Chemicals Controlling Insect Behavior

WITH A FOREWORD BY
E. F. KNIPLING

EDITED BY MORTON BEROZA

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Foreword

As the result of increased interest and research on the biology and physiology of insects, scientists are beginning to recognize the vital role that chemical attractants and repellents play in the behavior of insects. Pheromones produced by insects provide a necessary means of communication in the reproductive processes of many insects. They also seem to be the key to the well-coordinated behavior patterns characteristic of the social insects. Chemists and biochemists are making rapid advances in the techniques of isolation, identification, and synthesis of these highly active and naturally occurring compounds. Structural elucidation of the natural products opens the way for a new and important field of organic chemistry and permits the exploration of new, potentially useful chemicals for controlling insect pests.

These developments are of great interest because the need for effective, economical, and safer means of insect control is more urgent than ever in the past. The expanding world population is creating a greater demand for more food, fiber, and lumber, and this increased production must be met on diminishing land available for agricultural uses. People the world over are also demanding greater protection from the hoards of insects that undermine their health and comfort. Fortunately, scientists have made remarkable progress in dealing with the multitudes of insects that compete for man's food and which threaten his health, even though insects still take a high toll of our agricultural production and insect-borne diseases persist as a major threat to the health of hundreds of millions of people in various parts of the globe. Available methods of insect control depend largely on the use of chemical insecticides having broad-spectrum biological activity. Their use in many situations is not acceptable because of the side effects they produce to nontarget organisms in the environment. Also, insects have a remarkable capability of developing resistance to some of the currently used insect control chemicals. Thus, there is an urgent need for alternative ways to control insects, ways that assure more dependable and permanent effects and yet are not deleterious to other values.

The use of insect attractants and repellents highly selective in action against destructive insects can play an important role in achieving the long-range goals of managing insect populations effectively, economically, and with complete safety to man and his environment. Substantial progress has already been made on chemicals that influence insect behavior, as is evidenced by information contained in this publication. This book brings up-to-date much of the available information on insect pheromones, insect defense mechanisms, and on other insect attractants and repellents. It should lay the groundwork for even greater and more rapid progress in the years ahead. An understanding of the nature of the chemicals that regulate or influence insect behavior is a prerequisite for detailed biological investigations on their potential value in the management of insect populations and in their use for practical insect control.

E. F. KNIPLING

Preface

The increasing use of insecticides and the findings that many of these materials and their metabolites are permeating and contaminating our air, food, water, soil, wildlife, and even our bodies have aroused the concern of a broad spectrum of our community—scientists, public health officials, politicians, and laymen alike—and have engendered a thrust toward exploring noninsecticidal means of insect control. Although this approach is not new, its practical value and present status, as well as the technology involved, are not generally understood or appreciated. The symposium proceedings presented in this volume provide such information on chemicals for controlling insect behavior; such chemicals may prove useful either for direct control or for making other control measures more efficient.

Although certain parts of the book may interest the layman, the contents are directed mainly to the chemist, biochemist, biologist, entomologist, and others working to control insect pests. This broad interest reflects the fact that success has invariably been the product of an interdisciplinary approach. However, interest in the book will not necessarily be limited to those dealing with insects since the means of isolating and identifying microgram and sometimes submicrogram amounts of compounds, such as sex attractants and other pheromones, and biological and behavioral studies with these chemicals are likely to intrigue scientists dealing with natural products and those in the life sciences generally. The scope and treatment of the subject, which must be considered relatively new, are deliberately exemplary rather than exhaustive, with emphasis placed on current trends and practices.

While the safety aspects of the use of nontoxic behavior-controlling chemicals are readily apparent, realistic appraisal of the potential utility of these chemicals for insect control requires adequate background information on structures, modes of action, means of isolation or synthesis, synthetic alternatives, bioassays, and results of field studies. The accomplishments detailed in this work leave little doubt that the use of modern instrumentation and methodology and the rapidly developing expertise of our scientists will bring rapid progress in this area. The elucidation of the chemical structure of minute amounts of insect secretions, their syntheses, the demonstration of their fantastic potency, and the clarification of the biological mechanisms involved are exciting research exploits laden with potential for pest control. It is clear now that many insects depend on chemicals for survival—for finding a mate, for defending themselves, for maintaining their social organization, for finding food, and for appropriate placement of eggs. Clearly, the key to insect control in many instances may very well be the key that unlocks the structure of their secretions or of chemicals that attract or repel them.

