Pheromone and Its Application to Agricultural Chemicals

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Introduction

After World War II, various powerful organo-phoshoric insecticides have been developed and used widely for extermination of insect pests. And they have played a prominent part in the increase of agricultural production. On the other hand, their wide and increasing use, however, has given rise to public discussion recently regarding the contamination of the natural world and the remnant toxicity of them to man and beast. Accordingly, there is a demand to develop harmless pesticides. In this respect, the insect attractant is drawing the attention of persons concerned.

Insects are attracted to various agents. The fact that the common cabbage worm, *Pieris rapae*, is parasitic only on cruciferous plants and the larva of the swallow tail only on citrus plants must be considered to be due to the presence of some attracting agents in these plants. It is believed that some kinds of moths (Noctuidae) gather to ripen peaches and grapes by sucking them at night being drawn by some attractants in them. In addition to such food attraction there are different kinds of attraction. A certain kind of insect is attracted to a specific plant for oviposition. It was proved, by the experiments on the behavior of the silkworm to mulberry leaves, that some other substances which induce the insect to bite and swallow the food are also related to it in addition to more food-attractancy.[1] Insects can be attracted not only by such chemical compounds as mentioned above but also by physical agents, as sound and light. In all these cases, however, the stimulating substances or factors concerned are external for the insects.

A male and a female of the bisexual insect, which were far apart from each other at first, can come close and mutually copulate. It is believed, in this case, that some kind of information between the individuals makes it poossible for them to meet. The information is carried out by an extremely small amount of subrtance called sex attractant which is usually secreted from certain organs of the females outside the body. It reaches the receptor of the males by dispersion, and induces a specific stimulus in the latter. A substance which is produced by organisms and carries information to the partner or other individuals as a "chemical messenger" is called pheromone. It means "to carry excitement"[2]

In addition to the sex attractant as mentioned above, there are other pheromones, as the trail making substance found in the group of bees and ants, alarm substance and aggregation pheromone. There is also a pheromone which acts *per os* as seen in the queen substance of bees. From the viewpoint of the extermination of insect pests, however, the one which may be practicall used is sex pheromone, that is, sex attractant.

Pheromone, in general, has a striking physiological effect at an extremely small amount. And its effect is species-specific to each kind of insect. Accordingly, it will be favorably applied to control only the aimed pest, if pheromones of various insects are studied chemically and can be synthesized for practical use. The investigation of pheromone, however, is so difficult that the chemical structure has so far been made clear only in several cases.

The following is an outline of the results of investigations hitherto made on the insect pheromone with some examples of the practical application of pheromone to agriculture:

Sex pheromone (Sex attractant)

The first example of the chemical investigations of pheromone is the sex attractat of the silkworm moth (***Bombyx mori***). This pheromone is an unsaturated alcohol named Bombykol. The substacne obtained from 500,000 female moths was only 10 mg or so in the from of a derivative. According to the attraction experiment, it, however, has such an astonishing effect as it can stimulate the male at an extremely low concentration as 10^{-12} μg/ml.[3]

The silkworm moth was used in the investigation in order to obtain materials. The first insect pest in which chemical investigation of sex attractant was carried out by Jacobson and others[4] is the gypsy moth. The effective substance of this insect was named Gyptol. Its amount obtained from 500,000 female moths was only 20 mg or so. This substance is said to be able to attract the male moths at the concentration of 10^{-7} μg/ml in the field.

Investigations had been made to obtain cheaper homologs of it for practical use. And Gyplure with 18 carbons was found to be considerably high in the effect (about 1/100 of Gyptol in the effect). This can be easily synthesized from ricinoleic acid which is the main component of castoroil. Gyplure was put on the market and proved to be greatly effective for luring gypsy moths and forecasting their occurrence. This was the first and epoch-making fact in the practical application of pheromone to extermine insect pests.

$$CH_3\text{-}(CH_2)_5\text{-}\underset{\substack{|\\ OAc}}{CH}\text{-}CH_2\text{-}CH{=}CH\text{-}(CH_2)_7CH_2OH$$

Gyplure

Stimulated by the two pioneering works, many investigations on the sex attractant of insect have been carried out in various quarters. The results are shown in Table 1.

