Chemistry of Sex Attractant of Insects*

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I. INTRODUCTION

In the earlier times, the abnormal spread of injurious pests over the crops was one of the most important causes which made agriculture unsteady. This unexpectable and hateful damage of harvests has been hitherto prevented practically by many sorts of agricultural pesticides. Hence, enabling the introduction of new techniques, such as saving of labor and early plantation of crops etc., the agricultural productivity is brought up at a very high level. Although there is fluctuation of the prices of products due to the diminution and unbalanced supply by the unseasonable weathers and speculative plantations, it may be fairly said that the present farming is stabilized by the agricultural pesticides. Furthermore, some of these drugs are widely applied for the extermination of the injurious insects swaring to domestic animals and fowls in back yards, and play an important rôle in the prevention from the plaugues in the field of environmental sanitation.

As the results of the repeated application of the same pesticides, however, some of insects have acquired the resistance against the pesticides and now can not be exterminated easily. At the same time, the useful organisms were also unselectively killed and then the unexpected and undesirable disturbance of natural balance resulted in the living world. On the other hand, it is well known that a lot of social problems were derived from the frequent hazards owing to direct or residual toxicity associated with the occasional use of very poisonous pesticides, in the expectation of the greater harvest and because of the lack of non-toxic alternatives.

To avoid these dangers, it was recommended not to scatter successively the same pesticides, and moreover, studies have been directed to search for less poisonous pesticides. In the consequence, now, many less poisonous pesticides have been developed and already employed in fields. Although the rash of new pesticides may continue in future, at the same time, the nonclassical methods will be developed in the field of biological control, which has been well known for a long time and makes use of the habits of insects. Then good results have been obtained experimentally by some of them, and several of them are practically applied indeed.

** 大 野 稔

* There are already some other reviews (in Japanese) about *Bombykol* by Tomita[18-b)], and about *Bombykol*, *Gyptol* and the sex attractant of American cockroach by Inouye[18-a)] and by Hatanaka[18-c)].

Everyone of the organisms repeats its own living history which fit to the native environments of the species. Insects, too, repeat to be born, grow and to breed in the miracle cycle of Nature.

Some species of insects look instinctively for a special host to obtain food and water for growth and live. This phenomena may be ascribed to that the host organisms release some sorts of flavors and honey, to which the insects favor to be attracted. Accordingly, it is superior to the method of pesticides that we apply this habit of insects to attract these injustices by the *food-type attractant* which possess the advantage of spacial spread and kill them together.

Further, some species of insects are in the habit of laying eggs on the host which the larva of the next generation likes to eat, or at the places where plants, such as fungus, which are necessary for growth of them will spring up in due time, or to the symbiotic organisms. Then it is an effective method for eradication of insects to attract, induce breeding and at last to kill them with use of this habits. This type of substance is called "*oviposition attractant*".

Adult insects look for the different sex of the same species to mate. Some species of insects are attracted by colors, flavors and honey of flowers and brought about together, and happen to mate in these opportunities. The insects are induced by many sorts of physical media, such as light and noise or song to copulate by another chance. Moreover, it has also been well known for a long time that some species of butterflies, especially the moths excrete some sorts of substances which attract the other sex[1a-b]. For example, a female moth in the cage placed out-door attracts male moths at a long distance. On the other hand, a male moth does not find easily the female moth in the glass cases, although she is in his sight. We can find in the literature that 127 male moths were attracted for 6 and half an hour to a cage of virgin females of *Saturunia pavonia L*, (one of the species of Japanese name ; *Yamamayu-ga*) at the window side[2]. In another paper, when the males of silk-worm moth in China (one of the species of Japanese name ; *Kaiko-ga*) were carried by rail and then made free at 4,1 km distance, 40% of them came back to the female in cage, and 26%, at 11 km indeed[3]. And in others[3], the females of *Philosamia cyrthia Dr*, (Japanese name ; *Himasan-ga*) attract the male from 2.4 km away[4] ; and the male of *gypsy moth*, *Porthetria dispar* (one of the species of Japanese name ; *mai-mai-ga*) flies to seek and find the females at about 3.8 km distance[4].

In the body of these insects, there is an organ, *sacculi lateralis*, which secretes a special organic substance, and in it, of the different sex, an exquisitely sense organ, *Grubenbegelsensillen* or *Sinnehaare* to detect the substance[1]. We call generally this type of substance which sexually attracts insects, "*sex attractant*".

It is feasible practically to prevent the propagation of the next generation by rearing and releasing of adult insects, which are sterile by exposure to γ-ray irradiation or bait containing chemisterilants. Furthermore, insects die of diseases, too, one may get rid of them by the infection of pathogenic organisms, such as fungi, bacteria and viruses.

Some insects have long wings to fly to the suitable places for diapause or to tide over the winter, but on the other hand, in the favorable climates, they have short wings, because of unnecessity to fly for seeking foods and diapause. Moreover, when insects of different heredity cross over, the offspring can grow up only in a special condition. Accordingly, it is also expected to eradicate the insects by releasing the strain which carries different genetic factors.

The methods described above, are a few examples of the recent biological control. In this review, the author wishes to describe the chemistry of attractants, in particular the sex attractants of insects.

The sex attractancy of insects has long been known, but the chemistry has not been elucidated at all until recently.

The studies that will be described later, are very excellent, and provide one with a key to open the door to the wonderful and mysterious Nature.

Some of these biological control have already been applied practically, and each of them, especially sex attractants, is highly specific for only one species of insects, and not effective for others at all.

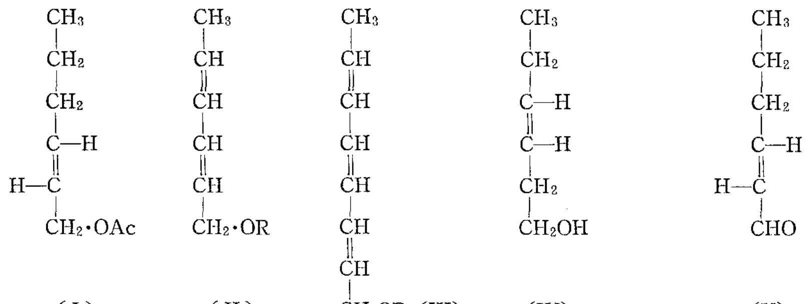
II. SEX ATTRACTANT OF INSECT

1. The sex attractant of Water-bug.

The male water-bug; *Leuthocerus indicus*, *Belostoma indica*, (Japanese name; *Tagame*) which is native of *Canbodia*, has two needle-tubes, 4 cm by length and 2-3 mm by diameter, at the abdomen in which is contained about 0.02 ml of transparent liquid with cinnamon-like odor. This is used as spices for foods by *Southeast Asian*. Butenandt et al.[5a-c] clarified the main fraction as *trans*-2-hexen-1-ol-acetate (I). Although the efficiency was not clear at the first time, afterwards it was proved to attract or excite the females of the water-bug[1].

The synthetic higher homologues of (I), that is 2, 4-hexadien-1-ol (II), 2, 4, 6-octatrien-1-ol (III), and also their acetates[6] gain more attractive potency with the number of double bonds increased.

Leaf alcohol and leaf aldehyde, *cis*-3-hexen-1-ol (IV) and *trans*-2-hexen-1-al (V), are widely distributed in green leaves[7] and are responsible for the flavors characteristic of fresh green leaves, hence the names. Furthermore, they may be the intermediate for synthesis of several perfumes of the natural origin, such as *jasmon*[8], *violet leaf aldehyde*[9] and *cucumber alcohol*[10]. It is due to the attractancy of (IV) and (V) that the larva or worms favors to eat the green leaves[11a-c].



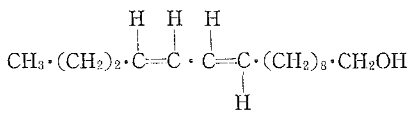
(I) (II) (III) (IV) (V)

R=H or Ac.

