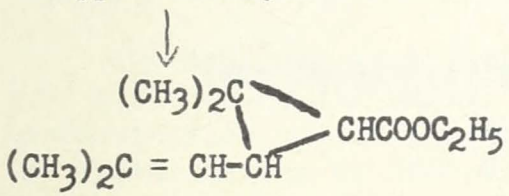
↓

$C_2H_5OOCCHN_2$ (Diazoacetic acid ethyl ester)

+ $(CH_3)_2C = CHCH = C(CH_3)_2$ (2,5-Dimethyl-2,4-hexadiene)

+ Copper catalyst

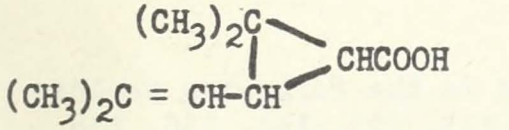
↓



(Chrysanthemum monocarboxylic acid ethyl ester)

+ Alkali

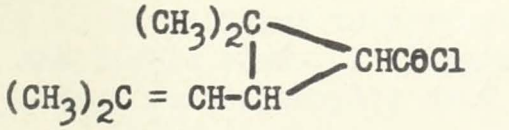
↓



(Chrysanthemum monocarboxylic acid)

+ $SOCl_2$ (Thionyl chloride)

↓



(Chrysanthemum monocarboxylic acid chloride)

Synthesis of 2,5-Dimethyl-2,4-Hexadiene

$CH \equiv CH$ (Acetylene)

+ CH_3COCH_3 (Acetone)

+ KOH (Potassium hydroxide)

↓

$(CH_3)_2C(OH)C \equiv CC(OH)(CH_3)_2$ (2,5-Dimethyl-3-hexyne-2,5-diol)

+ Catalyst + H_2 (Hydrogen)

↓

$(CH_3)_2C(OH)CH_2CH_2C(OH)(CH_3)_2$ (2,5-Dimethylhexane-2,5-diol)

+ Catalyst

$(CH_3)_2C = CHCH = C(CH_3)_2$ (2,5-Dimethyl-2,4-hexadiene)

Alternative Synthesis of 2,5-Dimethyl-2,4-Hexadiene

$CH_2 = C(CH_3)CH_2Cl$ (Methallyl chloride)

+ Mg (Magnesium)

↓

$CH_2 = C(CH_3)CH_2CH_2C(CH_3) = CH_2$ (2,5-Dimethyl-1,5-hexadiene)

+ Catalyst

↓

$(CH_3)_2C = CHCH = C(CH_3)_2$ (2,5-Dimethyl-2,4-hexadiene)

The details of the reactions are described in the following papers: 55, 57, 58, 59, 60, 61, 95, 97, 100, 105, 108, 113, 123, 154, 155, 156, 157, 158, 160, 161.

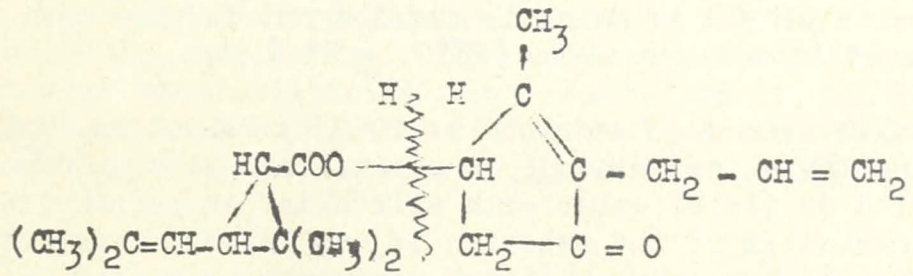
Cupples (62, 63) determined the infrared spectra of natural cinerolone and synthetic 2-(2-butenyl)-4-hydroxy-3-methyl-2-cyclopenten-1-one over the wave length of 2 to 15 microns. The spectra indicate that the compounds are cis-trans isomers and that the naturally occurring compound is the cis form and the synthetic compound the trans form. The spectra confirm the molecular structures as determined by Harper and by LaForge and coworkers.

In 1952 LaForge et al.(113) reported that esters of allethrolone are saponified to the combined acid and to 2-allyl-3-methyl-2,4-cyclopentadienone which undergoes the Diels-Alder reaction yielding a dimeric compound as the main product. The dimer exhibits the reactions characteristic of carbonyl bridge compounds. It furnishes both a mono- and a disemicarbazone and upon heating sheds carbon monoxide with formation of a tetrasubstituted indanone. These reactions of allethrolone esters on saponification probably would occur with all esters of 4-hydroxycyclopentenones including the pyrethrins.

ANALYSIS

Technical allethrin as produced commercially contains between 75 and 95 percent of allethrin. Of the methods proposed for the assay of technical allethrin, the hydrogenolysis method and the ethylenediamine method are the two that are chiefly used at present. Both are considered tentative methods by the Insecticide Chemical Analysis Committee of the Chemical Specialties Manufacturers Association.--Haring (93, 94).

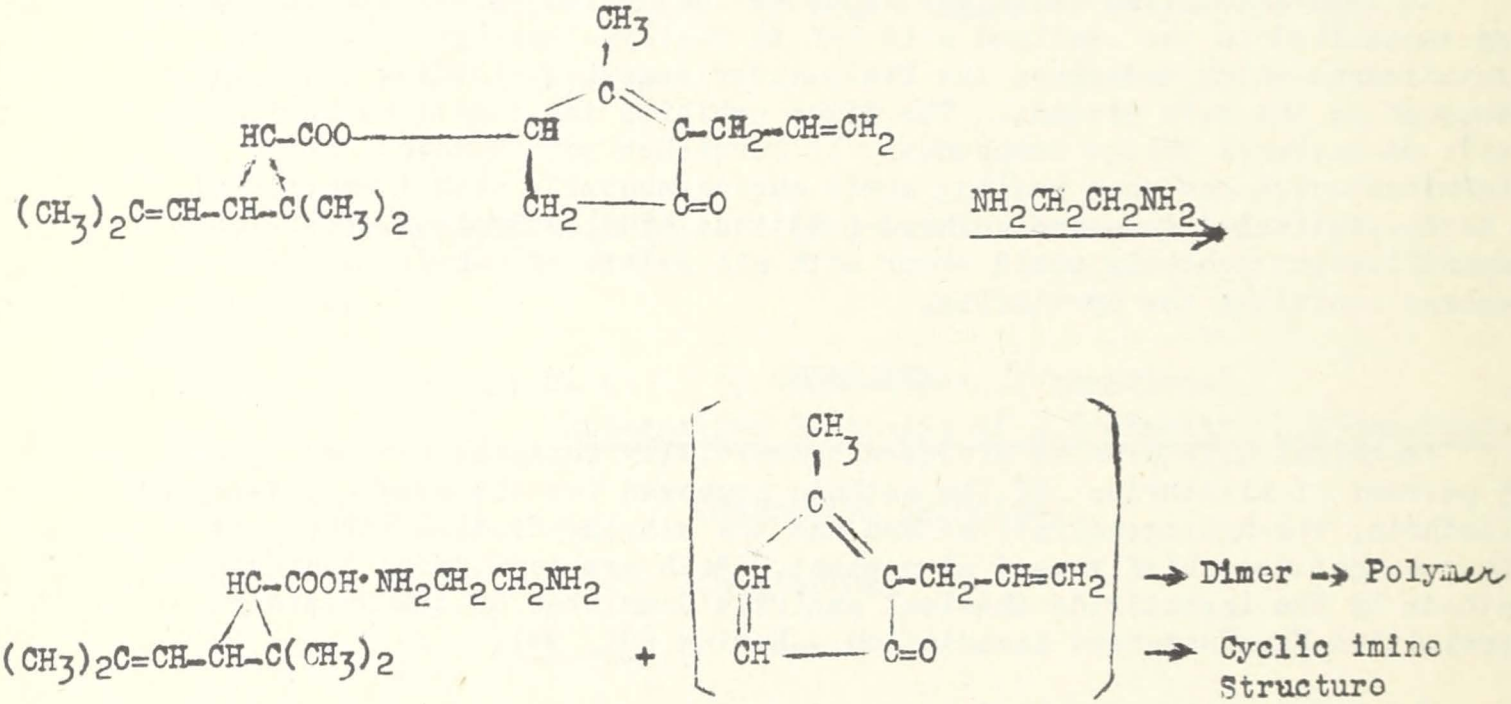
The hydrogenolysis method is based on the method proposed by LaForge and Acree (Soap and Sanit. Chem. 17(1): 95-98, 115) in 1941 for the determination of the pyrethrins and depends on the cleavage of the ester by hydrogenation of the sample in isopropanol employing a palladium oxide-barium sulfate catalyst. The location of the cleavage is shown in the following structural formula:



In addition to hydrogenolysis of the ester group and saturation of the double bonds, it is probable that the cyclopropane ring of chrysanthemum monocarboxylic acid is opened. The acidity produced is titrated

after filtration of the solution. In one version of the method, the titration is carried out at the boiling point, whereas in a later version, the titration is performed at room temperature. In the latter case, an amount of alkali equivalent to the free acidity of the sample plus 1.00 ml. of 0.1 N alkali is added to the solution before hydrogenation to activate the catalyst. Appropriate corrections are made for the free acidity originally present in the sample, for reagent blanks and for the catalyst activity.

The ethylenediamine method proposed by the Carbide and Carbon Chemicals Company depends on the following reaction of allethrin with ethylenediamine:



After the addition of pyridine, the chrysanthemum monocarboxylic acid is titrated with 0.1 N sodium methylate in pyridine. Suitable corrections are made for blanks on reagents, and for chrysanthemum monocarboxylic acid, acid chloride, and acid anhydride originally present in the sample. The reaction with ethylenediamine is carried out for 1/2 hour at 98° C. or for two hours at room temperature (25°C. ± 2° C.).

A color test for allethrin was described in 1952 by Feinstein (72). A solution of 2-(2-aminoethylamino) ethanol in ethanol and alcoholic potassium hydroxide will give a red or violet color with allethrin (or pyrethrins) if sulfur is added. The mechanism of the reaction is not known. Pure allethrolone, allethrolone semicarbazone, chrysanthemum monocarboxylic acid and pyruvic aldehyde do not react under the conditions present.