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MORTON BEROZA

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INTRODUCTION

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The development of synthetic insecticides during the past several decades stands as one of the great achievements of our times. The saving of millions of lives from insect-borne diseases and the high uninterrupted production of food and fiber from our agricultural community attest to the tremendous value of these chemicals (Whitten, 1966).

Unfortunately, problems relating to the use of insecticides have arisen; some are serious and are causing considerable concern in scientific as well as in lay circles. The problem of resistance to insecticides has been cited frequently (Crow, 1966), and recently we have been alerted to unforeseen disruptive effects of insecticide residues on nontarget ecological systems, systems that were not generally considered in the development of the synthetic insecticides (Barrett, 1968; Hunt, 1966; Moore, 1967; Newsom, 1967). Considering the appearance of residues in our foods, humans may be included as part of one of these nontarget ecosystems. In any event, we are learning more and more about these problems, and a concerted effort has been underway for some time to understand and eliminate these problems as they appear.

Responsible authorities agree that sufficient food to support the world's population cannot be produced without insecticides. With few exceptions, attempts employing biological control alone have not been successful. The same authorities also recognize that new and fresh approaches to pest control must be formulated to minimize pesticide residues, to make the use of pesticides more selective in their attack, and to utilize all means available, including biological control, to overcome insect depredation in a safe manner (Chant, 1966).

As a possible aid in solving some of these problems, we asked leading scientists to discuss chemicals controlling insect behavior. It is fairly certain now that outright killing is not the only way, or even the best way to get rid of our insect competitors. We are seeking more subtle and perhaps more effective means of causing their demise, and – in fact – their eradication if this objective appears feasible. That is why we are interested in disrupting insect growth processes with the insect's own hormones, or in controlling insect behavior patterns on which insects depend for survival. As will become evident in the course of the presentations, investigations along these avenues are not as straightforward as those dealing with the development of insecticides; but we can have confidence that some of the alternative approaches to pest control will in the future prove most useful. We may very well be entering a new era of scientific pest control that will embrace approaches more sophisticated than any used in the past (Knipling, 1966; Smith, 1966).

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SEX PHEROMONES OF THE LEPIDOPTERA. RECENT PROGRESS AND STRUCTURE—ACTIVITY RELATIONSHIPS

Martin Jacobson, Nathan Green, David Warthen, Charles Harding, and H. Harold Toba

I. INTRODUCTION

The term "pheromone" was coined by Karlson and Butenandt (1959) to designate substances secreted by an animal to influence the behavior of other animals of the same species. It comes from the Greek "pherein" (to carry) and "horman" (to excite, stimulate). As applied to insects, the term "sex pheromones" is now commonly used to include the chemical substances produced and released by one sex to attract or excite the opposite sex for mating. Although the sex pheromones released by female insects may attract males from a distance, they may also serve to excite the male sexually before copulation. Sex pheromones released by males are usually for the purpose of sexually exciting the female, making her more receptive to the male's advances; they are thus in the nature of aphrodisiacs.

The comprehensive review of insect sex attractants by Jacobson (1965) lists 159 species in which sex pheromones produced by the female have been demonstrated; of these, 109 species are members of the order Lepidoptera, which includes the moths and butterflies. A total of 53 species, of which 40 are lepidopterous insects, is given in which the pheromone is produced by the male.

In 1965, Jacobson (1965) stated "that the insect sex attractant literature has recently grown by leaps and bounds is due in no small measure to the fascinating fact that these substances, produced by the insects themselves as a requisite to their reproduction, may be used for their destruction." He cited 425 references on the subject appearing between 1837 and 1965. The field has seen an even greater growth since then, however; more than 400 additional references on insect sex pheromones have appeared in the literature during the past 4 years.