The substances (IV) and (V) are regarded as a factor to decide the protective coloring of nymphs of *Papilio xuthus* (Japanese name; *Agehacho*)[12]. Leaf aldehyde (V), is excreted with some other odorous substances by cockroach, *Eurycotis floridana* (*Walker*)[13], black cocktail ant, *Crematogaster* (*Atropogyne*) *africana Mayr*[14] and *Pentatomidae, Coreidae*[15]. These peculiar odors effect as the so-called, *odor trail* to come back its own nest from a long distance and also as the *defensive* and *protective* substance against enemies.

2. Bombyx mori L,.

After 20 year's studies of a sex attractant of silkworm moth, Butenandt and his co-worker isolated a pure substance, 15 mg, from 500,000 abdominal segments of virgin female of *Bombyx mori L.*, (Japanese name; *Kaiko-ga*), which was designated *Bombykol*, $C_{16}H_{30}O$, and determined its structure as 10, 12-hexadecadien-1-ol[16a–d]. The amount of the sample, however, was so small that the *cis-trans* geometry of the conjugated double bond in this molecule could not be decided at the same time. Later, it was established as 10-*trans*-12-*cis*-hexadecadien-1-ol (VI), comparing the natural *Bombykol* with all the synthetic stereo-isomers in the physico-chemical characters and also with bioassay[17a–c].



(VI)

Tab,. 1. Comparative Activity of *Bombykol* and its geometrical Isomers to male *Bombyx mori L,.*

Chemicals		LE γ/ml*)
1.	Natural *Bombykol*	10^{-10}**)
2.	10-*cis*-12-*cis*-Hexadecadien-l-ol	1
3.	10-*cis*-12-*trans*- ,,	10^{-3}
4.	10-*trans*-12-*cis*- ,,	12^{-12}
5.	10-*trans*-12-*trans*- ,,	10

*) LE means Lockstoffeinheit in German, i. e, the concentration: γ/ml at which, when a glass rod coated with suitable sex attractant dissolved in petroleum ether is allowed to come about 1 cm distance near the antennas of a male insect in a glass dish for 1 to 2 seconds, and when the experiment is repeated on 150 males individually, the half of the test insects are excited sexually.

**) The geometrical structure of 1 and 4 is the same. Although the synthetic 4 was superior to the natural 1 in bioassay, the difference may be permitted in the micro-order.

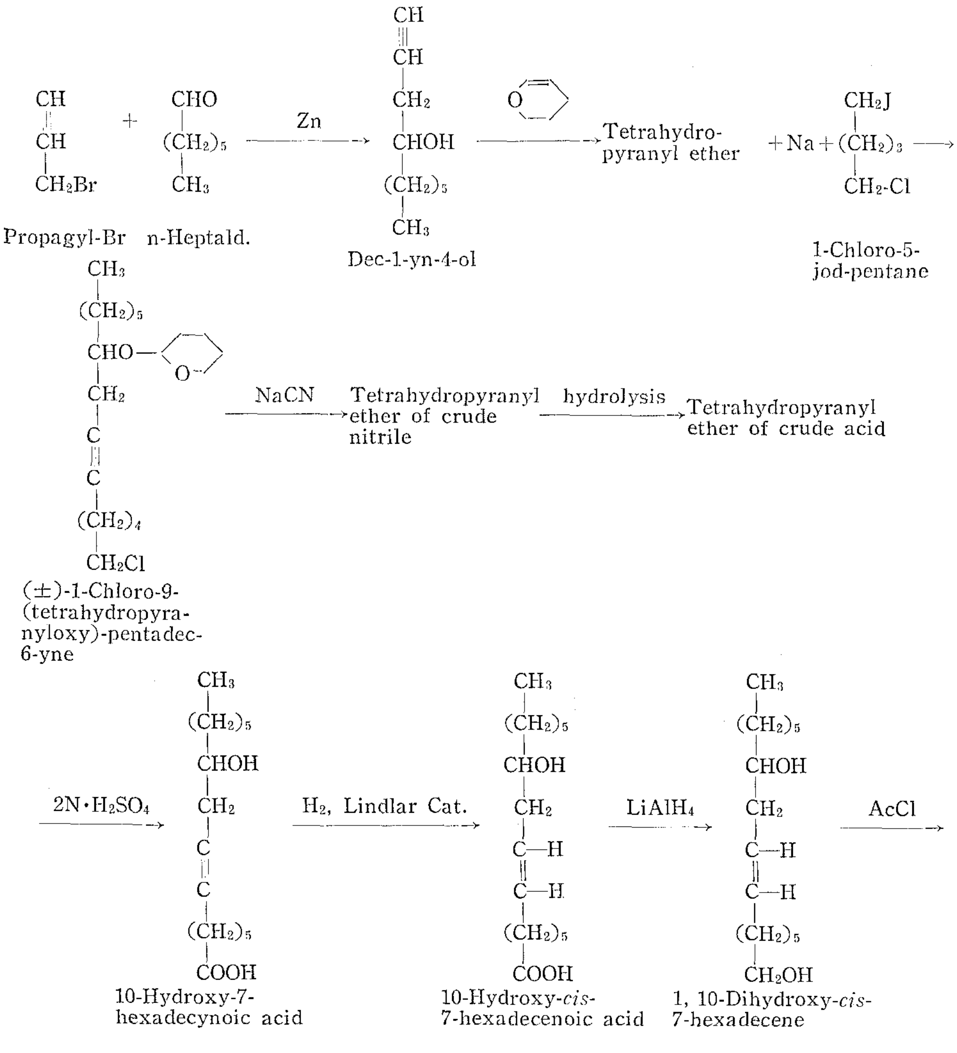
Karlson et al.[19] named "*Pheromone*" such substances as *Bombykol*, which are excreted one organism and after received by another of the same species to initiate some special excitations. The name of *pheromone* comes from *pherein* and *horman* in Greek, meaning transportation and excitement, respectively, and then that is, so to speak, the chemical language among individuals. These expression belongs to the same category as *hormone*, *gamone* (substance to feccundate), *termome* (substance to decide sex) and so on.

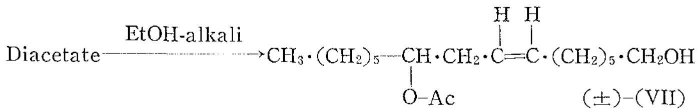
3. Gypsy moth.

It has been well known for a long time that the gypsy moth, *Porthetria dispar L.* which causes damages of several hundred-million dollors to the orchards in Europe and to the forests in America every year, the female gypsy moth excretes some kinds of sex pheromone. The chemists in U. S. A. had been studying that pheromone since 1932.

Jacobson et al.[20-21] caught 200,000 of virgin females of gypsy moth in Connecticut State in U. S. A. and 300,000 in Spain in 1956, and then purified the benzene extract of two abdominal segments to obtain 20 mg of pure, colorless and fluorescent liquid which was crystallized at low temperature. The liquid has such characters as follows; molecular formula, $C_{18}H_{34}O_3$; $[\alpha]_D^{23}+7.9$ (=1.0 in $CHCl_3$); LE $10^{-12}\mu g$.