All the sex attractants of insects shown in Table 1. are unsaturated aliphatic alcohols or their acetates with 12-16 frame carbons. But they are not always alcoholic compounds. It seems that the sex attractant of the Erisilkworm moth is a carbonyl compound.[13]

Researchers of Bayer in Germany, however, reported recently enexpected results on Gyptol, Propylure and Gyplure mentioned in the table.[14] They say that those substances synthesized in the ways somewhat different from those of Jacobson and others were not attractive to the respective insects. It, however, is true that Gyplure is useful in the practical extermination of gypsy moths, and Propylure has also been proved to be effective in the field.[15] Jacobson and others synthesized those substances and proved their attractiveness. What is the reason of this difference ? Early solution of the problem is anticipated. It may be said that this fact shows the difficulty of the study of pheromone.

There are a few researches on the pheromones of Coleopterous insects (Table 1).

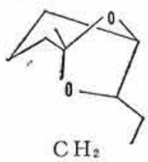
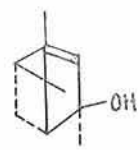
Studies were also made by Jacobson some years ago on the sex pheromone of cockroaches, especially American cockroach, which are important sanitary insects.[16] Other researchers, however, pointed out mistakes in the chemical structure reported by him on the basis of their synthetic studies.[17]

Aggregation pheromone

There are substances called aggregation pheromone which is recently focussing the reseachers' attention together with sex pheromone. When some bark beetles or ambrosia beetles(Coleopter: Scolytidae) burrow into the phloem tissue of a host tree, many males and females of the beetles gather there. In this case pheromone is secreted by either of the male or the female. It is secreted by the male in ***Ips confusus***.

In case a male of the insect attacks a suitable tree and burrows into the phloem tissue, it secret pheromone from the hind or Malpighian tubules, and excretes feces covered with the pheromone. Attracted to it, males and females in the vicinity assemble there, and the females try to enter the galleries of the males which are secreting the pheromone, while the newcomer males attempt to make new galleries there. In this case, therefore, it has an effect as a sex phero-

Table 1. Sex attractants of insects

Name of Insects	Chemical Name of Attractants	Chemical Structure	Literature
Lepidoptera			
Silkwom moth (Bombyx mori)	10-trans-12-cis-hexadecadienol (Bombykol)	$HO-(CH_2)_9-CH\overset{t}{=}CH-$ $-CH\overset{c}{=}CH-(CH_2)_2-CH_3$	3)
Gypsy moth (Porthetria)	(+)-10-acetoxy-7-cis-hexadecenol (Gyptol)	$HO-(CH_2)_6-CH\overset{c}{=}CH-$ $-CH_2-\underset{OAc}{\underset{\mid}{C}}H-(CH_2)_5-CH_3$	4)
Pink bollwom moth (Pectinophora gosypiella)	10-propyl-5-trans-9 -tridecadienol acetate (propylure)	$AcO-(CH_4)_4-CH\overset{t}{=}CH(CH_2)_2-$ $-CH=C<\begin{smallmatrix}CH_2-CH_2-CH_3\\CH_2-CH_2-CH_3\end{smallmatrix}$	5)
Cabbage looper (Tricoplusia ni)	7-cis-dodecenol acetate	$AcO-(CH_2)_6-CH\overset{c}{=}CH(CH_2)_3-CH_3$	6)
Fall army worm moth (Spodoptera frugiperda)	9-cis-tetradecenol acetate	$AcO-(CH_2)_8-CH\overset{c}{=}CH-(CH_2)_3-CH_3$	7)
Coleoptera			
Black carpet beetle (Attagenus megatoma)	3-trans-5-cis-tetra-decadienoic acid	$CH_3-(CH_2)_7-CH\overset{c}{=}CH-$ $-CH\overset{t}{=}CH-CH_2-COOH$	8)
Spring beetle (Limonius californicus)	n-veleric acid	$CH_3-(CH_2)_3-COOH$	9)
Red banded leaf roller moth (Argyrotaenia relutinana)	cis-11-tetradecenyl acetate	$CH_3-CH_2-CH\overset{c}{=}CH-$ $-(CH_2)_{10}-O\underset{O}{\underset{\Vert}{C}}-CH_3$	10)
Pine-bark beetle (Dendroctonus berevinis)	exo-7-ethyl-5-methyl-6. 8-dioxabicyclo-[3. 2. 1]-octane		11)
Wood borer (Ips confusus)		1) $CH_2=CH-\overset{CH_2}{\overset{\Vert}{C}}-CH_2-\underset{OH}{\underset{\mid}{C}}H-$ $-CH_2-\overset{CH_3}{\overset{\mid}{C}}H-CH_3$ 2)  3) $CH_2=CH-\overset{CH_2}{\overset{\Vert}{C}}-CH_2-\underset{OH}{\underset{\mid}{C}}H-$ $-CH=\overset{CH_3}{\overset{\mid}{C}}-CH_3$	12)