Detected by the insect in fantastically minute amounts, the sex attractants are undoubtedly among the most potent physiologically active substances known today. Thus far, their main practical use has been in insect survey, catches in traps baited with the attractants indicating the size and location of infestations of destructive insects, so that control measures with insecticidal treatments could be limited to those areas where they might be needed. Recent investigations have shown however, that the sex attractants themselves may also be useful in insect control (Jacobson, 1965, pp. 112-121).

The sex pheromones are detected by the insect by means of sense organs located mainly in the antennae, and in the case of the Lepidoptera the antennae are probably the sole organs of chemoreception since moths deprived of both antennae cannot locate a mate and show no response when exposed to a pheromone. Schneider (1964, 1969) has shown that the sex pheromones are detected by moths through numerous sensory cells located in the antennae, from which he succeeded in recording action potentials (EAG's or electroantennograms).

Good reviews on various phases of insect sex pheromones are those by Wilson (1963), Jacobson and Beroza (1963, 1964), Jacobson (1966b), Butler (1967), Roth (1967), and Regnier and Law (1968).

II. RECENT DEVELOPMENTS

A. SEX PHEROMONE DEMONSTRATION

In the past 4 years the presence of sex pheromones has been demonstrated in 31 additional species of lepidopterous insects (Table I). In each of these cases, the pheromone is produced by the adult female in glands situated in the last few abdominal segments. In three of these species – the false codling moth *(Argyroploce leucotreta)* (Read *et al.*, 1968), the red-banded leaf roller *(Argyrotaenia velutinana)* (Roelofs

TABLE I

Lepidopterous Insects Demonstrated to Possess Sex Pheromone (1965-1969)

Scientific name	Common name	Reference
Acrolepia assectella (Zeller)	Leek moth	Rahn (1966)
Alabama argillacea (Hübner)	Cotton leafworm	Berger (1968)
Anagasta kühniella (Zeller)	Mediterranean flour moth	Traynier (1968)
Ancylis comptana fragariae (Walsh & Riley)	Strawberry leaf roller	Roelofs and Feng (1968)
Archips argyrospilus (Walker)	Fruit tree leaf roller	Roelofs and Feng (1968)
Archips mortuanus Kearfott	–	Roelofs and Feng (1968)
Argyroploce leucotreta Meyr.	False codling moth	Read *et al.* (1968)
Argyrotaenia quadrifasciana (Fernald)	–	Roelofs and Feng (1968)
Argyrotaenia velutinana (Walker)	Red-banded leaf roller	Roelofs (1966)
Autographa biloba (Stephens)	–	Berger and Canerday (1968)
Choristoneura fumiferana (Clemens)	Spruce budworm moth	Findlay and MacDonald (1966)
Choristoneura rosaceana (Harris)	Oblique-banded leaf roller	Roelofs and Feng (1968)
Chrysopeleia ostryaella Chambers	Leaf miner	Lindquist and Bowser (1966)
Crambus trisectus (Walker)	Webworm	Banerjee (1967)
Diparopsis castanea (Hampson)	Red bollworm	Tunstall (1965)
Epiphyas postvittana (Walker)	–	Bartell and Shorey (1969)
Feltia subterranea (F.)	Granulate cutworm	Jefferson *et al.* (1968)
Grapholitha funebrana (Treitschke	Plum fruit moth	Saringer *et al.* (1968)
Hedya nubiferana (Haworth)	–	Roelofs and Feng (1968)
Heliothis phloxiphagus Grote & Robinson	–	Jefferson *et al.* (1968)
Hemileuca maia (Drury)	Buck moth	Earle (1967)
Pandemis limitata (Robinson)	Three-lined leaf roller	Roelofs and Feng (1968)
Prionoxystus robiniae (Peck)	Carpenterworm	Solomon and Morris (1966)
Pseudoplusia includens (Walker)	–	Shorey *et al.* (1968); Berger and Canerday (1968)
Rachiplusia ou (Guenée)	–	Shorey *et al.* (1968); Berger and Canerday (1968)
Sitotroga cerealella (Olivier)	Angoumois grain moth	Keys and Mills (1968)
Spodoptera frugiperda (J. E. Smith)	Fall armyworm	Sekul and Cox (1965)
Thyridopteryx ephemeraeformis (Haworth)	Evergreen bagworm moth	Kaufmann (1968)
Vitula edmandsae (Packard)	Bumble bee wax moth	Weatherston and Percy (1968)
Zeadiatraea grandiosella (Dyar)	Southwestern corn borer	Davis and Henderson (1967)

and Arn, 1968a,b), and the fall armyworm *(Spodoptera frugiperda)* (Sekul and Sparks, 1967)—the pheromone has been identified (see below).