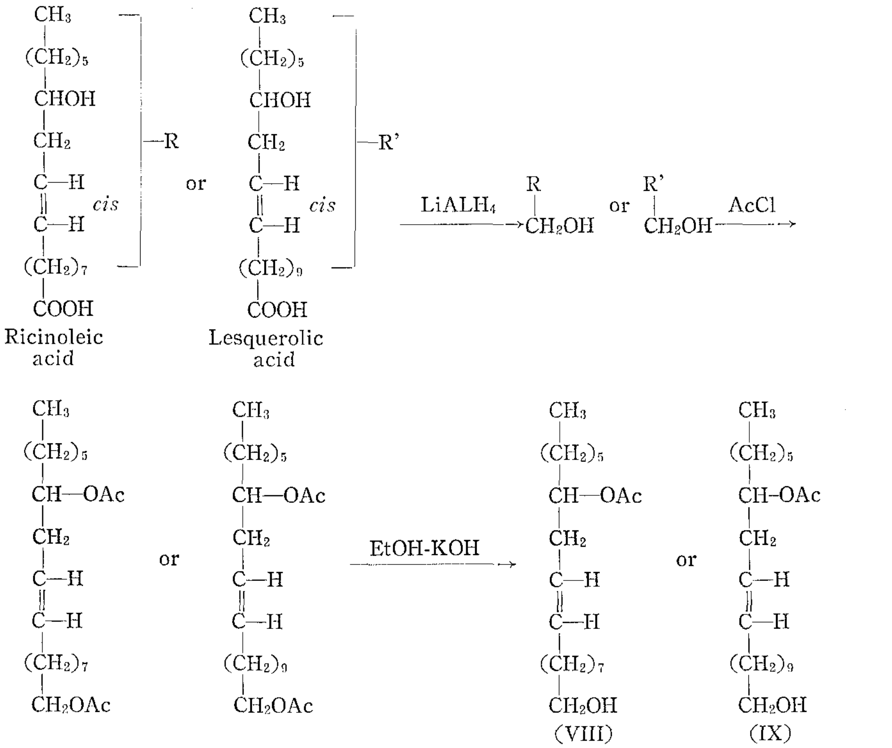
Its structure was decided as (+)-10-acetoxy-*cis*-7-hexadecen-1-ol (VII), by means of physico-chemical methods and also total synthesis[20]. The scheme of the total synthesis of (VII), which was named "*Gyptol*", is shown below;





The compound of (+)-(VII) was obtained by optical resolution[21] from racemic (±)-(VII) and was completely identical with the natural *gyptol*.

Jacobson et al. also synthetized its homo-acetates, (VIII) and (IX) from recinoleic acid[22a–b] and lesquerolic acid[22–b] [(+)-14-hydroxy-*cis*-11-eicosenoic acid[23]],



(VIII) 12-Acetoxy-1-hydroxy-*cis*-9-octadecene bp. 182°/0.5mm. $[\alpha]_D^{30}$ +7.4.

(IX) 14-Acetoxy-*cis*-11-eicosen-1-ol bp. 183°/0.3mm.

Tab. 2. Comparative Attractancy of *Gyptol* (natural), *Gyplure* and its Homologues to Male *Gypsy Moth*[22–b]

Compound	Attractancy μg	
	Laboratory	Field
Gyptol (VII) natural.	10^{-12}	10^{-7}
(+)−(VII) synthetic.	10^{-12}	10^{-7}
Gyplure(VIII) synthetic.	10^{-12}	10^{-5}
trans-isomer(X) of (VII).	10^{4}	$>2.5\times10^{5}$
Propoxy isomer(XI) of (VII)	Completely unattractive	
Butoxy isomer(XII) of (VII)	Completely unattractive	
Dihydro-gyptol	10^{-2}	10^{-2}

as the starting materials which has additional two or four carbon atoms, respectively. The attractancy of (VIII) is equal to that of natural *gyptol* in laboratory experiments, but a little inferior in field. The synthetic (VIII) was named "*Gyplure*" and is, perhaps, practically used now, since it can be obtained in a high yield from easily accessible ricinoleic acid.

There is little or no attractancy in *trans-isomer* (X), 12-propoxy-isomer (XI) and 12-butoxy-isomer (XII) of (VII)[22-b)].

Although (II, III), and (IV) mentioned above excite the larva of silk worm,[11a-b)] but these are not involved in the pheromone group. Moreover synthetic hexadecan-1, 2-diol (XIII) and that epoxide (XIV), give effect to the *gypsy moth* as attractant,[24a-b)] either of them is not included in the *pheromone* group, and they are considerably less attractive with use of 0.5 g per trap in field.

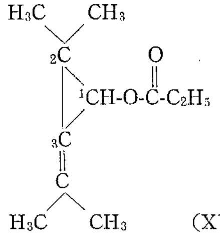
$$CH_3\cdot(CH_2)_{13}\cdot CH(OH)\cdot CH_2OH \quad \text{(XIII)}$$

$$CH_3\cdot(CH_2)_{13}\cdot CH\!-\!CH_2 \text{ (epoxide, bridged by O)} \quad \text{(XIV)}.$$

4. American Cockroach.

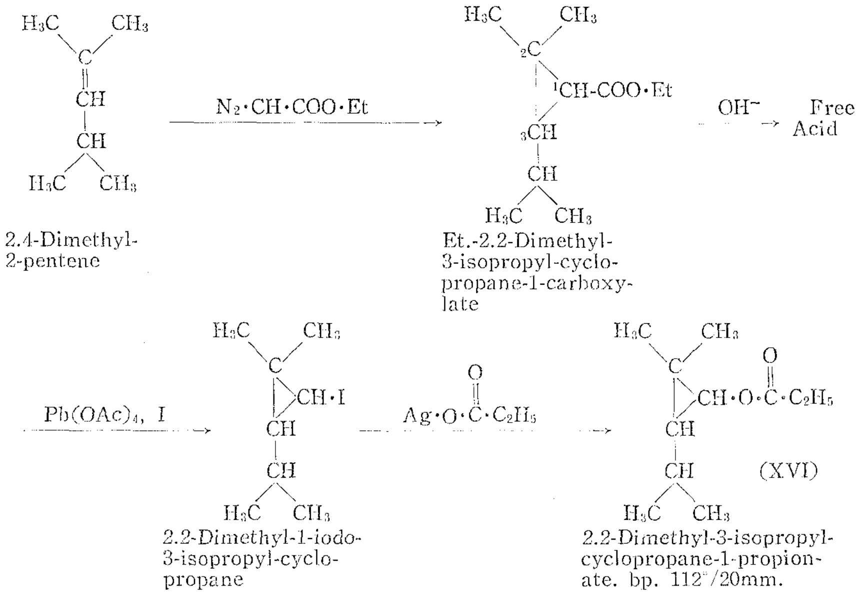
The female of *Periplaneta americana L.* (Japanese name; *Wamongokiburi*) secretes a sex attractant which excites the males and makes some characteristic sexual motions of spreading their wings. Wharton et al.[25)] obtained 25 μg of a pure substance with sex attractancy from the filter papers on which many females of the american cockroach had crawed around, but they could not elucidate its chemical structure.

On the other hand, Jacobson et al.[26)] obtained a 12.2 mg quantity of pure sex attractant from total 10 thousands of female american cockroach by the following procedure. The air was allowed to flow continuously for nine months through the metal containers in which a number of virgin females of the cockroach are custodied. Then the flowing out vapor was passed a small amount of 0.1 % hydrochloric acid solution in a chilled vessel. Then after, the condensate was extracted with *n*-hexane. The hexane extract was isolated and purified by chromatographic method. The obtained material had a strong sex attractancy of LE 10^{-14} μg to the male cockroach. The U. S. workers deduced the structure (XV), for this substance by the analyses, such as physico-chemical methods, IR., elemental analysis, elution times and also by the chemical evidence that the dihydro-isomer derived from the natural one was identical with a dihydro derivative (XVI) synthetized as below;



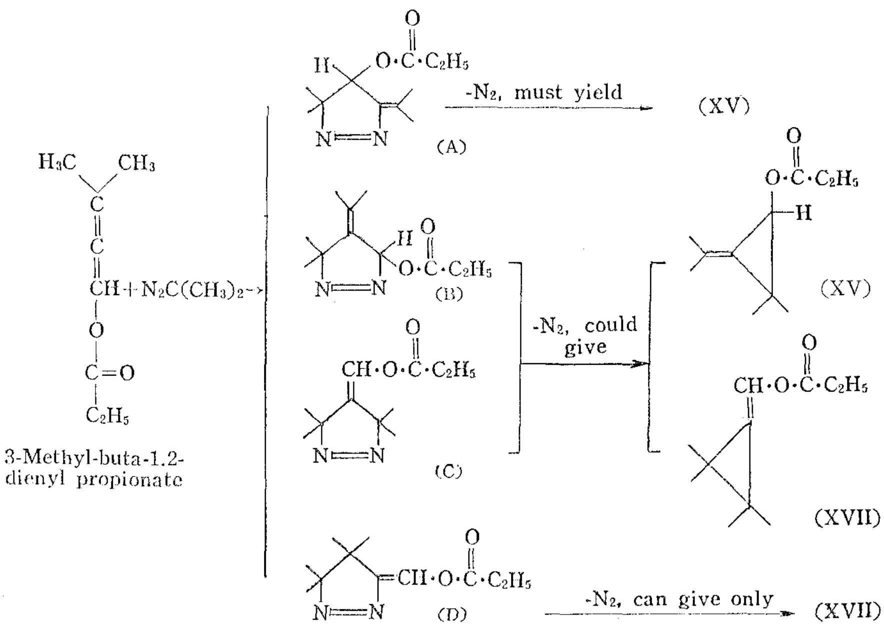
(XV)