PRODUCTION

In November 1951 the rate of commercial production of allethrin was as follows:

	Pounds per Year
Benzol Products	25,000
Carbide and Carbon	20 to 25,000
U. S. Industrial Chemicals	none

The future production was estimated to be:

Benzol Products	100,000
Carbide and Carbon	450 to 500,000
U. S. Industrial Chemicals	100,000

In the autumn of 1951 it was announced that Carbide and Carbon Chemicals Company was starting construction of a 6-million dollar plant at Institute (near Charleston), West Virginia for the production of allethrin. The first allethrin produced in this plant will be available in 1954.

The commercial production of allethrin within a year of the announcement of its synthesis in the laboratory was an outstanding accomplishment and Haller (183) stated that industry should be congratulated for having done a fine job in so short a time.

In April 1952 the U. S. Industrial Chemicals Company (191) announced that its new allethrin plant in Baltimore would be completed and in operation by July 1952.

Benzol Products Company's plant at Piscataway, New Jersey in June 1952 doubled its capacity for making allethrin pushing it to 100,000 pounds a year. The new capacity is an eight-fold increase in less than two years.--Anon. (41).

The allethrin produced since full scale production began more than one year ago is equivalent to approximately half of the high content pyrethrum imported during the same period. Such a consumption demonstrates conclusively its effectiveness when skillfully used. More than 12,000,000 allethrin aerosol bombs have been sold, and millions more are now being produced.--McLaughlin Gormley King and Company (119) and Anon. (38).

Availability

The National Production Authority (141) at a meeting held January 30, 1952 announced that no shortage of allethrin had developed so far. Military requirements for use in aerosol bombs have not been sufficient to limit availability for civilian use.

Price

The price of allethrin (100 percent basis) has declined from $55 a pound in 1950 to $32 a pound in August 1952.--Torpin (178) and Anon. (42).

PATENTS

On February 8, 1949 Schechter and LaForge (158) filed an application for a patent in the United States Patent Office for a process of making hydroxydiketones which can be cyclized to cyclopentenolones utilizable as intermediates in the synthesis of esters closely related to the pyrethrins and having their characteristic insecticidal properties. On November 13, 1951 part of this application was granted as U. S. patent no. 2,574,500. This patent is dedicated to the free use of the people in the territory of the United States.

U. S. Patent 2,603,652 granted Schechter and LaForge (159) on July 15, 1952 covers allethrin and similar esters. The methods of making allethrolone and analogous cyclopentenolones and of acylating these compounds are described. The knockdown and mortality of houseflies sprayed with solutions and aerosols of different esters are given.

The foreign rights to this invention and to the inventions described in pending United States patents describing the synthesis of pyrethrin-like chemicals were acquired early in 1950 by U. S. Industrial Chemicals, Inc. (Anon. 16). Corresponding applications have been filed in all major foreign countries including the United Kingdom, France, Australia, India, Brazil, Sweden, Pakistan, South Africa, and many others.

SPECIFICATIONS

Allethrin has been approved by the United States Department of Agriculture for use in sprays and dusts in meat packing plants subject to the same restrictions that govern the use of pyrethrum.--Miller (128, 129).

The U. S. Department of the Army (187) on December 6, 1950 issued military specification MIL-I-10745 (QMC) for a 12-ounce insecticide aerosol dispenser. This specifies the use of 0.6 percent of allethrin (not less than 75 percent purity) for the type A insecticide or 0.4 percent of pyrethrins for the type B.

On March 20, 1952 this specification was superseded by MIL-I-10745A (189) which specifies a minimum content of 0.6 percent by weight of allethrin for the type I insecticide. The technical allethrin shall contain not less than 75 percent allethrin nor more than 8.0 percent total free acidity when calculated as chrysanthemum monocarobxylic acid. The material shall have not more than 0.5 percent dichlorodifluoromethane insoluble material as determined by the method described in Munitions Board Purchase Specification P-42 for pyrethrum extract.

Military specification MIL-I-11355 (188) dated August 14, 1951 for insecticide powder calls for a minimum of 0.30 percent by weight of allethrin for the type I insecticide. Other ingredients are 0.2 percent of pyrethrins, 2 percent of sulfoxide, 5 percent of chloromethyl p-chlorophenyl sulfone, 0.25 percent of antioxidant, 2.7 to 3.3 percent of conditioner and diluent (pyrophyllite) to make 100 percent.

In July 1951 the Department of the Army revised purchase directives for the space spray covered by the Military Specification MIL-I-10177 and substituted allethrin at0.15 percent in place of pyrethrins at .1 percent. During 1951 85,000 gallons of this allethrin space spray were purchased.

The General Services Administration (190) on April 1, 1952 issued interim federal specification O-I-511 (GSA-FSS) for a liquid space spray insecticide which calls for 0.15 to 0.18 percent by weight of allethrin, 0.75 to 0.85 percent of piperonyl butoxide, 0.95 to 1.05 percent of DDT, 0.04 to 0.06 percent of odor neutralizer and deodorized kerosene to make 100 percent.

ALLETHRIN IN AEROSOLS

As soon as allethrin became commercially available it was tested as a replacement for pyrethrum extract in liquefied gas aerosols.

Schroeder and Berlin (163) in 1950 reported that when applied in low pressure aerosols containing 15 percent of non-volatile material and 85 percent of a mixture of Freon 11 and Freon 12 as a propellent, allethrin at 1.2 and 1.4 percent concentration was slightly superior to pyrethrins at the same concentration in both knockdown and kill. These aerosols were tested at an average dosage of 4 grams per 1000 cu. ft. Combinations of allethrin with piperonyl butoxide were about one-half as effective as similar combinations of pyrethrins with piperonyl butoxide. The addition of 2 percent of DDT did not change this ratio. Mixtures of allethrin and pyrethrins in combination with piperonyl butoxide showed only the addition effect of two materials having dissimilar synergistic relationships.

Maughan *et al.* (125) tested aerosol formulations containing allethrin or pyrethrins with DDT, MGK 264 and lethane 384 against 5-day old house flies of the CSMA strain. Four percent of lethane 384 adequately replaced 0.3 percent of allethrin when 2-percent of DDT was present in both formulations. It was concluded that combinations of allethrin, lethane 384, and a synergist (MGK 264, n-propyl isome, Sulfoxide or piperonyl butoxide) will result in highly satisfactory aerosol formulations with or without pyrethrins.

Fales (67) at the 1951 mid-year meeting of the Chemical Specialties Manufacturers Association reported that allethrin had proved acceptable for use in aerosols, and may be used in combination with pyrethrins, or lethane. One very effective formula contains the usual DDT, 2 and 4 percent lethane, and 0.1 percent allethrin with no synergist. In a typical aerosol formula, containing 0.2 percent pyrethrins and synergists, part of the pyrethrins (as much as one-half) may be substituted by allethrin. Aerosol formulas

recommended for use on aircraft contain one or 1.2 percent pyrethrins. These combinations have been reformulated, using allethrin with a resulting increase in performance.

As the result of these and other reports (cf. Moore 133) of favorable results of tests Rohwer (151) on October 26, 1950 announced that formulas containing allethrin were acceptable for use in gas-propelled aerosols.

Shortly after this announcement was made it was reported (Anon. 23-25) that the army had okayed use of allethrin in low pressure aerosols, to replace hard-to-get natural pyrethrin insecticides, and was asking bids for more than 2 million low pressure aerosols to contain 0.6 percent allethrin, 2 percent DDT, 5 percent alkylated naphthalene, 7.2 percent deodorized kerosene, and 85 percent of a mixture of Freon 11 and Freon 12.

In October 1951 it was announced that the Army would purchase 5,000,000 12-ounce aerosol bombs containing 0.6 percent allethrin through July 1952. At 2 grams per bomb this purchase requires 22,000 pounds of allethrin.

Resnick and Crowell (148) of the U. S. Public Health Service in 1951 reported that allethrin could be substituted for pyrethrum in the standard G-382 aerosol formulation without loss of effectiveness. The synergistic action of piperonyl butoxide and MGK 264 has not been as evident in formulations containing allethrin as in those containing pyrethrum extract. These tests were made on house flies in a modified Peet-Grady chamber.

The U. S. Department of Agriculture has approved about 35 formulas containing allethrin for use under the licensing agreement governing the method of applying parasiticides covered by the Goodhue-Sullivan patent no. 2,321,023 of June 8, 1943. These formulas usually contain from 0.10 to 0.4 percent ofallethrin plus DDT, methoxychlor, lethane 384, Thanite, pyrethrins and various synergists and solvents in a 50:50 mixture of Freon 11 and Freon 12.

STABILITY OF ALLETHRIN AND ITS FORMULATIONS

When exposed to ultraviolet light for 5 hours (equivalent to 5 days exposure to mid-day sun) and to heat (110° F. for 24 hours and to 120° F. for an additional 48 hours) allethrin proved more stable than pyrethrins. These tests were made on mosquito larvae and house flies. An allethrin residue of 144 mg. per sq. ft. persisted for several months against house flies and when a synergist (piperonyl butoxide or sulfoxide) was added the amount of residue could be reduced to 28 mg. per sq. ft.--Granett et al. (86).

Fales et al. (70) in 1951 reported that a high pressure aerosol containing 1 percent of allethrin held at room temperature for four months was equal in effectiveness against house flies to a freshly made sample.

Fales et al. (68) also found that allethrin when formulated into a high pressure aerosol and stored for 15 months lost none of its effectivness against house flies. There was no loss in effectiveness when a mixture of this material and DDT (in a low pressure aerosol) was stored for 10 months. Allethrin in kerosene sprays showed no loss in effectiveness after 6 months storage.

Fales and associates (71) also reported that in storage tests with sprays and aerosols containing the ester made with the natural d-trans acid there was no loss in effectiveness against house flies.

Schreiber (162) found that the decomposition, in thin layers, of pyrethrins was reduced to about one-half when mixed with at least an equal weight of MGK 264 and irradiated under equal conditions with a mercury vapor quartz lamp (Hanovia Alpine) for six hours at temperatures not exceeding 135° F. The irradiation described produced a vivid greenish yellow fluorescence in accordance with Stokes law. A similar though slightly smaller protective effect was obtained in the irradiation of allethrin. In each case the degree of decomposition was checked by the Seil method for the determination of pyrethrin I since the alkaline treatment required tends to decompose also part of MGK 264 thus rendering a determination of pyrethrin II quite vague.