mone, too.[18] Three kinds of terpenoids are confirmed to be the effective substances as shown in Table 1.

Cockroaches, especially in the larval stage, live in aggregation. In fact their growth is faster and more uniform in mass rearing than in single. It seems that the aggregation is induced by the effect of a pheromone which is produced by them. When the feces of cookroaches adhering to their natural aggregating places are transferred to any place, the larvae of cockroaches are attracted there to aggregate. This aggrgation occurs even in the dark condition, though the insect deprived of the antennae do not. A piece of filter paper can also be a place for their aggregation in case it is infiltrated with the extract of the feces with some organic solvent, showing that the feces contain aggregation-inducing substance.

As the result of investigations to trace up the origin of the substance, Ishii and others concluded that it was secreted by a gland of the rectum pad, being excreted with feces. Chemical investigation of this effective substance is now in progress.[19]

This aggregation pheromone is attractive not only to the larvae but also to the adults. For example, when a bottle containing a piece of the filter paper spread with the feces extract is put on a place where the cockroaches are likely to pass through, it can be observed that some larvae and adults of the insect are in the bottle within a few days. The effect of this pheromone is not species-specific, but rather common among such different species as ***Periplaneta fuliginosa***, ***Blattela germanica*** and ***Periplaneta americana***). It is highly possible that this pheromone is put to practical use.

Aggregation pheromone ie also confirmed to be secreted by the termite, ***Calotermes flovicollis***. Larvae of this termite secrete a substance highly attractive to the larvae and nymphs of the same species. 'The effective component of it is said to be hexen-3-ol.[20]

There is a substance which is a little different from aggregation pheromone. A volatile substance secreted from the hypodermal gland of migratory locusta, ***Locusta migratoria migratorioides***, promotes the maturation of sexual glands and the change of body color in the individuals of the same group by mutual effect. The chemical structure of this substance is unknown.[21]

Other pheromones

There is the queen substance of the honey-bee in this group. This substance from the queen functions ***per os*** on all the worker bees of the colony to inhibit them to become queens. One of the active substancee is identified as 9-oxo-trans-2-decenoic acid. A similar substance to this is known in ants.[22]

The trail marking substance is also a kind of pheromone. Its presence is confirmed in more than 17 species of ants. Ants can trace down the foregoer without fail to the place where they will find food, guided by the smell secreted by the foregoer.

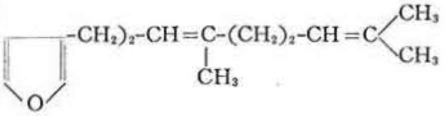
A certain kind of ant has an alarm substance to give warning of danger to the individuals of its colony. The members of the colony thus can take proper steps to counter the situation. There are some alarm substances whose chemical structures have been clarified (Table 2.)[23] It is interesting to note that terpenoid substances, as citral, have such an effect.