2.2-Dimethyl-3-isopropenyl-cyclopropyl-1-propionate (proposed structure by Jacobson et al.[26)])

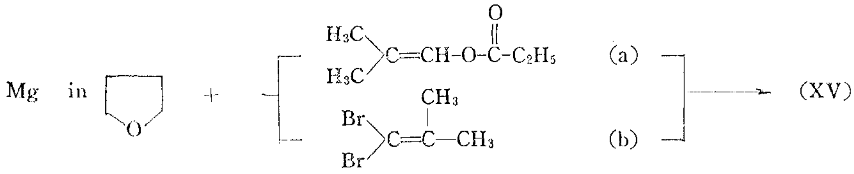


The cockroach haunts kitchen and lavatory, and very disagreeable, because of their carrying disease-germ. Then it is often used as the word meaning a detestable one. Many chemists paid attention to this report by Jacobson et al. and total synthesis of (XV) was attempted in several laboratories in all over the world[27,29a-c,33].

Day et al.[27] carried out a reaction of 3-methyl-buta-1, 2-dienyl propionate[28] with diazopropane at 0-20°, and obtained a single product. It must be one among (A-D) in that structure. Then the single product was photolyzed with a mercury lamp through a pyrex filter at 35° to give a mixture (XV) : (XVII), 37 : 63. Then one of possibility, (A) and (D) was omitted by this observation.



On the other hand, the synthetic (XV) was completely identified in the data of n. m. r. and IR. spectrum with a synthetic in a different way by Wakabayashi[29-a)], illustrated below.

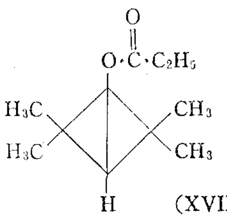


mixture of 2-methyl-1-propenyl propionate (a) and 1,1-dibromo-2-methyl-propene (b).

It was, however, different from the proposed structure for natural sex attractant (XV), in comparing of retention time in V. P. C., IR, and other chemical evidences, and further the synthetic (XV) was inactive in bioassay.

It is now obvious that Jacobson et al.[26)] were wrong in their structure deduction and that a bicyclobutane structure (XVIII),[27)] may be more reasonable for the (XV), sex pheromone of American cockroach by the analysis of the data.[26)]

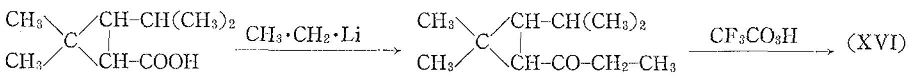
They also admitted their error on that point and said in a paper[30)] that the structure (XVIII), was one of the probability until (XV) was chosen finally.



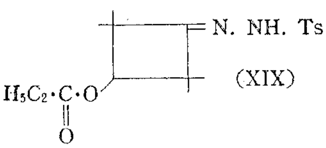
(XVIII)

Suggested structure for sex pheromone of American cockroach by A.C. Day et al[27)].

Apart from their discussion, Quelle et al.[31)] and Matsui et al.[32)] tried to synthetize a dihydro-isomer (XVI) by Jacobson's procedure, respectively, but they obtained different substances compared with (XVI). At the same time Matsui et al.[32)] synthetized dihydro-isomer (XVI) by a different way as follow;



Singh[33)] also made an approach to synthesis of proposed structure (XV), by a thermal decomposition of (XIX), but could not obtain (XV) as yet.

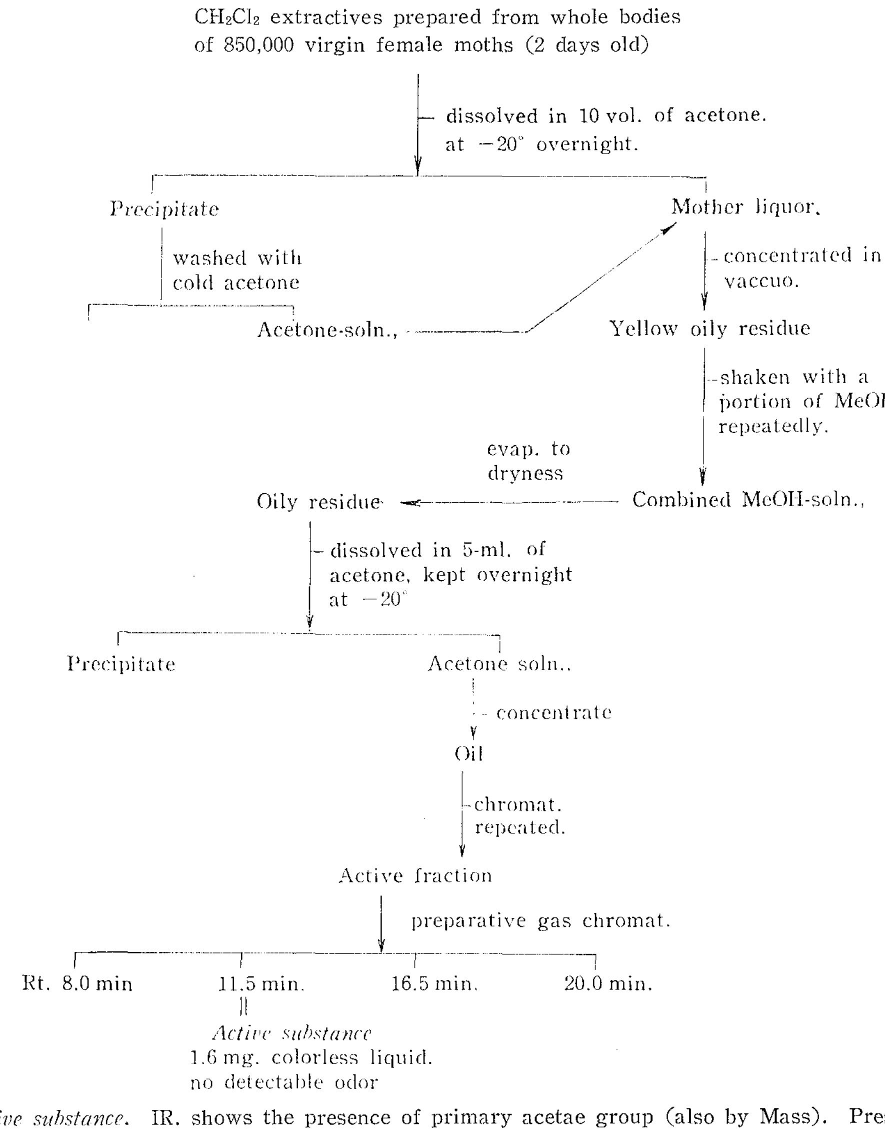


(XIX)

Accordingly, the structure of the sex pheromone of American cockroach remains to be determined in future.

5. Pinc Bollworm Moth

The larva of pinc bollworm moth, *Pectinophora gossypiella* (*Saunders*), (Japanese name; *Wataakami-mushi*) is one of the most destructive pests in the cotton growing areas of the world. They devour the seed in husks or ovary of the flower buds of cotton. It was clarified in 1957[34] that the female moth had some sex pheromones, and found in 1962 by Ouye et al.[35] that the males were attracted by the methylene chloride extract of the copulating insects. Further Berger et

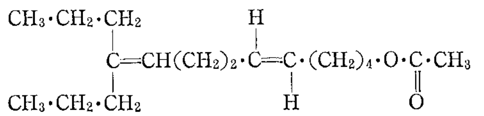


Active substance. IR. shows the presence of primary acetae group (also by Mass). Presence of unsaturation, *trans*-double bond, unbroken chain of at least 4-methylene groups.

Hydrogenolytic gas chromat., Presence of the branching in its structure.