USE OF SYNERGISTS WITH ALLETHRIN

Allethrin in aerosols is not activated by the usual pyrethrin synergists to the extent that the pyrethrins are (Fales 67). The same observation holds true for sprays. This lack of a good allethrin synergist has stimulated a great deal of testing of compounds for possible synergistic value but to date nothing outstanding has been found. Stage (169) in 1951 reported that approximately 150 compounds have been tested at Corvallis, Oregon to determine whether they enhance the effectiveness of allethrin when used as a residual treatment against adults of Aedes vexans (Meig.), and A. sticticus (Meig.). Only 16 of the materials showed some promise as synergists, and none of these were especially outstanding.

MGK 264

MGK 264, which is N-2-ethylhexyl bicyclo-(2.2.1)-5-heptene-2,3-dicarboximide, is a valuable synergist when combined with allethrin and pyrethrins for roach control in both aerosols and liquid sprays. In aerosols MGK 264 may be used at ratios of five to 15 to 1 part pyrethrins or allethrin.--Moore (132).

With the use of MGK 264 with allethrin, aerosol formulations can be arrived at which are at least equal in effect and often superior to the tentative official test aerosol of CSMA not only against flies but also against roaches. Such formulations may contain, for example, 2-3 percent of DDT, 2 percent MGK 264, and either from 0.10-0.15 percent each of allethrin and of pyrethrins or 0.25 percent of allethrin or 0.20-0.25 percent of pyrethrins. Also in experimental dusts for agricultural use combinations of allethrin and 264 have proved effective, for example, against flea beetle, cabbage worm, and small tarnished plant bug.--Schreiber (162).

n-Propyl isome

n-Propyl isome is a condensation product of isosafrole and di-n-propyl maleate (Synerholm and Hartzell, Boyce Thompson Inst. Contrib. 14: 85-86, 1945. U. S. patent 2,431,845, Dec. 2, 1947). According to Penick and Company (144) it is a synergist for allethrin.

Sulfoxide

This is the name given to n-octylsulfoxide of isosafrole by Penick and Company. It was formerly written "sulfox-cide."

Starr (170) in 1950 reported that in preliminary tests, a 16 day old residue of 44 mg. of allethrin and 220 mg. of sulfoxide per square foot on kraft paper, gave a knockdown of house flies of more than 95 percent in 30 minutes and a kill of better than 95 percent in 24 hours. Exposure was limited to two hours. After aging 37 days, the knockdown was better than 95 percent in two hours, but the kill dropped to 35 percent. Doubling the quantities of materials in the residue increased the time of effectiveness from 16 days to 11 weeks.

According to Starr (171) a high grade emulsion can be made using allethrin and sulfoxide. Starr also gave the following formulas for aerosols containing allethrin.

Aerosol formulation 105 contains:

Allethrin	1 percent
Sulfoxide (n-octylsulfoxide of isosafrole)	5 percent
Ultrasene	4 percent
Freon 11	45 percent
Freon 12	45 percent

A formula containing:

Allethrin	0.2 percent
DDT	2 percent
Sulfoxide	1 percent

was above CSMA's TOTA in both 15 minute knockdown and 24 hour kill at either 3 or 4 grams per 1000 cubic feet.

Piperonyl butoxide

This synergist contains as its principal constituent alpha-[2-(2-butoxyethoxy)-ethoxy]-4,5-methylenedioxy-2-propyltoluene.

Schroeder and Berlin (163) in 1950 reported that when applied in low pressure aerosols containing 15 percent of non-volatile material and 85 percent of a mixture of equal parts of Freon 11 and Freon 12 as a propellent, allethrin at 1.2 and 1.4 percent concentration was slightly superior to pyrethrins at the same concentration in both knockdown and kill. These aerosols were tested at an average dosage of 4 grams per 1000 cu. ft. Combination of allethrin with piperonyl butoxide are about one-half as effective as similar combinations of pyrethrins with piperonyl butoxide. The addition of 2 percent of DDT did not change this ratio. Mixtures of allethrin and pyrethrins in combination with piperonyl butoxide showed only the additive effect of two materials having dissimilar synergistic relationships.

Against resistant house flies in Florida allethrin and pyrethrins plus piperonyl butoxide were moderately effective early in 1950, but by the end of the season none of them provided satisfactory control.--Wilson et al. (194).

Incho and Greenberg (104) tested the synergistic effect of piperonyl butoxide when mixed with pyrethrins and with its four constituents separately and also with allethrin and allethrolone esters against house flies by the turntable method. By the use of a value representing relative synergistic effect it was shown that the cinerins exhibited a somewhat greater degree of synergism in a combination with piperonyl butoxide thandid the pyrethrins, although pyrethrins I and II showed superior effectiveness to the corresponding cinerins, both alone and in combination with piperonyl butoxide.

Since none of the separated active components of pyrethrum showed greater synergistic activity than the standard pyrethrum extract, it may be concluded that no one of the components of pyrethrum contributed the major portion of the synergism found with combinations of piperonyl butoxide and pyrethrins.

Although optical and geometric isomerism in the acid portion of the molecule have a marked influence onthe insecticidal effectiveness of allethrolone esters of chrysanthemum monocarboxylic acid when used alone or in combination with piperonyl butoxide, they have little effect on comparative synergistic activity.

m-Nitrobenzamides

Gertler et al. (83) in 1952 reported the results of tests of certain meta-nitrobenzamides for synergistic action in allethrin fly sprays. The concentration was 0.5 mg. allethrin and 20 mg. adjunct per ml. and all tests were made against house flies by the Campbell turntable method. Acetone was used as an auxiliary solvent to increase the solubility of the amides in kerosene. Ten of 22 materials caused significant increase in toxicity. These were the N,N-dibutyl, diethyl, diisobutyl, diisopropyl, dimethyl, and dipropyl and the N-isobutyl and isopropyl derivatives of meta-nitrobenzamide; 1, meta-nitrobenzoylpiperidine and meta-nitro-N-propylbenzamide. The adjuncts alone showed negligible toxicity.

Comparative value of synergists for allethrin

The comparative effect of piperonyl butoxide, n-propyl isome, and MGK 264 in sprays oontaining either allethrin or pyrethrins in the proportion of 10 times as much adjunct as insecticide was determined by Gersdorff et al. (81) in tests against the house fly, by the turntable method. The joint action of each of the three pyrethrum synergists with allethrin was of the synergistic type.

Piperonyl butoxide synergized pyrethrins more effectively than it did allethrin, the mixed spray with the natural insecticide being about 13 times as toxic as pyrethrins and mixed spray with the synthetic insecticide being but two and one half times as toxic as allethrin. The synergistic effect was

therefore five times as great with pyrethrins as it was with allethrin. Because of the greater toxicity of allethrin, however, this disparity was decreased somewhat, and mixed sprays containing the synthetic product were about half as toxic as those containing the natural product.

The synergistic effect of n-propyl isome was about three times as great with pyrethrins as with allethrin, since the pyrethrins mixture was but little more toxic than the allethrin mixture. The allethrin mixture was nearly as toxic as the mixture of allethrin and piperonyl butoxide, but less than half as toxic as the mixture of pyrethrins and piperonyl butoxide.

Synergist MGK 264 was not so effective a synergist as piperonyl butoxide, increasing the effectiveness of the spray by two-thirds when included with pyrethrins and by one-third when included with allethrin. The synergistic effect was therefore one and one-fourth times as great with pyrethrins as it was with allethrin. However, because of the greater toxicity of allethrin the mixture containing allethrin was about twice as toxic as that containing pyrethrins.

The relative effectiveness of the insecticidal materials, with and without a synergist, is in the following ascending order, whether the evaluation is based on the principal toxicant only or on the insecticide equivalent: (1) pyrethrins, (2) pyrethrins plus synergist MGK 264, (3) allethrin, (4) allethrin plus synergist MGK 264, (5) pyrethrins plus n-propyl isome, allethrin plus n-propyl isome, and allethrin plus piperonyl butoxide, and (6) pyrethrins plus piperonyl butoxide. The last mixture was 17 times as effective as pyrethrins by the first criterion and 13 times by the second.

Allethrin caused slightly slower knockdown than did natural pyrethrins. However, all sprays caused complete or nearly complete knockdown at the low concentration of 0.25 mg. of insecticide per milliliter of kerosene.

Piquett (145) in 1949 reported that piperonyl butoxide, piperonyl cyclonene and n-propyl isome increased the toxicity of allethrin to adult male American cockroaches when applied as dusts containing 0.6 percent of allethrin and 3 percent of the synergist. Sesame oil was ineffective in synergising allethrin. Allethrin alone killed 65 percent of the roaches in 4 days, pyrethrins alone killed 83 percent and the mixtures of allethrin with the effective synergists killed 75 to 87 percent.

Starr (171) in 1950 gave formulas for the use of MGK 264, n-propyl isome and sulfoxide with allethrin. Allethrin mixed with n-propyl isome (1:5), MGK 264 (1:10), sesame oil extractives (1:3.75), and piperonyl butoxide (1:8) and tested against house flies by the Peet-Grady method was in general less effective than similar mixtures of pyrethrins with the synergists. MGK 264 appeared to be almost equally as effective with pyrethrins at the 50 percent mortality level. The difference in effectiveness between allethrin and pyrethrins with synergists appears to be more pronounced against German roaches than against house flies. In surface deposit tests on glass plates about 3 times the dosage of allethrin with piperonyl butoxide is required to obtain the mortality of roaches given by the pyrethrins-butoxide combination.

Jones et al. (107) in 1950 reported on the first thorough study of allethrin in combination with the four commercially available pyrethrum synergists. In Peet-Grady tests with house flies they found that with sesame oil extractives it required somewhat less than twice, with n-propyl isome about twice, and with piperonyl butoxide over twice as much allethrin with synergist as pyrethrins with synergist to produce 50 percent mortalities. Synergist 264 appeared to be almost as effective with allethrin as with pyrethrins at the 50 percent mortality level.

They also reported that against grain insects such as the confused flour beetle and the rice weevil, surface deposits of allethrin with piperonyl butoxide may be less than one-third as effective as those of pyrethrins and piperonyl butoxide. In dusts against certain truck crop insects a combination of allethrin with piperonyl cyclonene was generally less effective than that of pyrethrins with piperonyl cyclonenes, but the difference in effectiveness varied greatly with the insect species. For example, against Mexican bean beetle adults and larvae the allethrin-cyclonene dust gave almost the same mortality as the pyrethrins-cyclonene dust, while against squash bug adults and nymphs the allethrin combination was very much less effective than the pyrethrins combination.