Male butterflies of the genus *Lycorea* possess a pair of extrusible, odoriferous, brushlike structures on the posterior of their abdomens called "hair pencils." While in aerial pursuit of the female, the male extrudes his "hair pencils" and brushes them against the female's antennae, thus inducing her to alight. The male continues "hair penciling" the female until she is acquiescent and copulation then occurs. Such use of a form of aphrodisiac by the male has been reported by Brower *et al.* (1965) in the queen butterfly *Danaus gilippus berenice* (Cramer), and by Meinwald *et al.* (1966) in *Lycorea ceres ceres* (Cramer), from which 1-hexadecanol (cetyl) acetate, *cis*-11-octadecen-l-ol acetate, and 2,3-dihydro-7-methyl-1*H*-pyrrolizidin-1-one have been isolated (Meinwald and Meinwald, 1966).

A very interesting development has been reported by Riddiford and Williams (1967a,b), who have shown that polyphemus moths *Antherea polyphemus* (Cramer) can normally mate only in the presence of leaves of the red oak *Quercus rubra*. A volatile leaf emanation, identified by Riddiford (1967) as *trans*-2-hexenal, impinges on the sensory receptors of the female's antennae, triggering the release of her sex pheromone (unidentified), which, in turn, is necessary for the sexual activation of the male.

B. *IDENTIFICATION AND SYNTHESIS OF SEX PHEROMONES*

In the past 4 years the sex pheromones of five destructive lepidopterous insects have been isolated, identified, and synthesized.

1. Pink Bollworm Moth, *Pectinophora gossypiella* (Saunders)

By means of column and preparative gas chromatography of a methylene chloride extract of 850,000 virgin female moths, Jones *et al.* (1966) isolated 1.5 mg of the pheromone, which they identified as 10-propyl-*trans*-5,9-tridecadien-l-ol acetate (I).

$$(CH_3CH_2CH_2)_2C{=}CH(CH_2)_2\overset{H}{C}{=}\underset{H}{C}(CH_2)_4O\overset{O}{\overset{\|}{C}}CH_3$$

(I)

The material, which they designated "propylure," proved to be highly exciting to males in laboratory cages, but did not attract males to field traps, although the crude female extract was attractive in the field. Extract from which the propylure had been separated however, was not attractive in the field (Table II). Jones and Jacobson (1968) subsequently found that *N,N*-diethyl-*m*-toluamide (Deet), present in the crude extract, activates propylure so that 1:10 mixtures of 50 female equivalents of propylure and Deet will lure males in the field, although catches are not as high as those obtained with the crude extract; it is probable that a second activator may also be necessary in the mixture to give optimum catches. It is interesting to note that Deet, present in large amount in the adult female moth, has never before been reported from a natural source, but it is a very effective mosquito repellent (McCabe *et al.*, 1954). Propylure has been synthesized by Jones *et al.* (1966), Eiter *et al.* (1967), and Pattenden (1968). Although the preparation of Eiter *et al.* (1967) failed to excite caged males in the laboratory, this was due to a masking problem which will be discussed later.

TABLE II

Attractiveness of Propylure to Male Pink Bollworms in the Laboratory and in Outdoor Cages

Material tested (50 female equiv.)	Laboratory bioassay	Number of males caught (out of 100)		
		Night 1	Night 2	Night 3
Propylure				
Synthetic	Strong	3	2	1
Natural	Strong	0	0	0
Inactive extract (40 mg)	Negative	0	0	0
Propylure + inactives	Strong	52	56	41
Natural extract (standard)	Strong	62	97	52

2. Cabbage Looper Moth, *Trichoplusia ni* (Hubner)

The pheromone, which excites caged males in the laboratory and attracts males in the field, was isolated from a methylene chloride extract of the last two or three abdominal segments of virgin female moths; it was identified as *cis*-7-dodecen-l-ol acetate (II) by Berger (1966).