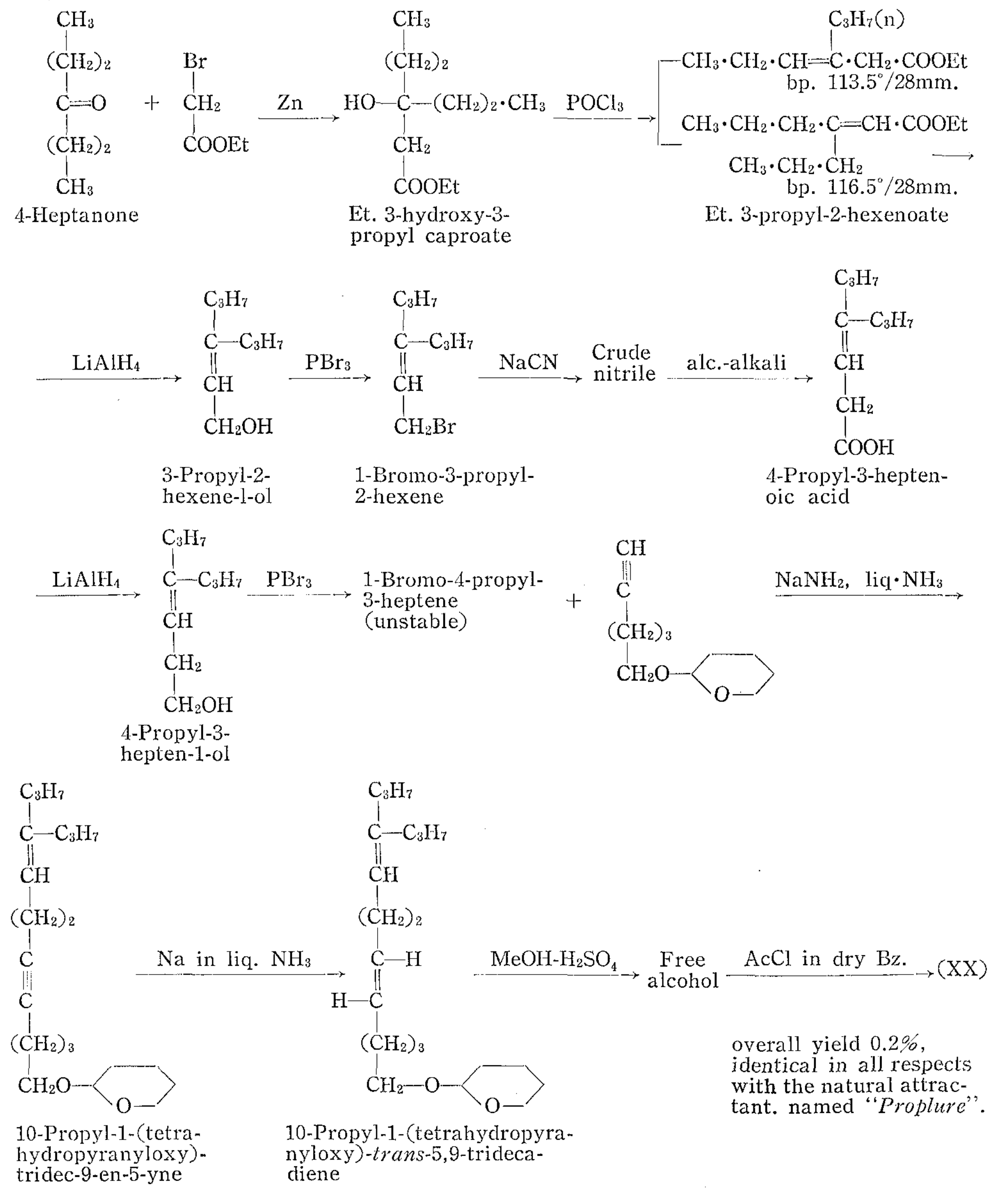
Mass. M=280. $C_{18}H_{32}O_2$ and n. m. r. spectra, the only structure for this sex pheromone is (XX).

al.[36] reported that the males were elicited by the extract from the abdomens of vergin females to dance in characteristic manners, such as excited flight, rapid wing vibration and upward curving of the abdomen. Although this substance was known only as C_{18}-ester until 1964, Jones et al.[37] succeeded in the isolation, identification and total synthesis of the pheromone.



(XX) 10-Proply-*trans*-5,9-tridecadienyl acetate

Synthesis of (XX).[37]



6. Cabbage Looper.

Berger[38] obtained approximately 200 mg quantity of crude extract of a sex pheromone from about 2,500 abdominal tips of the female of cabbage looper, *Trichoplusia ni*, (one of the species of Japanese name; *Uwaba-ga*). And a amount of 8-10 mg of impure but highly active material was prepared with further purification. The structure was decided as (XXI) by physico-chemical analyses and total synthesis.

The synthetic (XXI) was identical with the naturally derived compound by the IR. spectrum, Rf-value and minimum effective concentration, 0.1 μg/ml. or the equivalent of 0.05 females/ml, to stimulate the male of cabbage looper.

$$CH_3\cdot(CH_2)_3\cdot\overset{H}{\underset{|}{C}}=\overset{H}{\underset{|}{C}}\cdot(CH_2)_5\cdot CH_2O\text{-}\overset{O}{\overset{\|}{C}}\cdot CH_3 \qquad (XXI)$$

cis-7-Dodecen-1-ol acetate

7. Ips confusus.

The male of *Ips confusus* (one of the species of Japanese name; *Kikuimushi*) bores a hole on ponderosa pine and other conifers to produce the frass, (a mixture of phloem fragments and excrement pellets) including a pheromone. The frass attracts both sexes, especially the females. Both males and females crowed at the frass in the gallery. At this time, females assemble to make mass around the frass producing male. The males are stimulated by this aggregation to run away and to bore other hole on ponderosa pine. The tree will be finally blasted by the sequence of these masses. The female is evoked by 3×10^{-8} g of the frass.

Pitman et al.[39] isolated α-pinene, myrcence, β-pinene, Δ^3-carene, limonene and some kinds of unknown substance by gas chromatography of the extract from

Refuse or excrement left
by 21,000 males[40-(a)]

↓

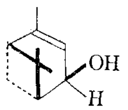
Frass . . . 3 kg.

↓ by sequence extraction, short pass distillation, coloum chromat., and gas chromat.,

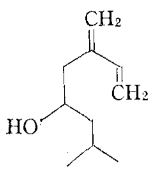
Highly potent
fraction. 0.0007%/frass

↓ gas chromat.,

- First broad fraction
  - ↓ Nonanal $CH_3\cdot(CH_2)_7\cdot CHO$ (XXII)
  - Geranyl acetate (XXIII)
- further fract., on carbowax 20 M.
  - Comp. 1. Rt. 17-22 min. 260 mg
  - Comp. 2. Rt. 26-29 min. 26 mg.

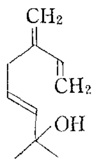


(XXVI)



(XXIV)

(−)-2-Me-
6-methylene-
7-octen-4-ol.



(XXV)

(+)-*trans*-2-Me-
6-methylene-3.
7-octadiene-2-ol.

frasses. These compounds, however, may be attributed to terpene components in the phloem fragment.

Silverstein et al.[40-a] clarified that the attractive substances in the frass, that is pheromone, were nonanal (XXII), geranyl acetate (XXIII) and two kinds of new terpene alcohol (XXIV and XXV). There is another literature[40-b] reporting the presence of (+)-*cis*-verbenol (XXVI)*), in the frass.

In the laboratory bioassay, a typical attractant response was elicited by each of two mixtures:

1 μg of compound (XXIV) with 0.01 μg of compound (XXVI), and

1 μg of compound (XXIV) with 1 μg of compound (XXV).

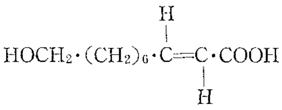
The compound alone was inactive at these levels: compound (XXIV) at 100 μg, compound (XXVI) at 20 μg and compound (XXV) at 100 μg.[40-c]

The compounds (XXIV, XXV) were synthetized, and the mass, IR, nmr and UV spectra were identical with those of natural substances.[40-c]

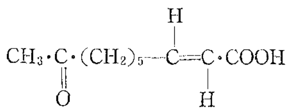
8. One of the mating attractant of Honey Bee.