In tests with high-pressure aerosols against house flies piperonyl butoxide, n-propyl isome, and sesame oil extractives all showed synergism with allethrin. There was considerable recovery of flies knocked down with sesame oil extractives formulation. The formulas containing n-propyl isome acted similarly with allethrin and with natural pyrethrins. The MGK 264 formulas appeared to give slightly better kill when allethrin was used. The knockdown was lower, but the mortality was the same, when piperonyl butoxide was used with allethrin.--Fales et al. (70).

Di-n-butyl hexahydrophthalate and dibutyl cis-bicyclo[2.2.1]-heptene-2,3-dicarboxylate (dibutyl carbate) as synergists produced better results with allethrin than with pyrethrins when tested against the deerfly.--Hoffman and Lindquist (103).

The comparative effect of sulfoxide and 3,4-methylenedioxybenzyl n-propyl ether in oil sprays containing either allethrin or pyrethrins in the proportion of five times as much adjunct as insecticide was determined by Gersdorff et al. (82) in tests against the house fly by the turntable method. The two pyrethrum synergists also synergized allethrin but to a lesser degree than they did pyrethrins. The intensity of synergism with sulfoxide was 4.7 and with the benzyl propyl ether 1.3 as great in the pyrethrum mixtures as in the allethrin mixtures. The mixture of sulfoxide and pyrethrins was 10.8 as toxic as pyrethrins, whereas the mixture of sulfoxide and allethrin was but 2.3 as toxic as allethrin. The mixture of the benzyl propyl ether and pyrethrins was 1.8 as toxic as pyrethrin, whereas the mixture of the benzyl propyl ether and allethrin was 1.4 as toxic as allethrin. However, when consideration is given to the greater toxicity of allethrin as compared with pyrethrins as well as synergistic effect, the relative effectiveness of the insecticidal materials falls in the following ascending order, whether the

evaluation is based on principal toxicant only or on insecticide equivalent: (1) pyrethrins, (2) pyrethrins plus the benzyl propyl ether, (3) allethrin, (4) allethrin plus the benzyl propyl ether, (5) allethrin plus sulfoxide, and (6) pyrethrins plus sulfoxide. The last-named mixture is nearly 12 times as toxic as pyrethrins on the first basis and nearly 11 times on the second. Knockdown of flies was of high order for all mixtures.

Laboratory tests against house flies indicate that the pyrethrum synergists sulfoxide, n-propyl isome, and MGK 264 can be substituted for piperonyl butoxide in the MIL-STD-129 or Type II Interim Federal Specification O-I-511 space spray. Substitution can be made at equal concentration levels but sulfoxide and n-propyl isome require auxiliary solvents.--Nelson et al. (142).

In tests against house flies by the Peet-Grady method, four synergists were tested at a concentration of 0.80 percent by weight in deodorized kerosene solutions of allethrin (0.16 percent). It was concluded that there are no significant differences between piperonyl butoxide, isome, sulfoxide and sulfone.--Calsetta (54).

In tests of piperonyl butoxide and sulfoxide as synergists for pyrethrins and allethrin against the flour beetle Hewlett (102) found sulfoxide to be six times as potent as piperonyl butoxide when used with pyrethrins and 1.8 times as potent when used with allethrin. In comparisons of insecticides pyrethrins and allethrins were equally toxic.

Hewlett (101) in 1952 reported that 5 percent of piperonyl butoxide synergized 3.5 percent of allethrin in solution in Shell oil P-31 in tests on the flour beetle Tribolium castaneum (Hbst.). The beetles were either exposed on films of the insecticides on filter paper at 25° C. or were directly sprayed and afterwards kept at 25° C. The response in the groups of beetles was determined six and nine days after the start of their exposure to insecticide.

ALLETHRIN STEREOISOMERS

Allethrin is a mixture of 8 stereoisomers which differ in insecticidal value. This fact should be kept in mind in evaluating reports of its tests against various species of insects. In this respect commercial allethrin is analogous to crude benzene hexachloride from which 5 of the 8 theoretically possible stereoisomers have been isolated. The gamma isomer of BHC accounts for practically all the insecticidal value of the product, whereas the beta isomer is responsible for the chronic toxicity of BHC to mammals. By separating the gamma isomer of BHC from the crude mixture a product (lindane) of superior insecticidal value has been obtained and at the same time the less desirable properties of the other isomers have been left behind. Although no simple procedure for separating the isomers in commercial allethrin isknown, such an achievement is not impossible.

The 8 isomers in allethrin are:

cis form of l-acid esterified with l-allethrolone
" " " l-acid " " d-allethrolone
" " " d-acid " " l-allethrolone
" " " d-acid " " d-allethrolone

trans form of l-acid esterified with l-allethrolone
" " " l-acid " " d-allethrolone
" " " d-acid " " l-allethrolone
" " " d-acid " " d-allethrolone

Schechter and associates inthe Division of Insecticide Investigations, Bureau of Entomology and Plant Quarantine are now working on the separation of these isomers in order to determine their individual activities to different species of insects.

A step in this direction has been accomplished by the separation of crystalline allethrin, m.p. 50.5-51° C., from molecularly distilled allethrin by cooling to about 4° C., or by low temperature crystallization from low boiling petroleum ether. This crystalline product called the alpha-dl-trans isomer must consist of one of the racemic ester pairs, d-trans acid with d-allethrolone plus l-trans acid with l-allethrolone, or d-trans acid with l-allethrolone plus l-trans acid with d-allethrolone; the beta-dl-trans isomer consists of the other pair. Entomological tests on house flies indicate the alpha-dl-trans isomer to be less effective and the beta-dl-trans isomer to be more effective than allethrin.--Schechter et al. (160).

In 1949 Gersdorff (76) reported that the d-chrysanthemum monocarboxylic acid ester of synthetic 2-(2-butenyl)-4-hydroxy-3-methyl-2-cyclopenten-1-one (probably a geometric isomer of cinerolone) was as toxic as natural cinerin I, about one and one-half times as toxic as the mixture of "pyrethrins" contained in the ordinary pyrethrum-kerosene extract. The replacement of the 2-butenyl side chain of these compounds with the allyl group was accompanied by a nearly 5-fold increase in toxicity whether the acid component was the dextro natural one or a racemic cis or trans synthetic one. The allyl compound with the natural acid component was the most toxic of any of the known pyrethroids, 6 to 7 times as toxic as the mixture of "pyrethrins." No difference in toxicity was found between the compounds of the cis and trans forms of the acid component for both classes of compounds, the 2-butenyl and the allyl. (However, see more recent work below). For both classes the ester with the natural dextro acid component was about 3.8 times as toxic as an ester with a synthetic racemic acid component. The completely synthetic isomers of cinerin I were about 0.39 times as toxic as the mixture of "pyrethrins." The completely synthetic allyl compounds were about 1.8 times as toxic as the "pyrethrins." The effect of other changes in chemical structures on toxicity was determined. Knockdown effect was of high order for all the compounds.

The marked difference in insecticidal value of the allethrin stereoisomers due to optical activity was demonstrated by Gersdorff (77). He reported that the ester made from synthetic allethrolone and natural d-trans chrysanthemum acid was 6 times as toxic as the natural pyrethrins against house flies, whereas the completely synthetic ester(synthetic allethrolone esterified with synthetic dl-cis-trans chrysanthemum acid) was 3 times as toxic; that is, the optically active isomer was twice as toxic as the optically inactive ester.

More recently Gersdorff and Mitlin (79) reported that the dl-trans fraction of allethrin was 1.56 as toxic as the dl-cis fraction. The toxic action of the two fractions when applied in mixtures was identified as similar action. The trans fraction was 1.33 and the cis fraction 0.85 as toxic as this sample of allethrin. On this basis the allethrin used in this study contained about 69 percent cis isomers and about 31 percent trans isomers. A crystalline compound, separated from the trans fraction, was only 0.35 as toxic as allethrin and constituted 8 percent of that insecticide. The remainder of the trans fraction was 1.69 as toxic as allethrin and constituted 23 percent of that insecticide. It is deduced that half of each of these portions of the trans fraction is relatively nontoxic and that one of the remaining two isomers, d-trans acid with d-allethrolone and d-trans acid with l-allethrolone, is 0.70 as toxic and the other 3.38 as toxic as allethrin. All the separated constituents possessed high knockdown value. All these tests were made on the housefly by the Campbell turntable method.

Elliott (65) has discussed the relationship of chemical constitution to the insecticidal activity of substances related to the pyrethrins.

ANALOGS OF ALLETHRIN

When the high insecticidal value of allethrin and the method of its synthesis were announced, chemists prepared analogous compounds by combining synthetic chrysanthemoyl chloride with substituted cyclopentenolones. In Japan Inoue and associates (106) synthesized lower alkyl- and alkenyl cinerin homologs in this way. They also synthesized fifty kinds of pyrethroids from aromatic, aliphatic, terpenic alcohols, dialkylamino-ethylalcohols, monoalkylethylene alcohols and chrysanthemoyl chloride in an analogous manner. Insecticidal activity of these compounds was tested against the common house fly in kerosene space spray.

Nagasawa et al. (136) prepared the ethyl analog of allethrin, called ethythrin. The toxicity of allethrin to pupae of the common house mosquito (Culex pipiens var. pallens Coquillett) when applied in water emulsion was approximately 10 times that of ethythrin. From the test results of a 1:2 mixture of allethrin and ethythrin it was concluded that these two toxicants act similarly on mosquito pupae.

Matsui (124) in Japan and LaForge, Green, and Schechter at Beltsville have synthesized an insecticidal ester named furethrin of the type of allethrin but with a 2-furfuryl side chain. The procedures follow those employed in the synthesis of allethrin with furfurylacetone as a starting material.

Tests on house flies by Gersdorff and Mitlin (80) show that furethrin compares favorably with allethrin in toxicity to house flies. Of all compounds analogous to allethrin, furethrin is the most promising. In tests against the house fly by the turntable method furethrin (synthesized in Beltsville) had a relative toxicity of 1.1 as compared to a toxicity of 1 for the pyrethrins. The ester made by combining natural (d-trans) chrysanthemum monocarboxylic acid with furethrolone had a relative toxicity of 1.9. Both products had high knockdown value.