Artificial attractants and their application to the extermination of insect pests

The pheromone itself is not always necessary to exterminate insect pests, but some active substances equivalent to it in effect can also be used for the purpose. Gyplure which is mentioned above is an example of easily synthesized homologs of pheromone. Some powerful attractants can often be found among the pure synthetic substances which have no relation to pheromone. Examples are: Medlure (sec-and tert-butyl ester of 4 (or 5)-chloro and bromo-2-methylcyclohexane carboxylic acid) for ***Ceratitis capitata***; "cue lure" (4-(p-acetoxyphenyl)-2-butanone(for the melon fly, ***Dacus cucurbitae***; and methyl eugenol for the male of the fruit oriental fly, ***Dacus dorsalis Hendel***. Those substances are powerful in the attracting effect, respectively.

Yeast and some hydrolysates of protein are highly attractive to some kinds of fruit flies

Table 2. Alarm subustances of ants

Insects name	Effective substance	Chemical structure	Litera-ture
Pogonomyrmex	4-methyl-3-heptanone	$CH_3-(CH_2)_2-CH(CH_3)-C(=O)-CH_2-CH_3$	23)
Lasius fuliginosus	dendrolasin(=β-(4. 8-di-methyl-nonadien-(3. 7)-yl) furan		24)
Atta rubropilosa, Acanthomyops claviger	citral	$(CH_3)_2C=CH-(CH_2)_2-C(CH_3)=CH-CHO$	24)
Acanthomyops claviger	citronellal	$(CH_3)_2C=CH-(CH_2)_2-CH(CH_3)-CH_2-CHO$	24)
Dolichoderinae	methyl heptenone	$(CH_3)_2C=CH-(CH_2)_2-C(=C)-CH_3$	24)
Tapinoma nigerrimum	propyl isobutyl ketone	$(CH_3)_2CH-CH_2-C(=C)-(CH_2)_2-CH_3$	24)
Iridomyrmex pruinosus, Conomyrma pyramica	2-heptanone	$CH_3-(CH_2)_4-C(=O)-CH_3$	24)

and Diptera insects in general.[25]

There are two ways for application of attractants to exterminate insect pests. One is the indirect method by which time and density of the occurrence of insect pests are forecast for the guidance of chemical extermination. It is also useful to judge of the effect of chemical extirpation. The sex attractants of gypsy moths and fruit flies are widely used for this purpose.

The other is the direct method by the application of attractants to luring of insects, or by using them in combination with poisonous substances for the same purpose. For this purpose light can be utilized with attractants to increase the luring effect. As mentioned above, hydrolysates of casein and other proteins are known to be food attractants. So a mixture of the hydrolysate and Malathon was scattered from airplanes to exterminate *Ceratitis capitata* which occurred in Florida. The total expenses of this work was 11 million dollars in 1956, 1962 and 1963, but it is said that the damage caused by the fly estimated at 180 million dollars could be prevented in nine years.

On the other hand, a mixture of methyl-eugenol, an attractant to the male of the oriental fruit fly, and Dibrom, a kind of organophosphoric insecticides, was dropped from planes for eradication of the fly in Rota Island of the Mariana Islands. It was reported that the fly which had been settled there for 35 years was totally destroyed by this dusting, and the expense of the chemicals was less than 4 pounds per square mile. Application of the attractant at more than a certain concentration induces disturbance of copulation in the male of *Trichoplusia ni*. So it is said that such a concentrated application of attractant may be more effective than the application of it to lure only males.[26] It is also possible to attract males to make them sterile by the use of chemosterilant in mixture with the attractant. The males are then set free to copulate with the females in the field to disturb fertilization. Such innovations will be tried in the future.

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