Honey bees, *Aphis mellifica* (Japanese name; *Mitsubachi*), and also ants constitute a characteristic community in which every individual works in a quota system. There are number of pheromones in the aggregation which are taken in *via os* and manifest a controlling effect of the massif.[41]

Although the queen bee is female as are the workers, the foods for the larva to raise a queen differ largely in quality and quantity[41] from those for the latter. The royal jelly which the queen bee takes is not yet clear in its biochemical meaning, but contains a large quantity of royal jelly acid, 10-hydroxy-*trans*-2-decenoic acid (XXVII).[42] The queen bee flies several score meters high and mate with male in air. A substance of 9-oxo-*trans*-2-decenoic acid (XXVIII)[43] is one of the mating attractant[44] in her body.



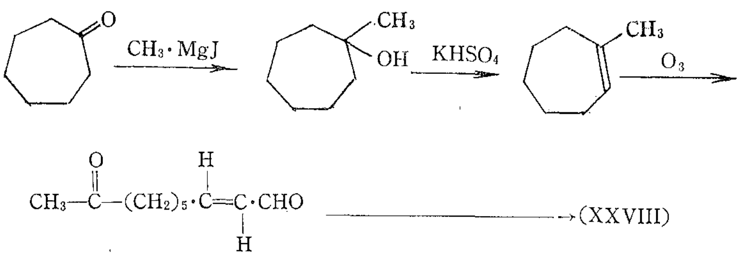
(XXVII)



(XXVIII)

Synthesis of (XXVII)[45a-b]

Synthesis of (XXVIII) from cycloheptanone[43], from pimelic acid[45-b]

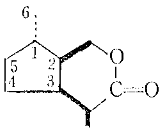


*) Adult females of *Dendroctonus frontalis Zimm.* & *D. brevicomis* (*Lec.*) (bark beetle) produce the same major volatile compound, which was identified as *trans*-verbenol. Males of the two species produce the same major component, verbenone. (J.A.A. Renwick. *Contrib. Boyce Thompson Institute* 23, 355 (1967)).

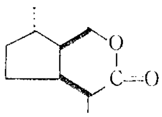
9. Sex Attractant for male Lace Wing.

S. Ishii[46] and T. Sakan et al.[47] reported that the male lace wing, *Chrysopa septenpuncta Wesmale* (Japanese name; *Yotsuboshi-kusakagero*)*) is attracted by the extract of *Actinidia polygoma Mig* (Japanese name; *Matatabi*). This plant contains some matatabilactone, which make the cat family exhibit the so-called matatabi-dance. This fraction is a homolactone mixture,[48] in which the secretions of Argentine and Austlarian ant, *Irdomyrmex* genus, i. e. iridomyrmecin (XXIX) and isoiridomyrmecin (XXX), are included.

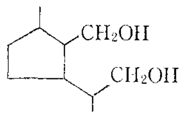
T. Sakan et al.[47] found, moreover, that some other homologues are included in the product of the plant, such as iridodiols (XXXI), 5-hydroxy-(XXXII), 7-hydroxy-matatabiether (XXXIII), matatabiol (XXXIV), allomatatabiol (XXXV) and neo-matatabiol (XXXVI), and also reported that the compounds, (XXXII) to (XXX-IV) and (XXXVI) stimulate sexually to the male lace wing.



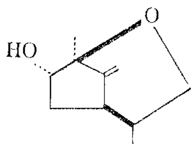
(XXIX)
Iridomrymecin



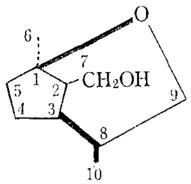
(XXX)
Isoiridomyrmecin



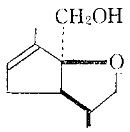
(XXXI)
$\alpha \sim \delta$-, *cis*-
Iridodiol



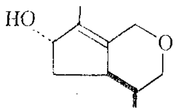
(XXXII)
5-Hydroxymatatabi-ether LF 1γ



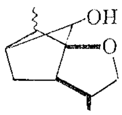
(XXXIII)
7-Hydroxymatatabi-ether LE 1γ



(XXXIV)
Matatabiol
LE $10^{-3}\gamma$



(XXXV)
Allo-matatabi-ether



(XXXVI)
Neo-matatabiol
LE $10^{-6}\gamma$

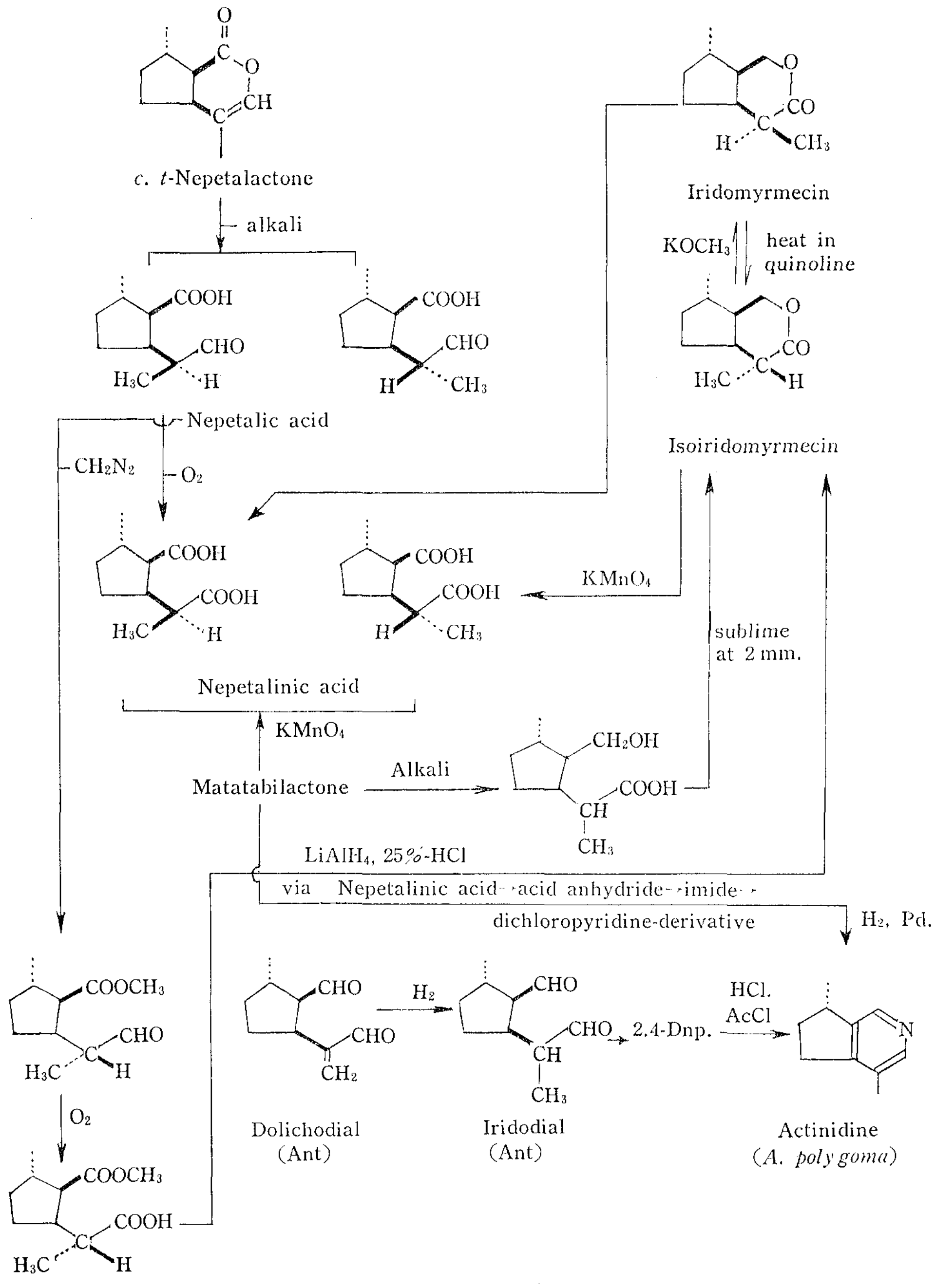
It is interesting that iridomyrmecin, isoiridomyrmecin and others are contained in *Iridomyrmex ant* of animal kingdom, and that matatabilactone, which is a mixture of the formers, in *A. polygoma Mig* of plant world. Further it is very interesting that nepetalactone[49] which is found in a genus of catnip, *Nepeta cataria* (Japanese name; *Inuhakka*) and has the same carbon skelton as irido-lactone, excites the cat family. The interconversion of these substances is shown as follows;

As to biogenesis of these substances, Cavill et al.[50] inferred that they may be derived from citral. It is sure that citral is found widely in the plant kingdom and was isolated also from some kinds of ant. Then the Cavill's hypothesis suggests a possible pathway, although it is not generally recognized as yet.