Gersdorff and Mitlin (78) tested the insecticidal value of certain allethrin analogs to house flies. Five substituted cyclopentenolones were acylated with a mixture of cis and trans dl-chrysanthemum monocarboxylic acids and the purified esters dissolved in refined kerosene for testing by the Campbell turntable method. Two compounds, each with one chlorine atom introduced into the allyl side chain characteristic of allethrin, were one and one-half times as toxic as pyrethrins. No difference in toxicity was demonstrated whether the attachment was on the second or third carbon atom. A compound with a triple bond in the side chain (2-butynyl) of the cyclopentenolone component was about three-fourths as toxic as pyrethrins. A compound with a chlorine atom introduced at the third carbon atom in the 2-butenyl side chain was one-fifth as toxic as pyrethrins. A compound with an allyl side chain attached to the carbon atom in position 5 of the cyclopentenolone nucleus as well as in position 2 was about two-fifths as toxic as pyrethrins.

LaForge et al. (112) in 1952 reported that all allethrin type esters of a number of cyclopropanecarboxylic acids were less toxic than allethrin to house flies by the turntable method. The most toxic ester, that of dl-dihydrochrysanthemum monocarboxylic acid, was as toxic as natural pyrethrins. Since the l-trans-acid ester was but 2 percent as toxic as the d-trans-acid ester, configuration in the acid component is of great importance with respect to toxicity. The toxicity ratio of the type I ester to the type II ester for the allethrin-type esters of the natural d-trans-chrysanthemum acids was 4.4 to 1, which is about the same as for pyrethrins I and II and cinerins I and II.

TOXICOLOGY

Starr et al. (172) in1950 reported that chronic toxicity tests on white rats showed allethrin to be nontoxic when used as a spray or incorporated with food. The allethrin tested was a technical grade product manufactured by the Carbide and Carbon Chemicals Corporation. A diet containing 0.2 percent of allethrin had no noticeable harmful effect on rats or their offspring over a period of 24 weeks and at that time control and experimental rats were approximately the same size. Inhalation of 1 percent allethrin aerosol sprays in large amounts did no apparent damage to rats during 22 weeks' exposure, 30 minutes per day, 6 days per week. The rate of growth of new-born rats subjected to the treatment was the same as the control group. In none of the experimental animals was any abnormality found which could be correlated with the application of allethrin.

At the June 1950 meeting of the Chemical Specialties Manufacturers Association, Inc., Starr et al. (173) presented additional data on the toxicity of allethrin to rats. After feeding for 41 weeks on dog-food containing 0.2 percent of allethrin (dosage approximately 200 mg./kg. per day) rats were in good condition with body weight equal to controls. All female rats gave birth to at least two normal litters. In aerosol inhalation tests the rats were sprayed with 800 g. per 1000 cu. ft. and exposed 30 minutes per day six days a week in their regular cages. During a period of 39 weeks none of the experimental rats including 48 new born rats were harmed by the aerosol which contained 1 percent of allethrin, 9 percent of petroleum distillate (Bayol D), 45 percent of Freon 11 and 45 percent of Freon 12. Another aerosol formula contained 1 percent of allethrin, 5 percent of sulfoxide, 4 percent of petroleum distillate (Ultrasene), 45 percent of Freon 11 and 45 percent of Freon 12. Eight rats were sprayed with this formula as in the other test, except that 1600 g. per 1000 cu. ft. were tested in addition to the 800 g. exposure. There were no deaths in seven weeks and weight gains were normal. A total of 40 rats which were representative of the experimental animals exposed to allethrin in the diet or aerosol were sacrificed at various times from one to eight months after the start of the experiments. Autopsy showed no visible damage or gross pathology in any of the internal organs. Microscopic examination of the organs was made. In none of the experimental animals was any abnormality found which could be correlated with the insecticide treatments.

Carpenter et al. (56) of the Mellon Institute of Industrial Research in October 1950 reported on the comparative acute and subacute toxicities of allethrin and pyrethrins.

Two separate inhalation studies on aerosols containing 1 percent by weight of allethrin or of pyrethrins, 9 percent of peanut oil and 90 percent of Freon 12 were carried out at concentrations in excess of 50 g. of total formulation per 1000 cu. ft. of space.

In the first study laboratory-produced allethrin and the comparative aerosols casued no detectable injurious effects on rats exposed twice daily for 30-minute periods up to a total of 85 such periods within 67 calendar days. In a second similar study a sample representing commercially produced allethrin (92 percent allethrin) caused no injury to rats or dogs receiving 40 exposures, each of 30 minutes duration, within 27 calendar days.

Single 30 minute exposures of rats to concentrations of aerosols of commercial allethrin and pyrethrins on the order of 350 times the level used for the repeated exposures caused no visible damage, nor did they depress weight gain during[a] subsequent 14-day observation period.

A fog of commercial allethrin produced by a vaponefrin nebulizer was lethal to one of 10 rats in a two-hour exposure at a concentration of 19 mg./l., and only four of 10 succumbed in a four-hour exposure to 13.8 mg./l. These massive concentrations of allethrin are respectively 10,000 and 7,000 times the amounts that would be present in the aerosols utilized in freeing aircraft from insects. The extreme viscosity of an 84 percent pyrethrin concentrate and its unavailability made comparison by this method impossible.

The single dose acute oral LD-50's of commercial allethrin for rodents fed 20-percent dilutions in deodorized kerosene are as follows: mice 0.48, rats 0.92, and rabbits 4.29 g./kg. Two different samples of purified pyrethrins, 20 percent in petroleum distillate, gave LD-50 values of 0.82 and 1.87 g./kg. for rats.

The LD-50 of undiluted commercial allethrin for rabbits by the percutaneous route is 11.2 ml./kg. Dilution in deodorized kerosene markedly increases toxicity by skin penetration, but dimethyl phthalate appears not to aid penetration.

Undiluted commercial allethrin and dilutions in deodorized kerosene are harmless to rabbit eyes, but they cause moderate erythema of the clipped skin of the rabbit belly when applied in single or repeated applications. Drill cloth impregnated with this allethrin at the rate of 4 g. per square foot caused marked erythema of the hair-free trunk of rabbits when worn for three days. Subsequently these reactions subsided even though the impregnated bands were reapplied twice each week during a 21-day period of wear. No systemic injury, as judged by weight changes, resulted, and all skin reactions had subsided in this interval.

Guinea pigs could not be sensitized by a course of eight intracutaneous injections of a 0.1-percent dispersion of allethrin in 3.3-percent propylene glycol in isotonic sodium chloride solution followed by a 21-day incubation period before retest.

Carpenter et al. concluded that commercial allethrin is of the same relative order of toxicity as pyrethrins and that it may be used safely as an insecticide in sprays and aerosols.

Lehman (115) of the Food and Drug Administration in 1951 stated that the acute toxicity of allethrin to the rat (approximate LD-50 mg./kg.) was 680 and that of the pyrethrins was 200. In these tests the dosages were administered by stomach tube to fasted animals. Allethrin causes tremors and convulsions. The onset of the symptoms of poisoning is within 30 minutes, the duration 6 hours. Fatalities appear to be rare 24 hours after poisoning. Death is due to respiratory paralysis.

Ambrose and Robbins (43) of the Western Regional Research Laboratory of the U. S. Department of Agriculture have reported a study of the comparative toxicity of pyrethrins and allethrin.

Purified pyrethrins containing 86.2 percent total pyrethrins and synthetic allethrin containing 93.6 percent allethrin administered gastrically or subcutaneously to rats in doses of 2.6 and 1.6 gm./kg., respectively, produced no toxic reactions. When rubbed into the skin of rats in amounts of 50 mg. daily for 30 days, they produced no local reactions. On albino guinea pigs and on the anterior cubital surface of three humans, purified pyrethrins or allethrin produced no signs of local irritation. With less pure allethrin some transitory skin irritation was observed. Albino guinea pigs were not sensitized by topical application or intracutaneous injection of purified allethrin. The effect of prolonged oral ingestion of one sample

of commercial allethrin and a purified sample of commercial allethrin, assaying 72.4 and 92 percent allethrin, respectively, was studied in rats on diets containing 78, 156, 312, 625, 1225, 2500 and 5000 ppm of the respective allethrin samples. Rats on the diet containing 5000 ppm commercial allethrin showed a slight decrease in growth as compared with rats on the diet containing the same concentration of purified allethrins. Hematological findings on rats on the various dietary levels of the two allethrin samples were indistinguishable from those of the controls. From these preliminary observations it is concluded that purified allethrin is no more toxic than purified pyrethrins. The toxic reaction observed after topical application or after prolonged oral ingestion is undoubtedly due to impurities. More extensive studies on chronic toxicity are in progress.

Lehman (116) has expressed the opinion that the pyrethrins in combination with any of the three activators, piperonyl butoxide, n-propyl isome and MKG 264 appear to be among the safest of insecticides. "We have yet to demonstrate adverse effects in our animals on chronic feeding experiments at levels considerably above what might be expected as contaminants of food when these materials are properly used. Allethrin is showing every indication of being in the same category, toxicologically, as the natural pyrethrins. The dermal and acute oral toxicities, and the preliminary chronic feeding data coincide very well with our results on the natural products."

CLASSIFICATION OF INSECTS AGAINST WHICH ALLETHRIN HAS BEEN TESTED

The literature records the results of tests of allethrin against 67 identified species of insects and other arthropods belonging to 60 genera, 37 families and 10 orders. In addition allethrin has been tried against many insects unidentified as to species such as ants, lice, and mosquitoes.

In the following summary of these tests the families and genera of insects are placed alphabetically under the orders which are arranged according to increasing complexity of structure from Orthoptera to Hymenoptera.

ORTHOPTERA

Blattidae

Blattella germanica (L.), the German cockroach

Allethrin at 100 and 200 mg. per 100 ml. was inferior to pyrethrins in knockdown in 1 hour and mortality in 24 hours.---Stoddard and Dove (177).

Allethrin was inferior to pyrethrins. In tests on roaches the addition of piperonyl butoxide, MGK 264 and two homologs thereof to allethrin increased the kill.--Moore (134).

When tested in oil solution by the direct spray method allethrin was 1/2 as effective as the pyrethrins in knockdown and kill. When tested by the settling mist method at concentrations of 0.10 and 0.20 percent, allethrin was nearly equivalent to pyrethrins in knockdown and kill.--Nash (139).

When tested in Deobase solution by the settling mist method allethrin was slower in knockdown than pyrethrins and caused 0.7 to 0.9 as much mortality of female roaches in 48 hours.--Granett et al. (86).