---

*) A day-fly, ephemera (Japanese name; Kagerō) eats the plant-louses, aphid (Japanese name; Aburamushi) which swarm and hurt the fresh leaves. Then the former is a useful insect for man.

Relationships between Nepetalactone, Iridolactones and Matatabilactone.



10. Hairpencil Secretion of Trinidad Butterfly.

Biology has been developed by the interesting studies by Brower et al.[51] on the courtship behavior of Queen butterfly, *Danaus gilipus berenice (Cremer)*, and on the sexual habits of *Lepidoptera* (Japanese name; *Rinshimoku-kontyu*).

The male of the tropical subfamily *Danainae* has generally a pair of exquisite organ, so to speak hairpencils, which can be extruded from the end of its abdomen. In the Queen butterfly, the male has been observed to brush the hairpencils across the anterior of the female in flight. This treatment appears to introduce the female to settle on available herbage. After continued hairpencilling copulation occurs.

The secretion of hairpencils and their associated glandular cells is thought to play an important role in producing copulation. This secretion is not a sex attractant, but a pheromone. And nothing was found about the chemical characters of it at his time.

On the other hand, Meinwald et al.[52] later isolated and purified three kinds of component from the hairpencil secretion of Trinidad butterfly *Lycorea ceres ceres (Cramer)*, a member of the *Lycoreini tribe* of *Danainae* subfamily, and they revealed each of the chemical structure. Its hairs were carefully removed from the extruded hairpencils at the end of the abdomen of several hundreds of the living male caught in Trinidad, and then those were immediately treated to extract with methylene chloride or carbondisulfide. The extract was purified and divided to obtain a few mg of compounds of ester-I, -II and a ketone, respectively.

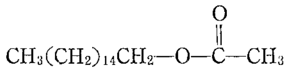
Hairpencils from 100 live male.
↓
soaked in 5 ml. of CH_2Cl_2 or CS_2
— after four such extraction, no further extracted material was obtained.
— concentrated to 1 ml.
↓
Combined extract
Glpc analysis at 180° (5% SE 30 column) showed three major components. Rt. 1.7, 10.5 and 20 min.,
↓
Chromat. on 15 g of Silicic acid

eluted, CH_2Cl_2 → Ester-Fraction . . . Glpc anal., showed two main comp.
Preparative gas chromat. 5% SE 30 culumn, at 200°
→ Ester-I (Rt. 5 min.) 4.5 mg. Structure (XXXVII)
→ Ester-II (Rt. 8.5 min.) 8.5 mg. Structure (XXXVIII)

eluted, CH_2Cl_2-MeOH (1%) → Ketonic Fraction about 10mg . . . solidify on standing in refrigeartor, mp. 63-66°
— Sublimation at 60-65°/0.5 mm.
↓
Colorless needles. 2.3mg mp. 74~5°.

A more efficient preparative technique for separation of ketonic fraction proved to be preferential vacuum sublimation of this crude extract, and the esters by chromatography of the residue.

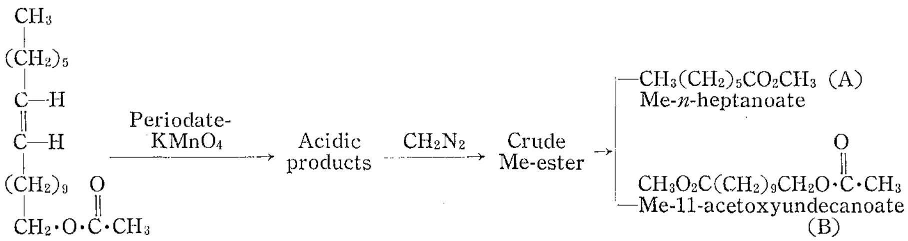
Ester-I is an acetate including a trace of some unknown unsaturated materials. This ester was unchanged when it was subjected to catalytic hydrogenation, and was identical with the authentic sample of *n*-hexadecyl (cetyl) acetate (XXXVII) by the analyses of physical measurements, such as IR and mass spectra.



(XXXVII) Cetyl acetate (Ester-I)

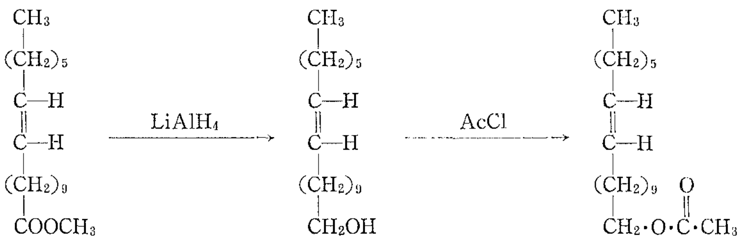
Ester-II is also identified as an acetate, (XXXVIII) of a molecular weight 130 involving one *cis*-double bond. It was converted to *n*-octadecyl (stearyl) acetate by hydrogenation. Oxydative cleavage of ester-II gave methyl heptanoate (A), and methyl 11-acetoxyundecanoate (B).

Moreover it was identical with a synthetic (XXXVIII-s) from methyl-*cis*-vaccenoate. Then it is clear that ester-II is *cis*-octadec-11-enyl (*cis*-vaccenyl) acetate.



cis-Octadec-11-enyl (*cis*-Vaccenyl) acetate (XXXVIII)

Synthesis of Ester-II (XXXVIII).

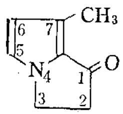


Me-*cis*-vaccenoate (XXXVIII-s)

Carbonyl compound has a molecular formula, C_8H_9ON, including one conjugated ketone (—C═C—C═O), as a partial structure. The structure of this ketone is decided as (XXXIX) which has a methyl group at 7-position, by the comparison of n.m.r. data with 2, 3-dihydropyrrolidin-1-one (XXXX).

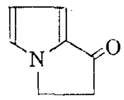
It is not yet convinced whether the above two acetate and synthetic (XXXIX-s) have the same pheromone activity as the natural substances, for ester-I contains a trace of some other unsaturated compound and synthetic ketone (XXXIX-s) has not sweet odor.

In Table 3 are summarized the sex pheromones, attractants and related sub-



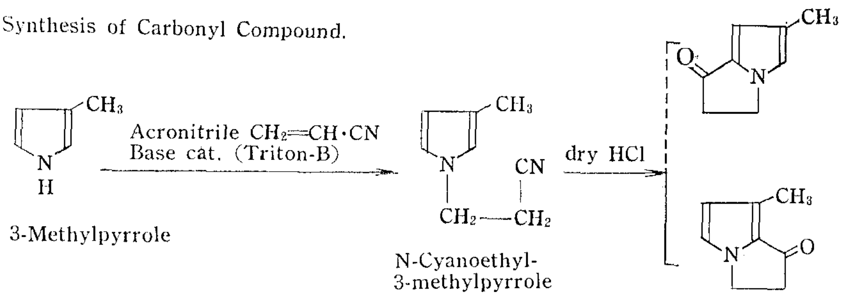
(XXXIX)

2, 3-Dihydro-7-methyl-
1 H-pyrrolidin-1-one

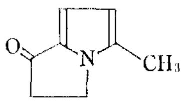


(XXXX)

Synthesis of Carbonyl Compound.



(XXXIX-s)



(XXXXI)

were synthetized, but clear differed from natural ketone.

(XXXIX-s) identical with natural ketone in mixed mp, UV. IR. and mass, but lacked characteristic sweet odor of the natural ketone.

stances described above. One can find some interesting structural relationship among these compounds.

Studies on sex pheromone are currently in progress, in particular with female insect excretions, such as codling moth *Carpocapsa pomonella* (*L.,*), several species of *Dermestidae* (Japanese name; *Katsuobushi-mushi*), black carpet beetle *Attagenus piceus* (*Oliber*)*⁾, tobacco hornworm *Protoparce sexta* (*Johnson*), carpenterworm moth *Prionoxystus robiniae* (*Peck*), red pine scale *Matsucoccus resinosae Bean Godwin* and screw worm fly (male) *Cochlimyia hominiborax* (*Coquerel*) and so on.

Then we can expect numerous sex pheromones of insects in future. Each of sex pheromone exhibits a high specific potency to the different sex of the same species of insect and takes part in the instinctive behavior of its own species. Consequently, some of the sex pheromones and synthetics are practically applied in field to eradicate injurious insects by inverting of this character, and moreover numbers of the attractant will increase to be supplied hereafter.

Little is known in the field of *molecular biochemistry* or "*chemical language*" of pheromone, and a question, "how a pheromone language is perceived by the receptor of insects of different sex?" is not answered as yet and awaits further developments in future.

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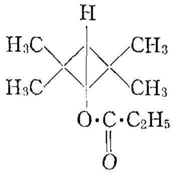
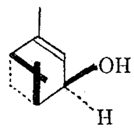
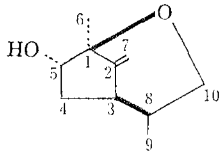
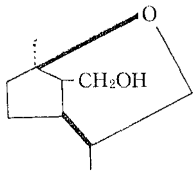
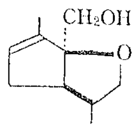
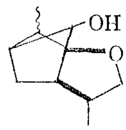
*⁾ A carpet beetle *Attagenus megatoma* (*Fabsicius*) attractant has been isolated, identified and synthesized. This attractant is a carboxylic acid, *trans*-3-*cis*-5-tetradecadienoic, acid,

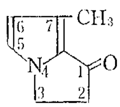
$$CH_3(CH_2)_7\overset{H}{C}{=}\overset{H}{C}{-}\overset{H}{C}{=}\underset{H}{C}{-}CH_2\cdot COOH$$, and is a sex attractant for the male carpet beetle.

Chem. and Eng. News. **1967** July 17. page 35. *Science.* **158**, 85 (1967)

Table 3. Sex Pheromones, Sex Attractant and Stimulant for Insects.

Insect	Produced by	Sex Pheromene	
Belostoma indica	male	$CH_3(CH_2)_2\overset{H}{C}=\underset{H}{C}CH_2\cdot O\cdot \underset{O}{\underset{\|}{C}}\cdot CH_3$	2-*trans*-Hexen-1-ol-acetate
Bombyx mori (Silk worm moth)	female	$CH_3(CH_2)_2\underset{H}{C}=\underset{H}{C}\cdot\overset{H}{C}=\underset{H}{C}\cdot(CH_2)_8CH_2OH$	10-*trans*-12-*cis*-Hexadecadien-1-ol
Portheria dispar (Gypsy moth)	female	$CH_3(CH_2)_5\underset{OCOCH_3}{CH}\cdot CH_2\cdot\overset{H}{C}=\overset{H}{C}(CH_2)_5\cdot CH_2OH$	(+)-10-Acetoxy-1-hydroxy-7-*cis*-hexadecene
Periplaneta americana (American cockroach)	female	 (?) (proposed by A. C. Day)	2, 2, 4, 4-Tetramethyl-bi-cyclobutane (0. 1. 1.)-1-propionate
Pectinophora gossypiella (Pink bollworm moth)	female	$(CH_3\cdot CH_2\cdot CH_2)_2C=CH(CH_2)_2\overset{H}{C}=\underset{H}{C}\cdot-$ $(CH_2)_4O\cdot\underset{O}{\underset{\|}{C}}\cdot CH_3$	10-Propyl-5-*trans*-9-tridecadienyl acetate
Trichloplusia ni (Cabbage Looper)	female	$CH_3(CH_2)_3\overset{H}{C}=\overset{H}{C}(CH_2)_5CH_2O\overset{O}{\overset{\|}{C}}CH_3$	7-*cis*-Dodecen-1-ol-acetate
Aphis mellifera (in Queen bee)	female	$CH_3\cdot\overset{O}{\overset{\|}{C}}(CH_2)_5\overset{H}{C}=\underset{H}{C}\cdot COOH$	9-Oxo-2-*trans*-decenoic acid
Ips confusus	male		*cis*-Verbenol
		$CH_3(CH_2)_7CHO$	n-Nonanal
		$(CH_3)_2C=CH(CH_2)_2\cdot\underset{CH_3}{C}=CH\cdot CH_2\cdot O\cdot\underset{O}{\underset{\|}{C}}\cdot CH_3$	Geranyl acetate
		$(CH_3)_2CHCH_2\underset{OH}{CH}CH_2\underset{\underset{CH_2}{\|}}{C}CH=CH_2$	(−)-2-Me-6-methylene-7-octen-4-ol
		$(CH_3)_2\underset{OH}{C}\cdot\overset{H}{C}=\underset{H}{C}CH_2\underset{\underset{CH_2}{\|}}{C}\cdot CH=CH_2$	(+)-2-Me-6-methylene-*trans*-3, 7-octadiene-2-ol
Attagenus megatoma (Fabsicius)	female	$CH_3(CH_2)_7\overset{H}{C}=\overset{H}{C}-\overset{H}{C}=\underset{H}{C}-CH_2\cdot COOH$	3-*trans*-5-*cis*-Tetradecadienoic acid.

Insect	Origin	Sex Attractant	
Chrysopa septenpunctata Wesmale (Lace Wing)	*A. polygoma* (Matatabi)		5-Hydroxy-matatabi-ether
			7-Hydroxy-matatabi-ether
			Matatabiol
			Neo-matatabiol

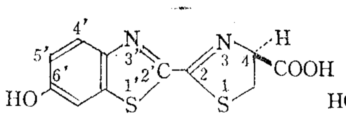
Insect	Produced by	Sex Stimulant (?)	
Lycorea ceres ceres (Cramer) (Trinidad Butterfly)	male	$CH_3(CH_2)_{14}CH_2OC(=O)CH_3$	Cetyl acetate
		$CH_3(CH_2)_5CH{=}CH\cdot(CH_2)_9\cdot CH_2\cdot O\cdot C(=O)\cdot CH_3$	*cis*-Octadec-11-enyl acetate
			2, 3-Dihydro-7-Me-pyrrolidin-1-one

Before closing this review, an additional mention is made to an interesting pheromone(?) bearing a relation to courtship.

The fireflies (*Japanese name*; *Hotaru*) assemble each other, being attracted by their small lanterns and happen to mate on the occasion.

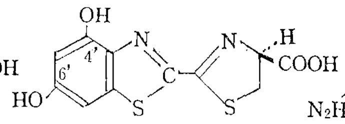
Bitler et al. isolated this luciferin[53] and White et al.[54a-b] decided the structure as (XXXXII) and synthetized[54b-d].

This (XXXXII) luciferin emit light by biochemical systems that a hydrogen

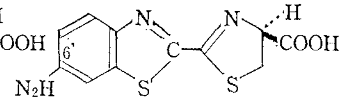


(XXXXII)

Firefly Luciferin
D-(−)-2-(6'-Hydroxy-2'-benzothiazolyl)-Δ^2-thiazoline-4-carboxylic acid



(XXXXIII)



(XXXXIV)

ion is removed and attached alternatively in 6'-position. The firefly luciferin and the homologues were synthetized[54-c)]. In them, 4,' 6'-dihydroxy-(XXXIII) and 6'-aminoisomer (XXXIV) emit red light in biochemical systems.

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