Periplaneta americana (L.), the American cockroach

An aerosol containing 1 percent of allethrin applied at a dosage of 35 g./1000 cu. ft. killed no adult females in 5 days and only 12 percent of large nymphs; pyrethrins killed 42 percent of the adult females and 18 percent of the large nymphs. The roaches were confined in a pen on the floor of a Peet-Grady chamber.--Fales et al. (70).

Allethrin was inferior to pyrethrins.--Moore (134).

By the injection method the approximate LD-50 for female nymphs was 3.25 micrograms per gram for allethrin, and 1.375 micrograms per gram for pyrethrins indicating the natural material to be about 2.4 times as toxic as allethrin when tested in this way.--Bishopp (48).

When tested in Deobase solution by the settling mist method allethrin was 1/4 to 1/6 as toxic as pyrethrins to female roaches; 0.2 percent pyrethrins caused the same knockdown in 30 minutes and the same kill in 4 days as 1.2 percent allethrin.--Granett et al. (86).

THYSANOPTERA

Thripidae

Hercinothrips femoralis (Reut.), the banded greenhouse thrips

In greenhouse tests aerosols of allethrin and of pyrethrins gave equally good control.--Roark (149).

HOMOPTERA

Aleyrodidae

Aleurocanthus woglumi Ashby, the citrus blackfly

In laboratory tests allethrin in Deobase was slightly superior to a similar solution of pyrethrins.--Bishopp (48).

Aphidae

Aphis fabae Scop., the bean aphid

Allethrin at the rate of 0.06 pound per 100 gallons of water plus an equal quantity of Dreft killed 100 percent of the aphids; pyrethrins did likewise. Dreft alone killed only 2 percent of the aphids.--Bishopp (48).

In laboratory spraying tests against adult apterous viviparous parthogenetic females pyrethrins were about 14 times as toxic as allethrin. --Elliott et al. (66).

Aphis gossypii Glov., the cotton aphid

In tests against the cotton aphid 1 and 2 percent allethrin dusts caused about the same mortality as 0.1 and 0.2 percent pyrethrins dusts, that is 10 to 14 percent. Even at 10 percent allethrin killed only 53.3 percent. When tested in a greenhouse as liquefied gas aerosols containing 1 percent of toxicant, pyrethrins were slightly superior to allethrin. --Bishopp (48).

When tested in the laboratory in the form of dusts by a modification of the settling tower method pyrethrins were better than allethrin against nymphs.--Stoddard and Dove. (177).

Brevicoryne brassicae (L.), the cabbage aphid

Allethrin dust was inferior to pyrethrins dust.--Roark (149).

Macrosiphoniella sanborni (Gill.), the chrysanthemum aphid

When tested in a greenhouse as liquefied gas aerosols containing 1 percent of toxicant pyrethrins were slightly superior to allethrin.-- Bishopp (48).

Macrosiphum pisi (Kltb.), the pea aphid

Allethrin dust was 1/2 as effective as pyrethrins dust; allethrin spray was less effective than pyrethrins spray.--Bishopp (48).

Pyrethrin dusts were from 2 to 3.4 times more effective than allethrin against 2-day old nymphs at 3 dosage levels. Liquid dosages of 0.0125 percent v/v of both materials were about equally effective. At intermediate and low mortality levels allethrin was less effective.--Bottger and Yerington (52).

In laboratory tests allethrin and pyrethrins in the form of pyrophyllite dusts and aqueous emulsions (made by adding an acetone solution to water) compared as follows on the basis of 50-percent mortality values:

pyrethrins = 14. x allethrin (dusts)
pyrethrins = 3.8 x allethrin (dips) --Bottger (50).

Macrosiphum solanifolii (Ashm.), the potato aphid

In laboratory spraying tests in England allethrin was only 1/16 as toxic as pyrethrins.--Elliott et al. (66).

Myzus solani (Kltb.), foxglove aphid

In greenhouse tests aerosols of allethrin and of pyrethrins were equally effective.-- Roark (149).

Myzus persicae (Sulz.), the green peach aphid

Allethrin dust was inferior to pyrethrins dust.--Roark (149).

Aphis rosarum Kltb.,

Allethrin at the rate of 0.06 pounds per 100 gallons of water killed 100 percent of the aphids; pyrethrins at the same strength killed 97 percent. Dreft (used as a wetting agent at 0.06 pound per 100 gallons of water) alone killed 37 percent of the aphids.--Bishopp (48).

Cicadellidae

Circulifer tenellus (Baker), the beet leafhopper

Allethrin dust was inferior to pyrethrins dust.--Roark (149).

Macrosteles divisus (Uhl.), the six-spotted leafhopper

Emulsions and dusts of pyrethrins were more effective than those of allethrin.--Moore (134).

In greenhouse tests of aerosols, allethrin proved inferior to pyrethrins.--Roark (149).

Coccidae

Phenacoccus gossypii T. & C., the Mexican mealybug

Allethrin, 0.125 pound per 100 gallons of water plus 0.08 pound of Dreft killed 84 percent, pyrethrins 92 percent, and Dreft alone 14 percent. When tested as liquefied gas aerosols containing 1 percent of toxicant in a greenhouse pyrethrins were slightly superior to allethrin.--Bishopp (48).

HETEROPTERA

Coreidae

Anasa tristis (Deg.), the squash bug

In the form of water emulsion sprays pyrethrins were 3 times as effective as allethrin and a dust containing 0.23 percent of pyrethrins killed 46 percent,

whereas a dust containing 0.46 percent of allethrin killed 21 percent.--Moore (134).

Pyrethrin dust was better than allethrin dust against nymphs and adults. --Stoddard and Dove (177).

Lygaeidae

Oncopeltus fasciatus (Dall.), the large milkweed bug

When tested as dusts allethrin was 1/2 as effective as pyrethrins: when tested as sprays allethrin was twice as effective as pyrethrins.--Bishopp(48).

Pyrethrin dusts were twice as effective as allethrin against 3rd instar nymphs. When tested as 0.0125-percent sprays allethrin was twice as effective as pyrethrins and when the dosage was reduced to 0.0055 in the allethrin it was 5 times more effective than pyrethrins.--Bottger and Yerington (52).

In laboratory tests allethrin and pyrethrins in the form of aqueous emulsions (made by adding an acetone solution to water) compared as follows on the basis of 50 percent mortality values.

allethrin = 2.5 x pyrethrins (sprays) --Bottger (50).

Miridae

Lygus oblineatus (Say), the tarnished plant bug

In greenhouse tests allethrin spray (32 ounces of 4 percent solution per 100 gallons equivalent to 0.01-percent concentration) was ineffective; the control 96 hours after spraying was 25 percent.--Zia-Din (195).

Pentatomidae

Murgantia histrionica (Hahn), the harlequin bug

When tested in the laboratory in the form of dusts by a modification of the settling tower method pyrethrins were better than allethrin.--Stoddard and Dove (177).

ANOPLURA

Haematopinidae

Haematopinus eurysternus (Nitx.), the short-nosed cattle louse

When 0.05-percent sprays were applied to cattle infested with the short-nosed louse, motile forms were killed by both pyrethrins and allethrin. --Roark (149).

Pediculidae

Pediculus humanus corporis Deg., the body louse

Laboratory tests indicated that body lice in Korea which were highly resistant to DDT were about as susceptible to allethrin as normal laboratory

colony lice at Orlando, Florida. In beaker tests (cloth impregnation) 0.05-percent allethrin caused 100 percent mortality after 24 hours exposure; 0.01-percent caused 62 percent mortality. In laboratory tests on residual effectiveness, the pyrethrin 2,4-dinitroanisole formulations appeared somewhat more effective than similar formulation containing allethrin in place of 2,4-dinitroanisole. Six pyrethrin and allethrin powder formulations caused good reductions of lice in field tests after one treatment and almost complete eradication of lice after three treatments. All six formulas appeared equally effective under the conditions in which the tests were made. Pyrethrins and allethrin at a concentration of 0.1 percent caused 100 percent mortality of lice in 24 hours. Both caused complete knockdown at a concentration of 0.05 percent, but the pyrethrins did not give complete mortality in 24 hours. At a concentration of 0.025 percent neither material caused complete knockdown or kill in 24 hours. In recent tests with the non-resistant strain of lice at the Orlando, Florida laboratory, a concentration of 0.05 percent of either material generally caused complete knockdown but rather low mortalities in 24 hours. It would appear, therefore, that there is little difference in the susceptibility of normal and DDT-resistant Korean strains of body lice to allethrin and pyrethrins. --Eddy (64).

COLEOPTERA

Anobiidae

Lasioderma serricorne (F.), the cigarette beetle

A spray containing allethrin was inferior to one containing pyrethrins. --Roark(149).

Chrysomelidae

Acalymma vittata (F.), the striped cucumber beetle

See under *Diabrotica*.--Stoddard and Dove (177).

Altica ambiens (Lec.), the alder flea beetle

Allethrin was more effective than pyrethrins both in dusts and in sprays. --Bishopp (48).

Allethrin dust was 17 percent more toxic than pyrethrins dust. Allethrin spray 0.05 percent v/v killed 29 percent of the test insects, whereas pyrethrins at 0.10 percent v/v killed none.--Bottger and Yerington (52).

Diabrotica undecimpunctata howardi Barb., the spotted cucumber beetle

When tested in the form of dust in the laboratory by a modification of the settling tower method allethrin proved inferior to pyrethrins.--Stoddard and Dove (177).

Diabrotica sp.

In cage tests of impregnated dusts a dust containing 0.23 percent of pyrethrins was better than one containing 0.46 percent of allethrin.--Moore (134).

Leptinotarsa decemlineata (Say), the Colorado potato beetle

When tested in the laboratory in the form of dusts by a modification of the settling tower method pyrethrins were better than allethrin.--Stoddard and Dove (177).

Phaedon cochleariae (F.), the mustard beetle

In laboratory spraying tests pyrethrins were 5 times as toxic as allethrin to adult beetles.--Elliott et al. (66).

Coccinellidae

Epilachna varivestis Muls., the Mexican bean beetle

When tested in the laboratory in the form of dusts by a modification of the settling tower method pyrethrins were better than allethrin against adults and larvae.--Stoddard and Dove (177).

Cucujidae

Oryzaephilus surinamensis (L.), the saw-toothed grain beetle

In laboratory spraying tests on adult beetles pyrethrins were about 2 1/2 times as toxic as allethrin.--Elliott et al, (66).

Curculionidae

Listroderes costirostris obliquus Klug, the vegetable weevil

A dust containing allethrin was inferior to a pyrethrins dust.--Roark (149).

Sitrophilus oryza (L.), the rice weevil

Adult weevils were immersed for 5 minutes in 0.5-percent emulsions of allethrin and pyrethrins at 20° C. Allethrin caused less mortality than pyrethrins 24 hours after treatment, but more mortality at 48 hours and 72 hours after treatment.--Sakai et al. (153).

Dermestidae

Attagenus piceus (Oliv.), the black carpet beetle

Beetle larvae were exposed to cloth impregnated with acetone solutions of toxicants. Allethrin at 5 mg./sq. ft. produced slightly less knockdown but higher mortality and a longer residual action than pyrethrins. At 15 mg./sq. ft. allethrin exhibited about the same knockdown, slightly lower mortality and longer residual effectiveness than pyrethrins. Piperonyl butoxide and n-propyl

isome increased the knockdown of allethrin but not the mortality.--Bishopp (48).

Scarabaeidae

Popillia japonica Newm., the Japanese beetle

When tested in the laboratory in the form of dusts by a modification of the settling tower method pyrethrins were superior to allethrin.--Stoddard and Dove (177).

Tenebrionidae

Tribolium confusum Duv., the confused flour beetle

By the glass plate method residues of allethrin and pyrethrins caused equal mortality after 12 days contact and one synergist (sulfoxide) greatly increased the kill with allethrin.--Bishopp (48).

Deposits of allethrin on glass plates paralyzed adult beetles less rapidly than did deposits of pyrethrins and the beetles recovered much more rapidly and completely than those that had been exposed to the pyrethrins.--Stoddard and Dove (177).

Sprays containing 0.5 percent pyrethrum or allethrin are recommended by the Bureau of Entomology and Plant Quarantine for combating insects in empty grain bins, These sprays should be applied at the rate of 2 gallons per 1,000 square feet of wall or floor surface.--U. S. Dept. Agr. (184).

LEPIDOPTERA

Hyponomeutidae

Plutella maculipennis (Curt.), the diamondback moth

In labortory spraying tests in England against final instar larvae allethrin was nearly twice as effective as pyrethins.--Elliott et al. (66).

During the spring of 1950 natural pyrethrum powder and allethrin, were compared in the laboratory and in field plots in South Carolina. In general, allethrin dusts proved less toxic than those of similar pyrethrin content. Higher dosages of allethrin, however, showed considerable promise. In a small field test, a 1-percent allethrin dust was about as effective as a 0.3-percent allethrin dust against a mixed infestation of the cabbage looper, the imported cabbageworm, and the diamondback moth.--Reid and Cuthbert (147).

Papilionidae

Papilio polyxenes F.

Emulsions and dusts of pyrethrins were more effective than those of allethrin.--Moore (134).

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Phalaenidae

Alabama argillacea (Hbn.), the cotton leafworm

When tested against the cotton leafworm as 1- and 2-percent dusts at 10 pounds per acre allethrin showed 5 to 15 percent kill while pyrethrins at 0.5 percent gave a 25 percent kill.--Bishopp (48).

Pseudaletia unipuncta (Haw.), the armyworm

When tested as dusts allethrin was more effective than pyrethrins, but in the form of sprays there was no difference.--Bishopp (48).

At low and intermediate levels allethrin dust was 40 and 10 percent respectively more toxic than pyrethrins; at high levels pyrethrins were 31 percent more effective than allethrin. As sprays allethrin and pyrethrins exhibited similar toxicity.--Bottger and Yerington (52).

In laboratory tests allethrin and pyrethrins in the form of pyrophyllite dusts and aqueous emulsions (made by adding an acetone solution to water) compared as follows on the basis of 50-percent mortality values:

pyrethrins = 2.8 x allethrin (dusts)
pyrethrins =10.9 x allethrin (sprays) --Bottger (50)

Heliothis armigera (Hbn.) the corn earworm

When tested in the laboratory in the form of dusts by a modification of the settling tower method pyrethrins were better than allethrin.--Stoddard and Dove (177).

In injection tests in California in which the toxicants were dissolved in USP mineral oil, Saybolt viscosity 145 to 155 seconds, 0.4 percent of allethrin plus 2 percent of MGK 264 was inferior to 0.1 percent of pyrethrins plus 2 percent of the same synergist. However, both allethrin and pyrethrum mixtures gave poor control in these tests.--Anderson et al. (45).

Trichoplusia ni (Hbn.), the cabbage looper

Emulsions and dusts of pyrethrins were more effective than those of allethrin.--Moore (134).

See also under Plutella maculipennis.--Reid and Cuthbert (147).

Phycitidae

Ephestia eleutella (Hbn.), the tobacco moth

An oil spray containing 0.2 percent of allethrin killed as many moths as a pyrethrins-oil spray.--Roark (149).

Pieridae

Pieris rapae (L.), the imported cabbage worm

Emulsions and dusts of pyrethrins were more effective than those of allethrin.--Moore (134).

See also under Plutella maculipennis.--Reid and Cuthbert (147).

Pyraustidae

Diaphania nitidalis (Stoll), the pickleworm

Allethrin dust was inferior to pyrethrins dust.--Roark (149).

Phlyctaenia rubigalis (Guen.), the celery leaf tier

Allethrin was 1/4 as effective as pyrethrins when tested as dusts, but was 10 times as effective when tested as sprays.--Bishopp (48).

Against 3rd instar celery leaf tier larvae pyrethrins sprays were 27.6 times as toxic as allethrin sprays and when tested as dusts pyrethrins were 13 times as toxic as allethrin.--Bottger and Mayer (51).

Pyrethrins dust was about 4 1/2 times as effective as allethrin dust against 3rd instar larvae, but allethrin was roughly 10 times more effective than pyrethrins when tested as sprays.--Bottger and Yerington (52).

Pyrausta nubilalis (Hbn.), the European corn borer

Allethrin at 0.5 ounce for 100 gallons of water caused 100 percent mortality of newly hatched larvae. At 1/8 ounce the mortality was 33.7 percent. Pyrethrins in the form of powdered pyrethrum flowers at 1/100 pound per 100 gallons water gave a kill of 100 percent and at 1/2 this dosage the kill was 23 percent. Pyrethrins were thus about 3 times as toxic to young corn borers as allethrin. In these tests the toxicity of allethrin was increased as much as 8 fold with the addition of various synergists.--Bishopp (48).

Emulsions and dusts of pyrethrins were more effective than those of allethrin against 3rd and 5th instar larvae.--Moore (134).

Sphingidae

Protoparce sexta (Johan.), the tobacco hornworm

Allethrin dust was inferior to pyrethrins dust.--Roark (149).

HYMENOPTERA

Formicidae

Monomorium minimum Buckl., the little black ant

Ants were exposed for 30 minutes on pads treated with insecticides. When the pads were aged 8 days after treatment pyrethrins caused 12 percent mortality as compared to 31 percent for allethrin. The addition of piperonyl butoxide or n-propyl isome did not materially improve the effectiveness of either product. When the pads were aged only one day the mortality at the 48 hour reading was increased to some extent by the addition of these synergists. --Bishopp (48).

DIPTERA

Culicidae

Aedes aegypti (L.), the yellow-fever mosquito

Tests with 0.1 and 0.2-percent solutions of allethrin and pyrethrins alone applied as space sprays showed allethrin to be slightly less effective. The addition of 2 percent of piperonyl butoxide materially stepped up the action of allethrin but did not enhance that of the pyrethrins.--Bishopp (48).

Against 3rd instar larvae allethrin was approximately 1/3 as toxic as pyrethrins at the LD-50 level; 0.19 ppm as compared to 0.059 ppm. The addition of sulfoxide (5 parts) or piperonyl butoxide (5 parts) to one part of allethrin did not enhance its toxicity whereas these synergists did slightly raise the toxicity of pyrethrins.--Granett et al. (86).

Allethrin in sprays (1 mg./ml.) at a dosage of 55.56 ml./1000 cu. ft. killed 100 percent of the males and 99 percent of the females in 1 day; pyrethrins (0.2 mg./ml.) killed 82 percent of the males and 62 percent of the females.--Fales et al. (70).

Aedes spp., flood-water mosquitoes

Allethrin and pyrethrins were applied to cages at the rate of 0.5 mg. per sq. ft. and 24 hours later mosquitoes were introduced and exposed for 2 minutes. Pyrethrins gave a mortality of 74 percent and two samples of allethrin 58 and 44 percent. When piperonyl butoxide was added to each product all the mosquitoes exposed 2 hours in cages treated with pyrethrins were killed; when exposed in cages treated with allethrin the kills were 63 and 45 percent. --Bishopp (48).

Anopheles quadrimaculatus Say, the common malaria mosquito

Allethrin spray, 1 mg./ml. at a dosage of 9.26 ml./1000 cu. ft. killed 65 percent of the males and 16 percent of the females in 1 day; pyrethrins at 0.2 mg./ml. at the same dosage killed 73 percent of the males and 43 percent of the females. At a dosage of 55.56 ml./1000 cu. ft. allethrin killed 100

percent of the males and 99 percent of the females; pyrethrins killed (at a dosage of 9.26 ml./1000 cu. ft.) 67 percent of the males and 38 percent of the females.--Fales et al. (70).

Culex pipiens var. pallens Coq.

In Japan Nagasawa et al. (138) reported that mosquito incense containing allethrin was about 1.5 times as effective as a similar pyrethrin incense to adults. When applied in oil solution to the pupae allethrin was about 0.06 times as toxic as pyrethrins at LD-99.87.--Nagasawa et al. (137).

Fales et al. (69) reported that in Peet-Grady tests with allethrin on free-flying laboratory reared Aedes aegypti, Anopheles quadrimaculatus and Culex pipiens the Aedes were the least resistant and the Culex were the most resistant. When the mortality figures for Aedes females were plotted, it was found that the LC-50 of allethrin was eight times that of the pyrethrins. With Anopheles twice and with Culex approximately five and one-half times the amount of allethrin was required. Against male Aedes, the amount allethrin required was again eight times that of pyrethrins. With Anopheles the materials gave nearly equal performances. With Culex the lowest concentration of allethrin (3.2 mg./ml.) gave approximately the same results as the highest concentration of pyrethrins (1.6 mg./ml.).

Drosophilidae

Drosophila melanogaster Mg., the pomace fly

Sakai et al. (152) tested the action of insecticides on the "vestigial form" of the pomace fly by immersing the insects into emulsions of the insecticides for 2 minutes at 20° C. and determining the mortality after 30 minutes. In experiments on insecticide alone, pyrethrins were markedly more toxic than the other insecticides, but allethrin was more toxic than the other synthetic insecticides as regards MLD values. On the basis of the MLD, the toxicities of each contact insecticide were expressed in order of effectiveness as follows, 1) pyrethrins, 2) allethrin, 3) rotenone, 4) gamma BHC, 5) TEPP, 6) pp'DDT, 7) op'DDT, 8) parathion, 9) O,O-diethyl-O-para-nitrophenylphosphate, 10) dieldrin, 11) nicotine, 12) aldrin and 13) toxaphene. Although chlordane was tested in the present investigation, it was not toxic against the pomace fly. Synergism was exhibited by a mixture of allethrin and BHC and antagonism by allethrin plus rotenone, and allethrin plus pyrethrins.

Hippoboscidae

Melophagus ovinus (L.), the sheep tick

Sprays of pyrethrins were superior to those of allethrin.--Roark (149).

Mycetophilidae

Bradysia fenestralis (Zett.)

Megaselia agarici (Lint.)

Adults of both species of mushroom flies appeared more susceptible to pyrethrins dust than to allethrin dust.--Roark (149).

Muscidae

Musca domestica L., the house fly

When applied as space sprays against house flies natural pyrethrins were slightly more effective than allethrin at 0.1 percent, but at 0.2 percent the reverse was true. When piperonyl butoxide was added to allethrin in a 5:1 ratio there was a 34 percent increase in toxicity as compared with a 54 percent increase when the pyrethrins were used. Cages were dipped in acetone solution containing 0.1 percent of various toxicants and after 24 hours flies were introduced. Allethrin killed 74 percent and pyrethrins 47 percent of the flies. When 1 percent of piperonyl butoxide was added the toxicity of the pyrethrins was increased to 92 percent whereas the toxicity of allethrin remained unaffected.--Bishopp (48).

When tested by the Peet-Grady method allethrin was less effective than pyrethrins at low concentrations (below approximately 125 mg./100 ml.) but was more effective at concentrations above this. To give 50 percent kill of the house flies 145 mg./100 ml. of allethrin were required as compared to 165 mg./100 ml. of pyrethrins. An allethrin residue on a glass plate was more effective in knockdown and kill than an equal residue of pyrethrins. A 1 percent allethrin aerosol was almost, but not quite, the equivalent of a 1 percent pyrethrin aerosol.--Nash (139).

Blackith (49) in 1951 stated that in his experience and in that of Elliott et al., allethrin gives parallel regression lines with the natural extracts.

In tests with sprays containing 1 mg. of toxicant per milliliter of deodorized kerosene allethrin and pyrethrins gave the same kill (25 percent in 1 day) and essentially the same knockdown in 10 minutes (87 and 84 percent, respectively). In tests with aerosols (89 percent of Freon 12, 6 percent of methylene chloride, 4 percent of deodorized kerosene and 1 percent of toxicant) applied at a dosage of 4.63 grams per 1000 cu. ft. allethrin and pyrethrins gave the same kill (32 percent in 1 day) and almost the same knockdown in 10 minutes (69 and 73 percent, respectively).--Fales et al. (70).

When tested in aerosols allethrin is equal to pyrethrins in knockdown and kill. The addition of 2 percent of DDT enhances the kill of both materials. The synergistic effect of piperonyl butoxide is considerably less with allethrin than with pyrethrins.--Moore (134).

When sprayed in 0.1-percent Deobase solution on adult flies allethrin was superior to pyrethrins in both 10-minute knockdown and 24-hour kill. When exposed to ultraviolet light for 5 hours (equivalent to 5 days exposure to mid-day sun) and to heat (110°F. for 24 hours and to 120°F. for an additional 48 hours) allethrin proved more stable than pyrethrins. These tests were made on mosquito larvae and house flies. An allethrin residue of 144 mg. per sq. ft. persisted for several months against house flies and when a synergist (piperonyl butoxide or sulfoxide) was added the amount of residue could be reduced to 28 mg. per sq. ft.--Granett et al. (86).

In tests made by the turntable method allethrin was about 3 times as toxic as the pyrethrins.--Gersdorff (77).

In England Crombie et al. (61) quote Parkin and Green of the Pest Infestation Laboratory as reporting that when allethrin and pyrethrins were tested over the concentration range 0.05-0.4 percent w/v in odorless distillate by a modified Peet-Grady method "There was no difference in toxicity between the two sets of corresponding solutions either in knock-down in 10 minutes or in kill in 24 hours."

March and Metcalf (122) in 1950 reported that resistant and nonresistant houseflies showed approximately the same level of susceptibility to pyrethrins and allethrin. In these tests the insecticides in acetone solution were applied to flies with a micro-syringe. The 24-hour LD-50's in micrograms per female fly were:

	Laboratory strain	Bellflower strain	Pollard strain
Pyrethrins	1.0	0.94	1.6
Allethrin	0.43	0.97	0.5

On the basis of LD-50's the Bellflower strain of flies was more than 300 times as resistant to DDT as the non-resistant laboratory strain and the Pollard strain was even more resistant. On the basis of LD-95's the Bellflower strain was more than 1500 times as resistant to DDT as the laboratory strain. The authors conclude that the use of space sprays or aerosols containing pyrethrins or the equivalent represents the only satisfactory means for the chemical control of flies resistant to both DDT and BHC.

Houseflies from a dairy near Orlando, Florida that were [illegible] times as resistant as regular flies to DDT exhibited no increased resistance to pyrethrins plus piperonyl butoxide and allethrin plus piperonyl butoxide.--Knipling (110).

Quarterman (129) of the U. S. Public Health Service at the 19th Annual Convention of the National Pest Control Association held in Boston October 30, 1951 stated that for the control of resistant flies pyrethrum with synergists can be used successfully. Allethrin is a promising substitute for pyrethrum in some cases but not in others.

Houseflies which were resistant to DDT in 1949 acquired increased resistance to five additional chlorinated hydrocarbons in 1950, but little or none to allethrin and pyrethrins.--Gilbert et al. (84).

Against resistant flies in Florida allethrin and pyrethrins plus piperonyl butoxide were moderately effective early in 1950, but by the end of the season none of them provided satisfactory control.--Wilson et al. (194).

Siphona irritans (L.), the horn fly

A dust containing 0.5 percent of allethrin applied at the rate of 2.3 to 2.5 ounces per animal caused 53 percent reduction in the number of horn flies

on cattle in tests at Oswego, New York in 1950. A spray of Pyrenone 1-5 caused the greatest reduction - 96 percent.--Goodwin et al. (85).

Stomoxys calcitrans (L.), the stable fly

To test the residual effectiveness of allethrin and pyrethrins screen-wire cages were dipped into 0.1-percent solutions of these toxicants alone and with the addition of 1 percent of piperonyl butoxide. Stable flies were introduced one day later and exposed for 24 hours. In two tests pyrethrins gave a 100 percent knockdown and kill with and without the synergist whereas allethrin alone gave 60 and 92 percent knockdowns and 40 and 85 percent kills and the mixture 87 and 82 percent knockdowns and 72 and 70 percent kills. Additional tests with stable flies introduced 4 days after treatment indicated that pyrethrins were much more effective than allethrin from a residual standpoint and the addition of piperonyl butoxide did not enhance the effectiveness of allethrin.--Bishopp (48).

Tabanidae

Chrysops discalis Will., the deer fly

Tabanus sonomensis O.S.)
) horse flies
T. punctifer O.S.)

A concentration of 1 mg. per square foot or greater was necessary to obtain knockdown of the deerfly in less than two hours with either natural pyrethrins or allethrin when used alone. Natural pyrethrins plus synergists usually produced superior results to those obtained with allethrin and the same synergist. At 0.5 mg. per square foot of pyrethrins and 5 mg. per square foot of synergist, piperonyl butoxide was the most effective synergist, resulting in complete knockdown in an average of 3 minutes with either natural pyrethrins or allethrin and a 100 percent mortality in 8 hours after an exposure of 1 1/2 minutes to the treated surfaces. Lower dosages, however, provided greatly reduced effectiveness particularly in relation to the synthetic product.--Hoffman and Lindquist (103).

Tabanus quinquevittatus Weidemann

A dust containing 0.5 percent of allethrin applied at the rate of 2.3 to 2.5 ounces per animal caused 45 percent reduction in the number of horse flies on cattle in tests at Oswego, New York in 1950. A spray of Pyrenone 1-10 caused the greatest reduction -93 percent.--Goodwin et al. (85).

ACARINA

Argasidae

Otobius megnini (Duges), the ear tick

Allethrin was less effective than pyrethrins in tests against spinose ear ticks and winter ticks in which the ticks were dipped in acetone solution of the insecticides.--Roark (149).

Ixodidae

Dermacentor albipictus (Pack.), the winter tick

See under spinose ear tick.

Tetranychidae

Paratetranychus citri (McG.), the citrus red mite

Allethrin and pyrethrins as 2-percent dusts were ineffective; as sprays 11-percent v/v dosages of both materials gave 100 percent mortality.--Bottger and Yerington (52).

Tetranychus bimaculatus Harvey, the two spotted spider mite

Allethrin at 0.125 pounds per 100 gallons caused 56 percent dead and moribund; twice this concentration raised the percentage to 72. The corresponding figures for pyrethrins were 8 and 89 percent. These toxicants were dispersed in water with Dreft. When tested in a greenhouse as liquefied gas aerosols containing 1 percent of toxicant pyrethrins were slightly superior to allethrin. A spray of allethrin was about equal to one of pyrethrins, but allethrin dust was 1 1/2 times as effective as pyrethrins dust.--Bishopp (48).

Allethrin dust was about 73 percent more effective than pyrethrins dust. When tested as sprays of 0.1 percent concentration allethrin was slightly superior to pyrethrins.--Bottger and Yerington (52).

Tetranychus sp., red spider

Against the red spider on cotton a dust containing 0.1 percent of the toxicant in Attaclay was applied at the rate of 10 pounds per acre. The kill after 60 hours was 19.7 percent for allethrin and 4.6 percent for pyrethrins. The addition of piperonyl butoxide failed to increase the kill.--Bishopp (48).

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